Room-temperature photoluminescence in erbium-doped deuterated amorphous carbon prepared by low-temperature MO-PECVD

Raymond Y. C. Tsai1, Li Qian1,*, Hossein Alizadeh1, and Nazir P. Kherani1,2,3

1Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Ontario, Canada M5S 3G4
2Department of Materials Science and Engineering, University of Toronto, 184 College Street, Toronto, Ontario, Canada M5S 3E4
3kherani@ecf.utoronto.ca

Abstract: We report on a novel optical thin film material, erbium-doped deuterated amorphous carbon, fabricated directly on silicon substrate at room-temperature via controlled thermal evaporation of a Metal-Organic compound in a Plasma-Enhanced Chemical Vapour Deposition (MO-PECVD) system. High erbium concentrations (up to 2.3 at.%) and room-temperature photoluminescence at 1.54 µm are successfully demonstrated. Concentration quenching due to erbium clustering is reduced by adopting an appropriate MO precursor—Er(tmhd)3. Another quenching mechanism, caused by non-radiative C-H and O-H vibrational transitions, is shown for the first time to be significantly reduced by deuteration instead of hydrogenation of amorphous carbon. Our results suggest that erbium-doped deuterated amorphous carbon is a promising new class of photonic material for silicon-compatible optoelectronics applications in the technologically important 1.5 µm wavelength region.

©2009 Optical Society of America

OCIS codes: (130.3130) Integrated optics materials; (160.5690) Rare-earth-doped materials

References and links
26. Y. Haas, G. Stein, and E. Wurzberg, “Radiationless transitions in solutions: Isotope and proximity effects on potential application in integrated optoelectronics. Most recent breakthroughs include the optically pumped micro-laser based on erbium-implanted SiO2 characteristic in SRSO(Er) waveguides [3,4], and the realization of an ultra-low threshold in light-emitting diodes [2], the observation of optically pumped gain and amplifier erbium doping in a variety of silicon-based materials has been investigated [1] for their 


1. Introduction

Integration of electronic and optical communication devices on a single silicon chip is challenged by silicon’s inability to readily emit or amplify light on the one hand, and its incompatibility with predominantly III-V high speed photonic devices on the other. Realization of electrical and optical functions co-existing on a single chip requires the development of silicon-compatible light emitting materials. Due to Er3+ emission in the 1.5 µm region, the wavelength preferred by the majority of optical communication devices, erbium doping in a variety of silicon-based materials has been investigated [1] for their potential application in integrated optoelectronics. Most recent breakthroughs include the demonstration of electroluminescence in erbium-doped silicon-rich silicon oxide (SRSO(Er)) light-emitting diodes [2], the observation of optically pumped gain and amplifier characteristic in SRSO(Er) waveguides [3,4], and the realization of an ultra-low threshold in optically pumped micro-laser based on erbium-implanted SiO2 [5]. Extensive efforts in seeking promising host candidates are still going strong. Other than crystalline silicon and silica, it was shown that photo- or electro-luminescence at 1.5-4µm also exists in hydrogenated
amorphous silicon [2], in silicon carbide [6,7], and in Er silicate [8], and more recently, optical gain was observed in Yb$^{3+}$-sensitized Er-doped porous silicon [9].

Notwithstanding the extensive research on Er-doped silicon-based materials, Er-doping in carbon materials has received little scrutiny, despite the fact that carbon-based materials are compatible with silicon substrates and offer a number of advantages as a host. Take hydrogenated amorphous carbon (a-C:H) as an example, which can be readily prepared using a low-temperature plasma enhanced chemical vapour deposition (PECVD) process. (Here, hydrogenation of amorphous carbon stabilizes the structure by terminating the π dangling bonds.) This material is promising because of its high film quality, its easy integration with current metal-oxide-semiconductor (CMOS) technology, and its low cost and reproducibility. Moreover, it is feasible to obtain a-C:H films with a wide range of opto-electronic properties by adjusting the deposition parameters in the growth process. In particular, a-C:H offers the following desirable properties [10]: (i) it can be directly deposited on silicon substrate and easily etched by an oxygen plasma, allowing easy integration; (ii) it has large tailor able optical band gap (0.9 – 4.3 eV) covering from IR to visible; (iii) its conductivity can be altered by two orders of magnitude ($5 \times 10^3 – 5 \times 10^5$ S m$^{-1}$) through p- or n-doping; (iv) its refractive index can be altered from 1.47 – 2.76, providing more flexibility in waveguide design and mode confinement. These flexible opto-electronic properties of a-C:H allows one to tailor the host material for specific optoelectronic applications.

Major difficulties with obtaining light emission near 1.54 µm in Er-doped a-C:H films is due to the severe quenching of radiative emission by the C-H and O-H vibrational modes [11,12]. Herein we report, for the first time, that deuteration, instead of hydrogenation, can effectively overcome the quenching of ErP$^{3+}$ luminescence caused C-H and O-H bonds. Erbium-doped deuterated amorphous carbon (a-C:D(Er)) films are fabricated directly on silicon substrate at room-temperature via an MO-PECVD system. We show that high erbium concentrations and significantly enhanced room-temperature photoluminescence (PL) at 1.54 µm can be obtained in a-C:D(Er). Our results suggest that a-C:D(Er) is a promising photonic material for silicon-compatible optoelectronics applications.

2. Amorphous carbon as a host material

2.1 The metal-organic precursor

One important concern regarding the host material for erbium is its ability to reduce concentration quenching effects associated with erbium ion clustering at high concentrations. Such quenching effects limit the optical gain that can be obtained from Er-doped hosts, as a result of co-operative upconversion and energy migration [13,14]. At high erbium concentrations, an Er ion in the excited state is more likely to release its energy non-radiatively to cause an upward transition in a nearby Er ion, a process known as co-operative upconversion, than to de-excite radiatively. The upconversion process is then likely to repeat through a chain of ion-ion interactions, resulting in energy migration in a host until a quenching centre is encountered, where the energy is dissipated non-radiatively. This quenching process causes a decrease in luminescence efficiency [15].

To reduce concentration quenching, we selected tris(2,2,6,6-tetramethyl-1-3-5-heptanedionato) Erbium(III), abbreviated Er(tmhd)$_3$, as the metal-organic precursor in our MO-PECVD process. Its chemical composition is Er(C$_{11}$H$_{19}$O$_2$)$_3$, which is illustrated in Fig. 1. Under appropriate deposition conditions, the Er(tmhd)$_3$ molecule can be incorporated into the host material while preserving the Er-O bonds, as well as the long carbon chains (ligands). Thus, large separation between erbium ions is ensured, and accordingly, Er-Er co-operative upconversion is reduced. Moreover, the hydro-carbon ligands provide the framework for seamless integration into a hydrogenated (or deuterated) amorphous carbon network, allowing high solubility of erbium. Erbium concentration as high as 8.74 at.% in carbon films was reported [16]. Furthermore, the ligands in Er(tmhd)$_3$ act as sensitzers, which absorb optical excitation energy and transfer it to the encapsulated Er ion [17–20]. Thus, the effective absorption cross-section of Er$^{3+}$ is increased, making it more amenable to optical pumping.
Other advantages of using Er(tmhd)$_3$ as a precursor include: (i) Er(tmhd)$_3$ has a high vapour pressure of 0.1 mm Hg at 160 °C [21], allowing us to deliver a controlled evaporant using a low-temperature deposition technique; (ii) unlike ion-implantation, which is expensive and creates film damage during the implantation process, our low-temperature MO-PECVD technique does not require subsequent high-temperature annealing to repair film damage; (iii) each Er(tmhd)$_3$ molecule contains an erbium ion in the Er$^{3+}$ form (which emits at 1.54 mm) surrounded by six oxygen atoms [22], which can be directly incorporated in the host material without needing a post-growth process to activate erbium; and, (iv) Er(tmhd)$_3$ does not give rise to contamination problems often associated with using other metal-organic sources for Er [23].

![Illustration of the erbium metal organic precursor, tris(2,2,6,6-tetramethyl-3,5-heptanedionato) Erbium(III), abbreviated Er(tmhd)$_3$. The large central atom (purple) represents Er, the immediately surrounding 6 atoms (red) represent O, the larger atoms (dark grey) attached to the oxygen atoms are C atoms, while the smaller atoms (light grey) attached to carbon atoms represent H atoms. Note, the hydro-carbon ligands provide the framework for seamless integration into a hydrogenated/deuterated amorphous carbon network.]

2.2 Hydrogenation versus deuteration

Another important issue concerning a host for Er is the existence of non-radiative deactivation channels intrinsically within the host material. For amorphous carbon, it is well known that C-H vibrations in the vicinity of Er$^{3+}$ play an important role in quenching the luminescence lifetime of Er$^{3+}$ [11], and hydroxyl groups (O-H) was also shown to resonate with the Er$^{3+}$ 1.5 μm emission in silicate glass [12]. A systematic comparison between Er-implanted silicate glasses with different O-H impurity contents showed a correlation between O-H content and luminescence lifetime [24]. In Fig. 2, it can be clearly seen that the radiative transition in Er$^{3+}$ (~6500 cm$^{-1}$), between the ground state $^4$I$_{132}$ and the first excited state $^4$I$_{152}$, approximately matches the second harmonics of C-H and O-H bond vibrations (5900 and 6900 cm$^{-1}$, respectively) of the host material. Hence, excited Er ions can efficiently perturb the nearby C-H or O-H oscillators, resulting in a non-radiative transition. It is therefore not surprising that so far only one publication, by Speranza et al. [25], reported a study of Er luminescence in a a-C:H host, observing very weak Er photoluminescence (PL) despite applying a high optical excitation power on a sample of high Er concentration (~1.2 at.%).

To effectively suppress this inherent quenching of Er emission by C-H and O-H vibration modes, in this study, we remove the C-H bonds in the host by substituting hydrogen atoms with heavier deuterium atoms (H → D), consequently presenting a first demonstration of significantly enhanced room-temperature photoluminescence in erbium-doped deuterated amorphous carbon (a-C:D(Er)) films.
As can be seen from Fig. 2, deuteration modifies the harmonic number, \( \nu \), of the transitions that overlap with the radiative transition of Er, from \( \nu = 2 \) (for C-H and O-H) to \( \nu = 3 \) (for C-D and O-D). The interaction strength between Er\(^{3+}\) and the third harmonic of C-D vibrations, is much weaker than that between Er\(^{3+}\) and the second harmonic of C-H vibrations [26]. Therefore transition probability between Er\(^{3+}\) and the vibration modes of the host material is reduced through deuteration. The transition probabilities of \( \nu = 2 \) and \( \nu = 3 \) can be quantitatively compared by adopting the Franck-Condon factor, \( F \), with an approximation of the undistorted oscillator model [27]:

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

where \( k \) is force constant, \( \bar{q} \) and \( \bar{q}^0 \) are equilibrium positions of the oscillators, \( \hbar \) is Planck's constant, and \( \omega \) is frequency. Equation (1) suggests that the factor \( F \) decrease as \( \nu \) increases. As an example, \( F \) are 0.076 and 0.012 for \( \nu = 2 \) and \( \nu = 3 \), respectively, assuming \( \gamma = 0.5 \).

To verify experimentally the effectiveness of suppressing the quenching effect by replacing H with D, simple PL measurements were carried out to compare the Er emission from 1.1 mol% of Er(tmhd)\(_3\) diluted in methanol and that from the same concentration of Er(tmhd)\(_3\) diluted in deuterated methanol. With 86% of the hydrogen replaced by deuterium, the peak PL intensity is enhanced by ten-fold, as seen in Fig. 3(a). Moreover, we compare the PL intensity of an erbium-doped hydrogenated amorphous carbon (a-C:H(Er)) film, prepared using methane (CH\(_4\)) as a precursor gas, and that of an erbium-doped deuterated amorphous carbon (a-C:D(Er)) film, prepared under the same deposition conditions except the precursor gas was replaced by deuterated methane (CD\(_4\)). (Details on sample preparation and characterization are provided in the next two sections.) As in the cases for the Er(tmhd)\(_3\) solutions, a ten-fold enhancement in Er PL is observed (Fig. 3(b)), suggesting that most of the
C-H bonds are similarly replaced by C-D bonds in the deuterated film. This result confirms that Er luminescence efficiency can be dramatically improved through deuteration of amorphous carbon in a one-step deposition procedure.

![Graph showing PL comparison between 1.1 mol% of Er(tmhd) diluted in methanol (CH₃OH) and deuterated methanol (CD₃OD). The peak intensity is improved by ten-fold when Er(tmhd) is dissolved in C-H free solvent.](image1)

![Graph showing PL comparison between a-C:H(Er: 2.0%) and a-C:D(Er: 2.3%) films prepared under same deposition conditions except for the different precursor gas, CH₄ for a-C:H(Er) and CD₄ for a-C:D(Er). By deuteration of host material, the intensity of Er PL at 1540 nm is enhanced by ten-fold.](image2)

3. Sample fabrication

![Diagram of metal organic – dc saddle-field plasma enhanced chemical vapour deposition system used for the preparation of erbium doped deuterated amorphous carbon. The grey region surrounding the semi-transparent electrodes (mesh) represents the deuterated methane plasma.](image3)
Four a-C:D(Er) samples with varying Er concentrations were prepared by dc saddle-field PECVD (DCSF-PECVD) [28–30] at room temperature using deuterated methane (CD$_4$) as the precursor gas. The films were deposited on a 0.6-mm-thick 10-20 Ωcm crystalline silicon ⟨100⟩ and 1-mm-thick fused silica substrates. Erbium incorporation was achieved through thermal evaporation of metal-organic precursor Er(tmhd)$_3$, inside the deposition chamber as illustrated in Fig. 4.

The semi-transparent mesh anode is situated symmetrically between two parallel electrically grounded semi-transparent mesh cathodes. The resulting symmetric electric field serves to significantly extend the electron mean free path, thus permitting lower pressure dc discharges ordinarily not attainable with dc diode electrode configuration.

The evaporator containing the metal-organic precursor is placed ~8 cm away from the edge of the substrate holder. The Er doping concentration was controlled by modulating the evaporator temperature, and accordingly, the evaporant flux.

4. Sample characterization techniques

Three characterization tools were applied to study the material and the optical properties of our thin-film samples: X-ray photoelectron spectroscopy (XPS) was used to determine the composition of the film; Photoluminescence (PL) spectra were used to compare the relative photo emission intensities from different samples in the 1.5 µm region; and the binding energy (BE) spectra were used to study the oxidation state of Er. Below we provide details on the tools and procedures of the film characterizations.

XPS spectra were recorded on a K-Alpha monochromated XPS spectrometer (Thermo scientific, East Grinstead, UK) which included a monochromatic Al K-Alpha (1486.6 eV) x-ray source used for excitation and an ultra high vacuum chamber (operating pressure ~7.5 × 10$^{-8}$ Torr) with the vast majority of the residual pressure due to argon from the operation of the surface charge compensation flood gun. The elemental composition and depth distribution was determined by dividing the individual peak area, after background subtraction [31], by their respective atomic sensitivity factor (ASF) provided by the manufacturer.

The BE used to study the oxidation state of Er was calibrated by using the peak of adventitious carbon, setting it to 285 eV. High resolution spectra were fitted using Gaussian-Lorentzian curves in order to more accurately determine the BE of Er 4d core level. Prior to curve fitting, a background was subtracted.

PL measurements were performed on the samples to verify the optical activity of Er in a-C:D films. The optical pumping source for the PL measurement was the 514 nm line of an Ar$^+$ laser, operating at 600mW. It is focused down to 1 mm spot size on the surface of the sample. The energy from the laser is near resonant with $^2\text{H}_{11/2}$ excited level of Er ions. The excited Er ions decay to the $^4\text{I}_{13/2}$ level through fast non-radiative transition and then emit at 1.54 µm through the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ transition. The emission spectrum from Er ions is dispersed by double-grating monochromator, with a 70-µm input/output slit size, and detected by a thermoelectric-cooled InGaAs photodetector using a standard lock-in technique.

5. Results and discussion

Erbium concentrations of 0.47, 0.75, 1.4, and 2.3 at.% in a-C:D film samples were measured using XPS, and the atomic concentrations in the films are summarized in Table 1. Figure 5 depicts Er, O, and C concentrations for Sample #4 (the one with the highest Er content) as a function of the distance from the film surface, showing uniform erbium concentration across the thickness of the sample, which is 2 µm. The drop in the Er concentration near the surface is associated with the depletion of the Er MO reservoir; on the other hand, the increase of the O concentration near the surface could be caused by surface contamination. The analysis also suggests some C and O penetration into the Si substrate, likely an effect of the sputtering process during the XPS. The O/Er ratio is observed to be approximately 6 in the film region, suggesting that the source of O is mainly from the metal-organic ligands, as intended.
Table 1. Atomic concentrations of a-C:D(Er) samples computed from XPS spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>C%</th>
<th>O%</th>
<th>Er%</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>94.3</td>
<td>5.1</td>
<td>0.47</td>
</tr>
<tr>
<td>#2</td>
<td>91</td>
<td>8.2</td>
<td>0.75</td>
</tr>
<tr>
<td>#3</td>
<td>87.2</td>
<td>11.2</td>
<td>1.4</td>
</tr>
<tr>
<td>#4</td>
<td>83.8</td>
<td>13.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>

As seen in Fig. 6 (a), room-temperature PL spectra peaked at 1540 nm, corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er$^{3+}$ and its full width at half-maximum (FWHM) is about 70 nm. This FWHM is wider than those of other Er-doped silicate glasses, suggesting that Er$^{3+}$ have different local environments in the amorphous carbon matrix. The wider emission bandwidth indicates the potential of enabling a wide gain bandwidth for optical amplification.

To study the concentration dependence of the Er luminescence efficiency in more detail, the peak PL intensity is normalized to film thickness, denoted by $I_{nor}$, and then plotted as a function of Er concentration $N_{Er}$. Under cw laser excitation, $I_{nor}$ is proportional to $\sigma \varphi N_{Er} \tau_{rad}$, where $\sigma$ is the excitation cross section, $\varphi$ is the photon flux, $N$ is the optically active Er.
concentration, $\tau$ is the lifetime, and $\tau_{\text{rad}}$ is the radiative lifetime. If all incorporated Er atoms are optically active, i.e., $N \approx N_{\text{Er}}$, and if there are no quenching effects that would affect $\sigma$ and $\tau/\tau_{\text{rad}}$, an increase in $N_{\text{Er}}$ should be accompanied by a linear increase in $I_{\text{nor}}$. In Fig. 6(b), $I_{\text{nor}}$ increases linearly up to 1.4 at.% of Er and then begins to drop, suggesting a reduction in $\tau$ as $N_{\text{Er}}$ increases beyond this point; this indicates that concentration quenching is beginning to become significant only after the Er concentration has reached 1.4 at.% and beyond.

In order to verify that the majority of the incorporated erbium is in the optically active form of Er$^{3+}$, surrounded by oxygen atoms (as illustrated in Fig. 1), binding energy (BE) analysis using XPS was carried out. The shape of the BE spectrum is indicative of the oxidation state of Er in the material, and the BE spectra of the Er(tmdh)$_3$ powder, the evaporated film of Er(tmdh)$_3$, and all a-C:D(Er) samples were compared. The normalized 4d spectra of Er are given in Fig. 7, showing a characteristic spectral feature near 169 eV. Such feature is attributed to the 4d levels in Er$^{3+}$ forming a multiplet through an interaction with the unfilled shell [32]. Spectral multiplets at ~169 eV with essentially the same features as shown in Fig. 6 were observed in the 4d photoemission spectra obtained from the erbium state of 4f$^{11}$/Er$^{3+}$ [32], as well as from Er$_2$O$_3$ [33]. The existence of the multiplet near 169 eV for all the cases we measured suggests that the oxidation state of Er in Er(tmdh)$_3$ powder did not change markedly during evaporation and the deposition of the Er(tmdh)$_3$ film, nor did it change significantly during the MO-PECVD process. We therefore conclude that the incorporation of Er into the a-C:D(Er) samples essentially preserves the Er$^{3+}$ state, forming efficient emission centers.

![Er 4d XPS spectra](image)

**Fig. 7.** Er 4d XPS spectra of the four a-C:D(Er) film samples, an Er(tmdh)$_3$R film (prepared by evaporating the powder) and the Er(tmdh)$_3$R powder. Each spectrum is normalized to its maximum intensity after a background subtraction and offset vertically for clarity of presentation.

### 6. Conclusion

We have demonstrated significantly enhanced room-temperature Er photoluminescence in a-C:D(Er) thin films deposited by metal-organic PECVD. Our simple fabrication technique offers four essential advantages of the a-C:D(Er) material: (i) controllable and uniform Er concentration as large as 2.3 at.%, the highest reported in amorphous carbon as a host material; (ii) the possibility of obtaining a wide range of tailorable optoelectronic properties; (iii) the elimination of the annealing step (a required step in many Er-doped materials); and, (iv) deuteration for suppressing quenching. All these concur in an easy one-step film growth procedure. Film thicknesses up to 2000 nm have been achieved using this technique. No concentration quenching effects have been observed up to 1.4 at.% Er$^{3+}$. Binding energy analysis confirmed that the Er ions in a-C:D(Er) having the optically active oxidation state of...
Er⁺³ can be incorporated at room-temperature. It has also been shown that deuteration of amorphous carbon has effectively removed the non-radiative second order C-H and O-H vibrational modes, resulting in a significant enhancement in PL at 1.5 µm in a-C:D(Er) in contrast to that in a-C:H(Er). The efficient Er emission in a-C:D(Er) films, along with its wide range of tailorable conductivity, optical bandgap and refractive index, suggests a-C:D(Er) is a promising material for realizing integrated light-emitting and light-amplifying devices using CMOS technology.

Acknowledgements

We thank the following researchers who assisted with this work: G. Weiser for technical discussion on the selection of metal-organic Er compounds, V. Sukvatkin for assistance with the PL measurements, P. Broderson for performing XPS analysis, D. Yeghikyan and T. Kosteski for assistance with the fabrication facility, and A. Chutinan with the illustration of the metal-organic Er precursor. This work was supported through grants from the Natural Sciences and Engineering Research Council of Canada, Ontario Centres of Excellence, and Ontario Research Fund – Research Excellence program.