Rare-Earth Doped Amorphous Carbon Thin Films Using Plasma-Enhanced Metalorganic Chemical Vapor Deposition: A Potential Photonic Material

by

Hui-Lin Hsu

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Electrical and Computer Engineering
University of Toronto

© Copyright by Hui-Lin Hsu 2015
Rare-Earth Doped Amorphous Carbon Thin Films Using Plasma-Enhanced Metalorganic Chemical Vapor Deposition: A Potential Photonic Material

Hui-Lin Hsu
Doctor of Philosophy
Electrical and Computer Engineering
University of Toronto
2015

Abstract

Thin films of rare-earth doped amorphous carbon (a-C(X), X= Er or Yb) were grown on silicon substrates at low temperatures (< 200 °C) using a simple yet versatile one-step radio frequency plasma-enhanced metalorganic chemical vapor deposition technique, motivated by the potential of this new family of rare-earth doped carbon-based photonic materials for direct integration on Si CMOS chip during back end-of-line processing.

Prior to the synthesis of a-C(X) films, we show that a-C host films with wider optical bandgap and lower percentage of $sp^2$ carbon bonding are obtained on the anode. Doped amorphous carbon films were synthesized using partially fluorinated metalorganic compound, X(fod)₃. Room temperature (RT) photoluminescence (PL) is observed in a-C:H(Er) films at 1.54 μm notwithstanding the use of hydrogenated a-C host. High concentration of Er ([Er]), direct incorporation of Er$^{3+}$ ions, partial fluorination of the organic ligands, and the large optical bandgap of the a-C:H host conspire to yield RT PL despite the abundance of C-H quenching modes. This
facile synthesis technique affords the ability to attain vertically uniform dopant concentration or user defined concentration profiles.

Six-fold enhancement of RT PL in Er doped films was demonstrated by deuteration of the a-C host. The enhancement is principally a result of the weaker interaction strength between Er$^{3+}$ and the C–D$_x$ and O–D third harmonic vibrations, compared to the interaction strength between Er$^{3+}$ and the C–H$_x$ and O–H second harmonic vibrations. Also, PL signal is observed to increase with increasing RF power, which is attributed to an increase in [O]/[Er] ratio. Moreover, PL decreases with increasing substrate temperature, which is attributed to decrease in [Er]. Also, the onset of [Er] quenching was observed at ~2.2 at% and continued to increase until 5.5 at% in the studied a-C:D(Er) matrix.

RT PL at 1 µm was attained via direct incorporation of optically active Yb$^{3+}$ ions in the carbon films. A four-fold enhancement of Yb PL was also demonstrated via deuteration of the a-C host. The film growth temperature was observed to greatly influence the relative deposition rate of the plasma dissociated metalorganic species, and hence the concentration of the rare earth elements. PL was limited by the concentration of Yb within the film, the concentration of Yb ions in the +3 state, and the relative amount of quenching due to the various de-excitation pathways associated with the vibrational modes of the host a-C network. The observed wide full width at half-maximum PL signal is a result of the variety of local bonding environments prevalent in the a-C matrix, and the bonding of the Yb$^{3+}$ ions to O and/or F ions as determined by X-ray photoelectron spectroscopy analyses.

This work constitutes the first comprehensive study of incorporating multiple dopant elements which are optically active in amorphous carbon.
Dedication

To my beloved mom and my dear brother
Acknowledgments

First, I would like to thank my supervisors, Professor Li Qian and Professor Nazir P. Kherani. Over the past four years, Professor Qian and Kherani have motivated, inspired, and guided me to levels of great academic achievement. This thesis would not be possible without their instruction, discussion and support. I also wish to acknowledge the funding support from the Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery grants, the NSERC CREATE program in Nanoscience and Nanotechnology, the Ontario Research Fund – Research Excellence program and the Departments of Electrical and Computer Engineering and Materials Science and Engineering at the University of Toronto.

I would like to express my deepest appreciation to Dr. Keith R. Leong, Dr. Davit Yeghikyan, Dr. Tome Kosteski, Dr. Pratish Mahtani, and Dr. Paul O’Brien. Starting from the first day of my Ph.D. degree pursuit, you have been my closest colleagues in the lab. Thank you for teaching me both the scientific and fundamental hands-on skills. A special thank you to Dr. Keith R. Leong for being my mentor and the closest friend in the APD Labs and for the countless occasions when he provided assistance in repairing/assembling the experimental equipment needed to conduct the research reported herein. More importantly, thank you for planning the research experiments, discussing the results and analyses methods with me to shape my knowledge of the field. I would also like to express my appreciation to Dr. Pratish Mahtani for bringing to bear his support and discussions pertaining to host a-C film deposition and analyses.

To all my colleagues in the APD Group, thank you for your support and friendship over the years. A special thank you to Andrew Flood, Yujin Kim, and Yang Yang for having fun together over a lot of nights, and in particular for being great company during those late nights working in the lab. Also, I would like to express my gratefulness to Joanne Kearney, whose organization, genuine concern and infinite patience have been essential in the success achieved by all members of the APD group.

I would also like to express my gratitude to all the summer internship students who worked with me. Thank you to Michael Halamicek for assisting with the FTIR measurements and analysis, Jerry Wang for performing Ag / Au nanoparticle experiments and obtaining UV-Vis spectra and
SEM micrographs, and Shirley Wu for photoconductance decay measurements and light soaking experiments.

I would like to express my gratitude to Dr. Rana Sodhi for valuable help with XPS and XAES measurements, Dr. I-Ju Teng, Dr. Jenh-Yih Juang and Dr. Sheng-Rui Jian for assisting in photoluminescence characterizations and XPS analyses, Dr. Alberto Tagliaferro for the discussion and valuable comments in this research and for providing suggestions for future work. Further, I would like to express my great appreciation to Prof. J. Stewart Aitchison, Prof. Benjamin D. Hatton and Prof. Giovanni Fanchini for the valued comments and input during the examination of this thesis.

Lastly, I would like to express my deepest and most heartfelt appreciation to my family and friends for providing support and encouragement throughout my Ph.D. degree pursuit. A special thank you to Monica Hsu and Andy Chen for treating me as close family in Toronto.
# Table of Contents

**Contents**

Dedication ............................................................................................................................... iv

Acknowledgments .................................................................................................................. v

Table of Contents ................................................................................................................ v

List of Tables ......................................................................................................................... xi

List of Figures ......................................................................................................................... xii

List of Symbols and Abbreviations ....................................................................................... xvii

1 Introduction ......................................................................................................................... 1

   1.1 Motivation ....................................................................................................................... 1

   1.2 Significance .................................................................................................................... 1

   1.3 State of Art ..................................................................................................................... 2

   1.4 Research Objective ......................................................................................................... 5

   1.5 Structure of Thesis ......................................................................................................... 6

2 Background: Literature Review ......................................................................................... 7

   2.1 Overview ......................................................................................................................... 7

   2.2 Si-Compatible Thin Film Photonic Materials and Methods ........................................ 7

      2.2.1 Si-based Low Dimensional Materials: Porous Si, Si nanocrystals, SOI superlattice ................................................................. 7

      2.2.2 III-V Wafer Bonding, Epitaxial III-V, Strained SiGe ........................................... 8

      2.2.3 Erbium Doped Thin Film Materials and Methods .............................................. 10

      2.2.4 Ytterbium Doped Thin Film Materials and Methods ......................................... 13

2.3 Amorphous Carbon and Hydrogenated Amorphous Carbon ......................................... 15

   2.3.1 Overview ..................................................................................................................... 15

   2.3.2 Microstructure and Role of Hydrogen ...................................................................... 16
2.3.3 Radio-Frequency Plasma-Enhanced Chemical Vapor Deposition (RF-PECVD) System .................................................20
2.3.4 Film Deposition Mechanism..............................................................24
2.3.5 Electronic Structure and Defects ..........................................................25
2.4 Erbium or Ytterbium Incorporated in Carbon Based Host Materials ..........27
  2.4.1 Sputtering and Laser ablation of Erbium Mixed Targets ......................27
  2.4.2 Erbium Metalorganic Complex with PECVD Method .........................28
  2.4.3 Erbium Doped in Polymer .................................................................29
  2.4.4 Ytterbium Doped in Carbon Based Materials ......................................29
2.5 Summary ..............................................................................................30
3 Film Growth and Characterization Techniques ........................................35
  3.1 Overview ..............................................................................................35
  3.2 Film Growth Process Flow ....................................................................35
    3.2.1 Metalorganic RF-Plasma-Enhanced Chemical Vapor Deposition System Design and Assembly ...................................................35
    3.2.2 Incorporating Rare Earth (Erbium or Ytterbium) Metalorganic Compound ..........38
    3.2.3 Deposition Procedure ........................................................................40
  3.3 Characterization Techniques ...............................................................43
    3.3.1 Spectroscopic Ellipsometry .................................................................43
    3.3.2 Fourier Transform Infrared Spectroscopy ..............................................44
    3.3.3 X-Ray Photoelectron and X-ray Excited Auger Electron Spectroscopy ..........47
    3.3.4 Photoluminescence Spectroscopy .........................................................51
3.4 Summary ..............................................................................................53
4 Hydrogenated Amorphous Carbon (a-C:H) in RF-PECVD: Results and Discussion ....54
  4.1 Overview ..............................................................................................54
  4.2 a-C:H Host: Influence of Different Electrodes and Varying RF Power on Film Deposition .........................................................................................................................54
List of Tables

Table 2.1. Categories of amorphous carbon films [103]................................................................. 18

Table 3.1. Vibrational frequencies of various molecular bonds commonly existing in a-C:H films [143].................................................................................................................................................. 46

Table 3.2. The respective properties obtained from the employed characterization tools in this thesis. ........................................................................................................................................................................ 53

Table 5.1. A summary of the energy levels and associated harmonic modes of C–Hₓ, C–Dₓ, O–H, O–D, and C–Fₓ bonds in the solid state. The range of energy levels of the first vibrational modes (υ = 1) of C–Hₓ, C–Dₓ, and C–Fₓ bonds were directly measured by FTIR technique while those for O–H and O–D bonds are taken from references [41, 48]. The higher vibrational modes are inferred from the first respective mode........................................................................................................................................................................ 71

Table 5.2. Ratios of atomic concentrations and relative/absolute atomic concentrations of relevant elements in as-received stoichiometric Er(fod)₃ compound, thermally evaporated (TE) Er(fod)₃, and in seven a-C:D(Er) films deposited under varying conditions as determined from XPS measurements. Table based on one published by Hsu et al. [131]........................................................................................................ 75

Table 6.1. Ratios of atomic concentrations and relative/absolute atomic concentrations of relevant elements in as-received stoichiometric Yb(fod)₃ compound, and in six a-C:D:F(Yb) films deposited under varying conditions as determined from XPS measurements. Table based on one published by Hsu et al. [132]........................................................................................................................................................................ 90
List of Figures

Figure 2.1. Schematic energy level diagram of Er$^{3+}$ as the free ion and as an occluded ion in a solid matrix, respectively. [14] ................................................................. 11

Figure 2.2. (a) Cooperative upconversion process (concentration quenching). (b) Excited-state absorption process. ........................................................................................................ 13

Figure 2.3. $sp^3$, $sp^2$, $sp^1$ bonding hybridizations for a carbon atom [46]. ......................... 17

Figure 2.4. Ternary phase diagram of bonding in amorphous carbon-hydrogen alloys [46]. The abbreviations are defined in Table 2.1. ........................................................................................................ 19

Figure 2.5. Schematic diagram of plasma generation in a conventional capacitively-coupled RF-PECVD. .................................................................................................................. 22

Figure 2.6. Schematic diagram of sheath region formations in a conventional capacitively-coupled RF-PECVD. ........................................................................................................ 23

Figure 2.7. Component processes in the deposition mechanism of a-C:H thin film [46]. ........... 24

Figure 2.8. Schematic density of states of carbon with $\sigma$ and $\pi$ states [46]. .......................... 26

Figure 3.1. Schematic diagram of the RF-PEMOCVD system used for the preparation of rare earth (Er or Yb) metalorganic doped a-C based films. ............................................................. 37

Figure 3.2. Illustration of the rare earth (Er or Yb) metalorganic compound, $X$(fod)$_3$ ($X=$ Er or Yb), with chemical structure $X(C_{10}H_{10}O_2F_7)_3$ ($X=$ Er or Yb). ......................................................... 40

Figure 3.3. Deposition procedure for host a-C-based thin films.............................................. 41

Figure 3.4. Deposition procedure for rare earth (Er or Yb) metalorganic doped a-C based films. ........................................................................................................................................ 42

Figure 3.5. (a) XPS process: measurement of photoelectrons emitted from the core-level due to x-ray absorption. (b) XAES: measurement of secondary photoelectrons emitted from the valence-
level carrying excess energy creating from core-level hole, created in process shown in (a), being filled.

Figure 3.6. Band diagram of relationship between binding energy ($E_{\text{binding}}$), work function of the sample ($\phi_{\text{sample}}$), work function of the spectrometer ($\phi_{\text{spectrometer}}$), Fermi level of the sample ($E_f$), measured kinetic energy of the photoelectron ($E_{\text{kinetic}}$), and the energy of the X-ray photons ($E_{\text{photon}}$). $E'_{\text{kinetic}}$ represents the kinetic energy of photoelectrons emitted from the sample, and $E_{\text{kinetic}}$ represents the kinetic energy of photoelectrons measured on the spectrometer.

Figure 3.7. Auger emission in $sp^3$ hybridized carbon atom.

Figure 3.8. Two potential Auger processes in $sp^2$ hybridized carbon atom that produces emission of electrons with unique kinetic energies.

Figure 3.9. Schematic diagram of Photoluminescence Spectroscopy apparatus.

Figure 4.1. The optical properties ($E_{04}$, $n$, $k$) and deposition rate of a-C:H films grown on the anode (solid line), and cathode (dash line), as a function of the applied RF power. Figure based on one published by Hsu et al. [130]. For clarity of presentation, error bars are not included; the estimated error in each measurement is less than +/- 10% of the measurement.

Figure 4.2. Deconvoluted FTIR spectra in the C-H$_x$ stretching region for a-C:H films grown at an RF power of 60 W on the (a) anode and (b) cathode, respectively. (c) The hydrogen concentration and (d) the C-H$_x$ $sp^2$ bonding concentration as a function of the applied RF power for a-C:H films grown on the anode (solid blue line) and on the cathode (dash black line). Figure based on one published by Hsu et al. [130].

Figure 4.3. The optical bandgap $E_{04}$ and extinction coefficient $k$ at 532 nm of the a-C:H films grown on the anode (solid blue line), and cathode (dash black line), as a function of the % $sp^2$ bonding. Figure based on one published by Hsu et al. [130].

Figure 5.1. Room temperature PL spectrum of a-C:H(Er) with peak centered at 1540 nm and FWHM of ~65 nm. Figure based on one published by Hsu et al. [130].

Figure 5.2. PL intensity comparison between a-C:D(Er: 3.92 at%) and a-C:H(Er: 3.92 at%) films prepared under the deposition condition of 40 W of RF power, 40 sccm of flow rate, 120 mTorr
of deposition pressure, 80 °C of substrate temperature, and 150 °C of evaporation temperature of the Er(fod)_3 powder. Figure based on one published by Hsu et al. [131].

Figure 5.3. The absorption spectra of Er(fod)_3 metalorganic compounds dissolved in d-chloroform solvent.

Figure 5.4. A simplified conceptual diagram illustrating the σ* and σ bands of a-C based host films, the energy levels of π* and π states originating from sp^2 C=C bonds, and Er^{3+} ions within the a-C matrix. Included is a 532 nm pump source whereby Er ions can be excited to 4S_{3/2} level, followed by non-radiative decay to the 4I_{13/2} level, and subsequent photoemission at 1.54 μm through the 4I_{13/2} to 4I_{15/2} transition. Also possible is the participation of localized density of states lying in the gap due to the sp^2 clusters in the host a-C matrix; these states can absorb incident photons and transfer the energy to the high energy- states of Er^{3+}, leading to PL emission around 1.54 µm. The non-radiative transitions are shown with broken arrows.

Figure 5.5. Illustration of energy levels of the vibrational modes for C–H_x, C–D_x, O–H, O–D, and C–F_x bonds in the solid state [151], where the range of each vibrational mode is inferred from FTIR spectra of the host a-C:H, a-C:D, and fluorinated a-C:D films as displayed in Figure 5.6. The grey band here is used to represent the highly varying bonding structure, which reflects the levels associated with the numerous combinations of nearest neighbors and the different local bonding environments. Figure based on one published by Hsu et al. [131].

Figure 5.6. FTIR spectra of the host a-C:H, a-C:D, and a-C:D:F (CF_4/[CF_4+CD_4] = 50 vol.%) films without rare earth (Er or Yb) metalorganic compound incorporation prepared under the same deposition condition except for the precursor gas. The range of the first vibrational mode illustrated in Figure 5.5 is inferred from this data. Figure based on one published by Hsu et al. [132].

Figure 5.7. The absorption spectra of various solvents comprising different combinations of C–H_x, C–D_x, and O–H bonds.

Figure 5.8. (a) The [O]/[Er] ratio (black triangle) and normalized PL peak intensity (blue triangle) as a function of the applied RF power with a substrate temperature of 80 °C. (b) The Er concentration (solid black circle) and normalized PL peak intensity (solid blue circle) as a function of the substrate temperature with an RF power of 60 W. The normalized PL peak intensity is shown.
to depend critically on the (c) \([O]/[Er]\) ratio, and (d) \([Er]\). The lines are guides to the eye. \(I_{nor}\) is defined as the PL intensity peaking at \(\sim 1540\) nm and normalized to the respective a-C(\(Er\)) film thickness indicated in Table 5.2. Figure based on one published by Hsu \textit{et al.} [131].............. 77

Figure 5.9. (a) XPS spectra of the three a-C:D(\(Er\)) films, \(\text{Er(fod)}_3\) film (evaporated in the vacuum chamber with \(\text{CD}_4\) precursor gas flowing without plasma ignition), and the as-received stoichiometric \(\text{Er(fod)}_3\) powder. The curves have been shifted vertically for clarity of presentation. Figure based on one published by Hsu \textit{et al.} [131]................................................................. 80

Figure 5.10. Depth profile of C, F, O, and \(\text{Er}\) concentrations in a-C(\(Er\)) film deposited at 60W of RF power and 80°C as determined from XPS measurements. Figure based on one published by Hsu \textit{et al.} [131]........................................................................................................... 81

Figure 6.1. Comparison of the PL intensity of \(\text{Yb(fod)}_3\) powder dissolved in (a) Chloroform (\(\text{CHCl}_3\)) and Chloroform-d (\(\text{CDCl}_3\)); in (b) Methanol (\(\text{CH}_3\text{OH}\)) and Methanol-d\(_4\) (\(\text{CD}_3\text{OD}\)). (c) Comparison of the PL intensity of a-C:D:F(\(\text{Yb}: 1.6\text{ at\%}\)) and a-C:H:F(\(\text{Yb}: 1.6\text{ at\%}\)) films prepared using RF power of 60 W, precursor gas flow rate of 20 sccm, deposition pressure of 60 mTorr, substrate temperature of 90 °C, and \(\text{Yb(fod)}_3\) powder evaporation temperature of 110 °C. Figure based on one published by Hsu \textit{et al.} [132]........................................................................................................ 85

Figure 6.2. Illustration of energy levels of the vibrational modes for O–H, O–D, C–H\(_x\), and C–D\(_x\) bonds in the solid state, where the range of each vibrational mode is inferred from FTIR spectra of a-C:H, a-C:D and fluorinated a-C:D host films as displayed in Figure 5.6 and summarized in Table 5.1. The grey band here is used to represent the highly varying bonding structure, which reflect the levels associated with the numerous combinations of nearest neighbors and the different local bonding environments. Figure based on one published by Hsu \textit{et al.} [132]......................... 86

Figure 6.3. (a) The \(\text{Yb}\) concentration (solid black circle) and normalized PL peak intensity, \(I_{nor}\), (solid blue circle) as a function of the substrate temperature for films deposited at an RF power of 60 W. The normalized PL peak intensity is shown to depend critically on the (b) \([O]/[Yb]\) ratio; and (c) \([Yb]\). The lines are guides to the eye. \(I_{nor}\) is defined as the total integrated area underneath the 3 deconvoluted peaks and normalized to the respective a-C(\(Yb\)) film thickness indicated in Table 6.1. (d) \(\text{Yb4d XPS spectra of the three a-C:D:F(Yb) films, and TE Yb(fod)}_3\) film (thermally evaporated \(\text{Yb(fod)}_3\) compound in the vacuum chamber with \(\text{CD}_4\) precursor gas flowing without
plasma ignition). The curves have been shifted vertically for clarity of presentation. Figure based on one published by Hsu et al. [132].

Figure 6.4. Deconvoluted XPS (a) C1s and (b) F1s spectra of the a-C:D:F(Yb) film with maximum \( I_{\text{nor}} \) prepared using RF power of 60 W, precursor gas flow rate of 20 sccm, deposition pressure of 60 mTorr, substrate temperature of 80 °C, and Yb(fod)\(_3\) powder evaporated at a temperature of 110 °C, and (c) C1s and (d) F1s spectra of the TE Yb(fod)\(_3\) film. Figure based on one published by Hsu et al. [132].

Figure 6.5. The optical bandgap, \( E_{04} \), of the host a-C:D:F films as a function of the introduced fluorinated precursor gas.

Figure 6.6. The absorption spectra of Yb(fod)\(_3\) metalorganic compounds dissolved in d-chloroform solvent.

Figure 6.7. A simplified conceptual diagram illustrating the \( \sigma^* \) and \( \sigma \) bands of the a-C based host films, the energy levels of \( \pi^* \) and \( \pi \) states originating from \( sp^2 \) C=C bonds, and Yb\(^{3+}\) ions within the a-C matrix. Included is the excitation associated with the 532 nm pump. Participation of the localized density of states lying in the gap due to the \( sp^2 \) clusters in the host a-C matrix lead to the absorption of incident photons and subsequent energy transfer to a higher energy state of Yb\(^{3+}\), and thus leading to PL emission around 1.1 \( \mu \)m. The non-radiative transitions are shown with broken arrows.

Figure 7.1. Simplified conceptual energy diagrams showing the energy transfer between Er and Yb for different pump wavelengths. At 980 nm pumping, Yb absorbs incident photons and transfers the excitation energy to the second excited state of Er, leading to a larger effective absorption cross section. For 532 nm and 488 nm pumping, the light is absorbed by the higher excited states of Er ions. From these higher lying levels, the excitation decays sequentially to the lower lying states and the branching is affected by energy transfer from the second excited state of Er to the Yb ions. The non-radiative relaxing transitions are shown with broken arrows.
List of Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$%_{sp^2}$ bonding</td>
<td>percent of sp$^2$-hydridized carbon atoms</td>
</tr>
<tr>
<td>[Er]</td>
<td>Er concentration</td>
</tr>
<tr>
<td>[Yb]</td>
<td>Yb concentration</td>
</tr>
<tr>
<td>a-C</td>
<td>amorphous carbon</td>
</tr>
<tr>
<td>a-C:H</td>
<td>hydrogenated amorphous carbon</td>
</tr>
<tr>
<td>A-RF</td>
<td>a-C:H films grown on the top grounded electrode (anode)</td>
</tr>
<tr>
<td>at%</td>
<td>atomic percent</td>
</tr>
<tr>
<td>BEOL</td>
<td>back end-of-line</td>
</tr>
<tr>
<td>CD$_4$</td>
<td>deuterated methane gas</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>methane gas</td>
</tr>
<tr>
<td>C-H$_x$</td>
<td>hydrocarbon molecule</td>
</tr>
<tr>
<td>CMOS</td>
<td>complementary metal-oxide-semiconductor</td>
</tr>
<tr>
<td>C-RF</td>
<td>a-C:H films grown on the bottom powered electrode (cathode)</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>CW</td>
<td>continuous wave</td>
</tr>
<tr>
<td>DC</td>
<td>direct-current</td>
</tr>
<tr>
<td>$E_{04}$ gap</td>
<td>photon energy at which the absorption coefficient reaches $10^4$ cm$^{-1}$</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
</tr>
<tr>
<td>Er</td>
<td>Erbium</td>
</tr>
<tr>
<td>ESA</td>
<td>excited-state absorption</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half-maximum</td>
</tr>
<tr>
<td>GaAs</td>
<td>gallium arsenide</td>
</tr>
<tr>
<td>Ge</td>
<td>Germanium</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Term</td>
</tr>
<tr>
<td>--------------</td>
<td>------</td>
</tr>
<tr>
<td>ICs</td>
<td>integrated circuits</td>
</tr>
<tr>
<td>InP</td>
<td>indium phosphide</td>
</tr>
<tr>
<td>$k$</td>
<td>extinction coefficient</td>
</tr>
<tr>
<td>LED</td>
<td>light-emitting devices</td>
</tr>
<tr>
<td>LPCVD</td>
<td>low pressure chemical vapor deposition</td>
</tr>
<tr>
<td>LPE</td>
<td>liquid phase epitaxial</td>
</tr>
<tr>
<td>MW</td>
<td>microwave</td>
</tr>
<tr>
<td>$n$</td>
<td>refractive index</td>
</tr>
<tr>
<td>nc-Si</td>
<td>nanocrystalline Si</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>PLD</td>
<td>pulsed laser ablation</td>
</tr>
<tr>
<td>RF-PECVD</td>
<td>radio frequency plasma enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>RF-PEMOCVD</td>
<td>radio frequency plasma enhanced metalorganic chemical vapor deposition</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SOI</td>
<td>Si-on-insulator</td>
</tr>
<tr>
<td>XAES</td>
<td>X-ray excited auger electron spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>YAG</td>
<td>$Y_3Al_5O_{12}$</td>
</tr>
<tr>
<td>Yb</td>
<td>Ytterbium</td>
</tr>
<tr>
<td>Yb:YAG</td>
<td>Ytterbium doped in $Y_3Al_5O_{12}$</td>
</tr>
<tr>
<td>YSO</td>
<td>$Y_2SiO_5$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>absorption coefficient</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
</tr>
<tr>
<td>$\nu$</td>
<td>wavenumber</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Motivation

Effective integration of optical-photonic technologies with microelectronic devices is essential in the quest to overcome the speed bottlenecks associated with the ever shrinking device length scale [1]. The optical interconnect is able to transfer and process data at rates that are orders of magnitude higher than traditional electronic technologies, both within the silicon (Si) chip and in chip-to-chip communication. In order to completely avail optical technologies, it is imperative to develop silicon compatible materials that enable light generation, guiding, switching, detection, modulation and amplification. High-speed photonic devices have been widely employed using III-V semiconductor-based materials, such as gallium arsenide (GaAs), indium phosphide (InP), and related compounds. However, the fabrication techniques for these materials are deemed less than ideal and incompatible with conventional Si-based integrated circuits (ICs) fabrication technologies [2, 3]. Notably, high lattice mismatches of 4.1% and 8.1%, and thermal expansion coefficient mismatches of 120.4 % and 76.9%, appear in GaAs and InP compared to Si substrate, respectively [4]. Moreover, given the inherent indirect bandgap characteristic of crystalline Si, it does not readily emit or amplify light, which exacerbates the integration of electronic and optical communication devices on a single Si chip. This issue is likely to become more acute in the near future as the information technology industry shifts to optical interconnects for board-to-board and chip-to-chip communication [1]. As a result, to realize the co-existence of electrical and optical functions on the same Si chip platform, it is essential to investigate and develop Si compatible photonic materials. Further, materials processing temperature of less than 400 °C is highly desirable [5] as this would meet the Si back end-of-line (BEOL) requirements in current Si IC fabrication technology.

1.2 Significance

Imagine what we could possibly achieve if 1,000 or even 10,000 photonic devices were integrated together on an existing Si chip platform; such chips would give us the ability to download an entire week’s worth of video footage in seconds, or allow entire music and photograph collections to be transferred from your computer to another mobile phone device simply by connecting a fiber or by direct wireless transfer between the two. In order to make this
a reality, advances in Si photonics have been driven not only by the need to develop more complex, higher functionality and lower cost photonics integrated circuits, but also by the constraints of pin count and communication power wherein developing new light emitting materials with the advantages of simple and controllable CMOS-compatible processing is particularly essential. We can in principle combine both technologies, silicon processing and lasers, on a single Si chip to benefit the society at large.

1.3 State of Art

A number of different photonic materials and fabrication techniques to implement such photonic materials on the Si platform have been researched, including Si-based nanostructure growth, direct epitaxial III-V-based film growth, rare earth elements doped in various thin film hosts, and III-V wafer bonding technique.

Crystalline Si is not readily amenable to light emission due to its inherent indirect bandgap characteristic. It has been shown that photoluminescence (PL) can be achieved through the creation of nanostructures and amorphous forms of crystalline Si. For instance, Si nanocrystals embedded in a silicon-rich SiO$_2$ matrix has been demonstrated to exhibit room temperature PL at visible wavelengths. However, high temperature annealing (> 1000 °C) under N$_2$ environment is required as it is critical to inducing phase separation/crystallization of Si nanocrystals [6-9]. Although the presented growth methods of SiO$_2$ matrix are compatible with CMOS processing, the subsequent necessary annealing step is incompatible with BEOL processing.

Directly growing InP, GaAs, and Ge based epitaxial lasing materials on Si substrates is another approach. However, a two-step growth in an ultrahigh vacuum chemical vapor deposition (CVD) system along with high temperature (> 850 °C) thermal cleaning of Si or Si-on-insulator (SOI) substrate [10, 11] is normally needed to achieve high quality epitaxial layer on Si as well as to eliminate the dangling bonds, followed by a high temperature (> 600 °C) growth process, and a post-growth high temperature annealing (> 750 °C) step to reduce the dislocation density [12] -processes which are costly and incompatible with the existing CMOS BEOL processes.

Doping rare earth elements in various thin film hosts is another promising approach. In particular, implanting erbium (Er) ions in a variety of Si-based [13-15], silica-based [14, 16], and ceramic [14] thin film hosts has been a leading approach in the effort to efficiently produce photons
from Si since standard CMOS-compatible ion-implantation techniques can be deployed. Also, excited Er\(^{3+}\) ions emit at 1.5 \(\mu\)m, which is a strategic wavelength for telecommunications. However, PL is severely quenched at room temperature in crystalline Si based hosts [17, 18]. As well, in order to reduce Er precipitation and increase the fraction of active Er\(^{3+}\) ions, co-implantation of additional O atoms is highly preferred [19]. For silica-based and ceramic thin film hosts, high processing and high post-annealing temperatures (> 700 °C) are required to grow good quality material and further to eliminate the ion implantation-induced damage, so as to optically activate the Er\(^{3+}\) ions and/or to enhance photoluminescence lifetime or quantum efficiency. However, these high temperature post-deposition annealing processes are incompatible with Si BEOL fabrication processes.

The ideal optical wavelength for applications on a Si chip and in chip-to-chip communications has not been determined. Yb has a long luminescence lifetime [20] (up to 1 ms), and a relatively large emission cross section, leading to a higher pumping efficiency [21] compared to Nd based solid lasers. Incorporation of Yb into ceramic-based (YAG [22-24], Y\(_2\)SiO\(_5\) (YSO) [25-27], KY(WO\(_4\))\(_2\) [28], NaLu(WO\(_4\))\(_2\) [29], and Al\(_2\)O\(_3\) [30, 31]) wide bandgap semiconductors, oxide-based semiconductors (ZnO [32-34], TiO\(_2\) [35, 36], In\(_2\)O\(_3\) [37]), III–V group based materials (AlN [38]), and Si-based [39] thin film hosts using various deposition techniques, has been shown to produce luminescence of peak wavelength of around 1 \(\mu\)m. For Yb doped ceramic based materials, liquid phase epitaxial growth (LPE) method with post-deposition annealing temperatures as high as 900–1300 °C to fabricate homogeneous crystalline films has been employed, albeit it is not compatible with current Si-based IC fabrication technology.

Lower substrate growth temperature (< 300 °C) via pulsed laser ablation and magnetron sputtering of Yb containing targets has been employed to deposit Yb-doped films and crystalline Yb\(_2\)O\(_3\) film [40] on Si-based and/or sapphire substrates. The disadvantage of the techniques with lower growth temperatures is that the concentration of the Yb (or Er) and the properties of the host material cannot be independently controlled. A high temperature (> 600 °C) post-deposition annealing step is always required to promote the formation of optically active Yb\(^{3+}\) (or Er\(^{3+}\)) ions and to enhance the PL efficiency, which is not amenable with current Si BEOL fabrication technology.
In addition to directly growing or depositing thin films on Si substrates, various techniques of integration of direct bandgap III-V epitaxial layer on top of SOI wafers [41-44] have been extensively investigated to produce light from Si wafers. However, most of the wafer bonding techniques are still rather involved with slow, complicated and costly multi-steps with little flexibility for ultimate laser design compared to directly growing the film on Si substrates. Accordingly, it is imperative to investigate and explore potential alternative Si compatible photonic materials that can overcome the challenges posed by the current cadre of materials.

Hydrogenated amorphous carbon (a-C:H) films can be grown at low temperatures by a variety of methods including PECVD, an approach which is compatible with current CMOS fabrication technology [45]. Additionally, a-C based films possess a number of outstanding properties such as high chemical inertness, mechanical hardness, and transparency in the infrared [45, 46]. These unique and versatile properties provide an impetus to utilize PECVD-grown a-C:H films for specific passive optoelectronic applications [45]. It has been demonstrated that it is possible to prepare carbon based planar waveguides with an attenuation of less than 1 dB/cm at wavelength of 633 nm [47]. Having low optical losses in photonic materials is one of the most important prerequisites for employing a given material in integrated optics. However, Er [48-52] or Yb [53-56] doping in carbon based hosts for active photonic device applications has received minimal attention.

The first demonstration of room temperature PL at 1.54 μm in a-C:H(Er) thin films was published in 2002 [48]. a-C:H(Er) films were deposited by magnetron sputtering technique. The Er concentration in a-C:H(Er) films was varied from 0.15 at% to 1.2 at%. However, the PL intensity was relatively low. This was caused by non-radiative relaxation pathways provided by C-H vibrational modes [51] and low optical bandgap. In this technique, in order to achieve high Er concentration, high Ar ion energy and flux are required. However, this causes a high concentration of sp² carbon and a low optical bandgap.

The incorporation of Er into a carbon layer by radio frequency PECVD (RF-PECVD) was demonstrated by Prajzlera et al. [50] in 2003, however, no PL spectra was reported. In 2009, a-C:H(Er) and a-C:D(Er) films were grown via in situ thermal evaporation of tris(2,2,6,6-tetramethyl-3-5 heptanedionato) erbium(+III), or simply Er(tmhd)₃, compound in a DC saddle-field PECVD system. However, the relative PL intensity from a-C:H(Er) was at least 10 times
lower than from a-C:D(Er), attributed to the optical quenching from the highly abundant C-H bonds. Also, a-C:H films have been deployed as a host for co-doping of Er and Yb. However, the attempted PL enhancement of Er via Yb sensitization was not attained for samples prepared by sputtering of a hybrid Er/Yb/carbon target [56].

It is the potential of carbon-based photoluminescence that motivates us to specifically explore Er or Yb doped carbon-based materials and in particular to develop the corresponding deposition techniques and processes whereby synthesis temperatures are below 400 °C so as to be compatible with Si BEOL fabrication processes.

1.4 Research Objective

The primary objective of this thesis is to systematically explore and develop the synthesis of novel rare-earth doped amorphous carbon based photonic materials using radio frequency plasma-enhanced metalorganic chemical vapor deposition (RF-PEMOCVD) technique.

Specifically, the optical properties of intrinsic amorphous carbon (a-C) based materials are investigated and analyzed with respect to their corresponding microstructural and local binding features in relation to a range of deposition conditions in the radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) system - prior to performing rare earth (Er or Yb) metalorganic doping of a-C thin films. Thereafter, the feasibility of in situ growth of Er/Yb metalorganic doped amorphous carbon based (a-C(Er or Yb)) thin films on Si substrates at low temperature (< 200 °C) by simple occlusion of a metalorganic compound in a radio frequency plasma-enhanced chemical vapor deposition (RF-PEMOCVD) system is explored. The properties of the a-C host film and the concentration of the incorporated Er/ Yb are independently controlled. The enhancement of room temperature photoluminescence by substitution of O–H and C–Hx bonds with O–D and C–Dx bonds via deuteration of the a-C host is probed and analyzed in detail. The effect of processing conditions on the photoluminescence of a-C(Er or Yb) films is investigated and correlated to film microstructure and bonding environment. The change in the optical properties of the a-C host upon incorporation of fluorinated Er /Yb metalorganic compound is also discussed.
1.5 **Structure of Thesis**

The structure of the thesis is as follows. Chapter 2 provides background on Si-compatible thin film photonic materials and their respective growth methods, fundamental a-C film properties, and Er and Yb doped carbon based materials and their deposition methods. Chapter 3 presents the experimental process flow, the film growth systems, the employed precursor gases, the selected metalorganic compounds, and the characterization techniques employed. Chapter 4 presents the characterization of a-C host films and explores the appropriate growth condition of a-C host amenable to subsequent rare earth metalorganic compound incorporation. Chapter 5 investigates the feasibility of *in situ* growth of Er-doped a-C based thin films (a-C(Er)) using the RF-PEMOCVD system. Also, the effect of RF power and substrate temperature on the photoluminescence of a-C(Er) films is systematically investigated in order to obtain optimized PL with the current growth method. The respective PL is also correlated to the film structure and concentration of the incorporated Er. In Chapter 6, the synthesis of a-C(Yb) films is presented and the effect of the substrate temperature on photoluminescence of a-C(Yb) films is investigated and correlated to film microstructure and bonding environment. The change in the optical properties of the a-C host upon incorporation of fluorinated Yb metalorganic compound is also discussed. In Chapters 5 and 6, the enhancement of photoluminescence by substitution of O–H and C–H₅ bonds with O–D and C–D₅ bonds via deuteration of the a-C host is probed and discussed in detail. The rare earth doped amorphous carbon (a-C(X), X= Er or Yb) films explored in Chapters 5 and 6 have the potential of being utilized for light amplifier applications. Chapter 7 presents the conclusions of this research; specifically, key results emerging from this study are presented and follow-up research activities are discussed.
2 Background: Literature Review

2.1 Overview

In this chapter, scientific background is provided on the key concepts pertaining to that exploration in this thesis. This includes background on Si-compatible thin film photonic materials and their growth methods, on material properties of a-C films and associated fundamentals and growth mechanism, and on Er and Yb doped amorphous carbon based materials and their deposition methods. This chapter provides a framework which forms the basis for the experimental methods, described in Chapter 3, and results, discussed in Chapters 4 to 6, that follow.

2.2 Si-Compatible Thin Film Photonic Materials and Methods

2.2.1 Si-based Low Dimensional Materials: Porous Si, Si nanocrystals, SOI superlattice

Crystalline Si is not readily amenable to light emission due to its inherent indirect bandgap characteristic. Through the creation of nanostructured or amorphous forms of the crystalline materials, it is possible to relax traditional phonon-selection rules in indirect-gap crystalline materials as a result of breaking the crystal-symmetry. Consequently, the optical transitions in these nanostructured or amorphous materials occur with a certain degree of assistance from incoherent phonons, and the trend of the optical absorption coefficient has been shown to be a function of the photon energy [57]. A number of low-dimensional Si materials, including porous Si [58, 59], Si nanocrystal [9], Si-on-insulator (SOI) superlattices [60], photonic crystal like nanopatterns [61], and Si nanopillars [62], have been reported to show light-emitting properties, leading to potentially a path for Si-based photonic integrated circuits. Porous Si can be produced by electrochemical etching of crystalline silicon wafers, and room temperature photoluminescence at visible wavelengths was first observed in 1990 [63, 64]. However, highly porous Si materials are very fragile and generally are not able to resist subsequent standard CMOS fabrication steps. Thus Si nanocrystals or nanocrystalline Si (nc-Si) embedded in a silicon-rich SiO₂ matrix have been proposed as an alternative. These materials have been observed to generate room temperature photoluminescence at visible wavelengths [9]. The origin of photoluminescence in Si nanocrystals and/or porous Si arises from transitions between highly localized defects states at the Si/SiO₂
interface due to the lattice mismatch [65-67], quantum confinement of excitons of Si nanocrystals [68-70], and the localized states of amorphous Si clusters. These defects were probed to be the dominant source of light based on measurements under high magnetic fields [6]. Hydrogen passivation of the sample reduces defects, and the resulting photoluminescence can be ascribed to confined quantum states. However, the subsequent ultraviolet illumination may reintroduce the defects, leading to interface defect-dominant photoluminescence processes [6]. Furthermore, the photoluminescence is highly dependent on the Si nanocrystal size, density and surface chemistry [8, 65-67, 71]. Higher interface state density, in particular Si=O bonds, can be obtained as the size of Si nanocrystals becomes larger, making the interface state recombination process more beneficial than the quantum confinement process [71]. In order to attain the desirable photoluminescence, high temperature annealing (> 1000 °C) under N₂ environment is required and is crucial to induce phase separation / crystallization of Si nanocrystals [6-9]. Although a silicon-rich SiO₂ matrix can be synthesized via sputtering of Si rich oxides, Si ion implantation into high quality oxides, reactive evaporation of Si rich oxides, or chemical vapor deposition (CVD) deposition of sub-stoichiometric oxide films which are all compatible with CMOS processing, the unavoidable and necessary activating annealing step is incompatible with BEOL processing.

2.2.2 III-V Wafer Bonding, Epitaxial III-V, Strained SiGe

Integration of direct bandgap III-V epitaxial layer on top of the SOI wafers via flip-chip bonding [44] and semiconductor wafer bonding (adhesive semiconductor wafer bonding [41], molecular wafer bonding [42], and die-to-wafer bonding [43]) techniques has been also extensively investigated in an effort to produce light from Si wafers. For flip-chip integration, individual laser diode dies are flip-chipped on and coupled to an SOI waveguide circuit. As individual dies need to be accurately aligned and placed on the surface, the process is slow and costly. Also, the integration density is limited by the pitch and size of the bumps (physical undulations at the wafer surface). Semiconductor wafer bonding allows integration of high-quality III-V epitaxial layers on top of a Si platform by transferring the III-V layer stack from its original growth substrate to the SOI wafer. To decrease the cost of the integration process, a die-to-wafer bonding method was proposed in which unprocessed III-V dies are bonded, epitaxial layer are stripped, to the processed SOI wafer. This reduces the material consumption since III-V materials are only bonded when they are needed, and reduces the time required to complete the integration process compared with a flip-chip process. The drawback of this approach compared with a flip-
chip process is that good electrical and thermal interfaces are not directly established. The adhesive semiconductor wafer bonding employs the thermosetting polymer divinylsiloxyane-benzocyclobutene as a bonding agent. In the molecular wafer bonding approach, the processed SOI wafer surface is coated with a SiO₂ cladding layer and planarization is achieved by chemical mechanical polishing. Subsequently, the III-V epitaxial layer structure is coated with SiO₂. However, most of the wafer bonding techniques are still quite comprising slow, complicated and costly multiple steps with less flexibility for laser design compared to directly grown films on the Si substrate.

Another approach to obtain direct-bandgap lasing materials on indirect bandgap Si substrates is heteroepitaxial growth, in which epitaxial III-V materials are directly grown on Si substrates [4]. A number of methods, including the use of interfacial strained layers, superlattice buffer layers, low-temperature substrates, defect passivation, and growth on patterned substrates, have been introduced to reduce the dislocation density between the epitaxial III-V semiconductor, GaAs and InP, and the Si wafer from 10⁸ -10¹⁰ cm⁻² to 10² - 10⁶ cm⁻² [4]. However, it is still two orders of magnitude higher than in InP- or GaAs-based epitaxial wafers for room temperature continuous wave (CW) lasers. In addition, epitaxial growth of Ge on Si (or SiGe on Si) material system has been demonstrated for key photonic components, including p-i-n [72] and avalanche photodetectors [73] and modulators [74, 75]. Their performance is comparable with their III-V counterparts in certain aspects. Although Ge has an indirect bandgap of 0.664 eV, its direct bandgap of 0.8 eV, measured from the top of the valence band to the momentum-aligned Γ valley in the conduction band is able to be significantly reduced by the mismatching lattice constant and thermal expansion coefficient between <111> Ge and the Si wafer [12]. Applying an adequate thermal tensile strain of 0.2 – 0.25 % in Ge after growth on Si substrate reduces the energy difference between Γ and L valleys to 115 meV and simultaneously raises the light-hole band. This effectively increases the probability of radiative recombination between the Γ valley and the valence band [76]. Moreover, with the assistance of heavy n-type doping in Ge, the energy difference between the direct and the indirect bandgap of Ge can be compensated by filling electrons into the L valley, achieving light emission [12, 76, 77]. Nevertheless, in order to achieve high quality epitaxial layer on Si, a two-step growth is normally applied in an ultrahigh vacuum CVD system along with high temperature (> 850 °C) thermal cleaning of Si or SOI substrate [10, 11] needed to carry out to eliminate the dangling bonds, followed by high temperature (> 600 °C)
growth, and post-growth high temperature annealing (> 750 °C) to reduce the dislocation density [12] - processes which are costly and incompatible with the existing CMOS BEOL process.

2.2.3 Erbium Doped Thin Film Materials and Methods

2.2.3.1 Trivalent Erbium Ion

Erbium (Er), a rare earth element with atomic number of 68 belonging to the group of Lanthanides, has played an important role in the development of optical communication technology owing to their intra-4f emission at around 1.5 µm, wavelength at which the silica fibers exhibit minimum absorption loss. Trivalent erbium ion (Er$^{3+}$) exhibits an incomplete 4f electronic shell, which is shielded by the outer closed 5s and 5p shell. Therefore, these 4f sub-shells are weakly dependent on the host materials of Er$^{3+}$ dopants, and sharp optical intra-4f transitions can be achieved. Figure 2.1 shows the energy level diagram for Er$^{3+}$ in the solid, where Stark-splitting of Er manifolds is due to the electric field of the host material, leading to the emission band broadening. Er$^{3+}$ ions can be excited through optically or electrically generated charge carriers, and the generated carriers rapidly relax to the first excited state via multi-phonon emission with lifetimes in the nanosecond range. On the other hand, the radiative lifetime of the first excited state is in the millisecond range, depending on the host material, and the transition occurring from the first excited state to the ground state is around 0.8 eV, large compared to other upper state-transitions. Accordingly, photon emission corresponding to a wavelength of 1.54 µm is highly likely. Once the population inversion condition is created in the first excited $^4I_{13/2}$ state, trivalent Er$^{3+}$ ion is able to emit photons around the 1.5 µm wavelength range, followed by stimulated emission from $^4I_{13/2}$ to $^4I_{15/2}$ in the 4f orbital, as seen in Figure 2.1 [14], thus serving to amplify a high frequency telecommunication signal. Optical amplifiers are essential to compensate for the losses in processing and transferring of signals while maintaining high bandwidth and low crosstalk.

In additions to its telecommunication applications, Er has attracted great interest because of its ability to be incorporated into various thin film host materials in order to fabricate planar optical amplifiers or lasers. These can be integrated with other devices on the same Si chip for optoelectronic device applications. Compared to low dimensional Si and epitaxial materials described in Section 2.2.1 and 2.2.2, Er doped thin films exhibit potential advantages of low-cost and simple processing capability. Accordingly, for the next generation of data processing
technologies it is logical and desirable to employ the effective luminescence characteristics of Er and further develop CMOS BEOL-compatible hybrid optoelectronic integrated circuits - which can be directly connected to the fiber optic network and perform the functions of guiding, splitting, switching, wavelength multiplexing, and amplification of light on a single Si chip.

![Figure 2.1. Schematic energy level diagram of Er\textsuperscript{3+} as the free ion and as an occluded ion in a solid matrix, respectively.][14]

2.2.3.2 Erbium Incorporated Thin Film Hosts and Methods

Ion implantation of light-emitting impurities, such as Er, into a variety of silica-based [14, 16], ceramic [14], and Si-based [13, 14] thin film hosts, has been a leading technique available to the scientific community to produce photons from Si. The advantage of this approach is that standard Si technology can be deployed to introduce Er as a dopant. Moreover, Er doped Si / SiO\textsubscript{2} [78-83], ZnO [84, 85], TiO\textsubscript{2} [86], II-V [87, 88] based thin films have successfully served as active materials for light-emitting devices (LED) with 1.5 \textmu m emission. However, high processing temperatures are required to grow silica-based (SiO\textsubscript{2}, phosphosilicate, borosilicate) and ceramic based (Al\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, LiNbO\textsubscript{3}) thin film hosts. These are incompatible with Si BEOL fabrication
processes. Also, high temperature (> 700°C) post-deposition annealing processing is necessary to eliminate the ion implantation-induced damage, to optically activate the Er$^{3+}$ ions, and to enhance the photoluminescence lifetime or quantum efficiency [14]. However, in many cases, high temperature annealing is not sufficient to remove the defects. For instance, ion implantation-induced defects still exist in high Er fluence implanted borosilicate glass [89]. Despite subjecting the samples to a post-deposition annealing step, additional quenching sites coupled to O-H bonds are created. For crystalline Si based hosts, photoluminescence is severely quenched at room temperature as a result of the strong non-radiative processes that compete with the radiative Er de-excitation transitions. Co-implantation of additional O atoms (highly preferred) reduces the Er segregation/precipitation by forming Er-O complexes, and increases the fraction of active Er$^{3+}$ ions. To overcome the quenching issue, a SiO$_2$ matrix containing Er-doped Si nanocrystals has been applied. The Si nanocrystals act as efficient sensitizers, which is attributed to an effective Er excitation cross section that is more than two orders of magnitude larger than the Er resonant absorption of a photon [90]. However, high temperature post-deposition annealing processing is inevitable in order to form Si nanocrystals inside a SiO$_2$ matrix. High Er concentration and lower temperature quenching can be achieved in hydrogenated amorphous Si (a-Si:H) and/or porous Si. This is achieved by using low-temperature processing methods, such as low-pressure chemical vapor deposition (LPCVD) or plasma-enhanced chemical vapor deposition, both of which are Si BEOL compatible. Nevertheless, high temperature post-deposition annealing is required in order to observe photoluminescence in Er doped a-S:H and/or porous Si films [14].

### 2.2.3.3 Photoluminescence Quenching for Erbium ions

For the Er$^{3+}$ optically active centers, there are two major photoluminescence quenching factors, and, specifically, concentration quenching and excited-state absorption (ESA) as described in Figure 2.2. These limit photoluminescence performance and subsequent optical amplification of the device. The Er transitional cross sections are relatively small (typically 10$^{-20}$ – 10$^{-21}$ cm$^2$). Accordingly, high Er concentration (0.1 - 1 at%) is required to achieve a certain degree of population inversion. However, at high Er concentration the average distance between Er ions is small, leading to cooperative upconversion effect, in which two excited Er$^{3+}$ ions exchange energy through a dipole-dipole interaction, causing one Er$^{3+}$ ion to de-excite to the ground state non-radiatively and a nearby Er$^{3+}$ ion to transit upward to the higher $^4$I$_{9/2}$ state as seen in Figure 2.2(a). The upconversion process is then likely to repeat by a resonant interaction between Er ions,
resulting in energy migration through the host until a quenching center is encountered, where the energy is dissipated non-radiatively [14, 89, 91]. Consequently, the degree of Er$^{3+}$ population in the first excited $^4I_{13/2}$ state is significantly reduced at a given pumping power.

![Figure 2.2](image)

**Figure 2.2.** (a) Cooperative upconversion process (concentration quenching). (b) Excited-state absorption process.

Excited-state absorption often occurs at high pump power and becomes significant when the higher-lying states have appreciable lifetimes, leading to the population buildup in the higher excited states. This prevents photon emission between the first excited and ground state, resulting in no contribution to the optical gain. For example, an Er$^{3+}$ can be excited from $^4I_{13/2}$ state up to $^4I_{9/2}$ state by a $\sim$1.5 μm incident photon as seen in Figure 2.2(b). ESA process becomes important when high pump power is required to compensate the concentration quenching effect. Both processes limit the amplification performance. The strength of both processes determines the optimum Er concentration, maximum gain and the required pump power. Thus, Er$^{3+}$ concentration optimization and related photoluminescence quenching studies are imperative for the development of any new class of host material.

### 2.2.4 Ytterbium Doped Thin Film Materials and Methods

Er-implanted in Si, SiO$_2$, and ceramic based host thin films [14, 92] has been shown to efficiently produce photons from Er$^{3+}$ ions at 1.5 μm, a strategic wavelength for telecommunications. Nevertheless, the ideal optical wavelength for applications on a Si chip and in chip-to-chip communications has not been determined. In order to completely avail optical technologies, it is essential to explore each alternative Si compatible photonic material. Further,
the techniques of synthesize these materials need to be compatible with current Si IC fabrication technology. Moreover, it is desirable to develop material growth processes at temperatures below 400 °C in order to meet the Si BEOL requirements [5].

Ytterbium (Yb) doped yttrium-aluminum garnet $Y_3Al_5O_{12}$ (YAG) single crystals have appeared as a promising competitor to the traditional neodymium (Nd) based solid laser for high power diode pumped waveguides [93] and thin-disk lasers [94]. Yb exhibits a simple electronic structure with two manifold levels, a $^2F_{7/2}$ ground state and a $^2F_{5/2}$ excited state. It has been demonstrated that Yb:YAG lasers lack excited-state absorption, or up-conversion effect owing to a cross-relaxation between the active Yb$^{3+}$ ions [95]. Also, Yb doping concentration can be high due to the enhanced probability of Yb$^{3+}$ substitution of Y$^{3+}$ ions in YAG single crystals [96]. Moreover, Yb has a long luminescence lifetime [20] (up to 1 ms), and a relatively large emission cross section which results in a higher pumping efficiency [21] compared to Nd based solid lasers. However, Yb:YAG single crystals grown via the Czochralski technique possess an inhomogeneous distribution of the active impurities. In particular, the Czochralski technique is not suitable for the fabrication of planar thin film optoelectronic devices integrated on a Si chip platform without convoluted multi-wafer bonding schemes.

Incorporation of Yb into ceramic-based (YAG [22-24], $Y_2SiO_5$ (YSO) [25-27], KY(WO$_4$)$_2$ [28], NaLu(WO$_4$)$_2$ [29], and Al$_2$O$_3$ [30, 31]) wide bandgap semiconductors, oxide-based semiconductors (ZnO [32-34], TiO$_2$ [35, 36], In$_2$O$_3$ [37]), III-V group based materials (AlN [38]), and Si-based [39] thin film hosts using various deposition techniques, have been shown to produce luminescence at a wavelength of around 1 μm. For Yb doped YAG [22], YSO [25, 26], and KY(WO$_4$)$_2$ [28] thin films, the liquid phase epitaxial (LPE) method has been employed to fabricate homogeneous crystalline films from a molten solute diluted in a solvent. Their growth and post-deposition annealing temperatures are as high as 900-1300 °C so as to avoid growth defects and to further improve the film quality [22, 25, 26]. In addition, a flat oriented YAG and/or YSO single crystalline substrate is needed as seeds in the LPE method, since growth of the single crystal film is performed by dipping the substrate in a supersaturated melt solution [97]. Consequently, the LPE processing method is not compatible with current Si-based IC fabrication technology.

Lower substrate temperature growth (< 300 °C) of amorphous or polycrystalline/crystalline Yb-doped films (i.e., YAG [24], $Y_2O_3$ [98], Al$_2$O$_3$ [30, 31], CoSb$_3$ [99], ZnO
ITO [100], AlN [38], and Si-based [39] hosts) and crystalline Yb$_2$O$_3$ film [40] on Si-based and/or sapphire substrates was achieved via pulsed laser ablation (PLD) [24, 30, 31, 39, 40, 98, 99] and magnetron sputtering [34, 38, 100] of Yb containing targets. While it is highly desirable to directly employ Si as the host in optoelectronic devices, the bulk crystalline Si bandgap energy is not large enough to activate Yb luminescence. Thus, nanocrystalline silicon (nc-Si) hosts have been applied to act as an efficient sensitizer to transfer photo-induced carriers from the host to the Yb$^{3+}$ ions. Photoluminescence has been obtained at temperatures ranging from approximately 20 K to 300 K in Yb doped nc-Si films fabricated by ablating a Si:Yb$_2$O$_3$ mixture target [39]. Moreover, co-doping with O$_2$ was highly preferred during the ablation to enhance PL efficiency. Enhancement was achieved through the formation of Yb-O bonds and the reduction in Yb segregation. For PLD grown Yb$_2$O$_3$ films, room temperature PL was not observed [40]. This was attributed to high Yb concentrations, leading to fast energy migration from one Yb site to another and non-radiative de-excitation. Despite the achievement of lower growth temperatures, the concentration of Yb and the properties of the host material cannot be independently controlled with pulsed laser ablation and magnetron sputtering techniques. Also, multiple targets with varying Yb composition would be required to obtain different concentrations of Yb-doped films. In addition, a high temperature (> 600 °C) post-deposition annealing step is always required to promote the formation of optically active Yb$^{3+}$ ions and to enhance the PL efficiency. This post-deposition annealing step is not amenable with current Si BEOL fabrication technology. Therefore, this motivates us to develop new Yb doped host materials which are Si BEOL compatible and can be processed at temperatures below 400 °C.

2.3 Amorphous Carbon and Hydrogenated Amorphous Carbon

2.3.1 Overview

Hydrogenated amorphous carbon (a-C:H) films, for example grown by a low-temperature PECVD method, exhibit compatible processing parameters with current CMOS fabrication technology [45]. This methodology facilitates integration and allows for reproducible, low-cost films. In addition, a-C based films possess a number of outstanding properties such as high chemical inertness, mechanical hardness, biocompatibility [101], and transparency in the infrared [45, 46]. Due to their excellent tribological properties, a-C:H films are widely used as protective
coatings for hard disks and magnetic media, machine parts, optical windows and fibers, and other surfaces [102]. Specific properties of a-C:H films can be tailored over a wide range by adjusting the amount of $sp^3$ and $sp^2$ hybridized carbon and the incorporated hydrogen content in the film via various deposition parameters and methods [46]. In particular, a-C films provide the following desirable properties: (i) the refractive index, $n$, can be tuned from 1.5 to 2.8 [45] and the absorption coefficient $\alpha$ can be tailored along with $n$, providing flexibility in optical waveguide design and mode confinement; (ii) the optical bandgap can be varied from 0 to 5 eV from hydrogenated graphite-like a-C (GAC:H) to hydrogenated polymer-like a-C (PAC:H) [46, 103], where the wide bandgap allows the metalorganic compound doping for potential optical amplifier application; (iii) the conductivity of a-C film can be altered by two orders of magnitude (5x$10^3$ - 5x$10^5$ Sm$^{-1}$) through p- or n- dopant incorporation [103]. Moreover, PECVD-grown a-C:H films reveal atomically smooth surface and interface with surface roughness of order of magnitude of sub-visible-wavelength, which minimizes light scattering effects [104], and is uniform over a large area. These unique and versatile opto-electronic properties provide an impetus to further explore and utilize PECVD a-C:H films for specific optoelectronic applications. More importantly, it has been demonstrated that it is possible to prepare carbon based planar waveguides with an attenuation of less than 1 dB/cm at 633 nm wavelength [47]. Having low optical losses in photonic materials is one of the most important prerequisites for employing a given material in integrated optics.

2.3.2 Microstructure and Role of Hydrogen

The three common allotropic forms of carbon are diamond, graphite, and buckminster-fullerenes or buckyballs. Diamond is highly transparent, electrically insulating, extremely hard and thermally conductive. By contrast, graphite is opaque, electrically conducting, soft, and thermally insulating. Fullerenes were introduced in the 1980s and much of the research that has been conducted pertains to nano-science and nano-technology of carbon nanotubes.

The versatility of allotropes is attributed to three bonding hybridizations, $sp^3$, $sp^2$ and $sp^1$ as illustrated in Figure 2.3 that a carbon atom can form. The ground state electron configuration of the carbon atom is 1$s^2$2$s^2$2$p^2$, thus a carbon atom possesses four valence electrons, i.e., two in the 2$s$ orbital and two in the 2$p$ orbital. These four valence electrons can form different bonding hybridizations under specific synthesis conditions.
Figure 2.3. $sp^3$, $sp^2$, $sp^1$ bonding hybridizations for a carbon atom [46].

In the $sp^3$ configuration, four identical tetrahedral $\sigma$ bonds are formed and each bond is separated by 109.5°. For a $sp^2$-hybridized carbon atom, each of the four valence electrons is assigned to a fully tetrahedral $sp^3$ orbital, making a strong $\sigma$ bond to an adjacent carbon atom. Thus, there are four $\sigma$ bonds formed in the $sp^3$ configuration. This $\sigma$ bond is a covalent bond which is the strongest among all of the bonds and makes a $sp^2$-hybridized carbon atom closest to its neighbors. Diamond is known as a crystalline carbon-based material bonded in this $sp^3$ configuration which results in its transparent (wide optical bandgap of 5.5 eV), highly electrical resistive, largest room temperature thermal conductivity properties, and possessing the largest bulk modulus and the smallest thermal expansion coefficient of any solid.

In the $sp^2$ configuration, three trigonally identical $\sigma$ bonds are formed in a plane separated by 120° and a weaker $\pi$ bond is formed normal to the $\sigma$ bonding plane. For a $sp^2$-hybridized carbon atom, three valence electrons are in $sp^2$ orbitals and the fourth electron remains in 2p orbital whose axis is normal to the plane containing three $sp^2$ orbitals. Three valence electrons in $sp^2$ orbitals form three $\sigma$ bonds with the neighboring three $sp^2$-hybridized carbon atoms, while the remaining electron in 2p orbital overlaps with other electrons in 2p orbitals among the three nearest neighbors thus forming a distributed $\pi$ bond. The $\sigma$ bond is stronger than the $\pi$ bond since there is a greater overlap of orbitals among $\sigma$ bonds than in $\pi$ bonds. All four valence electrons are essentially bonded with coplanar atoms, so adjacent planes are only held together by weak Van Der Waals forces. Graphite is known as a crystalline carbon-based material bonded in this type of $sp^2$ configuration, which leads to opaque (zero optical bandgap due to the highly de-localized $\pi$
bonding and weak forces between the planes along the z axis.), high electrical conductivity, thermally insulating, and mechanically soft.

In the $sp^1$ configuration, two identical $\sigma$ bonds are formed and two weaker $\pi$ bonds are formed normal to the $\sigma$ bonding plane. For a $sp^1$-hybridized carbon, two of the four valence electrons enter $\sigma$ orbitals, each forming a $\sigma$ bond directed along the x axis, and two other electrons enter 2p orbitals forming $\pi$ bonds in the y and z directions.

Amorphous carbon (a-C) is a non-crystalline carbon-based material with the microstructure of short-range order. While two primary crystalline forms of carbon possess either 100% $sp^3$ bonding (diamond) or 100% $sp^2$ bonding (graphite), a-C films contain a mixture of $sp^3$, $sp^2$, and $sp^1$ bonding and their properties are primarily dependent of the fractions of $sp^3$ and $sp^2$ bonding configurations, with $sp^1$ bonding not contributing significantly to its properties. Moreover, the term a-C includes hydrogenated forms of non-crystalline carbon, which can be represented as a-C:H. The properties of a-C:H films are dependent on the deposition conditions and methods. In addition to the fraction of $sp^3$ and $sp^2$ bonding hybridization, H content plays an important role in determining the properties of a-C:H films. Based on the percentage of $sp^3$ bonds and the percentage of H content in the film, a-C:H films are classified into various catalogues as simply illustrated in Table 2.1. Their optical property, such as optical bandgap, and mechanical property, such as hardness, and physical property, such as density, are significantly a function of H content and ratio of $sp^3$/sp$^2$ bonding configuration in the films [46, 103]. In addition, it is convenient to display the composition of the various forms of amorphous carbon alloy on a ternary phase diagram as shown in Figure 2.4 [46, 105].

Table 2.1. Categories of amorphous carbon films [103].

<table>
<thead>
<tr>
<th>Category</th>
<th>Abbreviation</th>
<th>H (at%)</th>
<th>$sp^3$ (%)</th>
<th>Optical bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogenated diamond-like a-C</td>
<td>DAC:H</td>
<td>20 - 40</td>
<td>40 - 60</td>
<td>0.8 - 4.0</td>
</tr>
<tr>
<td>hydrogenated tetrahedral a-C</td>
<td>TAC:H</td>
<td>0 - 30</td>
<td>65 - 95</td>
<td>1.6 - 2.6</td>
</tr>
<tr>
<td>hydrogenated graphite-like a-C</td>
<td>GAC:H</td>
<td>0 - 40</td>
<td>0 - 30</td>
<td>0.0 - 0.6</td>
</tr>
<tr>
<td>hydrogenated polymer-like a-C</td>
<td>PAC:H</td>
<td>40 - 65</td>
<td>60 - 80</td>
<td>2.0 - 5.0</td>
</tr>
</tbody>
</table>
Figure 2.4. Ternary phase diagram of bonding in amorphous carbon-hydrogen alloys [46]. The abbreviations are defined in Table 2.1.

Diamond like amorphous carbon (DAC) is also popularly referred to as “DLC” in the published literature. However, DAC is not identified as the material that resembles the microstructure of diamond, that is, the unique properties of diamond due to its high C-C $sp^3$ bonding configuration as discussed above. Instead, tetrahedral amorphous carbon (TAC) possesses much lower hydrogen content and much higher $sp^3$ fraction of bonding configuration, which is mainly C-C $sp^3$, compared to DAC, and thus leading to high hardness and high density in TAC films. Graphite-like amorphous carbon (GAC) exhibits low hydrogen content and low $sp^3$ content, implying that high C=C $sp^2$ bonding configuration encompasses the GAC film which results in low-density soft, usually black, film with smaller optical band-gap. DAC exhibits moderate H content and $sp^3$ bonding ratio compared to TAC and GAC, where some of the $sp^3$ bonds are due to C-H $sp^3$ bonds, which leads DAC to be a wide optical bandgap material (0.8 – 4.3 eV). Polymer like amorphous carbon (PAC) possesses very high H content (40 – 65 at%) incorporated into the microstructure of the films and high fraction of $sp^3$ bonding configuration. However, this high $sp^3$ content within PAC films is due to the fact that the hydrogen bond prefers to terminate the carbon π dangling bond during the deposition process to form the $sp^3$ configuration. Accordingly, most of the $sp^3$ content within PAC film is due to C-H $sp^3$ instead of C-C $sp^3$, which causes PAC to become even softer with a lower density compared to GAC. Therefore, the optical properties of a-C:H films can be dramatically varied in correspondence to the range of deposition conditions and
methods availed. This remarkable versatility of the properties makes a-C:H a potentially promising for application in opto-electronic devices.

2.3.3 Radio-Frequency Plasma-Enhanced Chemical Vapor Deposition (RF-PECVD) System

The first part of this thesis investigates the optical properties of host a-C:H films and their correlation to the microstructure of the films. a-C based films were grown via radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD) method. Thus, it is instructive to review the basic concepts for the RF-PECVD technique and the film growth processes during the formation of a-C:H films.

2.3.3.1 Plasma Kinetics

Before discussing the various operational details of RF-PECVD, we briefly explain plasma generation and plasma kinetics.

Plasma, a state of matter similar to gas, can be generated by supplying energy to a neutral gas and causing the formation of charged particles, namely positively charged ions, negative electrons, and neutral radicals. Applying an external electric field to a neutral gas is the most common way to produce and sustain a low-temperature plasma [106]. Any volume of a neutral gas invariably contains a few electrons and ions owing to the interaction of cosmic ray or radioactive radiation with the gas. These free charged particles can be accelerated by an applied electric field, and then inelastically collide with the stable neutral atoms or molecules in the feed gas to create new particles. The lower-mass electrons respond rapidly to the applied electric field, gain most of the applied electric energy and play an important role in generating and sustaining a plasma. The key plasma processes are described below.

- **Ionization**: A process of converting a neutral molecule into a positively charged ion and an additional electron due to energy transfer from an inelastic collision with an energetic electron.

  Example: \( \text{CH}_4 + e^- \rightarrow \text{CH}_4^+ + 2e^- \)

  Ionization of ions is also referred to as an ionization process.
• **Dissociation**: A process in which a neutral stable molecule is separated or split into highly-reactive neutral molecular fragments, known as radicals and usually indicated by*, due to energy transfer from an energetic electron in an inelastic collision.

Example: \( \text{CH}_4 + e^- \rightarrow \text{CH}^+ + \text{H}_2 + \text{H}^+ + e^- \)

• **Excitation**: A process where photons are emitted by virtue of electrons in neutral molecules being promoted to higher energy states which in turn relax to their ground state. This relaxation process accounts for the visible glow commonly seen in plasmas.

The positive ions and active radicals produced in a plasma account for formation of a-C film, which will be discussed in Section 2.3.4 “Film Deposition Mechanism”. Various types of ions and radicals can be generated subject to the composition of precursor gases introduced during the plasma deposition process. For examples, \( \text{CH}_3^+ \), \( \text{CH}_3^* \), and \( \text{H}^* \) are three predominant species in a CH$_4$ plasma during film deposition [107-109].

2.3.3.2 **Fundamentals of Radio-Frequency Plasma-Enhanced Chemical Vapor Deposition System**

PECVD can be classified according to the power sources used to apply the electric field that generates the plasma. The primary types of sources are continuous dc or pulsed direct-current (DC), capacitively or inductively coupled radio-frequency (RF), and microwave (MW) [106]. DC-PECVD, with an external DC current applied to generate plasma, is not typically utilized for a-C deposition since highly resistive a-C film builds up on the DC powered electrode during deposition. Accordingly, it is increasingly difficult to maintain stable plasma using such a deposition process, especially when thick films are needed for specific opto-electronic applications. The most popular a-C deposition method is RF-PECVD. There are also advanced configurations developed within the RF-PECVD context; these include plasma beam source (PBS), electron cyclotron resonance (ECR) and electron cyclotron wave resonance (ECWR) source [46, 103].

Typical RF-PECVD system configuration consists of two electrodes, capacitively-coupled RF power source, impedance matching network, and inlet/outlet gas delivery and vacuum pumping system. The RF power source typically operates at 13.56 MHz connected in series to an impedance matching network to minimize the reflected RF power from the chamber and thus to maintain a
stable plasma during the deposition process. One electrode is powered while the other one is grounded along with the chamber wall. The detailed specifications of the RF-PECVD system used in this work will be described in Section 3.2.1 “Film Growth Process Flow”.

Figure 2.5. Schematic diagram of plasma generation in a conventional capacitively-coupled RF-PECVD.

As discussed in Section 2.3.3.1 Plasma Kinetics, electrons, positively charged ions, reactive radicals, and stable neutral molecules coexist in a plasma. The ions, reactive radicals, and stable neutral molecules, having lower mobilities by a factor of $10^2$ compared to that of electrons, remain relatively stationary while electrons with lower mass oscillate between the electrodes at 13.56 MHz. Electrons collide inelastically with the neutral molecules and radicals to induce ionization processes and generate more ions as electrons oscillate between two electrodes. The generated electrons participate in the existing oscillating flux of electrons and further induce additional ionizations while the generated ions remain relatively stationary. The process, as illustrated in Figure 2.5, continues until a steady-rate is approached between the generation of new charged particles and recombination of the existing charged particles. It should be noted that for simplicity, negatively-charged ions are not shown in Figure 2.5. This is a reasonable omission as negative ions have been reported to not play a significant role in the plasma or growth processes in a-C:H.

The dark space-charge regions also exist next to the electrodes known as sheath regions, in addition to the central glow region attributed to the relaxation of electrons at higher energy states. Due to the higher mobilities of electrons compared to the ions during the positive phase of electric field, the electron current towards a given electrode is significantly higher than the ion current to the
same electrode during the negative phase of the electric field. Accordingly, this leaves a positive and dark space charge region near the electrodes known as sheath regions as represented in Figure 2.6. Since the system is capacitively-coupled, the mean electron and ion currents must be balanced, thus a static electric field forms in the sheath regions such that the electrodes develop a negative DC potential with respect to the plasma. This negative potential is known as the self-bias potential.

Figure 2.6. Schematic diagram of sheath region formations in a conventional capacitively-coupled RF-PECVD.

Due to the capacitive characteristic of the sheaths, the applied RF voltage can be divided between the sheaths based on their inverse capacitance. The powered electrode (cathode) usually possesses a smaller area as opposed to the overall area of the grounded electrode (anode) and grounded chamber walls. Thus, the cathode acquires a larger DC potential [110]. Due to the configuration of the electric field in the sheath regions, ions entering the sheath are accelerated by the field and bombard the electrode with higher energy, in contrast with electrons that are decelerated by the field. Also, ions entering the sheath are able to collide with the neutral gas or neutral radicals, thus resulting in the plasma generation processes described in Section 2.3.3.1 Plasma Kinetics. Accordingly, the energetic radicals and ions impinging on the electrode contribute to the formation of a-C film. It is worth noting that the energy of the ions and radicals impinging on the substrate is strongly related to this DC bias voltage. This plays an important role during the formation of a-C films.
2.3.4 Film Deposition Mechanism

There are many processes during the deposition of a-C:H, as represented in Figure 2.7. The properties of plasma deposited a-C:H films depends strongly on bias voltage and hence on the ion energy, indicating that ions play an important role in the deposition and properties of a-C:H films. The action of ions is principally via subplantation, that is, an energetic molecular ion incident at the film surface dissociates into atomic ions and the incident energy is hence distributed evenly. Thus, each atomic ion will subplant independently with its corresponding energy.

![Component processes in the deposition mechanism of a-C:H thin film](image)

Figure 2.7. Component processes in the deposition mechanism of a-C:H thin film [46].

In addition to the physical process of subplantation, the chemical process of neutral species and dehydrogenation also occur during the growth of a-C:H films. The plasma deposition process can be separated into three general stages: (i) the reactions within the plasma (ionization and dissociation as mentioned in Section 2.3.3.1 Plasma Kinetics), (ii) the plasma-surface interaction, and (iii) the subsurface reactions in the film. The plasma species incident on the film is composed of ions and neutrals including a significant amount of atomic hydrogen H. The neutrals besides hydrogen consist of closed shell molecules, such as stable undissociated precursor gases, active mono-radicals such as CH₃, di-radicals and other unsaturated species such as C₂H₂.
It is known that neutral species contribute to the growth of the film since the mass deposition rate exceeds the rate due to ions alone. This leads to an effect which is of note, that is, the growth rate decreases with increasing deposition temperature which is due to the increasing etching rate of the film due to atomic hydrogen. The contribution of each neutral species to the growth rate depends on its sticking coefficient. The surface of a-C:H film is chemically inert since it is essentially covered with C-H bonds. The di-radicals and other unsaturated species react strongly with the film considering sticking coefficient of near unity and accordingly being able to directly insert into the surface via C-C or C-H bonds. However, the effect of stable neutral hydrocarbon species, like CH₄, can be neglected due to the low sticking coefficient of below 10⁻⁴. The mono-radicals, which have a moderate effect on film growth, can only react with the film to form C-C bonds provided existing dangling bonds appear on the surface. The dangling C bond must be created by removing an H from a surface C-H bond, which can occur via ion displacement or by an H atom abstracting reaction, or by radical abstracting reaction. It has been found that atomic hydrogen H is the most efficient species for hydrogen abstraction.

Neutral hydrocarbon species cannot penetrate the film and can only react at the surface. But, H atoms are so small and can penetrate to about 2 nm depth into the film, where they can abstract H from C-H bonds and create subsurface dangling bonds and H₂ molecules. Some of the dangling bonds will be re-saturated by incoming atomic H.

Ions can also penetrate the film. Carbon and hydrocarbon ions can cause subplantation. A more typical role of ions in a-C:H film is to displace H from C-H bonds. This H can then recombine with other atomic H to form H₂ molecules, and desorb from the film. This is the main process which causes the H content of PECVD a-C:H film to decrease with increasing bias. H⁺ ions can penetrate deepest into the film because of their low mass and undergo the same reactions as atomic H but at a far greater depth.

The preceding discussion on the deposition mechanism is limited to a-C:H. Interested readers can refer to [46] for a-C, especially TAC.

2.3.5 **Electronic Structure and Defects**

Carbon can exist in three hybridization configurations, \( sp³ \), \( sp² \), and \( sp^1 \) as discussed earlier. In the \( sp³ \) configuration, a carbon atom, with four \( sp³ \) orbitals, forms four strong \( \sigma \) bonds with four
adjacent atoms. In the $sp^2$ configuration, a carbon atom, with three $sp^2$ orbitals, forms three $\sigma$ bonds, the fourth $2p$ orbital forms a $\pi$ bond with a neighboring $2p$ orbital. The $\sigma$ bonds at all carbon-carbon sites or C-H bonds occupy $\sigma$ states in the valence band and empty $\sigma^*$ states in conduction band, thus separated by a wide $\sigma - \sigma^*$ gap. The $\pi$ bonds from $sp^2$ phases fill $\pi$ and empty $\pi^*$ states which lie deep in the gap. A simple band diagram, as illustrated in Figure 2.8, has been developed [111-114], where proposed $sp^2$ phases confined in clusters with 2-10 atoms are embedded within a $sp^3$ matrix forming localized tail states. The $sp^2$ clusters are likely nano sized crystals and embedded in the amorphous $sp^3$ matrix film [46]. The complex distribution of localized $\pi$ and $\pi^*$ states is related to the size and number of $sp^2$ clusters and shapes. Thus, the optical bandgap of a-C:H films exhibit a broader energy range, and the electronic and optical properties are largely controlled by these $sp^2$ localized states.

Defects are atomic configurations that create states deep in the bandgap. It is expected that $\pi$ defects will predominate as $\pi$ bonding is weaker than $\sigma$ bonding in a-C. Besides the three-coordinated dangling bond existing in a-C:H, any cluster with an odd number of $sp^2$ sites produce a state near the midgap. Electron paramagnetic resonance technique (EPR) can be utilized to determine the spin density $N_s$, defined on average as spin population divided by the sample volume, from the unpaired electrons reflecting the paramagnetic behavior.

![Figure 2.8. Schematic density of states of carbon with $\sigma$ and $\pi$ states](image-url)
2.4 Erbium or Ytterbium Incorporated in Carbon Based Host Materials

2.4.1 Sputtering and Laser ablation of Erbium Mixed Targets

The first reported demonstration of room temperature photoluminescence from Er at 1.54 μm in a-C:H(Er) thin films was published in 2002 [48]. a-C:H(Er) films were deposited by magnetron sputtering of a graphite target that was partially covered by Er platelets in an Ar/ C6H12 atmosphere. The Er concentration in the a-C:H(Er) films could be changed from 0.15 at% to 0.8 at% based on the processing conditions of magnetron sputtering. But, the PL spectra induced by a Xe lamp or Ti: sapphire laser could only be detected in the highest concentration 0.8 at% sample with an optical gap of 1.5 eV. Later, this group could incorporate Er concentration up to 1.2 at% using the same deposition technique. In 2008, another group employed a similar method and reported doped Er concentration ranging from 1.2 at% to 17.1 at%, the attained concentration being a function of the weight percentage of metallic erbium embedded within the graphite targets [115]. However, the PL intensity was still relatively low given the results reported by both groups. This was attributed to the low optical bandgap (~0.5 eV) of the samples and the non-radiative relaxation pathway induced by C-H vibrations [51].

In this deposition technique, the Er concentration highly depends on the degree of magnetron sputtering of the Er-graphite target. Accordingly, high Ar ion energy and flux are required to achieve high Er concentration. However, this causes a high concentration of sp2 carbon and a low optical bandgap. Although a correlation between the optical bandgaps of a-C:H(Er) films and the doped Er concentration was indicated in this work, the detailed photoluminescence mechanism and role of Er3+ ion playing in relation to the energy transitions within the a-C:H(Er) network were not fully understood.

Besides the magnetron sputtering technique, pulsed laser ablation of a graphite/ Er mixture target was utilized in 2009 to prepare diamond-like carbon (DLC) films doped with 0.5-2.0 at% of Er [49, 116]. Nevertheless, the study was primarily focused on the effects of heavy Er metal on the tribological property and adhesion strength of DLC films, suggesting that the presence of SiC at the surface with increasing Er fraction leads to the improvement of adhesion strength of the film; no photoluminescence spectra were reported. Neither sputtering nor laser ablation method
cannot achieve independent control of Er concentration and properties of the host a-C film. Thus, it is highly desired to seek an alternative deposition technique.

2.4.2 Erbium Metalorganic Complex with PECVD Method

The incorporation of an Er metalorganic compound into a carbon layer by one-step radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) method was demonstrated by Prajzler et al. [50] in 2003 and [115] in 2008. a-C:H(Er) thin films were prepared from gas mixture CH₄ and Er vapor by heating “erbium tris” ((Tris (2,2,6,6-tetramethyl-3,5-heptanedionato)x Er(qIII)), abbreviated as Er(tmhd)₃ with chemical structure Er(C₁₁H₁₉O)₃, at temperature ranges of 130 - 160 °C. High Er concentration of up to 8.7 at% could be obtained depending on the distance between erbium tris containing apparatus and substrate. However, the PL around 1.5 µm was not present. This was attributed to the non-radiative relaxation pathway induced by C-H and O-H vibrations. Besides Er(tmhd)₃, erbium isopropoxide having the chemical structure C₉H₂₁O₃Er was mixed with CH₄ and Ar plasma environment at temperatures ranging from 240 - 260 °C [115]. However, no Er concentration was detected in the carbon film. Another two-step method was also employed. The carbon film was initially deposited by RF-PECVD method, followed by exposure to the vapor of erbium nitrate Er(NO₃)₃ dissolved in glycerol solution [50]. However, low Er concentration, 0.11 - 0.25 mol%, was attained and found to depend on the diffusion time and heating temperature of the solution; further, a non-uniform Er depth distribution were observed. Although no PL around 1.5 µm were presented, incorporation of Er metalorganic compound via Er vapor into the carbon layer deposited by RF-PECVD method was first successfully demonstrated in the preceding described experiments.

In 2009, Tsai et al. [52] grew a-C:H(Er) and a-C:D(Er) films, where D in a-C:D(Er) is deuterium, the isotope of H, via in situ thermal evaporation of the Er(tmhd)₃ compound in a DC saddle-field PECVD system. High Er concentration (up to 2.3 at%) and room temperature photoluminescence at 1.54 µm were demonstrated. Photoluminescence was observed from both a-C:H(Er) and a-C:D(Er) films. However, the relative PL intensity from a-C:H(Er) was at least 10 times lower than from a-C:D(Er), attributed to the optical quenching from the highly abundant C-H bonds. Further, the Er(tmhd)₃ metalorganic compound contains a high percentage of C-H bonds, 59 at%. Hence, this precursor is inherently inefficient at promoting Er³⁺ photoluminescence. Moreover, the DC saddle-field PECVD system utilized for the preparation of these samples could
not provide a stable plasma condition for a long period of deposition time owing to the build-up of the highly insulating a-C film on the DC electrodes. This limitation presented significant challenges to growing a thick film with controllable deposition conditions which is essential for the ultimate design of waveguide devices. Moreover, the effect of the incorporated Er metalorganic compound on the morphology, microstructures, and optical properties of the host a-C films, as well as the role of host a-C matrix on PL energy transfer mechanism were not examined.

2.4.3 **Erbium Doped in Polymer**

Besides employing a number of vacuum techniques to deposit host a-C films as discussed in the previous sections, a variety of solution-based processed carbon based materials, polymers, especially commercial photoresists such as poly (methyl methacrylate) (PMMA), polyimide, and epoxy-based resin, have been utilized as carbon based hosts for rare earth lanthanide ions encapsulated in organic compounds [117]. However, there have been very few reports for Er 1.5 μm emission [118-120], the lack of which could be attributed to the presence of inherent C-H and OH quenching effect of the polymers. Accordingly, most of the studies concentrated on the neodymium (Nd³⁺) emission at 1060 nm [121-123] and europium (Eu³⁺) at 612 nm [124, 125]. Also, deuteration or fluorination of the polymer hosts and hydration of the lanthanide complexes by adding Lewis bases have been performed to increase the lifetime and photoluminescence intensity [126], and lower the intrinsic absorption loss and material dispersion of the polymer hosts as well [127, 128]. However, most of the studies limit their discussions to PL in organic complex solvents wherein complex powders are dissolved, and/or discussion of organic complex powder mixtures with KBr. These studies are also limited in that they do not examine thin film formation methods nor do they report the PL of thin films. Moreover, it has been reported that fluorocarbon polymers (C-F based bonds), for example polytetrafluoroethylene (PTFE, Teflon™), are not suitable for optoelectronic applications due to the poor adhesion of these materials to various substrates. This limits the processing capability of these solution-based approaches. However, it is interesting to note that plasma-polymerized fluorocarbon films do exhibit good adhesion to several substrates [129].

2.4.4 **Ytterbium Doped in Carbon Based Materials**

Although extensive research on Yb-doped ceramic and oxide thin films deposited using various methods of deposition has been performed (as introduced in Section 2.2.4), Yb doping in
carbon based hosts has received minimal attention. Yb nanocrystals have been incorporated in various polymers as hybrid materials using sol-gel for potential bio imaging [53, 54], gas adsorption, and catalytic activity [55] applications. Hydrogenated amorphous carbon has been used as a host for Er and Yb, however, the attempted PL enhancement of Er via Yb sensitization was not achieved for samples prepared by sputtering of a hybrid Er/Yb/carbon target [56].

2.5 Summary

A summary of the salient points emerging from the foregoing discussion is presented below.

- **Si-based Low Dimensional Materials: Porous Si, Si nanocrystals, SOI superlattice**

Creation of nanostructured Si makes it possible to relax traditional phonon-selection rules in indirect-gap materials by breaking the crystal-symmetry or by phonon localization, thus leading to materials that exhibit direct-gap-like characteristics. A number of low-dimensional Si materials, including porous Si [58, 59], Si nanocrystal [9], Si-on-insulator (SOI) superlattice [60], photonic crystal like nanopatterns [61], and Si nanopillars [62], have been reported to show light-emitting properties, potentially leading to a path for Si-based photonic integrated circuits. Highly porous Si materials are very fragile and generally are not able to resist subsequent standard Si fabrication steps. Si nanocrystals embedded in a silicon-rich SiO₂ matrix have been observed to generate room temperature PL at visible wavelengths as well. However, in order to attain the desirable photoluminescence, high temperature annealing (> 1000 °C) under N₂ environment is required as it is critical to inducing phase separation/crystallization of Si nanocrystals [6-9]. Although silicon-rich SiO₂ matrix can be synthesized via sputtering of Si rich oxides, Si ion implantation into high quality oxides, reactive evaporation of Si rich oxides, or chemical vapor deposition (CVD) of sub-stoichiometric oxide films that are compatible with CMOS processing, the subsequent necessary annealing step is incompatible with BEOL processing.

- **III-V Wafer Bonding, Epitaxial III-V, Strained SiGe**

Integration of direct bandgap III-V epitaxial layer on top of SOI wafers via flip-chip bonding [44] and semiconductor wafer bonding (adhesive semiconductor wafer bonding [41], molecular wafer bonding [42], and die-to-wafer bonding [43]) techniques have been extensively investigated to produce light from Si wafers. However, most of the wafer bonding techniques are
still rather involved with slow, complicated and costly multi-steps with little flexibility for ultimate laser design compared to directly growing the film on the Si substrate.

Another approach is to directly grow epitaxial lasing materials on Si substrates via a number of methods. However, it is still two orders of magnitude higher than in InP- or GaAs-based epitaxial wafers for room temperature continuous wave lasers. Also, epitaxial growth of Ge on Si (or SiGe on Si) material system has been demonstrated with performance comparable with their III-V counterparts in certain aspects. Moreover, with the assistance of heavy n-type doping in Ge, light emission was achieved [12, 76, 77]. Nevertheless, in order to achieve high quality epitaxial layer on Si, a two-step growth is normally applied in an ultrahigh vacuum CVD system along with high temperature (> 850 °C) thermal cleaning of Si or SOI substrate [10, 11] is needed so as to eliminate the dangling bonds, followed by a high temperature (> 600 °C) growth process, and a post-growth high temperature annealing (> 750 °C) step to reduce the dislocation density [12] - processes which are costly and incompatible with the existing CMOS BEOL process.

- **Erbium Doped Thin Film Materials and Methods**

Erbium ion implantation in a variety of Si-based [13-15], silica-based [14, 16], and ceramic [14] thin film hosts has a leading role in the effort to efficiently produce photons from Si. The advantage of this approach is that standard Si technology can be deployed to introduce Er as a dopant. In addition, excited Er$^{3+}$ ions emit at 1.5 μm, which is a strategic wavelength for telecommunication due to minimal absorption loss in silica fibers. However, photoluminescence is severely quenched at room temperature in crystalline Si based hosts [17, 18]. Also, co-implantation of additional O atoms is highly preferred in order to reduce Er precipitation and increase the fraction of active Er$^{3+}$ ions [19]. For silica-based and ceramic thin film hosts, a high processing temperature is required to grow good quality material. Also, high post-annealing temperatures (>700 °C) are typically necessary to eliminate the ion implantation-induced damage, to optically activate the Er$^{3+}$ ions, and/or to enhance photoluminescence lifetime or quantum efficiency. These high temperature post-deposition annealing processes are incompatible with Si BEOL fabrication processes.

- **Ytterbium Doped Thin Film Materials and Methods**
The ideal optical wavelength for applications on a Si chip and in chip-to-chip communications has not been determined. In order to make use of optical technologies fully, it is essential to explore each alternative Si compatible photonic material. Yb has a long luminescence lifetime [20] (up to 1 ms), and a relatively large emission cross section which results in a higher pumping efficiency[21] compared to Nd based solid lasers.

Incorporation of Yb into ceramic-based (YAG [22-24], Y₂SiO₅ (YSO) [25-27], KY(WO₄)₂ [28], NaLu(WO₄)₂ [29], and Al₂O₃ [30, 31]) wide bandgap semiconductors, oxide-based semiconductors (ZnO [32-34], TiO₂ [35, 36], In₂O₃ [37]), III–V group based materials (AlN [38]), and Si-based [39] thin film hosts using various deposition techniques, have been shown to produce luminescence at a wavelength of around 1 μm. For Yb doped ceramic based materials, liquid phase epitaxial growth method has been employed to fabricate homogeneous crystalline films and post-deposition annealing temperatures as high as 900–1300 °C have been required. These processes are not compatible with current Si-based IC fabrication technology. Lower substrate growth temperature (<300 °C) of amorphous or poly-crystalline/crystalline Yb-doped films and crystalline Yb₂O₃ film [40] on Si-based and/or sapphire substrates has been achieved via pulsed laser ablation and magnetron sputtering of Yb containing targets. PL has been demonstrated at temperatures ranging from approximately 20–300 K in Yb doped nc-Si films [39]. For PLD grown Yb₂O₃ films, room temperature PL was not observed [40]. Despite the achievement of lower growth temperatures, the concentration of the Yb and the properties of the host material cannot be independently controlled with PLD nor magnetron sputtering techniques. Also, a high temperature (>600 °C) post-deposition annealing step is always required to promote the formation of optically active Yb³⁺ ions and to enhance the PL efficiency. This post-deposition annealing step is not amenable with current Si BEOL fabrication technology.

- **a-C Advantages**

a-C:H films can be grown by low-temperature PECVD methods, an approach which is compatible with current CMOS fabrication technology [45]. This methodology facilitates integration and allows for reproducible and low-cost films. Additionally, a-C based films possess a number of outstanding properties such as high chemical resistance, mechanical hardness, and transparency in the infrared [45, 46]. The specific properties of a-C:H films can be tailored over a wide range by adjusting the sp³ to sp² hybridized carbon ratio, the type of sp³ (predominately C-C
or a mixture of C-C and C-H) and $sp^2$ (the number and size of the clusters) bonding configurations, and the amount of incorporated hydrogen in the film via various deposition parameters and deposition methods [46]. These unique and versatile properties provide an impetus to utilize PECVD a-C:H films for specific optoelectronic applications. More importantly, it has been demonstrated that it is possible to prepare carbon based planar waveguides with an attenuation of less than 1 dB/cm [47]. Having low optical losses in photonic materials is one of the most important prerequisites for employing a given material in integrated optics.

- **Erbium or Ytterbium Incorporated in Carbon Based Host Materials**

  While extensive research on Er-implanted silicon and silica-based materials or Yb-doped ceramic and oxide thin films deposited with various methods has been performed, Er [48-52] or Yb [53-56] doping in carbon based hosts has received minimal attention.

  The first reported demonstration of room temperature PL from Er at 1.54 μm in a-C:H(Er) thin films was published in 2002 [48]. a-C:H(Er) films were deposited by magnetron sputtering of a graphite target that was partially covered by Er platelets in an Ar/C$_6$H$_{12}$ atmosphere. The Er concentration in the a-C:H(Er) films could be changed from 0.15 at% to 1.2 at%. However, the PL intensity was relatively low. This was caused by the non-radiative relaxation pathways provided by C-H vibrations and the low optical bandgap (~0.5 eV) of the sample [51]. In this deposition technique, the Er concentration depends highly on the degree of magnetron sputtering of the Er/graphite target. Accordingly, high Ar ion energy and flux are required to achieve high Er concentration. However, this causes a high concentration of $sp^2$ carbon and a low optical bandgap. The incorporation of an Er metalorganic compound into a carbon layer by the radio frequency PECVD method was demonstrated by Prajzlera et al. [50] in 2003, however, no PL spectra were presented. In 2009, Tsai et al. [52] grew a-C:H(Er) and a-C:D(Er) films via *in situ* thermal evaporation of the Er(tmhd)$_3$ compound in a DC saddle-field PECVD system. A PL signal was observed from both a-C:H(Er) and a-C:D(Er) films. However, the relative PL intensity from a-C:H(Er) was at least 10 times lower than from a-C:D(Er), attributed to the optical quenching from the highly abundant C-H bonds. Further, the Er(tmhd)$_3$ metalorganic compound contains a high percentage of C-H bonds, 59 at%. Hence, this precursor is inherently inefficient at promoting Er$^{3+}$ photoluminescence.
Yb nanocrystals have been incorporated in various polymers as hybrid materials using sol-gel for potential bio imaging [53, 54], gas adsorption, and catalytic activity [55] applications. a-C:H film has been deployed as a host for Er and Yb. But, the attempted PL enhancement of Er via Yb sensitization was not achieved for samples prepared by sputtering of a hybrid Er/Yb/carbon target [56].

In summary, this motivates us to develop Er or Yb doped carbon-based materials and the corresponding deposition technique, which are Si BEOL compatible and can be processed at temperatures below 400 °C. Parts of this chapter have been reported in [130-132].
3 Film Growth and Characterization Techniques

3.1 Overview

In this chapter, the film growth method and characterization tools used in this research are described. Specifically, details are provided on the metalorganic radio frequency plasma-enhanced chemical vapor deposition (RF-PEMOCVD) system used to prepare rare earth (Er and Yb) metalorganic doped a-C (a-C(Er or Yb)) films, precursor metalorganic compounds, spectroscopic ellipsometry used to determine the thickness and optical properties \((n, k, E_{04})\) of the host a-C films, infrared spectroscopy employed to probe the microstructure (hydrogen concentration and C-H\(_x\) stretching absorption) in the host a-C films, x-ray photoelectron spectroscopy used to characterize the chemical bonding information in the host a-C and a-C(Er or Yb) films, and photoluminescence spectroscopy used to verify the luminescence property of a-C(Er or Yb) films.

3.2 Film Growth Process Flow

Prior to doping rare earth (Er or Yb) metalorganic compounds in a-C thin films, the optical properties of intrinsic a-C based films were examined and discussed with respect to their corresponding structural and local binding features via different RF power and substrate (on the anode or cathode) placement in radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) system. Later, the feasibility of in situ growth of rare earth (Er or Yb) doped a-C-based thin films on Si substrates at low temperature \(< 200 \, ^{\circ}\text{C}\) by a simple-step RF-PEMOCVD system was investigated.

3.2.1 Metalorganic RF-Plasma-Enhanced Chemical Vapor Deposition System Design and Assembly

A capacitively coupled RF-PEMOCVD system, shown in Figure 3.1, with a base pressure of \(5\times10^{-5}\) Torr was designed to deploy the rare earth (Er or Yb) metalorganic doped a-C based thin film growth.

3.2.1.1 RF-Plasma-Enhanced Chemical Vapor Deposition System Design and Assembly

The RF-PECVD system shown in Figure 3.1 in this work principally consists of the RF power generator operating at a frequency of 13.56 MHz, the impedance matching network,
vacuum inlet/outlet pumping gas system, and two circular electrodes in the vacuum chamber. In order to prevent or minimize the RF power reflection from the chamber during the deposition process, an impedance matching network system, composed of various series and shunt capacitances, is connected in series to the RF power generator. The impedance network is connected to a controller, which can automatically modify the impedance values in order to acquire zero reflected RF power from discharge in the chamber, so as to maintain the RF plasma stabilized during the deposition processes. The precursor gas is introduced from the bottom of the chamber. The outlet pumping system is composed of a turbo pump connected in series to a mechanical pump. Also, the ion gauge is attached between chamber and turbo pump for the monitor of the background pressure of the chamber before commencing film deposition. Moreover, there are two pressure gauges, which are situated on the top of the chamber and within the inlet gas line, respectively. These are to monitor the deposition pressure and inlet gas-line pressure during deposition process. Also, there is a convectron gauge located between the turbo and mechanical pump to ensure the chamber pressure to be below 500 mTorr before turning on the turbo pump so as to protect the turbo pump from being damage by large amount of gas.

Coiled heating wires along with a precise temperature controller system are attached on the top grounded electrode for obtaining various properties of the films via heating the substrate during the film growth. The temperature controller system consists of a primary controller and an extra temperature monitor which allows us to monitor the temperature of another location on the top grounded electrode (anode). This ensures that temperature is uniform across the anode during the heating process. Furthermore, the gas bypass system was constructed in order to allow the precursor gas directly flow from the inlet gas line to the outlet gas line. This enhances the efficiency of multi-depositions in series as well as helps to meet the criterion of high vacuum condition in the inlet gas line.

The bottom powered electrode (cathode) and the anode for the system are made of stainless steel plate with a diameter of 125 mm. The substrates can be either placed on the cathode or anode. Furthermore, the chamber wall and the top/bottom flanges, also made of stainless steel, are all held at ground potential, and the system has two viewports that enables the plasma and sheath regions to be monitored during deposition processes.
3.2.1.2 Thermal Evaporator System Design and Assembly

An ac-powered thermal evaporator was designed to be situated next to the RF-powered electrode (cathode) within the deposition chamber and utilized to dope \textit{in situ} rare earth (Er, Yb) metalorganic compounds concurrent with the deposition of a-C film as schematically illustrated in Figure 3.1. Instead of heating the metalorganic compound outside the deposition chamber and further introducing the metalorganic vapor via the carrier gas Ar or via the hydrocarbon precursor gas into the deposition chamber [50, 115], the evaporator in this work was designed to be placed as close as possible to the electrode inside the deposition chamber so as to prevent the condensation of the rare earth (Er or Yb) metalorganic vapor in the inlet gas line.
Highly resistive Ni-Cr wires were selected as the heating components, which were entwined tightly around the outside surface of the stainless steel container and the vapor-delivering nozzle. The temperature of the vapor delivery nozzle was kept higher than that of the bottom of the container, by 30 - 50 °C, so as to avoid condensation of the rare earth (Er or Yb) metalorganic vapor on the delivery nozzle as well. AC power then was applied onto the two ends of the wire to heat the container and gas-delivery nozzle. A thermocouple is embedded on the bottom of the evaporator, providing feedback to the temperature controller for precise control of the evaporation temperature. A low pass filter is connected using copper conductors between the thermal evaporator inside the chamber and the external ac power supply in order to prevent the RF plasma power source from dissipating into the temperature controller or the ac power line.

3.2.2 Incorporating Rare Earth (Erbium or Ytterbium) Metalorganic Compound

The Er and Yb metalorganic compound tris(6,6,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) Erbium/Ytterbium(+III), abbreviated (X(fod)3, X= Er or Yb), having the chemical structure X(C10H10F7O2)3 (X= Er or Yb) as illustrated in Figure 3.2, are selected as the doping candidates for a-C(Er or Yb) films. It is presumed that the optically active Er3+ and Yb3+ ions originating from the X(fod)3 (X= Er or Yb) metalorganic compound can be preserved with the X-O bonds under appropriate deposition conditions in RF-PEMOCVD system. This could effectively enhance the luminescence efficiency. The Er and Yb in the X(fod)3 (X= Er or Yb) compound are coordinated by six oxygen atoms, which represents a similar bonding environment to Er(tmhd)3 [133, 134] and Yb(tmhd)3 [135] with chemical structure of X(C11H19O2)3 (X= Er or Yb). As in X(tmhd)3 (X= Er or Yb), Er and Yb in X(fod)3 are coordinated to six oxygen atoms as well. Accordingly, the Er and Yb ions would not require a high temperature post-deposition annealing step to be optically activated and/or to repair film damage. It has been demonstrated [134] that the Er local environment in an as-deposited a-Si:H(Er) sample prepared by PECVD with introduction of Er(tmhd)3 vapor is very similar to Er2O3. This bonding environment has efficiently promoted the optically emitting centers [134]. In addition, Yb(tmhd)3 has been employed as the precursor to dope Yb2O3 in Y2O3 films by atomic layer deposition method [135] in order to maintain the optically active Yb3+ state. The hydrocarbon ligands of the Er/Yb metalorganic compound are expected to promote a high Er/Yb concentration in the a-C host matrix as its structure matches the internal structure of the a-C host matrix. As well, large separation of X3+ ions and less ion clusters/
precipitates attributed to long hydrocarbon ligands between $X^{3+}$ ions are expected to reduce concentration quenching. Also, the metalorganic compound is expected not to cause excessive contamination problem for host carbon-based materials, thus no further reduction of photoluminescence is expected [136]. More importantly, the ligands can serve as the sensitziers, which act as an optical antenna by which energy transfer to the $X^{3+}$ ions could take place. Accordingly, the absorption cross section could be increased and/or the excitation of $X^{3+}$ ions at wavelengths where $X^{3+}$ ions themselves exhibits no absorption is permitted, leading to the enhanced efficiency of the photoluminescence and more amenable to optical pumping.

Moreover, by selecting the X(fod)$_3$ metalorganic compound (with chemical structure $X(C_{10}H_{10}F_7O_2)_3$) as the doping precursor instead of $X$(tmhd)$_3$ with chemical structure Yb(C$_{11}$H$_{19}$O$_2$)$_3$, partial fluorination of hydrogen-containing ligands is expected to reduce the non-radiative deactivation channels due to C-H bonds. This could result in an enhancement of the Er$^{3+}$ luminescence efficiency [126, 137]. Further, the Er(tmhd)$_3$ metalorganic compound contains a high percentage of C-H bonds, 59 at%. Hence, this precursor is inherently inefficient at promoting Er$^{3+}$ photoluminescence. Details regarding advantages of substituting C-F with C-H bonds will be discussed in Section 5.3.2 and Section 6.5. As well, fluorine is also incorporated via the partially fluorinated X(fod)$_3$ precursor in the films. The effect of fluorine on the structure and properties of the films will be discussed in Section 6.5.

The X(fod)$_3$ (X= Er or Yb) powders were obtained from Strem Chemicals Inc. and was loaded into the vacuum chamber without any special treatment. Moreover, in order to determine the proper wavelength of the pumping source for a-C(Er or Yb) films as well as to indirectly understand the role of host a-C matrix on PL energy transfer mechanism, the absorption spectra for the X(fod)$_3$ (X= Er or Yb) metalorganic compounds dissolved in a d-chloroform solvent were collected with a UV-Vis-NIR spectrometer.
3.2.3 Deposition Procedure

3.2.3.1 Host a-C based Films

The deposition process procedure of host a-C based films is illustrated in Figure 3.3. Following the cleaning procedures, the substrates were loaded into the RF-PECVD chamber. The chamber was sealed and pumped to achieve a background pressure of below $5 \times 10^{-5}$ Torr. Then the deposition process of the host a-C based films was performed. The first step is to set the substrate heater (if required, $Time = t_1$) and wait for the grounded electrode (anode) to be heated up under the vacuum to the desired deposition temperature ($Time = t_2$), at which time the precursor gas is introduced into the chamber to purge the chamber. Once the pre-set substrate temperature and the deposition pressure are both stabilized ($Time = t_3$), RF power is turned on to ignite the plasma to commence the deposition of host a-C based films.

Once the deposition is complete, the remaining gas is pumped out ($Time = t_4$), then the chamber is vented by $N_2$ to the atmosphere pressure after waiting for the substrate to cool down to around 30 °C (if required, $Time = t_5$). Reactive ion etching by $O_2$ plasma process is utilized to clean the chamber with coated insulating a-C films after each deposition. This prevents contamination and assists to maintain the stable plasma conditions for the future deposition. The resistance of each electrode was examined by an ohmmeter to ensure the each electrode is itself
electrically short before loading new substrates and commencing a new deposition run. By using O₂ plasma, C based bonds (C-C, C-H, C-F) on the electrode or chamber wall can be etched away or dissociated by O ions and radicals due to the formation of stable CO₂ and H₂ gas phase molecules and being pumped out of the chamber.

In this work, three different kinds of precursor gases were utilized. Methane (CH₄) with purity of 99.999% and tetrafluoromethane (CF₄) with purity of 99.996 % were purchased from Linde Canada Limited. Deuterated methane (CD₄) with isotopic purity of 99 at% D was purchased from Sigma-Aldrich.

![Figure 3.3. Deposition procedure for host a-C-based thin films.](image)

3.2.3.2 a-C(Er or Yb) Films

The deposition process procedure of rare earth (Er or Yb) metalorganic doped a-C based films is displayed in Figure 3.4. The deposition procedure is similar to Figure 3.3 except for in situ
introduction of rare earth metalorganic vapor via the designed thermal evaporator apparatus while the commencing the a-C based film deposition. While the precursor gas is introduced into the chamber from the inlet gas line, the heating process of the thermal evaporator apparatus starts simultaneously (Time = t’). Once the pre-set doping temperature (T_{doping}) and the deposition pressure are both stabilized (Time = t’), RF power is turned on to ignite the plasma to commence the deposition. Once the deposition is complete, the heating process of rare earth metalorganic compound is turned off and the remaining gas is pumped out (Time = t’), then the chamber is vented by N₂ to the atmosphere pressure after waiting for the substrate cooling down to around room temperature 30 °C (if required, Time = t).
3.3 Characterization Techniques

3.3.1 Spectroscopic Ellipsometry

The thickness (deposition rate), refractive index $n(\lambda)$, extinction coefficient $k(\lambda)$, and optical bandgap $E_{04}$ of the host a-C based films were probed through spectroscopic ellipsometry. $k(\lambda)$ corresponds to absorption of electromagnetic radiation propagating through the material \[138\]. Furthermore, the absorption coefficient, $\alpha(\lambda)$, of the films can be related to the extinction coefficient, $k(\lambda)$, by:

$$\alpha(\lambda) = \frac{4\pi k(\lambda)}{\lambda}$$

EQN (1)

The optical bandgap $E_{04}$, defined as the photon energy at which the absorption coefficient $\alpha(=4\pi k/\lambda)$ is equal to $10^4$ cm$^{-1}$, where $\lambda$ is the wavelength, is determined from the extinction coefficient $k$.

The principle of ellipsometry is based on measuring the variation of the polarization state of the light after reflection on a sample surface \[139\]. In particular, spectroscopic ellipsometry can analyze complex structures, such as multilayers, interface roughness, inhomogeneous layers, anisotropic layers with the advantages of non-destructive character, high sensitivity due to the measurement of the phase of the reflected light, large measurement range from single layers to micrometers, and the possibilities to control in real time complex processes.

The thickness and the complex index of refraction, $N(E) = n(E) + i \ k(E)$, can be probed by performing a regression fitting of the measured data against the theoretical change of polarization of light of the sample with an initial thickness approximation and theoretical dispersion model of a-C film provided. The first-order initial thickness approximation of the a-C film was estimated from profilometry measurements. Then, the continuous values for $n(E)$ and $k(E)$ values were obtained via fitting the measured data by Forouhi-Bloomer dispersion model \[140\].

From the Forouhi-Bloomer dispersion model, the extinction coefficient, $k(E)$, of the amorphous materials was derived as a function of photon energy $E$ using the following equation:

$$k(E) = \frac{A(E-E_g)^2}{E^2-BE+C}$$

EQN (2)
where $A$, $B$, and $C$ are positive nonzero constants characteristic of the medium such that $4C - B^2 > 0$, and $E_g$ represents the optical energy bandgap. The index of refraction, $n(E)$, was determined by the following equation by using Kramers-Kroning analysis:

$$n(E) = n(\infty) + \frac{B_0E + C_0}{E^2 - BE + C}$$

EQN (3)

where $B_0$ and $C_0$ are constants which are dependent on $A$, $B$, $C$, and $E_g$, and $n(\infty)$ is a constant greater than unity describing the index of refraction at large photon energies. Therefore, there are five independent constants, $A$, $B$, $C$, $E_g$, $n(\infty)$ in Forouhi-Bloomer dispersion model required to be solved in order to obtain $n(E)$ and $k(E)$ values.

The measurements were carried out using a Sopra wavenumber spectroscopic ellipsometer. The wavelength range was 350-1700 nm at an incident angle of 75°. The spectra were analyzed by regression fitting using the linear Levenberg-Marquard algorithm method with a maximum of 1000 iterations under a three-layer optical system comprising of void (ambient)/a-C layer/c-Si substrate. A first-order initial thickness approximation of the a-C film was estimated from profilomtery measurements. The five constants of Forouhi-Bloomer dispersion model [140] and thickness of the a-C layer were allowed to vary during the fitting process. The fits yielded a coefficient of regression $R^2 \sim 0.99$ and the error of the 6 fitting parameters was less than +/-10 %, indicating the model was appropriate for the a-C films. Based on reproducibility experiments, an error of less than +/-5 % was estimated for thickness, refractive index $n$, and extinction coefficient $k$.

### 3.3.2 Fourier Transform Infrared Spectroscopy

The hydrogen concentration and C-H$_x$ stretching absorption bands of the host a-C:H films were characterized by Fourier Transform Infra-Red (FTIR) Spectroscopy. Also, the relative wavenumber/wavelength positions and range of energy levels of the first vibrational modes ($\nu = 1$) of C–H$_x$, C–D$_x$, and C–F$_x$ bonds, shown in Figure 5.5 and Figure 6.2, were obtained from the absorption peaks of the host hydrogenated, deuterated and fluorinated a-C films measured by FTIR technique as displayed in Table 5.1 and Figure 5.6.

In FTIR technique, a broadband light source coupled with a Michelson interferometer is used to perform IR transmission and reflection measurements. Post-acquisition processing by
computer is necessary to convert the raw data, light absorption for each mirror position, into the desired result, light absorption for each wavelength, by performing a Fourier transform. Therefore, the measured transmission or reflection intensity as a function of wavenumber can be obtained [141, 142].

Chemical bonding information in solids or liquids is commonly acquired from FTIR spectroscopy. The measured IR spectra are based on the absorption from the vibrational modes of various molecular bonds. The specific molecular bond can be identified by its location of the wavenumber since each molecular bond possesses its own vibrational mode with certain frequency which generally lies in IR region. The IR absorption consists of C-H strength modes at 2800–3100 cm\(^{-1}\) and C-C mode and C-H bending modes below 2000 cm\(^{-1}\). Nine C-H stretching modes as seen in Table 3.1 have been identified through examination of free molecule vibrational frequencies which comprises the absorption spectra from 2700cm\(^{-1}\) to 3100cm\(^{-1}\) and can be found in Ristein et al. [143]. The features of a-C:H in FTIR spectra follows closely with hydrocarbon molecules C-H since they have strong vibration modes from strong IR absorption. However, the C-C and C=C bonds are more difficult to detect and analyze since they have weaker vibration modes due to less absorption in IR range. Thus, X-ray photoelectron spectroscopy and X-ray excited auger electron spectroscopy techniques are included in this work to investigate the \(sp^2\)-hybridized C=C and \(sp^3\)-hybridized C-C bonds as described later in Section 3.3.3.

To calculate the transmission spectra from the thin film alone, the background interference pattern due to the multiple reflections in the film, was subtracted from the raw transmission spectra. The background interference pattern was identified using polynomial curve-fit algorithm provided in the TableCurve 2D Automated Curve Fitting and Equation Discovery 5.0 software.

The absorption was determined using the following relation [144]:

\[
\alpha(\nu) = -\frac{1}{d} \ln T
\]

EQN (4)

where \(\nu\) is the wavenumber, \(\alpha(\nu)\) is the absorption constant, \(d\) is the thickness of the film, and \(T\) is the normalized transmission of the a-C film with the background removed.
Table 3.1. Vibrational frequencies of various molecular bonds commonly existing in a-C:H films [143].

<table>
<thead>
<tr>
<th>C-H Stretching Mode</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp³CH₂ sym</td>
<td>2840–2870</td>
</tr>
<tr>
<td>sp³CH₃ sym</td>
<td>2860–2885</td>
</tr>
<tr>
<td>sp³CH</td>
<td>2900 ± 15, 2890 ± 10</td>
</tr>
<tr>
<td>sp³CH₂ asy</td>
<td>2915–2950</td>
</tr>
<tr>
<td>sp³CH₃ asy</td>
<td>2950–2980</td>
</tr>
<tr>
<td>sp²CH₂ olef, sym</td>
<td>2980, 2985 ± 10</td>
</tr>
<tr>
<td>sp²CH olef</td>
<td>2995–3040</td>
</tr>
<tr>
<td>sp²CH aromat</td>
<td>3000–3100</td>
</tr>
<tr>
<td>sp²CH₂ olef, asy</td>
<td>3070–3100</td>
</tr>
</tbody>
</table>

The hydrogen concentration was determined by the following equation [143]

\[
H_{conc.} = \frac{A_s(CH_x)}{<\nu>} \int \alpha(\nu) \, d\nu \tag{5}
\]

where \(\alpha(\nu)\) is the absorption coefficient, \(A_s(CH_x)\) is the absorption cross section of individual stretching mode and \(<\nu>\) is the average wavenumber. The IR spectrum in the wavenumber region 2700–3100 cm⁻¹ was deconvoluted based on the various bond assignments and their corresponding wavenumber. \(A_s(CH_x)\) was calculated by considering the cross section in a vacuum environment and extrapolated refractive index \(n\) of each sample to 3.3 μm [143] – the extrapolation was based on measured \(n(\lambda)\) over the wavelength range of 350-1700 nm determined using the Spectroscopic Ellipsometry technique mentioned in Section 3.3.3. An error of less than 3% was estimated for the calculated hydrogen concentration. This error was based on comparing the calculated hydrogen concentration for different fits of the raw FTIR background spectra.

FTIR measurements are performed on a-C films deposited on the double-side polished crystalline Si wafers with resistivity of higher than 10 ohm-cm in the wavenumber range of 440–5200 cm⁻¹ using a Perkin Elmer 2000 spectrometer with the resolution of 4 cm⁻¹. High resistive prime Si wafers are selected as substrates due to the near-flat transmittance in the spectral range of interest. Before commencing a measurement, the samples are left in the sample compartment
for at least 20 min in order to allow desiccated air to purge the compartment. This prevents the absorption of water and CO$_2$ during measurement to influence the acquired data. FTIR spectrum of a bare Si substrate is also measured as a background reference. 20 measurements are taken as average for each sample with interval of 4 cm$^{-1}$.

3.3.3 X-Ray Photoelectron and X-ray Excited Auger Electron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was employed to quantitatively characterize the elemental composition, chemical bonding information, and the depth distribution for the intrinsic host a-C films and rare earth (Er and Yb) metalorganic doped a-C films. X-ray excited auger electron spectroscopy (XAES) was employed to estimate the ratio between the $sp^2$-hybridized and $sp^3$-hybridized carbon atoms in the host a-C films.

The principle of XPS and XAES analytical method is based on simultaneously measuring the quantity and kinetic energy of the emitted photoelectrons from the materials by an X-ray source irradiation under ultra-high vacuum conditions [145, 146]. In XPS, the energy and quantity of core-level photoelectrons emitted from the sample are measured, while in XAES the energy and quantity of photoelectrons emitted through the Auger process are analyzed, as shown in Figure 3.5. Core-level and Auger electrons are differentiated as the kinetic energy of electrons emitted from these two processes lie in different energy ranges.

Figure 3.5. (a) XPS process: measurement of photoelectrons emitted from the core-level due to x-ray absorption. (b) XAES: measurement of secondary photoelectrons emitted from the
valence-level carrying excess energy creating from core-level hole, created in process shown in (a), being filled.

The XPS and XAES spectra are collected from the surface of the sample using a monochromatic Al Kα X-ray source in a Thermo Scientific K-Alpha spectrometer located in Surface Interface Ontario center with an ultrahigh vacuum of order of $10^{-9}$ Torr. The samples were attached to a stainless steel holder using Cu conductive double-sided tape. The top of the sample was also grounded by Cu tape in order to prevent severe charging effects.

### 3.3.3.1 Elemental Composition

The elemental composition is characterized by its binding energy of the core-level electron, which can be correlated to the measured kinetic energy of the emitted photoelectrons through the following equation as long as the energy of a particular X-ray wavelength is known

$$E_{binding} = E_{photon} - E_{kinetic} - \varphi_{spectrometer} \tag{6}$$

where $E_{binding}$ is the binding energy of a particular element, $E_{photon}$ is the energy of the X-ray photons being used, $E_{kinetic}$ is the kinetic energy of the photoelectron measured by the instrument, and $\varphi_{spectrometer}$ is the work function of the spectrometer instead of the material itself. The relationship is illustrated in the band diagram in Figure 3.6. Since the binding energy is defined as the energy difference between the Fermi level and core electron energy level, it is unique and specific to different chemical element. Thus, the elemental composition of the sample can be identified by comparing the counts of photoelectrons occurring at different binding energies. Accordingly, once the XPS survey spectrum is collected, each respective peak can be assigned to a specific element based on the best match of the known core-level energy and the location of the measured peak [147]. Thus, the elemental composition (at%) can be quantitatively determined through the ratio of the area under each peak. It is worth noted that photoelectrons emitted from hydrogen and helium in XPS technique cannot be detected due to their low binding energies. Therefore, the hydrogen content of a-C:H samples are measured using FTIR technique in Section 3.3.2.
Figure 3.6. Band diagram of relationship between binding energy ($E_{binding}$), work function of the sample ($\varphi_{sample}$), work function of the spectrometer ($\varphi_{spectrometer}$), Fermi level of the sample ($E_f$), measured kinetic energy of the photoelectron ($E_{kinetic}$), and the energy of the X-ray photons ($E_{photon}$). $E_{kinetic}'$ represents the kinetic energy of photoelectrons emitted from the sample, and $E_{kinetic}$ represents the kinetic energy of photoelectrons measured on the spectrometer.

### 3.3.3.2 Chemical Bonding & Depth Profile

Another primary advantage of XPS is its ability to provide chemical state information, i.e. local bonding environment of the elements [145-148]. Different chemical bonds can be identified according to the shifts in the binding energies which originate in the heteropolar bonding configuration. Heteropolar bonding is covalent bonding where the bonded electrons are not equally shared by the atoms due to the differences in electronegativity of the atoms [145]. However, the increased electrical resistivity during the XPS measurement procedure can also lead to the shift in the binding energy, which is called charging effect. The increase of the built-in potential within the material leads to decrease the kinetic energy of the emitted photoelectrons and further decrease the measured binding energy. In order to exclude the charging effect of the highly insulating a-C films, the XPS spectrum is initially performed on 2 nm Ag/ a-C / Si sample, then it is shifted based on comparing the relative position of Ag 3d$^5$ measured from our sample to the exact position of
Ag 3d⁵ from the handbook (368.3 eV). By calibrating the position of Ag 3d⁵, it is found that C1s peak is located at 284.5 eV. Therefore, the positions of C1s primary peaks have always been shifted to 284.5 eV for all of the performed samples.

Another strength of XPS technique is to analyze the uniformity of elemental composition as a function of Ar ion beam etching or along depth of the sample. Thus, depth distributions of rare earth (Er, Yb) metalorganic doped a-C films are measured.

3.3.3.3 Carbon sp²/sp³ ratio

The ratio between the sp²-hybridized and sp³-hybridized carbon atoms in the host a-C films can be estimated via the empirical Lascovich method [149, 150]. The method depends on the fact that kinetic energy of an electron emitted from the Auger process is sensitive to the energy level present in the atom. As seen in Figure 3.7, a sp³-hybridized carbon atom has one core-level (1s) and one valence level (2sp³), therefore, only one type of Auger emission can occur. In contrast a sp²-hybridized carbon atom has one core-level (1s) and two valence levels (2sp² and 2p), and thus, multiple valence levels can be potentially involved in Auger emission as depicted in Figure 3.8. Accordingly, the kinetic energy of Auger electrons in sp² hybridized carbon atoms is expected to exhibit broader profile than that in sp³ hybridized carbon. This concept can be also extended from isolated atoms to condensed matter. The sp² hybridization results in the presence of π-bands and thus a broadening of the valence band.

![Figure 3.7. Auger emission in sp³ hybridized carbon atom.](image)
Figure 3.8. Two potential Auger processes in $sp^2$ hybridized carbon atom that produces emission of electrons with unique kinetic energies.

The percentage of $sp^2$ hybridized carbon is found through equation [149]

$$%sp^2 = \frac{(D_{sample}-D_{diamond})}{(D_{graphite}-D_{diamond})} \times 100 \%$$

EQN (7)

where D-parameter represents the distance between the maximum of the positive-going excursion and the minimum of the negative-going excursion, and it can be found in the derivative spectra of XAES measurements. An error of +/-1% was accounted for in the calculated value based on the step size used for this measurement.

3.3.4 Photoluminescence Spectroscopy

Photoluminescence spectra of rare earth (Er or Yb) doped a-C based films were collected at room temperature to verify the luminescence property of rare earth (Er or Yb) in the a-C based films. The principle of photoluminescence measurement is based on the detection of re-radiated photons by the de-excitation of the excited state in the materials, which are excited by incident photons. By analyzing the spectral position and relative intensity of the emitted light, electronic, optical, and microstructures of the materials may be further determined. The experimental apparatus of detecting PL signal primarily consist of an excitation source, a monochromator, and
an optical detection system. A schematic diagram of PL system is shown in Figure 3.9 and the components are illustrated as followings:

- **Excitation source**: A continuous wave diode-pumped solid-state 532 nm laser with a power density of 20 mW/mm² (the average output power is 500 mW) was used as the excitation source. The wavelength of the laser is near resonance with the $^4S_{3/2}$ excited level of Er ions as seen in Figure 2.1. The excited Er ions decay to $^4I_{13/2}$ level through the fast non-radiative transition and then emit at 1.54 μm through $^4I_{13/2}$ to $^4I_{15/2}$ transition. However, there is no direct energy resonance of Yb$^{3+}$ ions with the presently employed 532 nm laser, suggesting that the photogenerated carriers could transfer energy from the host a-C based films to the Yb$^{3+}$ ions, leading to PL emission. This will be briefly discussed in Section 6.5 and Figure 6.7.

- **Monochromator**: Cornerstone™ 260 1/4 m Monochromator with triple gratings assembly was utilized to disperse the emitted PL. The grating of model 74069 with 900 - 2800 nm range was utilized to disperse the emitted PL. (bandwidth resolution = 2 nm, inlet and outlet slit size = 3 mm, line density = 600 lines/mm)

**Figure 3.9. Schematic diagram of Photoluminescence Spectroscopy apparatus.**
Optical detection system: A thermoelectrically cooled InGaAs photodiode, with a 800-1700 nm detection range, with standard lock-in techniques was employed. PL signals were collected from rare earth (Er or Yb) doped a-C based films deposited on the double side polished Si wafer. The noise-equivalent power (NEP) is less than $5 \times 10^{-14} \text{W/Hz}^{1/2}$.

3.4 Summary

Table 3.2 represents a summary of the respective properties obtained from each characterization tool. Parts of this chapter have been reported in [130-132].

Table 3.2. The respective properties obtained from the employed characterization tools in this thesis.

<table>
<thead>
<tr>
<th>Characterization tool</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profilometer</td>
<td>initial film thickness</td>
</tr>
<tr>
<td>Spectroscopic Ellipsometry Spectroscopy</td>
<td>thickness</td>
</tr>
<tr>
<td></td>
<td>refractive index, $n$</td>
</tr>
<tr>
<td></td>
<td>extinction coefficient, $k$</td>
</tr>
<tr>
<td></td>
<td>optical bandgap, $E_{04}$</td>
</tr>
<tr>
<td>Fourier Transform Infrared Spectroscopy</td>
<td>C–H$_x$ modes</td>
</tr>
<tr>
<td></td>
<td>hydrogen concentration</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy</td>
<td>elemental composition</td>
</tr>
<tr>
<td></td>
<td>chemical bonding information</td>
</tr>
<tr>
<td></td>
<td>depth profile</td>
</tr>
<tr>
<td>Photoluminescence Spectroscopy</td>
<td>relative photoluminescence intensity</td>
</tr>
<tr>
<td></td>
<td>FWHM</td>
</tr>
<tr>
<td>X-ray excited auger electron spectroscopy</td>
<td>% sp$^2$-hybridized carbon atoms</td>
</tr>
</tbody>
</table>
4 Hydrogenated Amorphous Carbon (a-C:H) in RF-PECVD: Results and Discussion

4.1 Overview

In this chapter, the effects of the RF power and the placement of substrate on the properties of the host a-C:H films in the RF-PECVD system were systematically investigated prior to performing rare earth metalorganic doped a-C thin films. The optical and structural properties of the host a-C:H materials were obtained. For optical properties, refractive index $n$, extinction coefficient $k$ and optical bandgap $E_{04}$ were characterized by the spectroscopic ellipsometry technique. The tunable and large range of refractive index $n$ are essential for providing flexibility in waveguide design and mode confinement. Having low extinction coefficient $k$ or low optical losses is one of the most important prerequisites in photonic materials for employing a given material in integrated optics. Optical bandgap $E_{04}$ will assist us to obtain the general picture of relative bandgap values. These properties were evaluated and discussed with respect to the local bonding features. As a note, other deposition parameters, i.e., deposition pressure and flow rate of the methane precursor gas, and different precursor gases (i.e., C$_2$H$_2$, H$_2$, and Ar), were also scanned to obtain various properties of a-C:H films. Nevertheless, it was observed that the RF power and the electrode on which the substrate was placed are the two key/dominant parameters influencing the properties of the host a-C:H films in the present RF-PECVD system.

For a-C:H films, the methane (CH$_4$) flow rate was 40 sccm and the chamber pressure was 60 mTorr. The substrates were kept at room temperature, while the RF power was varied from 10 W to 300 W.

4.2 a-C:H Host: Influence of Different Electrodes and Varying RF Power on Film Deposition

4.2.1 Optical Properties

Figure 4.1 reveals the dependence of deposition rate, optical bandgap $E_{04}$, refractive index $n$ and extinction coefficient $k$ on the applied RF power for the a-C:H films grown on the bottom powered (cathode, i.e. C-RF) and top grounded (anode, i.e. A-RF) electrodes respectively. Both of the sample sets, C-RF and A-RF, reveal similar trends of an increase in the deposition rate,
decrease in the $E_{04}$ optical bandgap, increase in the refractive index $n$ and extinction coefficient $k$ with increasing RF power. However, the rate of change of $n$ and $k$ at 532 nm and $E_{04}$ is more rapid for the C-RF sample set. This indicates the placement of substrate in this work plays an important role in the film deposition process. As a note, $n$ and $k$ decreases monotonically with wavelength (data not shown here) notwithstanding the fact that the values presented in Figure 4.1 correspond only to 532 nm.

Figure 4.1. The optical properties ($E_{04}$, $n$, $k$) and deposition rate of a-C:H films grown on the anode (solid line), and cathode (dash line), as a function of the applied RF power. Figure based on one published by Hsu et al. [130]. For clarity of presentation, error bars are not included; the estimated error in each measurement is less than +/- 10% of the measurement.
As the RF power is increased there is a corresponding increase in the RF voltage and current. This increases the ion energy and the plasma density, and hence there is more ionization, excitation, and dissociation (as described in Section 2.3.3.1 Plasma Kinetics). This leads to an increase in the flux of ions, radicals, and electrons to the substrate surface which corresponds to an increase in the deposition rate for both the cathode and the anode. The deposition rate in the C-RF sample set is 10-15% higher than that in the A-RF sample set. This is attributed to the larger area of the electrically grounded surface and to the higher ion/radical energy impinging on the cathode. In a capacitively coupled RF-PECVD system, any asymmetry in the sheath capacitances (anode and cathode) results in a DC bias on the electrodes. Typically, and in the present case, the anode is grounded and the cathode is smaller than the anode. Since the capacitance varies with the electrode area, and the voltage across a capacitor is inversely proportional to its capacitance, a DC bias is developed on the smaller electrode, the cathode. Hence, the ions and radicals impinging on the cathode possess greater energy than those impinging on the anode. These higher energy ions and radicals can penetrate the surface of a growing film and bond to a carbon cluster within the bulk of the film, leading to a higher growth rate. The decreasing trend of $E_{04}$ bandgap and increasing trend of extinction coefficient $k$ with increasing RF power will be discussed later in Section 4.2.3.

4.2.2 Structural Properties – FTIR Characterization

The deconvoluted FTIR absorption spectra, normalized on the film thickness, provide insight into the presence of the different C-H$_x$ stretching modes in terms of the hybridization and bond configurations in the a-C:H films. Nine C-H stretching modes have been identified through examination of free molecule vibrational frequencies which comprises the absorption spectra from 2700cm$^{-1}$ to 3100cm$^{-1}$ and can be found in Ristein et al. [143]. Figure 4.2(a) and (b) displays the IR absorption coefficient for the a-C:H films grown on the anode and cathode with an RF power of 60W. For the film grown on the anode in Figure 4.2(a), there is a wide range of stretching modes. In particular, there is a significant contribution from the end groups $sp^3$CH$_3$ and $sp^3$CH$_2$ with an estimated concentration (from EQN (5)) of $1.78 \times 10^{22}$ and $7.75 \times 10^{21}$ cm$^{-3}$. In contrast, for the film grown on the cathode in Figure 4.2(b) there is a comparable amount in $sp^3$CH$_2$ (6.82 x 10$^{21}$ cm$^{-3}$), $sp^2$CH olefinic (3.12 x 10$^{21}$ cm$^{-3}$), and $sp^2$CH aromatic (5.18 x 10$^{21}$ cm$^{-3}$). The total hydrogen concentration of the a-C:H films decreases with increasing RF power as displayed in Figure 4.2(c). Moreover, the hydrogen concentration is lower for the a-C:H films deposited on the
cathode. As well, for the films on the cathode, there is larger rate of decrease of the hydrogen concentration with increasing RF power as seen in Figure 4.2(c).

![Deconvoluted FTIR spectra in the C-H x stretching region for a-C:H films grown at an RF power of 60 W on the (a) anode and (b) cathode, respectively. (c) The hydrogen concentration and (d) the C-H x sp² bonding concentration as a function of the applied RF power for a-C:H films grown on the anode (solid blue line) and on the cathode (dash black line). Figure based on one published by Hsu et al. [130].](image)

As the RF power increases the ion energy increases since the RF voltage increases. As well, the DC bias on the cathode is increased from 34 V to 543 V with increasing RF power from 10W to 300 W. Thus, ions striking the cathode possess a great deal and more energy than those striking on the anode. The increase in ion energy with RF power accounts for the decreasing trend of the hydrogen concentration in the a-C:H film. High energy hydrogen ions/radicals can penetrate into the bulk of the film to displace a bonded hydrogen atom, form H₂, and desorb from the film.
Nevertheless, for the A-RF sample set the hydrogen concentration initially increases then decreases with a peak at 60 W. This is thought to be due to the increased plasma density as the RF power is increased from 10 W to 60 W. Although the film density is not taken into account, it is recognized that a relatively low hydrogen atomic density (in atoms/ cm\(^3\)) may actually be transformed into a relatively high atomic percentage (in at%) if the film exhibits a low density. Moreover, the C-H\(_x\) \(sp^2\) bonding modes could provide a qualitative measure of the change in the relative H bonding configuration with RF power. Hydrogen prefers to bond to \(sp^3\) hybridized carbon atoms as it represents a lower energy state than \(sp^2\) hybridized carbon. Accordingly, the C-H\(_x\) \(sp^2\) would be less likely to occur unless the available \(sp^3\) carbon bonds are near saturation due to a high percentage of hydrogen in the film. As depicted in Figure 4.2(d), the C-H\(_x\) \(sp^2\) concentration also tends to decrease as RF power increases except for the A-RF sample set with low power. Furthermore, the rate of decline of the H concentration and the C-H\(_x\) \(sp^2\) concentration is significantly larger for the C-RF sample set. This is consistent with the prior discussion about the role of the ion bombardment energy.

4.2.3 Structural Properties – XAES Characterization

Both sample sets (A-RF and C-RF) show an increase in the percentage of \(sp^2\)-hybridized carbon bonding, from XAES results, as the RF power increases (plot not shown here). The C-RF sample set possesses much greater \(sp^2\) bonding than the A-RF sample set as indicated in Figure 4.3. The percentage of \(sp^2\) hybridization increases as the RF power increases due to large ion energy impinging on the film to lower film density. High energy ions process enough energy to overcome the penetration threshold energy of the film, i.e. 32 eV. The excess energy that these ions possess, above the threshold energy, will be transferred to the thermal energy to the film. This relaxes C-C \(sp^3\) bonds to the more stable C-C \(sp^2\) configuration [46], leading to a further increase in \%\(sp^2\) bonding of the film. The rapid increase in the \%\(sp^2\) for the C-RF samples compared to A-RF ones is due to the much larger ion energy impinging on the cathode.

Robertson [46] describes the microstructures of a-C as a continuous network of \(sp^3\) bonded carbon atoms with \(sp^2\) bonded carbon localized clusters embedded within the network. The \(sp^3\) bond configuration forms \(\sigma-\sigma^*\) bands and the \(sp^2\) sites creates \(\pi-\pi^*\) bands which form localized states. The size and quantity of the \(sp^2\) clusters dominates the film’s optical properties. Accordingly, the increasing \%\(sp^2\) in the film implies an increase in the localized density of states
lying deep in the gap. This leads to the decrease in $E_{04}$ bandgap and the increase in extinction coefficient $k$ as illustrated in Figure 4.3.

Figure 4.3. The optical bandgap $E_{04}$ and extinction coefficient $k$ at 532 nm of the a-C:H films grown on the anode (solid blue line), and cathode (dash black line), as a function of the %$sp^2$ bonding. Figure based on one published by Hsu et al. [130].
4.3 Summary

In aid of laying the experimental foundation for MO-RFPECVD depositions, the effects of RF power and the positional placement of the substrate on optical properties of the host a-C:H films grown in the RF-PECVD system were investigated and discussed in relation to microstructural and local bonding features.

Both of the sample sets, C-RF and A-RF, reveal similar trends in the change in deposition rate, $n$ and $k$, and $E_{04}$ with increasing RF power. However, the rate of change is more rapid for the C-RF sample set, indicating that the positional placement of the substrate in this study plays an important role in the film deposition process. The increase in the deposition rate for both the C-RF and A-RF sample set with increasing RF power is due to the increase in ion energy and plasma density, leading to an increase in the flux of ions, radicals, and electrons at the substrate surface. Higher growth rate (by 10-15%) for the C-RF sample set is attributed to the higher ion/radical energy impinging on the cathode—where the energetic particles can penetrate the surface of a growing film and ultimately bond with a carbon cluster deep within the bulk of the film.

Moreover, the deconvoluted FTIR absorption spectra show that the total hydrogen concentration as well as the C-H$_x$ $sp^2$ bonding modes of the a-C:H films decrease with increasing RF power, which is a result of the increase in ion energy with RF power. Higher energy hydrogen ions/radicals can penetrate deeper into the bulk of the film to displace bonded hydrogen atoms, lead to the formation of H$_2$, and subsequently desorb from the film. Also, the rate of decline in the H concentration and the C-H$_x$ $sp^2$ concentration is significantly larger for the C-RF sample set, which is consistent with the prior discussion about the role of ions and radicals with higher bombardment energy on the cathode.

From XAES results, $%sp^2$-hybridized carbon bonding increases for both A-RF and C-RF sample sets with increasing RF power. This is attributed to the greater energy of the ions impinging the film which in turn led to lower film density with increasing RF power. As high energy ions possess excess energy, over and above the penetration threshold energy of the film, the excess energy serves to relax C-C $sp^3$ bonds to the more stable C=C $sp^2$ configuration. Accordingly, it results in a further increase in $%sp^2$ bonding of the film. Similarly, the rapid increase in the $%sp^2$ for the C-RF samples compared to A-RF samples is due to the much larger ion energy impinging on the cathode.
The microstructure of a-C films constitutes a continuous network of $sp^3$ bonded carbon atoms forming $\sigma-\sigma^*$ bands with localized clusters of $sp^2$ bonded carbon embedded within the network. These $sp^2$ clusters create $\pi-\pi^*$ localized states lying deeper in the gap. Thus, the increase in $%sp^2$ bonding accounts for the decrease in $E_{04}$ bandgap and accordingly the increase in the extinction coefficient $k$ with increasing RF power.

In conclusion, the A-RF a-C:H films exhibit higher H concentration along with a wider range of C-H$_x$ stretching modes, a wider bandgap $E_{04}$ and lower $%sp^2$ carbon bonding compared to C-RF films—suggesting that A-RF a-C:H films are polymeric-like amorphous carbon. It is also noted that the refractive index values of the A-RF a-C:H films, as presented in Figure 4.1, match the refractive index range reported for polymeric-like amorphous carbon [45]. Accordingly, the absorption of the host a-C film around 1 µm and 1.5 µm wavelength range is expected to be lower. Consequently, it was determined that the substrates would be situated on the anode with RF power range from 40 W to 60 W while performing \textit{in situ} doping using the X(fod)$_3$ (X= Er or Yb) metalorganic compounds to synthesize the a-C(X) films as described in the following chapters—Chapter 5 and Chapter 6. Results presented in this chapter have been reported in [130].
5 Erbium Metalorganic doped a-C in RF-PEMOCVD

5.1 Overview

In this chapter, the feasibility of in situ growth of Er-doped a-C based thin films (a-C(Er)) at low temperatures (<200 °C) by simple occlusion of a metalorganic in a radio frequency plasma-enhanced chemical vapor deposition (RF-PEMOCVD) system is investigated. The properties of the a-C host film and the incorporated Er concentration are independently controlled via delivering of Er metalorganic vapor from a separate thermal evaporator system inside the vacuum chamber and followed by mixing of the evaporant with the hydrocarbon plasma leading to the formation of a-C(Er) film. The enhancement of photoluminescence in a-C(Er) via deuteration of a-C host is probed and discussed in detail. The effect of RF power and substrate temperature on the photoluminescence of a-C(Er) films is systematically investigated. The film structure, incorporated Er concentration, and the effect of the change in optical properties of host a-C are also discussed.

For a-C(Er) samples, the hydrocarbon gas flow rate was 20 sccm and the chamber pressure was 60 mTorr, which were the same deposition parameters used for a-C:H film formation described in Chapter 4. For the films where the RF power was varied, the power was varied from 40 W to 60 W while the substrate temperature was kept constant at 80 °C. The RF power range was selected to be from 40 W to 60 W so as to minimize the $sp^2$ content in the host a-C film based on the observation in Chapter 4. As well, it lowers the probability of dissociating the Er-O bonds in the pristine metalorganic compound due to energetic ions/radicals. For the films where the substrate temperature was varied, the temperature was varied from 80 °C to 150 °C while the RF power was kept constant at 60W. The substrate temperatures of 80 °C to 150 °C were used, as opposed to room temperature, so as to aid the uniformity of the prepared films as well as to avoid the direct condensation of the metalorganic vapor in powder form; precluding direct condensation ensures vapor-plasma chemistry leading to molecular occlusion of the dopant. In this chapter, a controlled vapor flux of Er(fod)$_3$ compound is introduced by thermal evaporation at 150 °C as the melting point of Er(fod)$_3$ compound is 157-163 °C. Herein, the new Er(fod)$_3$ metalorganic compound with partial fluorinated hydrogen-containing ligands is selected, as opposed to Er(tmhd)$_3$ [133, 134, 136]. The Er(tmhd)$_3$ metalorganic compound contains a high percentage of
C-H bonds, 59 at%. Hence, this precursor is inherently inefficient at promoting Er\textsuperscript{3+} photoluminescence. Details for advantages of substitution of C-F with C-H bonds will be discussed in Section 5.3.2 and Section 6.5. As well, fluorine is also incorporated via the partially fluorinated X(fod)\textsubscript{3} precursor in the films. The effect of fluorine on the structure and properties of the films will be discussed in Section 6.5.

5.2 Er Metalorganic Doped in Hydrogenated a-C film

As discussed in the chapter 4, the host a-C:H films deposited on the anode exhibit a wider bandgap and less % of \textit{sp}\textsuperscript{2} carbon bonding. Thus the host film absorption in 1540 nm wavelength range is expected to be lower. Hence, the substrates were situated on the anode while performing the \textit{in situ} doping using the Er(fod)\textsubscript{3} compound to synthesize the a-C:H(Er) film.

Figure 5.1. Room temperature PL spectrum of a-C:H(Er) with peak centered at 1540 nm and FWHM of ~65 nm. Figure based on one published by Hsu \textit{et al.} [130].

The room temperature PL spectrum centered at 1540 nm exhibited in Figure 5.1 corresponds to the \textit{4}I\textsubscript{13/2} to \textit{4}I\textsubscript{15/2} electronic transition of Er\textsuperscript{3+} ions. The 65 nm spectral width of the emission band is due to inhomogeneous and homogeneous broadening in addition to Stark splitting of the Er\textsuperscript{3+} excited and ground states. The PL peak is wider than that of other Er-implanted silicate glasses [14], indicating the Er\textsuperscript{3+} possesses a variety of local bonding environments in the a-C:H
matrix. Its full width at half-maximum (FWHM) suggests the potential of enabling a wide gain band width for optical amplification. From XPS analysis, the concentration of Er of a-C:H(Er) film is estimated to be 3.9 at%, which is much greater than those prepared by magnetron sputtering of up to 1.2 at% [50, 51], pulsed laser deposition of 0.5 mol % [49, 116], and DC Saddle-Field PECVD of up to 2.3 at% [52].

The prominent PL signal observed from the hydrogenated a-C:H(Er) film is attributed to several factors including a high Er concentration, the large optical bandgap of the a-C:H host, and the decrease in the C-H quenching. The long hydrocarbon ligands of the Er metalorganic compound matches the internal structure of the a-C:H host matrix. This is thought to result in a high solubility of the Er metalorganic compound, and hence promote a high Er concentration. The large optical bandgap of the a-C:H host is thought to increase the pumping and emission efficiency of the Er\(^{3+}\) ions without high absorption from a-C:H host itself. More importantly, the Er(fod)\(_3\) compound deployed in this work has the partial fluorination of the hydrogen-containing ligands which also reduces the C-H quenching effect. This was likely to have resulted in an enhancement in the Er\(^{3+}\) luminescence efficiency [126, 137]. Details for advantages of substitution of C-F with C-H bonds will be discussed later in Section 5.3.2 and Section 6.5. The ligands and coordinated solvent molecules of Er metalorganic compounds usually contain C-H and O-H bonds. Accordingly, if excited Er\(^{3+}\) ions are close to C-H and O-H oscillators, a non-radiative transition occurs [151]. This would dramatically reduce the luminescence efficiency. It has also been quantitatively demonstrated that a three order of magnitude increase in the radiative lifetime can be achieved by increasing the distance between the neighboring C-H and O-H bonds in the ligands and the Er\(^{3+}\) ion [152]. However, the presence of C-H vibrational oscillators within a sphere of at least 20 Å from the Er\(^{3+}\) ion can still be an effective de-excitation site [152]. By using Er(fod)\(_3\), the fraction of C-H bonds in the film would be lower than that due to the use of Er(tmhd)\(_3\). Further, it is conceivable that the distance between Er\(^{3+}\) ions and the nearest C-H bond could be greater than 20 Å.

The ratio of the O to Er concentration in the a-C:H(Er) film is approximately 1.5 in the film instead of 6 in the pristine Er(fod)\(_3\) compound. Table 5.2 lists the ratio of the atomic concentrations and the relative (and the absolute) atomic concentrations of the Er(fod)\(_3\) compound, thermally evaporated (TE) Er(fod)\(_3\), and the a-C:H(Er) form XPS measurements. The \(\text{[F]}/\text{[O]}\), \(\text{[C]}/\text{[O]}\), and \(\text{[C]}/\text{[F]}\) concentration ratios are approximately 5.9, 9.1, and 1.5, which are greater than the Er(fod)\(_3\).
stoichiometric ratios of 3.5, 5, and 1.4. However, the [F]/[Er] and [C]/[Er] concentration ratios are approximately 9 and 14, all less than the Er(fod)₃ stoichiometric ratios of 21 and 30. This implies that the plasma causes significant dissociation of the Er(fod)₃ metalorganic compound. It is noted that the TE Er(fod)₃ film possesses essentially the same relative concentration as the Er(fod)₃ compound, with the exception that the [C] is enhanced. The [F]/[O], [F]/[Er], and [O]/[Er] ratios are similar, while the [C]/[O], [C]/[F], and [C]/[Er] are much larger than the stoichiometric Er(fod)₃ compound. This increase in the [C] is thought to be due to the trapping or intermolecular bonding of methane like species in the Er(fod)₃ film.

5.3 Photoluminescence Enhancement in a-C(Er) by Deuteration of a-C host

In the Er metalorganic compound, non-radiative deactivation channels exist near the active Er³⁺ ions due to the surrounding ligands. Any additional C-H [52, 152] and O-H bonds [14, 153] from the host material would cause additional quenching of the Er³⁺ luminescence. Thus, it is not surprising that there are only a few publications [48, 50-52] as mentioned in Section 2.4.1–2.4.2, which demonstrate the photoluminescence of Er complexes in hydrogenated amorphous carbon (a-C:H), or other carbon-based related materials such as polymers [119, 120] as mentioned in Section 2.4.3. To suppress the quenching effect from the Er(fod)₃ compound and the host material, the precursor gas used to deposit the host a-C was changed from methane (CH₄) to deuterated methane (CD₄). The resultant room temperature PL spectra are depicted in Figure 5.2. It is observed that the intensity of PL is enhanced by a factor of 6 (defined by the ratio of integrated area underneath of the PL spectra of a-C:D(Er) compared to a-C:H(Er) films) with the same Er concentration in the a-C:D matrix. This confirms that Er luminescence is enhanced through the substitution of H with D in the host a-C samples prepared by the one-step RF-PEMOCVD method.
5.3.1 Photo Excitation Mechanism

Photo excitation of the a-C(Er) film may follow several pathways. As displayed in Figure 5.3, the absorption spectra for the Er(fod)$_3$ compound suggests that the potential excitation source can be near 520 nm. Therefore, Er ions can be excited to $^4S_{3/2}$ level as shown in Figure 5.4 by a 532 nm laser. This is followed by decaying non-radiatively to the $^4I_{13/2}$ level, which is subsequently followed by the photoemission at 1.54 μm through the $^4I_{13/2}$ to $^4I_{15/2}$ transition. Another photo excitation pathway may occur through the a-C host. The photogenerated carriers in the surrounding a-C host could be transferred from the a-C matrix via the localized density of π or π* states, which lie in the gap due to $sp^2$ C=C clusters, to Er$^{3+}$ - that is, its higher excited levels and/or $^4I_{13/2}$ level as seen in Figure 5.4. This would then be followed by decaying non-radiatively to the $^4I_{13/2}$ level and subsequently by photon emission due to $^4I_{13/2}$ to $^4I_{15/2}$ transition. The role of $\%sp^2$ (the number and size of the C=C clusters) and the electronic energy transfer mechanism between the host a-C matrix and Er$^{3+}$ ions are under investigation as part of the enlarging scope of the present study. This will be done via the application of multiple laser excitations (488 nm and 980 nm) –in addition to the
presently employed 532 nm laser source –as proposed in Section 7.3.2 Future Work – Energy Transfer Mechanism.

Figure 5.3. The absorption spectra of \( \text{Er}(\text{fod})_3 \) metalorganic compounds dissolved in d-chloroform solvent.
Figure 5.4. A simplified conceptual diagram illustrating the $\sigma^*$ and $\sigma$ bands of a-C based host films, the energy levels of $\pi^*$ and $\pi$ states originating from $sp^2$ C=C bonds, and Er$^{3+}$ ions within the a-C matrix. Included is a 532 nm pump source whereby Er ions can be excited to $^4S_{3/2}$ level, followed by non-radiative decay to the $^4I_{13/2}$ level, and subsequent photoemission at 1.54 $\mu$m through the $^4I_{13/2}$ to $^4I_{15/2}$ transition. Also possible is the participation of localized density of states lying in the gap due to the $sp^2$ clusters in the host a-C matrix; these states can absorb incident photons and transfer the energy to the high energy- states of Er$^{3+}$, leading to PL emission around 1.54 $\mu$m. The non-radiative transitions are shown with broken arrows.
5.3.2 Vibrational Energy Levels of Various Organic Bonds

In order to obtain the relative wavenumber/wavelength positions and the range of energy levels of the first vibrational modes ($\nu = 1$) of C–H$_x$, C–D$_x$, and C–F$_x$ bonds as shown in Figure 5.5, the absorption peaks of the host hydrogenated, deuterated and fluorinated a-C films were measured by FTIR technique as displayed in Figure 5.6. From Figure 5.6, it can be seen that the first vibrational modes ($\nu = 1$) of C–H$_x$ and C–D$_x$ bonds are located at 2800–3100 cm$^{-1}$ (blue curve) and 2000–2300 cm$^{-1}$ (green curve). Thus, it can be inferred that the second ($\nu = 2$) harmonic vibrational modes of C–H$_x$ peaks are at approximately 5600–6200 cm$^{-1}$, which match the radiative transition from the first excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$ in Er$^{3+}$ ions (at approximately 6060–6900 cm$^{-1}$ as determined from PL spectrum range of 1450-1650 nm in Figure 5.2) as shown in Figure 5.5. Also, the third harmonic vibrations ($\nu = 3$) of C–D$_x$ bonds can be inferred to be at 6000–6900 cm$^{-1}$, which match the radiative transition in Er$^{3+}$ ions as well. The first vibrational modes ($\nu = 1$) of O–H and O–D are approximately located at 3100–3800 cm$^{-1}$ centered at 3450 cm$^{-1}$ and 2150–2850 cm$^{-1}$ centered at 2500 cm$^{-1}$ from the cited reference papers [41, 48]. Accordingly, it can be inferred that the O–H second harmonic vibrational mode ($\nu = 2$) is at approximately 6200–7600 cm$^{-1}$ and the O–D third harmonic vibrational mode ($\nu = 3$) are at approximately 6450–8550 cm$^{-1}$ as shown in Figure 5.5. Furthermore, the first set of harmonic vibrational mode of C–F$_x$ is at 900–1400 cm$^{-1}$ as observed in Figure 5.6 (orange curve). Thus, it can be inferred that the 5$^{th}$ and 6$^{th}$ harmonic vibrational modes are at 4500-7000 cm$^{-1}$ and 5400-8400 cm$^{-1}$, which also overlap with the Er$^{3+}$ first excited state. The relative positions of the energy levels of various organic bonds in the solid state and their inferred harmonic modes are summarized in Table 5.1. Moreover, the darker sections of the band in Figure 5.5 signify a higher absorption coefficient. Hence, the grey band indicates the energy distribution of the vibrational levels.

Besides using the FTIR technique to obtain the range of energy levels of the first vibrational modes ($\nu = 1$) of C–H$_x$, C–D$_x$, and C–F$_x$ bonds from hydrogenated, deuterated, and fluorinated a-C films, the absorption spectra of various solvents (methanol, isohexane, IPA, methanol-d4, chloroform-d) possessing different combinations of C–H$_x$, C–D$_x$, and O–H bonds are shown in Figure 5.7, which roughly confirm the second ($\nu = 2$) harmonic vibrational modes of O–H, C–H$_x$, and O–D bonds in Figure 5.5.
Figure 5.5. Illustration of energy levels of the vibrational modes for C–H, C–D, O–H, O–D, and C–F bonds in the solid state [151], where the range of each vibrational mode is inferred from FTIR spectra of the host a-C:H, a-C:D and fluorinated a-C:D films as displayed in Figure 5.6. The grey band here is used to represent the highly varying bonding structure, which reflects the levels associated with the numerous combinations of nearest neighbors and the different local bonding environments. Figure based on one published by Hsu et al. [131].
Table 5.1. A summary of the energy levels and associated harmonic modes of C–H, C–D, O–H, O–D, and C–Fx bonds in the solid state. The range of energy levels of the first vibrational modes (υ = 1) of C–H, C–D, and C–Fx bonds were directly measured by FTIR technique while those for O–H and O–D bonds are taken from references [41, 48]. The higher vibrational modes are inferred from the first respective mode.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Range (cm⁻¹)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C–Hx</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2800–3100</td>
<td>a-C:H film</td>
</tr>
<tr>
<td>2</td>
<td>5600–6200</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8400–9300</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>11200–12400</td>
<td></td>
</tr>
<tr>
<td><strong>C–Dx</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2000–2300</td>
<td>a-C:D film</td>
</tr>
<tr>
<td>2</td>
<td>4000–4600</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6000–6900</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8000–9200</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>10000–11500</td>
<td></td>
</tr>
<tr>
<td><strong>O–H</strong></td>
<td></td>
<td>Literature</td>
</tr>
<tr>
<td>1</td>
<td>3100–3800</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6200–7600</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9300–11400</td>
<td></td>
</tr>
<tr>
<td><strong>O–D</strong></td>
<td></td>
<td>Literature</td>
</tr>
<tr>
<td>1</td>
<td>2150–2850</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4300–5700</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6450–8550</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8600–11400</td>
<td></td>
</tr>
<tr>
<td><strong>C–Fx</strong></td>
<td></td>
<td>a-C:D:F film</td>
</tr>
<tr>
<td>1</td>
<td>900–1400</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1800–2800</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2700–4200</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3600–5600</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4500–7000</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5400–8400</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>6300–9800</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>7200–11200</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>8100–12600</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.6. FTIR spectra of the host a-C:H, a-C:D, and a-C:D:F (CF<sub>4</sub>/[CF<sub>4</sub>+CD<sub>4</sub>] = 50 vol. %) films without rare earth (Er or Yb) metalorganic compound incorporation prepared under the same deposition condition except for the precursor gas. The range of the first vibrational mode illustrated in Figure 5.5 is inferred from this data. Figure based on one published by Hsu et al. [132].

Figure 5.7. The absorption spectra of various solvents comprising different combinations of C–H<sub>x</sub>, C–D<sub>x</sub>, and O–H bonds.
5.3.3  Photoluminescence Enhancement

The enhancement of PL is a result of the weaker interaction strength between Er\(^{3+}\) and the C–D\(_x\) and O–D third harmonic vibrations, compared to the interaction strength between Er\(^{3+}\) and the C–H\(_x\) and O–H second harmonic vibrations. The C–H\(_x\) and O–H second harmonic vibrations approximately match the radiative transition from the first excited state \(4I_{13/2}\) to the ground state \(4I_{15/2}\) in Er\(^{3+}\) ions [23] as seen in Figure 5.5. Accordingly, if excited Er\(^{3+}\) ions are disturbed nearby C–H\(_x\) and O–H oscillators, a non-radiative transition transpires. By applying the undistorted oscillator model [24], it is determined that the transition probability between Er\(^{3+}\) and the vibrational modes of the host a-C:D significantly decreases. The transition probability can be quantitatively estimated by the Franck-Condon factor, \(F\), from the approximation of the undistorted oscillator model [154]:

\[
F(E) = \frac{\nu^\nu e^{-\gamma}}{v!}, \quad \gamma = \frac{1}{2} k \frac{(q-q^0)^2}{\hbar w}
\]

where \(k\) is the force constant, \(q\) and \(q^0\) are equilibrium positions of the oscillators, \(\hbar\) is Planck’s constant and \(w\) is frequency. Consequently, the Franck-Condon factor \(F\) decreases as \(\nu\) increases and thus lowers the probability of the non-radiative transition. As an example, \(F\) are 0.076 and 0.012 for \(\nu = 2\) and \(\nu = 3\), respectively, assuming \(\gamma = 0.5\). The 5\(^{th}\) and 6\(^{th}\) harmonic vibrational modes of C–F\(_x\) overlap with the first excited state of Er\(^{3+}\), however they play a negligible role on PL quenching as these vibrational modes are much higher (\(\nu = 5, 6\)) compared to O–H (\(\nu = 2\)) and C–H\(_x\) (\(\nu = 2\)) modes. Hence, by selecting the Er(fod)\(_3\) metalorganic compound having the chemical structure Er(C\(_{10}\)H\(_{10}\)F\(_7\)O\(_2\))\(_3\) as the doping precursor instead of Er(tmhd)\(_3\), tris(2,2,6,6-tetramethyl-3,5-heptanedionato)Erbium(+III) with chemical structure Er(C\(_{11}\)H\(_{19}\)O\(_2\))\(_3\), the PL quenching by C–H\(_x\) is expected to be mitigated.

Furthermore, by directly comparing the FTIR spectra of the host a-C:H and a-C:D films, shown in Figure 5.6, the impact of the host a-C materials on Er\(^{3+}\) PL quenching can be seen. Deuteration of the host a-C effectively shifts the absorption of the first vibrational mode (\(\nu = 1\)) to lower wavenumber (longer wavelength). Also, the magnitude of the absorption has decreased by at least 50% as indicated in Figure 5.6. Moreover, the higher harmonic vibrational modes are much weaker, implying much lower absorption of C–D\(_x\) in the third harmonic (\(\nu = 3\)) than that of C–H\(_x\).
in the second harmonic ($\nu = 2$). Thus, this leads to an increase in the efficiency of the PL at 1540 nm for a-C:D(Er) films.
Table 5.2. Ratios of atomic concentrations and relative/absolute atomic concentrations of relevant elements in as-received stoichiometric Er(fod)$_3$ compound, thermally evaporated (TE) Er(fod)$_3$, and in seven a-C:D(Er) films deposited under varying conditions as determined from XPS measurements. Table based on one published by Hsu et al. [131].

<table>
<thead>
<tr>
<th>Sample</th>
<th>RF Power (W)</th>
<th>Substrate Temperature (°C)</th>
<th>C at%</th>
<th>Er at%</th>
<th>F at%</th>
<th>O at%</th>
<th>[O]/[Er]</th>
<th>[F]/[Er]</th>
<th>[C]/[Er]</th>
<th>[O]/[C]</th>
<th>[F]/[C]</th>
<th>[O]/[F]</th>
<th>Thickness (100 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er(fod)$_3$</td>
<td></td>
<td></td>
<td>34.1</td>
<td>1.1</td>
<td>23.9</td>
<td>6.8</td>
<td>6.00</td>
<td>21.00</td>
<td>30.00</td>
<td>0.20</td>
<td>0.70</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>TE Er(fod)$_3$</td>
<td></td>
<td></td>
<td>71.3</td>
<td>1.0</td>
<td>21.5</td>
<td>6.3</td>
<td>6.33</td>
<td>21.74</td>
<td>72.08</td>
<td>0.09</td>
<td>0.30</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>a-C:H(Er)</td>
<td>40</td>
<td>80</td>
<td>54.6</td>
<td>3.9</td>
<td>35.4</td>
<td>6.0</td>
<td>1.54</td>
<td>9.08</td>
<td>14.00</td>
<td>0.11</td>
<td>0.65</td>
<td>0.17</td>
<td>14.85</td>
</tr>
<tr>
<td>1</td>
<td>40</td>
<td>80</td>
<td>36.9</td>
<td>5.5</td>
<td>50.5</td>
<td>7.1</td>
<td>1.31</td>
<td>9.26</td>
<td>6.75</td>
<td>0.19</td>
<td>1.37</td>
<td>0.14</td>
<td>15.21</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>80</td>
<td>52.3</td>
<td>4.2</td>
<td>37.4</td>
<td>6.1</td>
<td>1.47</td>
<td>9.02</td>
<td>12.60</td>
<td>0.12</td>
<td>0.72</td>
<td>0.16</td>
<td>17.64</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>80</td>
<td>61.5</td>
<td>2.8</td>
<td>29.0</td>
<td>6.7</td>
<td>2.38</td>
<td>10.33</td>
<td>21.88</td>
<td>0.11</td>
<td>0.47</td>
<td>0.23</td>
<td>19.85</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>90</td>
<td>77.9</td>
<td>1.4</td>
<td>5.4</td>
<td>12.3</td>
<td>8.81</td>
<td>3.85</td>
<td>55.66</td>
<td>0.16</td>
<td>0.07</td>
<td>2.29</td>
<td>13.52</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>100</td>
<td>79.6</td>
<td>1.1</td>
<td>4.0</td>
<td>15.3</td>
<td>13.83</td>
<td>3.60</td>
<td>72.14</td>
<td>0.19</td>
<td>0.05</td>
<td>3.84</td>
<td>8.47</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>120</td>
<td>85.7</td>
<td>0.7</td>
<td>2.4</td>
<td>11.2</td>
<td>15.86</td>
<td>3.46</td>
<td>121.58</td>
<td>0.13</td>
<td>0.03</td>
<td>4.58</td>
<td>4.78</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>150</td>
<td>95.9</td>
<td>0.2</td>
<td>0.4</td>
<td>3.5</td>
<td>22.78</td>
<td>2.37</td>
<td>618.45</td>
<td>0.04</td>
<td>0.00</td>
<td>9.61</td>
<td>3.32</td>
</tr>
</tbody>
</table>
5.4 Effect of RF Power and Substrate Temperature on a-C:D(Er) Film

Two key parameters that are found to influence the concentration of Er occluded in the a-C:D(Er) film are the RF power and substrate temperature. Table 5.2 lists the ratios of the atomic concentrations and the relative (and absolute) atomic concentrations of the relevant elements in the as-received stoichiometric Er(fod)$_3$ compound, thermally evaporated (abbreviated TE) Er(fod)$_3$, a-C:H(Er), and in the seven a-C:D(Er) films deposited under varying conditions as determined from XPS measurements. In comparing the a-C:D(Er) film deposited at an RF power of 40W to the stoichiometric Er(fod)$_3$ compound, a few results are observed. The [O]/[C] ratios are very similar, ~ 0.19 in the a-C:D(Er) film compared to ~ 0.20 in the stoichiometric Er(fod)$_3$. Meanwhile, the [O]/[Er] and [C]/[Er] ratios are approximately 4.5× smaller in the film, while the [F]/[Er] ratio is 2.3× smaller in the film. This suggests that Er incorporation is being promoted in the film. Moreover, since the [F]/[C] ratio is 2× larger in the film, fluorine incorporation is also being promoted. Clearly, the plasma environment causes significant dissociation of the Er(fod)$_3$ compound. The loss of C and O atoms is attributed to the loss of large C$_x$O$_y$ (or deuterated C$_x$O$_y$) fragments. The increase in the F concentration is attributed to the selective incorporation of C$_m$F$_n$ fragments.

The Er concentration in a-C:D(Er) decreases with increasing RF power as seen in Table 5.2. This is evident from the increasing [O]/[Er], [F]/[Er], and [C]/[Er] ratios. The [C] increases with increasing RF power. This is observed through the increase in the [C]/[Er] ratio and decrease in the [O]/[C] and [F]/[C] ratios. The [O] increases when compared to the [F] with increasing RF power, as seen through the increase in the [O]/[F] ratio. The decrease in the relative Er, F, and O concentrations relative to [C] with increasing RF power is due to the increase in the plasma density. As the RF power increases, the dissociation of the precursors (CD$_4$ and Er(fod)$_3$) increases. Thus, more C is being incorporated via CD$_4$. The relative [F] is still quite large, 29 at% for the 60W sample, which is considered to aid the PL efficiency by further reducing the C-H quenching as discussed in the Section 5.3.2 and Figure 5.5. Also, note the decrease in the relative [Er], from 5.5 at% at 40W to 2.8 at% at 60W. Despite this decrease, the [O]/[Er] ratio increases from 1.31 to 2.38 as observed in Figure 5.8(a). The increase in [O]/[Er] ratio reflects the increase in the number of
erbium-oxygen bonded complexes, which are responsible for the increase in the PL signal with increasing RF power as indicated in Figure 5.8(a).

Figure 5.8. (a) The [O]/[Er] ratio (black triangle) and normalized PL peak intensity (blue triangle) as a function of the applied RF power with a substrate temperature of 80 °C. (b) The Er concentration (solid black circle) and normalized PL peak intensity (solid blue circle) as a function of the substrate temperature with an RF power of 60 W. The normalized PL peak intensity is shown to depend critically on the (c) [O]/[Er] ratio, and (d) [Er]. The lines are guides to the eye. $I_{\text{nor}}$ is defined as the PL intensity peaking at ~1540 nm and normalized to the respective a-C(Er) film thickness indicated in Table 5.2. Figure based on one published by Hsu et al. [131].
Another means of controlling the a-C:D(Er) film structure, and hence the PL efficiency, is through the temperature of the growth surface. The Er(fod)_3 evaporation temperature is 150 °C. Hence, the temperature of the substrate will affect the relative sticking coefficient of the Er metalorganic and its associated molecular fragments. Analyzing the XPS spectra for the films grown as the substrate temperature was varied from 80 °C to 150 °C yield a number of results as displayed in Table 5.2. The [F] decreases rapidly with increasing substrate temperature. This is seen through the increasing [O]/[F] ratio and the decreasing [F]/[Er] and [F]/[C] ratios. The [Er] is also decreasing with increasing substrate temperature as shown in Figure 5.8(b). This is evident from the increase in the [O]/[Er] and [C]/[Er] ratios. In examining the [O]/[C] ratio, the [O] increases, peaks at a substrate temperature of about 100 °C, then decreases as the substrate temperature increases. The considerable loss of F is associated with a drop in the deposition of fluorinated Er(fod)_3 molecular fragments. This is presumably due to either an increased desorption rate or a lower sticking coefficient of the fluorinated fragments. This is supported by the rise in the [O]/[C] ratio, which implies that oxygenated molecular fragments (C_xO_y) are preferentially incorporated into the film. The boiling temperatures of C_xO_y molecules are typically higher than C_mF_n molecules. Moreover, it is well known that the deposition rate of a-C:H decreases with increasing substrate temperature [155]. Hence, the increase in the [C] is not necessarily due to CD_4 species. Despite the relatively large decrease in the [F], and the smaller decrease in the [Er], the relative PL intensity slowly decreases as indicated in Figure 5.8(b). This is attributed to the increasing [O]/[Er] ratio as seen in Figure 5.8(c). Hence, more Er atoms are considered to be in the 3+ state. As well, the loss of a large fraction of the fluorinated ligands which in turn have likely been replaced by the deuterated film is considered to suppress the optical quenching of excited Er^{3+} ions.

As the substrate temperature is increased beyond 100 °C, there is an increase in the desorption rate or a lowering of the sticking coefficient of O containing species. At a substrate temperature of 150 °C, the majority of the film is deuterated amorphous carbon with minute O, F, and Er concentration. The [O]/[Er] ratio is 22.78 and a PL signal is present, although the peak is approximately 7× lower than the maximum PL signal due to the lower Er concentration. Examining the change in the optical properties of a-C:D host, it is observed that k increases from 1.65 x 10^{-3} to 3.2 x 10^{-3} and E_{04} decreases from 3.81 eV to 3.41 eV as the substrate temperature is
increased from 80 °C to 150 °C. This minute change is not expected to significantly influence the optical pumping, absorption and PL.

5.5 Er Quenching Concentration in a-C:D(Er) Film

In order to study the concentration dependence of the incorporated Er(fod)$_3$ on luminescence of the a-C:D matrix in more detail, the PL intensity which peaks at 1540 nm is normalized to the film thickness, denoted $I_{nor}$. Figure 5.8(d) plots the $I_{nor}$ as a function of the Er concentration, $N_{Er}$. $I_{nor}$ is proportional to $\sigma \phi N \Gamma / \Gamma_{rad}$ under the continuous laser pumping condition [156], where $\sigma$ is the excitation cross section, $\phi$ is the photon flux, $N$ is the optically active Er concentration, $\Gamma$ is the lifetime, and $\Gamma_{rad}$ is the radiative lifetime. The increase in $N_{Er}$ will result in a linear increase in $I_{nor}$ if all the incorporated Er atoms are optically active, i.e., $N \sim N_{Er}$, and if there are no quenching effects to adversely affect $\sigma$ and $\Gamma / \Gamma_{rad}$. In Figure 5.8(d) it is observed that $I_{nor}$ increases linearly up to an Er concentration of approximately 2.2 at% and thereafter begins to drop. The latter suggests a reduction in lifetime $\Gamma$ as $N_{Er}$ increases beyond this point. It indicates that the Er concentration quenching effect sets in after the Er concentration reaches ~ 2.2 at% and continues to increase until 5.5 at% at which point the PL becomes very weak.

The highest Er concentration achieved via RF-PEMOCVD system in this research is 5.5 at%, which is lower than 8.7 at%, the maximum concentration obtained by doping Er(tmhd)$_3$ in RF-PECVD method [115]. This could be attributed to the presently employed partially fluorinated metalorganic compound, Er(fod)$_3$ (Er(C$_{10}$H$_{10}$F$_7$O$_2$)$_3$), in this research, with partial replacement of C-H bonds with C-F bonds as opposed to Er(tmhd)$_3$ with its chemical structure of Er(C$_{11}$H$_{19}$O)$_3$. The covalent radius and Van der Waals radius of F atoms are 71 pm and 147 pm, respectively, which are larger than 37 pm and 120 pm for H atoms. Accordingly, the volume of the F related bonds (i.e., Er-F$_x$, Er-F$_2$O, Er-F$_2$-O, and C-F$_x$ bonds, will be discussed later in Section 6.5) should be higher than that of H-related bonds (i.e., C-H$_x$, O-H) in the a-C:H(Er) films prepared from Er(tmhd)$_3$. It is also worthy to note that the F at% in the film is as high as 50.5 at% as seen in Table 5.2. Thus, the high F incorporation could lead to a slightly lower Er incorporation. However, prominent RT PL at 1.54 µm in a-C:H:F(Er) with slightly lower Er concentration was obtained as shown in Figure 5.1 as opposed to no RT PL exhibited by the high 8.7 at% Er incorporated a-C:H(Er) film.
5.6 Er Oxidation State in a-C:D(Er) Film

The Er4d XPS spectra of the Er(fod)\(_3\) powder, the evaporated Er(fod)\(_3\) film, and the three a-C:D(Er) samples with different Er concentrations are compared in Figure 5.9. The spectra reveal similar spectral characteristic feature at a binding energy of approximately 169.5 eV for all of the samples. This is attributed to the 4d levels in the Er\(^{3+}\) ions forming a multiplet through the interaction with the unfilled shell [157]. Hence, the incorporated Er in a-C:D(Er) films is similar to the Er in the Er(fod)\(_3\) compound. Moreover, it suggests partial preservation of the Er\(^{3+}\) state in a-C:D(Er) films. The presence of a PL signal also supports this result, in spite of the fact that the O/Er ratio is less than 6 as is the case in the pristine Er(fod)\(_3\) powder.

![Figure 5.9. (a) XPS spectra of the three a-C:D(Er) films, Er(fod)\(_3\) film (evaporated in the vacuum chamber with CD\(_4\) precursor gas flowing without plasma ignition), and the as-received stoichiometric Er(fod)\(_3\) powder. The curves have been shifted vertically for clarity of presentation. Figure based on one published by Hsu et al. [131].](image)

5.7 Depth Distribution of a-C(Er) Film

The depth distribution measured by XPS technique as depicted in Figure 5.10 reveals a uniform concentration of Er throughout the film of 850 nm in thickness. It is noteworthy that the high oxygen concentration at the surface is simply surface contamination.
The in situ thermal evaporation technique provides the potential of doping Er in a vertically uniform profile as well as design specific concentration profiles via a controllable delivering vapor flux from Er metalorganic compound with high vapor pressure below 200 °C. This is in contrast to the ion-implantation technique [14], post solution immersion method, or vapor exposure to an Er source procedure [50], where the optically active ions are invariably located near the surface. Further, film damage caused by the high energy ions in the ion-implantation process is avoided. Moreover, the present approach does not require an additional sacrificial metal layer which is typical in the implantation process for non-metallic thin film hosts so as to prevent electrical charging. Also, compared to the co-sputtering [13] or pulsed laser ablation [49, 116] of an Er-containing target, this method enables independent control of the Er concentration profile and optical properties of the host material.

![Figure 5.10. Depth profile of C, F, O, and Er concentrations in a-C(Er) film deposited at 60W of RF power and 80°C as determined from XPS measurements. Figure based on one published by Hsu et al. [131].](image-url)
5.8 Summary

The feasibility of the *in situ* growth of Er-doped a-C thin films (a-C:(Er)) on Si substrates at low temperature (< 200 °C) by a simple one-step metalorganic radio frequency plasma-enhanced chemical vapor deposition system was successfully demonstrated. A high Er concentration (3.9 at\%) in a-C:H(Er) films was achieved and room temperature PL peaking at 1.54 μm was observed. By adopting a new Er metalorganic precursor with partial fluorination, Er(fod)$_3$, the optically active Er$^{3+}$ ions are conserved, thus avoiding a subsequent high temperature annealing procedure. In addition, non-radiative C-H vibrational quenching was expected to be significantly reduced by partial fluorination of the surrounding ligands. Therefore, room temperature PL was achieved despite the use of hydrogenated amorphous carbon as the host material.

Furthermore, the enhancement of the PL was demonstrated via deuteration of the a-C host by effectively shifting the quenching vibrational modes to lower wavenumbers and decreasing the respective magnitudes of absorption. The effect of RF power and substrate temperature on the Er concentration, [O]/[Er] ratio, and the respective PL intensity of the a-C:D(Er) film was investigated. It was observed that the PL signal increases with increasing RF power, which is attributed to an increase in [O]/[Er] ratio and hence the erbium-oxygen coordination number. The relatively large [F] is deemed to contribute to the enhancement in PL efficiency. In addition, PL intensity and [Er] decrease with increasing substrate temperature; the decrease in [Er] is attributed to an increased desorption rate or a lower sticking coefficient of the fluorinated fragments during film growth. By examining the relationship of the normalized PL intensity, $I_{nor}$, as a function of the Er concentration, it is observed that Er concentration quenching begins at ~ 2.7 at\% and continues to increase until 5.5 at\% at which point the PL is very weak. Furthermore, the foregoing indicate the preservation of the Er$^{3+}$ state in a-C:D(Er) films was achieved. The *in situ* thermal evaporation technique provides the capability of doping Er in a uniform profile vertically/depth-wise. More importantly, thickness of up 2 μm of a-C:D(Er) film was achieved, which provides flexibility in the design of optical waveguides. These properties suggest that a-C:D(Er) may be a promising material for active photonic devices to be integrated with the current Si CMOS platform. Results presented in this chapter have been reported in [130, 131].
6  Ytterbium Metalorganic doped a-C in RF-PEMOCVD

6.1  Overview

As mentioned in Section 2.2.4 and 2.4.4, Yb:YAG lasers lack excited-state absorption, as well. Yb$^{3+}$ ions have a long luminescence lifetime [20] (up to 1 ms) and a relatively large emission cross section, leading to a higher pumping efficiency [21] compared to Nd based solid lasers. While extensive research on Yb-doped ceramic and oxide thin films deposited with various methods has been performed as described in Section 2.2.4, Yb doping in carbon based hosts has been minimal.

In this chapter, Yb-doped a-C based thin films (a-C(Yb)) were prepared by simple occlusion of the metalorganic at low temperatures (< 200 °C) in a RF-PEMOCVD system. The enhancement of photoluminescence by substitution of O–H and C–H$_x$ bonds with O–D and C–D$_x$ bonds is probed and discussed in detail. The effect of the substrate temperature on the PL of a-C(Yb) films is investigated and correlated to the film microstructure and bonding environment. The change in the optical properties of the host a-C upon incorporation of fluorinated Yb metalorganic compound is also discussed.

For a-C(Yb) films, the substrate temperature was varied from 60 °C to 150 °C. The hydrocarbon gas flow rate was 20 sccm, chamber pressure was at 60 mTorr, and the RF power was kept constant at 60 W according to the results uncovered from the a-C(Er) study presented in Section 5.4. In this work, a controlled vapor flux of the Yb(fod)$_3$ compound is introduced by thermal evaporation at 110 °C as the melting point of Yb(fod)$_3$ compound is 108-111 °C. The vapor flux is mixed with the hydrocarbon plasma for a-C(Yb) film formation. Double-side polished crystalline silicon substrates with high resistivity were subjected to the standard CMOS cleaning procedure before being loaded into the chamber.

6.2  Photoluminescence Enhancement in a-C(Yb) Film by Deuteration of a-C host

The bonding environment of the Yb ions in the selected Yb(fod)$_3$ metalorganic compound, with the chemical structure Yb(C$_{10}$H$_{10}$F$_7$O$_2$)$_3$, is similar to that in Yb$_2$O$_3$. These optically active
Yb$^{3+}$ ions can be preserved under appropriate plasma deposition conditions without the need of a post-deposition annealing step. Fluorine is also incorporated via the partially fluorinated Yb(fod)$_3$ precursor. The effect of fluorine on the structure and properties of the films will be discussed in Section 6.5.

It is noteworthy that the resultant a-C:H:F(Yb) films may contain O–H bonds which form during the decomposition of the Yb(fod)$_3$ vapor flux which mixes with the methane (CH$_4$) plasma. Although the source of oxygen is limited in the Yb(fod)$_3$ precursor, the residual coordinated solvent molecules in the Yb(fod)$_3$ compound may also contribute to the overall source of oxygen and hydrogen. In addition, the resultant a-C:H:F(Yb) films will contain C-H bonds where the source of hydrogen includes the methane precursor gas and the existing ligands from Yb(fod)$_3$ vapor flux. Hence, prior to a-C:H:F(Yb) film formation via the RF-PEMOCVD method, the impact of the neighboring C–H$_x$ and O–H bonds in the host on the room temperature PL of the selected Yb(fod)$_3$ precursor was investigated.

The 0.5 mM Yb(fod)$_3$ powder was dissolved in Chloroform (CHCl$_3$), Methanol (CH$_3$OH), and their respective deuterated solvents, i.e., Chloroform-d (CDCl$_3$) and Methanol-d$_4$ (CD$_3$OD). It can be seen in Figure 6.1(a) that the PL intensity is enhanced by a factor of 2.6 (defined by the ratio of total integrated areas underneath the 3 deconvoluted peaks, the deconvoluted PL spectra not shown here) as the solvent CHCl$_3$ is replaced with CDCl$_3$. This suggests the Yb(fod)$_3$ PL is quenched by the C–H bonds in neighboring solvent molecules. Figure 6.1(b) displays the PL enhancement by a factor of 6.6 when using the CD$_3$OD solvent instead of the CH$_3$OH solvent. Since the CH$_3$OH host solvent molecules contain both C–H$_x$ and O–H bonds, the PL quenching of Yb(fod)$_3$ is more significant. As previously shown, O–H bonds contribute non-radiative deactivation channels for excited Yb$^{3+}$ ions [151, 158, 159]. It has been demonstrated that the Yb radiative lifetime is limited by the presence of O–H groups in the sol-gel silica glass host matrix [158]. Hence, hydrogen containing groups such as X–H (where X = O, C) appear to aid in PL quenching due to the proximity of their vibrational modes to the excited states of Yb ions as indicated in Figure 6.2. To suppress the O–H and C–H quenching effect near the Yb$^{3+}$ ions in a-C:H:F(Yb) films, the precursor gas was changed from methane (CH$_4$) to deuterated methane (CD$_4$). This reduces the formation of O–H and C–H$_x$ bonds which are now substituted by O–D and C–D$_x$ bonds [52, 131].
Figure 6.1. Comparison of the PL intensity of Yb(fod)$_3$ powder dissolved in (a) Chloroform (CHCl$_3$) and Chloroform-d (CDCl$_3$); in (b) Methanol (CH$_3$OH) and Methanol-d$_4$ (CD$_3$OD). (c) Comparison of the PL intensity of a-C:D:F(Yb: 1.6 at%) and a-C:H:F(Yb: 1.6 at%) films prepared using RF power of 60 W, precursor gas flow rate of 20 sccm, deposition pressure of 60 mTorr, substrate temperature of 90 °C, and Yb(fod)$_3$ powder evaporation temperature of 110 °C. Figure based on one published by Hsu et al. [132].
The room temperature PL spectra of a-C(Yb) samples shown in Figure 6.1(c), exhibit peaks around 985, 1013, and 1048 nm (the 3 deconvoluted PL peaks are not shown here), which correspond to the $^2F_{5/2}$ to $^2F_{7/2}$ electronic transition of Yb$^{3+}$ ions in Figure 6.2. For a-C:D:F(Yb) sample, its FWHM widths are approximately 20, 80, and 46 nm for the 3 deconvoluted PL peaks located near 985, 1013, and 1048 nm, respectively. The wide spectral width of the emission band is attributed to inhomogeneous and homogeneous broadening in addition to Stark splitting of the Yb$^{3+}$ excited and ground states. It suggests the potential of enabling a wide gain bandwidth for optical amplification and tunable laser design. In addition, the PL peak of the a-C(Yb) samples is wider
than those of other Yb doped ceramic and oxide based hosts [24, 36, 160, 161]. This suggests the Yb$^{3+}$ ion possesses a variety of local bonding environments in the a-C matrix, which will be discussed further in the XPS analysis in Section 6.5. Figure 6.1(c) shows the PL intensity is enhanced by a factor of 4.2 for the same Yb concentration in the deuterated a-C matrix as opposed to the hydrogenated a-C matrix. This suggests that Yb luminescence is enhanced through the substitution of O–H and C–H$_x$ groups with O–D and C–D$_x$ groups in the a-C(Yb) films prepared by the RF-PEMOCVD method. Nevertheless, the enhanced luminescence factor for the deuterated a-C(Yb) sample, i.e. 4.2, is lower than that of the Yb(fod)$_3$ deuterated methanol solution, i.e. 6.6, as shown in Figure 6.1(b). The factors that may contribute to the lower PL enhancement for the deuterated a-C(Yb) sample include the presence of C–H$_x$ bonds within the host that may reside in close proximity to the Yb$^{3+}$ ions for the given deposition conditions and/or some of the Yb ions in a-C(Yb) not being in the optically active 3+ state, which will be discussed in Section 6.4 and 6.5.

The enhancement of PL is primarily attributed to the weaker interaction strength between Yb$^{3+}$ and the O–D fourth harmonic vibration ($\nu = 4$) and the C–D$_x$ fourth and fifth harmonic vibrations ($\nu = 4, 5$) as compared to the interaction strength between Yb$^{3+}$ and the O–H third harmonic vibration ($\nu = 3$) and the C–H$_x$ third and fourth harmonic vibrations ($\nu = 3, 4$), as shown in Figure 6.2. The O–H third harmonic vibration mode (at approximately 9300-11400 cm$^{-1}$ [151, 162]) matches the radiative transition from the first excited state $^2F_{5/2}$ to the ground state $^2F_{7/2}$ in Yb$^{3+}$ ions (at approximately 9090–11110 cm$^{-1}$ as determined from the PL spectrum range of 900-1100 nm shown in Figure 6.1(c)), as shown in Figure 6.2. Also, the C–H$_x$ third and fourth harmonic vibration modes (at approximately 8400–9300 cm$^{-1}$ and 11200–12400 cm$^{-1}$ as inferred from FTIR spectra of C–H$_x$ peaks measured in a-C:H film as displayed in Figure 5.6) match the radiative transitions in Yb$^{3+}$ ions. The relative positions of the energy levels of various organic bonds in the solid state and their inferred harmonic modes are summarized in Table 5.1. The band indicated in Figure 6.2 is used to represent the highly varying bonding structure in the a-C matrix, which reflect the levels associated with the numerous combinations of nearest neighbors and the different local bonding environments. Accordingly, if excited Yb$^{3+}$ ions are disturbed by O–H and C–H$_x$ oscillators, a non-radiative transition occurs.

Considering the undistorted oscillator model [154] as described in Section 5.3.3, the transition probability between Yb$^{3+}$ and the O–D and C–D$_x$ vibrational modes of the host deuterated a-C film is lower than that between Yb$^{3+}$ and the O–H and C–H$_x$ vibrational modes.
This leads to an increase in the efficiency of the PL for a-C:D:F(Yb) films as shown in Figure 6.1(c). The 8th and 9th harmonic vibrational modes of C–F overlap with the Yb$^{3+}$ first excited state, however they play a negligible role on PL quenching as these vibrational modes are much higher ($\nu = 8, 9$) compared to O–H ($\nu = 3$) and C–H$_x$ ($\nu = 3, 4$) modes (C–F not shown here due to much higher vibrational modes). Hence, by selecting the Yb(fod)$_3$ metalorganic compound as the doping precursor instead of Yb(tmhd)$_3$, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)Ytterbium(+III) with chemical structure Yb(C$_{11}$H$_{19}$O$_2$)$_3$, the PL quenching by C–H$_x$ is expected to be mitigated.

The photoluminescence enhancement of Yb in a-C films was brought to fruition by changing the precursor gas from methane (CH$_4$) to deuterated methane (CD$_4$). This is similar to the photoluminescence enhancement of Er in a-C which was also achieved by changing the precursor gas from methane (CH$_4$) to deuterated methane (CD$_4$), as illustrated in Figure 5.2 of Section 5.3. However, while deuteration of Er doped a-C films exhibited a PL enhancement factor of 6, the PL enhancement factor of deuterated Yb doped a-C films was 4.2. This lower enhancement factor is attributed to the difference in the change of interaction strength for the two samples. That is, the change of interaction strength is greater for deuterated Er doped a-C samples compared to deuterated Yb doped a-C samples. This can be viewed through the change of the harmonic vibrational modes that align with Er and Yb. That is, for Er the interaction strength shifts from Er$^{3+}$ and the neighboring C–H$_x$ and O–H vibrational modes, at the $\nu = 2$ harmonic, to the interaction of Er$^{3+}$ and the neighboring C–D$_x$ and O–D vibrational modes, at the $\nu = 3$ harmonic. In the case of Yb, the interaction strength shifts from Yb$^{3+}$ and the neighboring C–H$_x$ and O–H, at harmonic modes of $\nu = 3$ and 4, to Yb$^{3+}$ and the neighboring C–D$_x$ and O–D, at harmonic modes of $\nu = 4$ and 5. Hence, for deuterated a-C(Er) films the shift is greater than the shift for deuterated a-C(Yb) films.

### 6.3 Effect of Substrate Temperature in a-C(Yb) Film

The temperature of the growth surface was found to influence the concentration of Yb occluded in the a-C:D:F(Yb) films, and hence the PL efficiency. Table 6.1 lists the ratios of the atomic concentrations and the relative (and absolute) atomic concentrations of the relevant elements in the as-received stoichiometric Yb(fod)$_3$ compound, and in the six a-C:D:F(Yb) films deposited under varying substrate temperatures as determined from XPS measurements. In comparing the a-C:D:F(Yb) film deposited at a substrate temperature of 60°C to the stoichiometric
Yb(fod)$_3$ compound, a few results are observed. The [O]/[Yb], [F]/[Yb], and [C]/[Yb] ratios are approximately 8×, 1.65×, and 2.2 × smaller, respectively, in the film. This suggests that Yb incorporation is being promoted in the film. Moreover, fluorine incorporation is being promoted since the [O]/[F] ratio is 4.8× larger in the film. The increase in the F concentration is attributed to the selective incorporation of $C_mF_n$ fragments. This film also exhibits a surprising reduction in the amount of bonded carbon as witnessed by the lower [C]/[Yb] ratio and the higher [F]/[C] ratio. One would expect the carbon concentration to increase since carbon can be sourced from CD$_4$ or the Yb(fod)$_3$ precursor. Evidently, significant dissociation of the Yb(fod)$_3$ compound occurs in the plasma environment. This is supported by the large variation in the atomic ratios ([C]/[Yb] = 13.64, [O]/[C] = 0.06, [F]/[C] = 0.93,) as compared to the stoichiometric samples ([C]/[Yb] = 30, [O]/[C] = 0.20, [F]/[C] = 0.7). The bond energies may provide a possible explanation for the relative exclusion of C and O in the a-C:D:F(Yb) film grown at a substrate temperature of 60°C. The C-C, C-O, and Yb-O bonds are expected to have a lower bond energy than C-F, C=C, and C=O bonds. Hence, it is expected that they will be heavily dissociated within the plasma and as a result may not be incorporated in the resultant film.

Analyzing the XPS spectra for the films grown as the substrate temperature was varied from 60 to 150 °C yields a number of results. The [F] monotonically decreases with increasing substrate temperature, as seen by the increasing [O]/[F] ratio and the decreasing [F]/[C] ratio. The [Yb] decreases rapidly and monotonically with increasing substrate temperature as shown in Figure 6.3(a). This is evident from the increase in the [O]/[Yb] and [C]/[Yb] ratios. The [C] increases monotonically as observed by the increase in the [C]/[Yb] ratio and the decrease in the [F]/[C] ratio. The [O] appears to show a slightly increasing trend. This is supported by the monotonic increase in the [O]/[Yb] ratio, the almost monotonic increase in the [O]/[F] ratio, and the slight increasing trend in the [O]/[C] ratio. The [F]/[Yb] ratio increases slightly, then decreases. It appears that the rate of decrease in the [Yb] is slightly sharper than the rate of decrease in the [F] as the substrate temperature increases from 60 °C to 90 °C. This is supported by the increase in the [C]/[Yb] ratio by a factor of 3.12, while the [C]/[F] ratio increases by a factor of 2.45. Increasing the substrate temperature above 90 °C, the [Yb] and [F] decrease with the [F] more quickly than with the [Yb].
Table 6.1. Ratios of atomic concentrations and relative/absolute atomic concentrations of relevant elements in as-received stoichiometric Yb(fod)$_3$ compound, and in six a-C:D:F(Yb) films deposited under varying conditions as determined from XPS measurements. Table based on one published by Hsu et al. [132].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate Temperature (°C)</th>
<th>C at%</th>
<th>O at%</th>
<th>F at%</th>
<th>Yb at%</th>
<th>[O]/[Yb]</th>
<th>[F]/[Yb]</th>
<th>[C]/[Yb]</th>
<th>[O]/[C]</th>
<th>[F]/[C]</th>
<th>[O]/[F]</th>
<th>Thickness (100 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb(fod)$_3$</td>
<td></td>
<td>34.1</td>
<td>6.8</td>
<td>23.9</td>
<td>1.1</td>
<td>6.00</td>
<td>21.00</td>
<td>30.00</td>
<td>0.20</td>
<td>0.70</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>48.5</td>
<td>2.7</td>
<td>45.2</td>
<td>3.6</td>
<td>0.75</td>
<td>12.72</td>
<td>13.64</td>
<td>0.06</td>
<td>0.93</td>
<td>0.06</td>
<td>33.21</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>59.9</td>
<td>2.5</td>
<td>35.0</td>
<td>2.6</td>
<td>0.94</td>
<td>13.23</td>
<td>22.64</td>
<td>0.04</td>
<td>0.58</td>
<td>0.07</td>
<td>27.65</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>63.4</td>
<td>3.6</td>
<td>30.9</td>
<td>2.1</td>
<td>1.68</td>
<td>14.61</td>
<td>29.94</td>
<td>0.06</td>
<td>0.49</td>
<td>0.12</td>
<td>20.23</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>68.9</td>
<td>3.2</td>
<td>26.3</td>
<td>1.6</td>
<td>1.99</td>
<td>16.25</td>
<td>42.63</td>
<td>0.05</td>
<td>0.38</td>
<td>0.12</td>
<td>14.52</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>86.4</td>
<td>7.2</td>
<td>5.5</td>
<td>0.9</td>
<td>8.00</td>
<td>6.05</td>
<td>95.73</td>
<td>0.08</td>
<td>0.06</td>
<td>1.32</td>
<td>5.67</td>
</tr>
<tr>
<td>6</td>
<td>150</td>
<td>91.8</td>
<td>6.1</td>
<td>1.7</td>
<td>0.4</td>
<td>17.50</td>
<td>4.84</td>
<td>261.64</td>
<td>0.07</td>
<td>0.02</td>
<td>3.62</td>
<td>3.51</td>
</tr>
</tbody>
</table>
Figure 6.3. (a) The Yb concentration (solid black circle) and normalized PL peak intensity, $I_{nor}$ (solid blue circle) as a function of the substrate temperature for films deposited at an RF power of 60 W. The normalized PL peak intensity is shown to depend critically on the (b) $[O]/[Yb]$ ratio; and (c) [Yb]. The lines are guides to the eye. $I_{nor}$ is defined as the total integrated area underneath the 3 deconvoluted peaks and normalized to the respective a-C(Yb) film thickness indicated in Table 6.1. (d) Yb4d XPS spectra of the three a-C:D:F(Yb) films, and TE Yb(fod)$_3$ film (thermally evaporated Yb(fod)$_3$ compound in the vacuum chamber with CD$_4$ precursor gas flowing without plasma ignition). The curves have been shifted vertically for clarity of presentation. Figure based on one published by Hsu et al. [132].

The considerable loss of F and Yb with increasing substrate temperature is associated with a drop in the deposition of C$_m$F$_n$, YbO$_x$, C$_m$F$_n$, Yb, and/or YbO$_x$ molecular fragments. The relative variation in the drop of the F and Yb concentration may be due to the temperature dependence of
the sticking coefficient or the desorption rate of Yb-containing fragments and F-containing fragments. Despite the decreasing [Yb] with increasing substrate temperature (black curve in Figure 6.3(a)), the relative PL intensity increases, peaks at a substrate temperature of 80°C, and then decreases as indicated in blue curve of Figure 6.3(a). The increasing PL intensity with substrate temperature is attributed to the increasing O concentration and hence an increasing [O]/[Yb] ratio as seen in Figure 6.3(b). Hence, more Yb atoms are considered to be in the 3+ state. Above a substrate temperature of 80 °C the PL intensity decreases even though the [O]/[Yb] ratio continues to increase. This is due to the decreasing [Yb] with increasing substrate temperature (Figure 6.3(a)). At a substrate temperature of 150 °C, the majority of the film is a-C:D with minute F and Yb concentrations as indicated in Table 6.1. A summary of the variation of the PL intensity with Yb concentration in a-C:D:F matrix is shown in Figure 6.3(c). \(I_{\text{tot}}\) increases linearly up to a Yb concentration of approximately 2.1 at% and thereafter begins to drop until 3.6 at% at which point the PL becomes very weak. The latter suggests a reduction in lifetime \(\Gamma\) beyond this point [156] due to energy transfer between optically active Yb\(^{3+}\) and Yb\(^{3+}\) ion pairs. Unlike Yb:YAG single crystals, Yb doping concentration can be high up to 10 at% without exhibiting concentration quenching phenomenon [96], which is attributed to the high probability of Yb\(^{3+}\) substitution of Y\(^{3+}\) ions in YAG single crystals. The host a-C films deployed here are in amorphous form.

### 6.4 Yb Oxidation State in a-C(Yb) Film

The Yb4d XPS spectra of the thermally evaporated (abbreviated TE) Yb(fod)\(_3\) film, and three a-C:D:F(Yb) samples with different Yb concentrations are compared in Figure 6.3(d). Yb ions appear in the 2+ state in the metal and in the 3+ state or slightly mixed 2+ and 3+ states in the sesquioxide. Yb\(^{2+}\) metal clusters show two distinct peaks located at 183 eV and 192 eV [163, 164]. Also, the partially oxidized metal shows the two distinct peaks, as well as a small peak around 186-187 eV [164]. However, the fully oxidized Yb in the 3+ state shows only one main peak around 186-187 eV with the broad peaks in the higher-binding energy region [163, 164]. The broad peaks are attributed to the 4d levels in the Yb\(^{3+}\) ions forming multiplet splitting with electro-static coupling of a 4d photohole to the unfilled valence shell of Yb\(^{3+}\)(4\(^{f13}\)) [163, 165]. From Figure 6.3(d), the spectra reveal similar characteristics for all of the samples, implying the environment of the incorporated Yb in a-C:D:F(Yb) films is similar to the Yb in the pristine Yb(fod)\(_3\) compound. More importantly, it confirms the preservation of the Yb\(^{3+}\) state in the a-C(Yb) samples. However, the fact that the [O]/[Yb] ratio is less than 6 (shown in Table 6.1), as is the case
for the pristine Yb(fod)$_3$ powder, suggests that some Yb ions may have undergone a shift in their electronic structure (the $2F_{5/2}$ and/or $2F_{7/2}$ energy levels) or may be optically inactive. A shift in the electronic structure would be supported by the larger width of the observed PL signal in Figure 6.1(c), as compared to the reported widths from Yb doped ceramic [22, 25, 29, 98], oxide [32, 33, 35, 36] based host films, and Yb$_2$O$_3$ crystalline films [40]. This wider luminescence spectra were also observed in Yb doped AlN films, where the host AlN films are essentially amorphous in form with AlN nanocrystals embedded in the matrix [166]. Nevertheless, the Yb4d XPS spectra suggests the Yb$^{3+}$ state is mostly preserved in the a-C:D:F(Yb) films, leading to the observed PL.

6.5 Structural Analyses of a-C(Yb) Film

From the XPS results the [O]/[Yb] ratio is less than 6, which is the coordination number of Yb$_2$O$_3$. Thus, suggesting the presence of optically inactive Yb ions (i.e., Yb-C, Yb-Yb, Yb-F). Hence, detailed XPS analyses were performed to examine the bonding details of the resultant a-C:D:F(Yb) film. In Figure 6.4(a), the deconvoluted C1s spectra indicate the majority of carbon bonds are C-C and/or C-D/C-H, with some C-F, C-O and/or C-CF, and very few C=O and/or C-F$_x$ bonds in the a-C:D:F(Yb) film. The deconvoluted F1s spectra displayed in Figure 6.4(b) show a small concentration of YbF$_x$ bonds exist in the a-C:D:F(Yb) film, while the majority of F atoms are bonded to carbon as C-F bonds, with some C-F$_2$ bonds and a minute amount of C-F$_3$ bonds. Note that the fitting error ($\Sigma \chi^2$) would be 33% higher without adding the YbF$_x$ bond peak at 683.6 eV during the F1s deconvolution process. This suggests that the probability of Yb bonding in the optically active 3+ state could be increased by formation of the Yb-F$_x$ bonds, in addition to the expected 3+ state as in the pristine Yb-O bonds of the Yb(fod)$_3$ compound. This additional bonding environment could further promote the luminescence efficiency of the a-C(Yb) film, as demonstrated by the observed luminescence from YbF$_3$ nanoparticles [167-169]. The different percentages of carbon and fluorine related bonds, as depicted in Figure 6.4, implies that significant dissociation of the Yb(fod)$_3$ compound occurs in the plasma environment. For instance, plasma dissociation of the C-F$_3$ and C-F$_2$ groups into C-F is shown by the decrease of the F1s C-F$_3$ and C-F$_2$ peaks in the a-C:D:F(Yb) film as seen in Figure 6.4 (b) compared to the TE Yb(fod)$_3$ film in Figure 6.4 (d). This is also supported by the increase in the C-F bond for the C1s peak, as well as the decrease in the C=O and/or C-F$_x$ and C-O and/or C-CF peak, relative to the TE Yb(fod)$_3$ film seen in Figure 6.4 (c). Note that no C1s C-Yb peak was observed. Thus, the resultant a-C:D:F(Yb) film contains Yb$^{3+}$ ions bonded to O and/or F (i.e., YbF$_3$, YbFO$_2$, YbF$_2$O, and YbO$_3$), and is
surrounded by a variety of local environments (with varying sizes of the Yb$^{3+}$ sites) due to the structural flexibility of the a-C matrix. Consequently, these structural observations may confirm the observed wider FWHM PL signal as seen in Figure 6.1(c), compared to other Yb doped ceramic [22, 25, 29, 98] and oxide [32, 33, 35, 36] based host films.

Figure 6.4. Deconvoluted XPS (a) C1s and (b) F1s spectra of the a-C:D:F(Yb) film with maximum $I_{nor}$ prepared using RF power of 60 W, precursor gas flow rate of 20 sccm, deposition pressure of 60 mTorr, substrate temperature of 80 °C, and Yb(fod)$_3$ powder evaporated at a temperature of 110 °C, and (c) C1s and (d) F1s spectra of the TE Yb(fod)$_3$ film. Figure based on one published by Hsu et al. [132].

The XPS measurements revealed that sample 1 and 2 contained a high fraction of fluorine as shown in Table 6.1. In order to probe the changes in the optical properties of the host a-C film
due to fluorination, fluorinated a-C:D (a-C:D:F) host films were prepared from deuterated methane (CD₄) and tetrafluoromethane (CF₄) mixtures. Figure 6.5 displays the dependence of optical bandgap $E_{04}$ on the CF₄/[CF₄+CD₄] gas mixture ratio for the resultant a-C:D:F films. It has been observed that as the relative F at% increases (i.e., CF₄/[CF₄+CD₄] ratio increases), the $E_{04}$ optical bandgap decreases. Robertson [46] describes the microstructures of a-C as a continuous network of $sp^3$ bonded carbon atoms (predominately C-C or a mixture of C-C and C-H) with $sp^2$ bonded carbon localized clusters (the number and size of the C=C) embedded within the network. The $sp^3$ bond configuration forms $\sigma-\sigma*$ bands and the $sp^2$ sites create $\pi-\pi*$ bands by forming the localized states. The size and quantity of the $sp^2$ clusters dominate the film’s optical properties. Accordingly, the increasing %$sp^2$ content in the film implies an increase in the localized density of states lying in the gap. Thus, the decrease in the optical bandgap $E_{04}$ as the relative F at% increases in the films could be attributed to the increase in %$sp^2$ bonding in the film [170-172].

![Graph showing the dependence of optical bandgap $E_{04}$ on the CF₄/[CF₄+CD₄] gas mixture ratio.]

Figure 6.5. The optical bandgap, $E_{04}$, of the host a-C:D:F films as a function of the introduced fluorinated precursor gas.

Although the $E_{04}$ of the a-C(Yb) films cannot be assessed at this moment, samples 1 and 2, as shown in Table 6.1, which represent a-C(Yb) films grown at the substrate temperature of 60°C and 70°C, respectively, and along with the PL shown in Figure 6.3(a) could be inferred to appear to have a lower $E_{04}$ compared to that of sample 3. This is due to higher incorporation of F [170-172] and Yb [49, 116] concentrations than those in sample 3 as seen in Table 6.1. As the relative
Fat% increases in the films, there is an increase in $\%sp^2$ bonding in the film which gives rise to a localized density of states lying in the gap [170-172]. This reduces the apparent $E_{04}$ optical bandgap. Moreover, with higher Yb incorporation, $\%sp^2$ is expected to further increase considering the observations of Er doped or Er oxide doped diamond like carbon films reported by Foong et al. [49, 116]. Accordingly, higher $\%sp^2$ could result in a higher probability of photoelectrons for non-radiative recombination in the a-C:D host, leading to a lower probability of photoelectrons transferring from the a-C:D host to Yb$^{3+}$ ions and further emitting 1 µm photons at room temperature. Thus, the higher $\%sp^2$ in sample 1 and 2 of the a-C(Yb) films might be another minor factor that contributes toward the lower PL intensity observed in addition to the concentration quenching effect from the high Yb concentration.

With respect to the change in film optical properties after incorporation of the Yb compound, the refractive index $n$ and extinction coefficient $k$ are expected to increase based on the results obtained from rare-earth ions doped PbTiO$_3$ thin films prepared by sol-gel method [173].

Moreover, from Figure 6.6, it can be clearly seen that there is no absorption peak around 532 nm for the Yb(fod)$_3$ compound. This also confirms that there are only two manifold levels, the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state, that appear with Yb$^{3+}$ ions, as shown in Figure 32. This is different when compared to the case of Er$^{3+}$ ions, where the energy of the 532 nm laser is near resonance with the $^4S_{3/2}$ excited level of Er ions as seen in Figure 1 and Figure 5.3. Accordingly, it is suspected that the photogenerated carriers in the $^2F_{5/2}$ excited states are likely due to electronic energy transfer from the host a-C matrix via localized density of states lying within the gap due to the $sp^2$ clusters as seen in Figure 6.7. The role of $\%sp^2$ (the number and size of the C=C) and energy transfer mechanism between the host a-C and Yb$^{3+}$ ions have not been determined. These topics are under investigation as part of the larger objectives of the present study, specifically via the application of multiple laser excitations (488 nm and 980 nm) —in addition to the presently employed 532 nm laser source —as proposed in Section 7.3.2 Future Work – Energy Transfer Mechanism.
Figure 6.6. The absorption spectra of Yb(fod)$_3$ metalorganic compounds dissolved in d-chloroform solvent.
Figure 6.7. A simplified conceptual diagram illustrating the $\sigma^*$ and $\sigma$ bands of the a-C based host films, the energy levels of $\pi^*$ and $\pi$ states originating from $sp^2$ C=C bonds, and Yb$^{3+}$ ions within the a-C matrix. Included is the excitation associated with the 532 nm pump. Participation of the localized density of states lying in the gap due to the $sp^2$ clusters in the host a-C matrix lead to the absorption of incident photons and subsequent energy transfer to a higher energy state of Yb$^{3+}$, and thus leading to PL emission around 1.1 $\mu$m. The non-radiative transitions are shown with broken arrows.
6.6 Summary

The in situ growth of Yb-doped a-C thin films on Si substrates at low temperature (<200 °C) was successfully demonstrated by a simple one-step RF-PEMOCVD system. Room temperature PL at a wavelength of around 1 µm was observed from these a-C(Yb) films. A subsequent high temperature post-deposition annealing procedure was not required. This is a result of the direct incorporation of the optically active Yb$^{3+}$ ions from the specially selected Yb(fod)$_3$ metalorganic compound. The PL was enhanced by a factor of 4.2 due to the use of deuteration as opposed to hydrogenation of the a-C host. This served to lower the interaction strength between the excited Yb$^{3+}$ and the neighboring harmonic vibrational modes. Moreover, fluorination of the a-C host may also assist in the suppression of the PL quenching effect through the partial substitution of C–H bonds with C–F bonds.

The substrate temperature was shown to greatly influence the relative deposition rates of the plasma dissociated metalorganic species. It was observed that the relative PL intensity increases, peaks at a substrate temperature of 80°C, and then decreases. The increasing PL intensity is attributed to an increase in [O]/[Yb] ratio, leading to more Yb atoms in the 3+ state. Above a substrate temperature of 80 °C the [O]/[Yb] ratio continues to increase, however the PL decreases. This is due to the considerable loss of the [Yb], which is associated with a drop in the temperature-dependent deposition of YbO$_x$C$_{m}$F$_n$, Yb, and/or YbO$_x$ molecular fragments. The relative PL intensity increases linearly with the Yb concentration up to a [Yb] of approximately 2.1 at%. Thereafter the PL intensity begins to drop suggesting a severe energy transfer between active Yb$^{3+}$ and Yb$^{3+}$ ion pairs beyond this point.

The Yb4d XPS spectra indicated that the environment of the incorporated Yb in a-C(Yb) films is similar to the Yb in the pristine Yb(fod)$_3$ compound. Although, the fact that the [O]/[Yb] ratio is less than 6 suggests some Yb ions may have their electronic structure shifted (the $^2F_{5/2}$ and/or $^2F_{7/2}$ energy levels) or have become optically inactive. By examining the C1s and F1s deconvoluted XPS spectra in detail, the Yb$^{3+}$ ions in the a-C(Yb) films are found to be bonded to O and/or F (i.e., YbF$_3$, YbFO$_2$, YbF$_2$O, YbO$_3$). The formation of the Yb-F$_3$ bonds increases the probability of Yb bonding in the optically active 3+ state, which may promote the luminescence efficiency of a-C(Yb) films. However, the relatively high F concentration in the host a-C matrix
could lead to an increase in the de-excitation pathways. This is due to the smaller bandgap or the increased states within the bandgap typically found in a-C:F materials.

In summary, the a-C:D:F(Yb) films synthesized by the RF-PEMOCVD method at low temperatures (<200 °C), exhibit room temperature luminescence owing to direct incorporation of Yb$^{3+}$ ions. Also, luminescence is enhanced by the substitution of C–D$x$, C–F$x$, and O–D bonds for C–H$x$ and O–H bonds. The wide FWHM observed is due to the various local bonding environments. More importantly, thickness of up to 3 μm of a-C(Yb) film was achieved, which provides flexibility in the design of optical waveguides. These properties suggest that a-C:D:F(Yb) may be a promising material for active photonic devices to be integrated with the current Si CMOS platform. Results presented in this chapter have been reported in [132].
7 Conclusions

7.1 Thesis Conclusions

This thesis undertakes a first in-depth investigation of the viability of in situ growth of Er and Yb metalorganic doped amorphous carbon based thin films on Si substrates at low temperature (< 200 °C) by simple occlusion of a metalorganic compound in a RF-PEMOCDV deposition system. Prior to the preparation of a-C(Er or Yb) thin films, the effects of RF power and positional placement of substrate (on the anode or cathode) on optical properties of the host a-C:H films grown by the RF-PECVD system were investigated and discussed with reference to microstructural and local bonding features. The enhancement of room temperature PL of a-C(Er or Yb) thin films via deuteration of the host a-C is probed and discussed in detail. The effect of different processing conditions on the PL of a-C(Er or Yb) films is investigated and correlated to the film microstructure and bonding environment. Also the bonding details of the resultant a-C:D:F(Yb) film was examined and discussed with reference to the FWHM of the emission bands. The results suggest that a-C(Er or Yb) could be a promising material for active photonic devices that can be integrated within the framework of the current Si CMOS platform.

The following is a summary of the key results emerging from the research presented in this thesis.

- Host a-C:H Films

Hydrogenated amorphous carbon films grown on the cathode (C-RF) and anode (A-RF) both reveal similar trends vis-à-vis changes in the deposition rate, refractive index \( n \) and extinction coefficient \( k \), and optical bandgap \( E_0 \) with increasing RF power. The increase in the deposition rate for both the C-RF and A-RF sample sets with increasing RF power is due to the increase in ion energy and plasma density. The total hydrogen concentration of the a-C:H films decreases with increasing RF power, which is attributed to the increase in ion energy with RF power whereby more of the bonded hydrogen atoms are displaced, leading to the formation of molecular H\(_2\), and its subsequent desorption from the film. Higher film growth rate and greater rate of decline in the H concentration for the C-RF sample set is a result of the higher energy ions/radicals impinging on the cathode. \( \% sp^2 \)-hybridized carbon bonding increases for both A-RF and C-RF sample sets with increasing RF power, which is a result of the increase in ion energy impinging on the film. The rapid increase in the \( \% sp^2 \) for the C-RF samples compared to A-RF ones is also due to the
much larger ion energy impinging on the cathode. These $sp^2$ clusters create $\pi-\pi^*$ localized states which lie in the gap and account for the decrease in $E_{04}$ bandgap and the increase in extinction coefficient $k$ with increasing RF power. The A-RF a-C:H films exhibit higher H content, a wider bandgap $E_{04}$ and lower $\%sp^2$ carbon bonding compared to C-RT films, suggesting that A-RF a-C:H films are more polymeric-like hydrogenated amorphous carbon and deemed a more suitable candidate host for Er or Yb metalorganic doping.

- **Fluorinated Metalorganic Compound via RF-PEMOCVD System**

Room temperature PL at wavelengths near 1.5 $\mu$m and 1 $\mu$m were observed from a-C(Er) and a-C(Yb) films, respectively, by adopting a new Er or Yb metalorganic precursor with partial fluorination, $X(fod)_3$ ($X$= Er or Yb, and fod represents 6,6,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedioate with chemical structure of $C_{10}H_{10}F_7O_2$). Subsequent high temperature post-deposition annealing was not required to activate the dopants, a result due to the direct incorporation of optically active $X^{3+}$ ions from the specially selected $X(fod)_3$ metalorganic compound. Moreover, partial fluorination of the ligands likely assists in the suppression of the PL quenching effect through the substitution of C–H bonds with C–F bonds. Accordingly, RT PL was achieved for a-C:H(Er) despite the use of hydrogenated amorphous carbon as the host material. The obtained PL in the present a-C:H(Er) film in this thesis is prominent as opposed to a-C:H(Er) thin films prepared by magnetron sputtering of Er/graphite mixed target [48, 115], by doping Er(tmhd)$_3$ (Er($C_{11}H_{19}O$)$_3$) via RF-PECVD [50, 115], and by doping Er(tmhd)$_3$ via DC Saddle Field PECVD [52] having extremely low PL intensity as mentioned in Section 2.4. In addition, the in situ thermal evaporation technique provides the capability of doping X in a uniform profile vertically, that is, depth-wise, compared to ion implantation technique [14]. Our work is the first successful demonstration of rare earth metalorganic compound doped in a-C films by RF-PEMOCVD system.

- **PL Enhancement by Deuteration of Host a-C**

The relative enhancement in PL due to deuteration of the a-C host was demonstrated. Specifically, enhancement factors of 6 and 4.2 were obtained for a-C(Er) and a-C(Yb) films, respectively, due to the use of deuterated as opposed to hydrogenated a-C host which resulted in the substitution of C–D$_x$, and O–D bonds for C–H$_x$ and O–H bonds, respectively. This served to lower the interaction strength between the excited $X^{3+}$ ions and the neighboring harmonic
vibrational modes by effectively shifting the quenching vibrational modes to lower wavenumbers by virtue of the mass effect.

- **a-C:D(Er) Films**

The effect of RF power and substrate temperature on Er concentration, [O]/[Er] concentration ratio, and PL intensity of the a-C:D(Er) film was investigated. It was observed that the PL signal increases with increasing RF power, which is attributed to an increase in [O]/[Er] ratio and hence the erbium-oxygen coordination number. In addition, the decrease in PL intensity and [Er] concentration with increasing substrate temperature are observed; the decrease in [Er] is attributed to an increased desorption rate or a lower sticking coefficient of the fluorinated fragments during film growth. By examining the relationship of the normalized PL intensity, $I_{nor}$, as a function of the Er concentration, it is observed that Er concentration quenching begins at ~2.7 at% and continues to increase until ~5.5 at% at which point the PL is very weak. The highest doping level of Er doping attained via the present RF-PEMOCVD method represents a great improvement as opposed to a-C:H(Er) thin films prepared by pulse laser ablation of graphite and Er mixed target (2 at%) [49], by RF-PECVD method using erbium isopropoxide with chemical structure C9H21O3Er (0 at%) [115], and by DC Saddle Field PECVD method using Er(tmhd)3 (2.3 at%) [52]. Although high 8.7 at% of Er by doping Er(tmhd)3 (Er(C11H19O)3) via RF-PECVD method [115] and 17.1 at% by sputtering of a graphite/Er target [115] have been reported, nevertheless in all these instances either no RT PL or extremely weak RT PL around 1.5 µm was obtained likely due to C-H and O-H quenching.

- **a-C:D(Yb) Films**

The substrate temperature was varied from 60 to 150 °C, and was shown to greatly influence the relative deposition rates of the plasma dissociated metalorganic species. It was observed that the relative PL intensity increases with temperature initially, peaks at a substrate temperature of 80°C, and then decreases with further increase in temperature. The increasing PL intensity is attributed to an increase in [O]/[Yb] ratio, leading to more Yb atoms in the 3+ state. Above a substrate temperature of 80 °C the [O]/[Yb] ratio continues to increase, however the PL decreases. This is due to the considerable loss of the [Yb], which is associated with a drop in the temperature-dependent deposition of YbOxCmFn, Yb, and/or YbOx molecular fragments. The relative PL intensity increases linearly with increasing Yb concentration up to a [Yb] of
approximately 2.1 at%. Thereafter, the PL intensity begins to drop—suggesting severe energy transfer between active Yb$^{3+}$ and Yb$^{3+}$ ion pairs beyond this point.

The Yb4d XPS spectra indicated that the environment of the incorporated Yb in a-C(Yb) films is similar to the Yb in the pristine Yb(fod)$_3$ compound. However, the fact that the [O]/[Yb] ratio is less than 6 suggests that some Yb ions may have their electronic structures shifted (the $^2F_{5/2}$ and/or $^2F_{7/2}$ energy levels) or may have become optically inactive. Our work is the first successful demonstration of Yb doped a-C films.

- **Local Bonding Structure in a-C(Yb) Films**

By examining the C1s and F1s deconvoluted XPS spectra in detail, the Yb$^{3+}$ ions in the a-C(Yb) films are found to be bonded to O and/or F (i.e., YbF$_3$, YbFO$_2$, YbF$_2$O, YbO$_3$), and is surrounded by a variety of local environments (with varying sizes of the Yb$^{3+}$ sites) due to the structural flexibility of the a-C matrix. The formation of Yb-F$_x$ bonds increases the probability of Yb bonding in the optically active 3+ state, which may promote the luminescence efficiency of a-C(Yb) films. Consequently, these structural observations appear to confirm the observed wider FWHM PL signal, compared to other Yb doped ceramic and oxide based materials. However, the relatively high F concentration in the host a-C matrix could lead to an increase in the de-excitation pathways, leading to lower PL efficiency. This is due to the increased density of states within the bandgap typically found in a-C:F materials.

### 7.2 Contribution to the Field

Feasibility of employing a-C based thin films as the promising host material for Er and Yb incorporation has been successfully demonstrated. More importantly, the optically active 3+ state of Er and Yb ions were directly incorporated in the host a-C via simple *in situ* occlusion of the metalorganic compound at low temperatures (< 200 °C) using a RF-PEMOCVD deposition system such that no post-deposition annealing was required to activate the dopants. The overall processing temperatures were controlled to be well below 400 °C in order to meet the Si BEOL requirements. This is the first definitive demonstration of incorporating multiple dopant elements which are optically active in amorphous carbon.

By using a selected fluorinated Er metalorganic compound (Er(C$_{10}$H$_{10}$F$_7$O)$_3$), room temperature photoluminescence at 1.5 μm was achieved for a-C(Er) in spite of using hydrogenated
a-C:H films as the host. Moreover, the photoluminescence of the a-C(Er or Yb) achieved was further enhanced by deuteration of the host a-C thereby decreasing the vibrational quenching strength between the Er$^{3+}$/Yb$^{3+}$ ions and the surrounding organic bonds by partial substitution of C–H and O–H with C–D and O–D bonds. The relative energy levels of various organic bonds were identified by the FTIR technique through the measurement of the transmission spectra of a-C:H, a-C:D and a-C:D:F films. Also, they were further confirmed by absorption spectra of various C–H, C–D, O–H, and O–D bonds containing organic solvents.

The effect of different processing conditions on the resultant photoluminescence of a-C(Er or Yb) films has been systematically investigated, and correlated to the incorporated concentration of various elements in the films and film microstructure. Also, the FWHM width was discussed respective to the variety of local environments in the complicated a-C matrix, suggesting the potential of enabling a wide gain band width for optical amplification. The results in this thesis indicate that a-C:D:F(Er or Yb) films may be a promising material for active photonic devices to be integrated within the current Si CMOS platform.

## 7.3 Future Work

### 7.3.1 Quantum Yield

Fundamental properties, such as photoluminescence quantum efficiency/quantum yield and radiative and non-radiative decay rate (lifetime) of the a-C(Er or Yb) films, will assist us to gain more insight into the proposed novel family of materials for future waveguide engineering and photonic device applications. Accordingly, the development of a characterization facility capable of measuring quantum efficiency and/or quantum yield will be the first prioritized work in the near future. For absolute quantum yield measurements, we will employ an integrating sphere mounted on the side of a monochromator and opposite to an excitation source, as demonstrated by M. Pokhrel et al. [174] and J. C. Boyer et al. [175]. The sample port of the integrating sphere faces the entrance port for laser excitation while the output port is at 90 degrees from the input and sample ports. The absolute quantum yield is defined as the ratio of the number photons emitted to the number of photons absorbed. Thus, the quantum yield can be obtained by finding the ratio of the area under the corrected emission spectra to the difference in the corrected area under the diffuse reflectance spectra for the sample and the reference [175].
7.3.2 Energy Transfer Mechanism

In order to have a better picture of the electronic energy transfer mechanism between Er\(^3+\)/Yb\(^{3+}\) ions and the host a-C and/or the role of $%sp^2$ (density of dangling bonds) in the host a-C matrix, PL measurements will be carried out via application of multiple laser excitations (488 nm and 980 nm) in addition to the presently employed 532 nm laser source. The energy transfer mechanism displayed in Figure 5.4 and Figure 6.7 is a preliminary sketch based on the results obtained via the presently employed 532 nm laser source. The possible energy transfer mechanism by various pumping laser sources is displayed in Figure 7.1. Moreover, the relative $%sp^2$ in the a-C(Er, Yb) films will be conducted via electron spin resonance (ESR) technique and furthermore will be correlated to the measured PL intensity. In addition, the Er and/or Yb metalorganic compounds can be introduced in the a-C films grown on the cathode electrode instead of the present anode electrode to investigate the effect of structural and compositional changes in the host a-C matrix. The a-C films grown on the cathode show less H content and higher $%sp^2$ in the host a-C as mentioned in Chapter 4. This can assist to understand the effect of $%sp^2$ on the resultant PL intensity and further provide a general picture of the energy transfer mechanism. Moreover, the relative $%sp^2$ quantity in the a-C(Er, Yb) films probed by ESR technique can be correlated to the refractive index $n$, extinction coefficient $k$ and optical bandgap $E_{04}$ of the a-C(Er, Yb) films using the Spectroscopic Ellipsometry technique. However, further efforts are also required in applying the proper dispersion model to fit the data considering that the deposited a-C(Er, Yb) films in this work is a relatively novel material with high occluded Er or Yb concentrations. Also, the photoluminescence lifetime can be obtained via time resolved PL characterization in order to help understand the energy transfer mechanism.

In addition, the deuterium/hydrogen (protium) bonding regime in a-C:D(Er) vs a-C:H(Er) should be considered further. In the current thesis, the impact of mass effect of D compared to H has been eliminated/minimized during the a-C(Er) film growth process by employing identical deposition parameters except for the introduced precursor gas (deuterated methane (CD\(_4\)) instead of (hydrogenated) methane (CH\(_4\))). Thus, it has been assumed that D/H atoms are bonded to O, Er/Yb, F, C atoms in a similar way in the a-C(Er) films. Detailed FTIR measurements of a-C:D(Er) and a-C:H(Er) films ought to be carried out to identify the effect of heteroatoms bonding between D and H atoms [176] considering that a distribution of heteroatom associated defects may lead to
different degrees of defect-induced non-radiative recombination and and hence lowering of PL intensity.

Figure 7.1. Simplified conceptual energy diagrams showing the energy transfer between Er and Yb for different pump wavelengths. At 980 nm pumping, Yb absorbs incident photons and transfers the excitation energy to the second excited state of Er, leading to a larger effective absorption cross section. For 532 nm and 488 nm pumping, the light is absorbed by the higher excited states of Er ions. From these higher lying levels, the excitation decays sequentially to the lower lying states and the branching is affected by energy transfer from the second excited state of Er to the Yb ions. The non-radiative relaxing transitions are shown with broken arrows.

7.3.2.1 \textbf{a-C(Er, Yb) Films}

To investigate the sensitization effect of Yb in a-C(Er), co-doping of Yb and Er in the proposed host a-C using a RF-PEMOCVD deposition system is highly suggested to be carried out. Yb$^{3+}$ ion has strong absorption at a wavelength of 980 nm, which is ten times higher than Er$^{3+}$ ions. The $^2F_{5/2}$ state of Yb$^{3+}$ and $^4I_{11/2}$ state of Er$^{3+}$ are nearly resonant in energy as seen in Figure 7.1. Accordingly, the pump radiation at the wavelength of 980 nm can be efficiently absorbed by Yb$^{3+}$
and then transferred to Er$^{3+}$, resulting in an increased number of excited Er$^{3+}$ per incoming photon. Besides down-converting PL measurement using the presently employed 532 nm laser excitation, the potential of upconversion effect in a-C(Er, Yb) films can be probed via 980 nm laser excitation.

7.3.2.2 Post-Deposition Annealing

To further enhance the PL intensity, a-C(X, X=Er, Yb) can be subjected to post-deposition annealing step under N$_2$ and O$_2$ environment albeit at temperatures below 400 °C. From XPS analysis, the [O]/[X] is less than six which is the coordination number of X$_2$O$_3$, suggesting a fraction of the X ions are not in the 3+ state. Thus the presence of optically inactive X ions may exist (i.e., X-C, X-X, X-F). By annealing the samples in O$_2$ environment, a possible increase in the quantity of X$^{3+}$ ions in the films may be realized. Also, the PL emission band (FWHM) can be further investigated with respect to changes in the local chemical states of the films after being subjected to the post-deposition annealing steps. Besides, the samples can be subjected to X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) analyses to see if the film is in the short or long range order and if any Er/ Yb cluster and/or C=C sp$^2$ nanocrystals are formed.

7.3.3 Device Application

After investigating the fundamental properties of a-C(Er, Yb) films in detail, the design and fabrication of optical waveguide/amplifier can be pursued, including the selection of potential cladding materials with appropriate refractive index $n$, modeling of range of viable thicknesses for cladding and core layers, and development of process parameters for the etching of a-C(Er, Yb) films. The propagation loss and gain can be further determined from the waveguide device. Also, the relationship between the gain and concentration of Er/ Yb can be characterized since high Er/ Yb concentration may lead to increased scattering losses and lower the optical gain. As for the waveguide structure, the F-based or Cl-based etchant gas can be applied in reactive ion etcher systems, but proper photolithography masks and detailed fabrication steps need further investigation.

In addition to the optical waveguide/amplifier device [47, 177, 178], applying a-C(Er) thin films as electroluminescent devices is potentially feasible, through integration in an all carbon based $p$-$n$ structure [103, 179], in metal-insulator-metal based structure [81, 180], or in heterostructure based structure [80, 86].
8 Publications and Other Scholarly Contributions

8.1 Journal Publications

Thesis Related


Non-Thesis Related


**8.2 Conference Presentations**

**Thesis Related – Oral Presentations**


**Thesis Related – Poster Presentations**


**Non-Thesis Related**


References


