

## Metastable defects in tritiated amorphous silicon

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### ABSTRACT

We have observed the growth of defects caused by tritium decay in tritiated a-Si:H instead of inducing defects optically. We kept the samples in liquid nitrogen for two years. After two years the ESR signal reached  $\sim 10^{19} \text{ cm}^{-3}$  with no evidence of saturation. However, the density is still less than the density of tritium that has decayed. We step-wise annealed (isochronally annealed) one sample up to 200 °C, where all of the defects were annealed out. Another sample was isothermally annealed at 300 K for several months. At this temperature, the defects anneal slowly.

### INTRODUCTION

The appearance of optically or electrically induced defects in hydrogenated amorphous silicon (a-Si:H), especially those that contribute to the Staebler-Wronski effect [1], has been the topic of numerous studies, yet the mechanism of defect creation and annealing is far from clarified. This paper presents another method to induce silicon dangling-bond defects by replacing some of the hydrogen,  $^1\text{H}$ , with tritium,  $^3\text{H}$ . Tritium decays to  $^3\text{He}$ , emitting a beta particle (average energy of 5.7 keV) and an antineutrino. This reaction has a half-life of 12.5 years. The samples discussed in this paper contain approximately 7 and 10.4 at. % tritium. In these tritium-doped a-Si:H samples each beta decay will create a defect by converting a tritium, which is bonded to silicon, to an interstitial helium, leaving behind a silicon dangling bond.

We have tracked these defects through electron spin resonance (ESR) and photothermal deflection spectroscopy (PDS) [2]. The densities we measured at room temperature were smaller by orders of magnitude – only about  $5 \times 10^{17} \text{ cm}^{-3}$ . Therefore, there should exist a mechanism of defect annealing that is capable of healing  $\sim 10^{20} \text{ cm}^{-3}$  defects at room temperature. In the present work, we extend these studies to 77K, in order to establish the saturation behavior at this temperature and the thermal stability of the Si dangling bond defects introduced by tritium decay.

### EXPERIMENTAL

Both samples studied were made at the University of Toronto in 1996. The tritium gas was mixed with  $\text{SiH}_4$ , and samples were deposited using a DC glow discharge deposition system at various substrate temperatures. The samples used in this experiment were deposited on glass

substrates at temperatures of 423 K (150 °C) (further referred to as G181) and 498 K (225 °C) (referred to as G83). The G181 sample used in this study was 1.5  $\mu\text{m}$  thick and the G83 sample used in this study was 0.26  $\mu\text{m}$  thick. Shortly after deposition, high temperature tritium effusion experiments determined the tritium concentration to be approximately 7.0 and 10.4 at. % in samples G181 and G83, respectively.

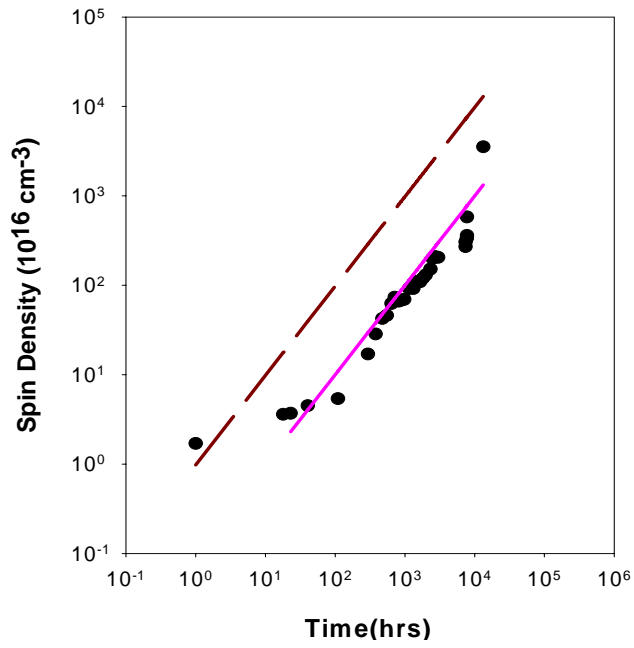
All ESR measurements were made using a Bruker ESR spectrometer operating at approximately 9.5 GHz with 4 gauss magnetic field modulation amplitude. ESR measures only the paramagnetic defects, such as neutral silicon dangling bonds. ESR does not measure the charged dangling bonds. Therefore, photo thermal deflection spectroscopy (PDS) was used to measure both the charged and uncharged defects in these samples at room temperature.

We expect the tritium decay to accumulate Si dangling bond defects because of the silicon-tritium bonds. The density of these defects is related to the number of tritium atoms that have decayed per unit volume. We first measured the samples 7 years after deposition, where the density of tritium atoms that had decayed since making the films was about  $6 \times 10^{20} \text{ cm}^{-3}$  [2]. However, both ESR and PDS measurements of the defect densities were lower by about 3 orders of magnitude because the defect density saturates at room temperature [2]. Next, we annealed the samples near the deposition temperature and kept the two samples at liquid nitrogen temperature for almost two years. During this time we used ESR to track the defect densities. After two years, the defect densities were about  $10^{19} \text{ cm}^{-3}$  for both samples

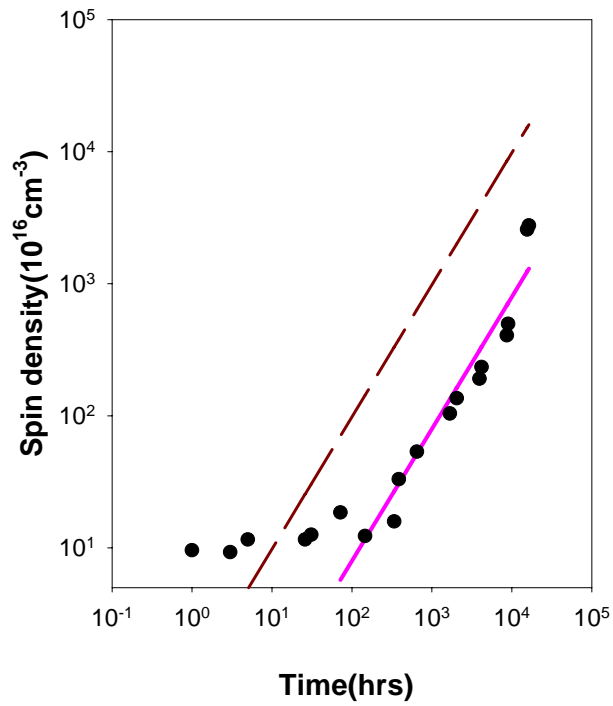
After two years in liquid nitrogen, we annealed the two samples. We step-wise annealed the G83 sample at successive temperatures up to 473 K isochronally while the G181 sample was annealed isothermally at 300 K.

## RESULTS AND DISCUSSION

After annealing the films, the defects began to accumulate in the dark at 77 K. The spin densities as functions of time stored at 77K are shown in Figs. 1 and 2 for samples G181 and G83, respectively. The data at the shortest times are the defect densities just after annealing. These densities are about  $10^{16} \text{ cm}^{-3}$  and  $10^{17} \text{ cm}^{-3}$  for G181 and G83, respectively. In both cases, the densities are probably due to surface or interface defects and not representative of residual densities in the bulk. The spin densities increase linearly with time. The final data points are the defect densities after about two years. In Fig.1, the final density is about  $3 \times 10^{19} \text{ cm}^{-3}$ , which is about 4 times lower than  $1.4 \times 10^{20} \text{ cm}^{-3}$ , the density of tritium atoms, which have decayed since the sample was annealed. In Fig. 2, the final density is about  $2 \times 10^{19} \text{ cm}^{-3}$ . In both samples there is no saturation in the growth as is the case at 300 K [2].

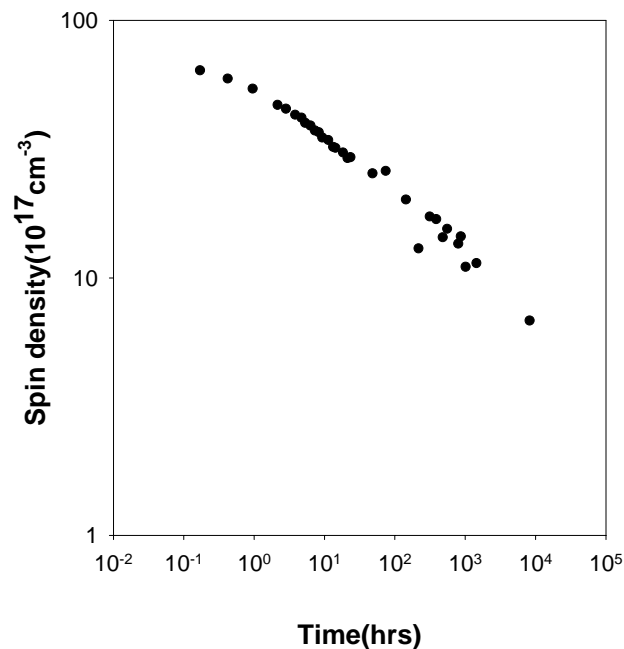


**Figure 1.** Increase of the defect densities of G181 as a function of time at 77 K.



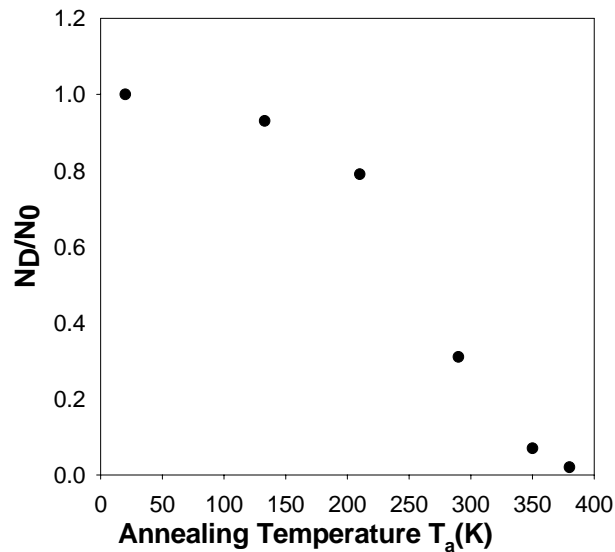
**Figure 2.** Increase of the defect density of G83 as a function of time at 77 K.

Figure 3 shows the decrease in defect densities after sample G181 was heated to room temperature and then kept at room temperature for several months. The defect densities were tracked by ESR. At 300 K, the defects created at 77 K anneal slowly. Even after several months, the density is still higher than the saturation density for defects created at room temperature, which is  $6 \times 10^{17} \text{ cm}^{-3}$ ; only after about one year does the defect density reach the saturated value at 300 K[2]. Because PDS measures both charged and uncharged defects in the sample, we used this method to check that the ESR was measuring all of the defects. The densities of defects as measured by ESR in these samples of a-Si: H are the same as those measured by PDS within a factor of two.



**Figure 3.** Decrease in the defect density after sample G181 was heated to room temperature and then kept at room temperature for several months of isothermal annealing.

Figure 4 shows data for stepwise annealing of the G83 sample up to 380 K. The sample was kept for 30 minutes at each annealing temperature,  $T_a$ . We continued annealing step by step up to 380 K, and after each annealing step we measured spin densities at 20 K. The data show that the defects are fully annealed at 473 K. The final density of approximately  $10^{17} \text{ cm}^{-3}$  matches the number after we annealed the sample at the start of the 77 K experiments. As mentioned above, this final “density” is due to surface defects and is not indicative of the remaining bulk spin density.



**Figure 4** . Relative decreases in defect density in sample G83 after stepwise annealing for 30 minutes at each successive annealing temperature,  $T_a$ .

At 77 K the defects accumulate almost linearly with the time. The spin density after two years is smaller than the density of tritium atoms that have decayed. This result possibly suggests that the tritium decay in a clustered hydrogen environment does not produce a dangling bond due to bond reconstruction as a result of emission of hydrogen from a nearby Si atom. This suggestion is similar to that proposed previously for thermal emission of hydrogen from the clustered phase [3, 7]. In addition, some tritium decays do not produce a silicon dangling bond because the tritium occurs in molecular form (trapped  $^3\text{H}-^1\text{H}$  or  $^3\text{H}-^3\text{H}$ ). The sample G83 was annealed step-by-step up to 473K. These annealing results are similar to those that are observed when defects are created with light (Staebler-Wronski effect) at low temperatures. In particular, two thirds of the defects decay near 300 K in both experiments [4, 5].

We checked that there is no effect of the energetic electrons that are emitted during the decay of tritium by electron irradiating a sample with an order of magnitude greater dose than that received in the tritium decay experiments. No increase in spin density was observed. There are two or three hydrogen-related signals that appear in the glass substrates, presumably after tritium decay. These signals are clearly in the glass substrates because their lineshapes correspond to centers commonly observed in oxide glasses on irradiation.

## SUMMARY

We have shown that the defect densities of two tritiated amorphous silicon samples at 77 K increase linearly in time up to  $10^{19} \text{ cm}^{-3}$ . The final densities, however, are factors of 4 to 8 smaller than the density of tritium atoms that decayed. From NMR experiments, we know that 3 at. % of the total atoms in the film (Si plus  $^1\text{H}$  plus  $^3\text{H}$ ) consist of hydrogen and tritium atoms that reside in a dilute phase and the rest of the hydrogen and tritium atoms exist in a clustered phase [9]. Therefore, some of the tritium atoms in the clustered phase probably do not produce

silicon dangling bonds at 77 K due to reconstruction. There is no evidence of saturation at 77 K. In our tritium experiments, hydrogen plays an important role in limiting the creation of the dangling bonds, even at 77 K. The annealing isochronal process of G83 is similar to that previously observed for Staebler-Wronski defects created at low temperature. This result provides further hints for the roles of hydrogen in creating and annealing defects in light soaked samples at low temperature, such as those suggested in [6-8].

## ACKNOWLEDGEMENTS

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