

RECOMBINATION IN TRITIATED AMORPHOUS SILICON

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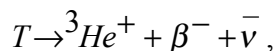
ABSTRACT

Tritiated amorphous silicon was used for the intrinsic layer of a p-i-n hydrogenated amorphous silicon diode. Current versus voltage measurements were carried out on the diode over time under dark and illuminated conditions. There was a decrease in the forward characteristic of the diode when measured under dark conditions and there was a decrease in photovoltaic power. These changes can be explained by the creation of dangling bonds when bonded tritium atoms decay. By annealing the diode at 125 °C, most of its photovoltaic properties could be recovered. It was also found that luminescence could be recovered in tritiated amorphous silicon by thermal annealing.

INTRODUCTION

The presence of metastable defects in hydrogenated amorphous silicon (a-Si:H) affects the performance of photovoltaic cells and thin film transistors. Stabler and Wronski [1] found that defects can be created by illuminating a-Si:H. The defects decreased the dark conductivity. Further, the dark conductivity could be restored by annealing the sample at 150 °C. Annealing has been used to restore photovoltaic power and luminescence of degraded a-Si:H [2,3].

Using tritium rather than hydrogen permits the study of dangling bonds unlike any other method. Tritium is a radioactive isotope of hydrogen and decays by the following reaction:



where $\bar{\nu}$ is an antineutrino and β^- is a beta particle. The half-life of tritium is 12.3 years and the mean energy of the beta particle is 5.69 keV. Chemically, tritium behaves like hydrogen and thereby can be used as a tracer to study hydrogen behaviour. The energy of the β particle and helium recoil (~ 3 eV) are insufficient to cause damage to the structure. Replacing hydrogen with tritium in a-Si provides an opportunity to directly observe the effects of dangling bonds produced by removing bonded hydrogen from the structure without otherwise changing the matrix.

Previous methods of creating dangling bonds, other than the use of light, have relied on high energy particle bombardment or hydrogen removal through heating of a-Si:H. Particle

bombardment will inflict serious damage to the structure of the material and high temperature hydrogen effusion will also change the matrix. The use of tritium ensures that after tritium decays the Si-T bond becomes a silicon dangling bond while the rest of the matrix remains relatively unchanged. Considering that the decay constant of tritium is $1.78 \times 10^{-9} \text{ s}^{-1}$ and that there can be over 10 atomic percent bonded tritium in the film, the density of dangling bonds will increase at a rate of over 10^{17} cm^{-3} per day.

Dangling bonds are expected to give rise to states deep in the band gap of the material. Photo-luminescence of undoped a-Si:H and the photovoltaic energy conversion of p-i-n junctions are greatly influenced by the number of deep states since these act as recombination centres. These centers provide a non-radiative recombination path for electron-hole pairs thereby reducing the luminescence and the carrier diffusion length in the material. A large density of mid-gap states also reduces the effective width of the depletion region in the diode. This then decreases the process of separation of photo-generated electron-hole pairs and thereby further decreases the power generation of the diode.

EXPERIMENTAL

The dc saddle-field system [4] was used to deposit p- and n- doped a-Si:H layers and undoped a-Si:H:T. p- and n- doping was achieved using diborane and phosphine, respectively. In order to produce intrinsic tritiated amorphous silicon, silane and tritium each flowed into the deposition system at 5 sccm and the chamber pressure was maintained at 90 mTorr. Due to the complexities of handling and delivery of tritium, the deposition parameters have not been optimized for photovoltaic cells. The structure of the device was glass/SnO₂/p-/i- a-Si:H:T/n-/Al. a-Si:H:T was also deposited on polished crystalline silicon for photo-luminescence measurements.

Current versus voltage (I-V) measurements were carried out using a Keithley 6517 electrometer. To establish dark conditions, the diode was placed in a light-tight enclosure that was fitted with electrical feedthroughs. Illuminated measurements were carried out by placing the sample under a halogen lamp system. To prevent any photo-induced instabilities the illumination was kept low. Annealing of the diode was carried out on a hot plate in ambient air at 125 °C for 1 hour.

Photo-luminescence measurements were carried out on a-Si:H:T films that were deposited onto polished silicon wafers. An argon ion laser was used to excite the film while the sample was held in a cryostat at 80 K. The cryostat system was also used to anneal the sample under vacuum at 130 °C.

RESULTS AND DISCUSSION

1. Photovoltaic devices

After the evaporation of aluminium contacts onto the p-i-n structure the device was

transferred into the light-tight metal box where dark I-V measurements were carried out. These measurements were repeated over a number of days and the results are shown in Figure 1. It can be seen that the I-V curve four hours after the deposition of the device exhibits a diode-like characteristic in the forward bias region. The shape of the curve in the low forward bias region and in the reverse bias region suggests the presence of a shunt resistance possibly related to surface leakage effects. Subsequent I-V measurements show that the forward current decreases as a function of time while the reverse current remains relatively unchanged. After about 300 hours the forward bias characteristic and the reverse bias characteristic overlap.

The I-V characteristics as a function of time of the same device when illuminated are shown in Figure 2. The light intensity was maintained low and the sample was illuminated only during acquisition of the I-V characteristic. From Figure 2 it can be seen that the short circuit current and the open circuit voltage decreased as a function of time. The open circuit voltage did not decrease as quickly as the short circuit current due to the fact that the open circuit voltage is logarithmically related to the short circuit current. After about 10 days the device's I-V characteristic is nearly linear which indicates that the device has developed a large series resistance. This is primarily a result of the produced dangling bonds pinning the Fermi level towards the center of the band gap. By pinning the Fermi level there is no longer a strong electric field across the entire intrinsic layer increasing the transit time and the recombination of carriers.

The sample was annealed at 125 °C for 1 hour in air. The dark and illuminated measurements were once again performed. Much of the initial illuminated I-V characteristic was recovered, followed again by a reduction of the short circuit current and the open circuit voltage as a function of time. The sample was annealed once more at 125 °C for 1 hour and I-V measurements were carried out over time. These are plotted in Figure 3. Again much of the photovoltaic properties of the sample were recovered and once again after a period 10 days the I-V characteristic developed a large series resistance.

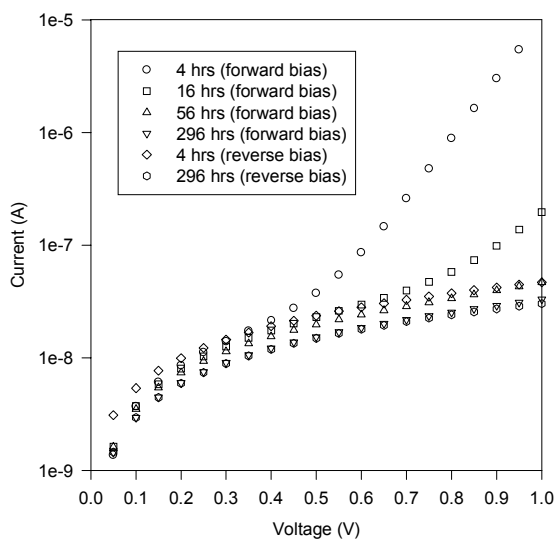


Figure 1. Dark current versus voltage of the p-i-n device.

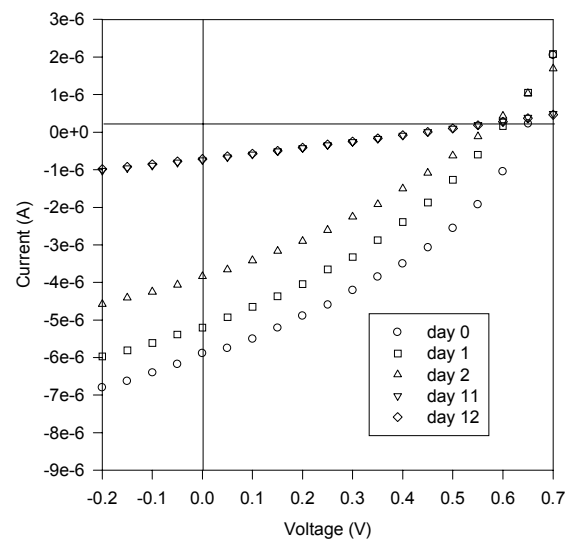


Figure 2. Illuminated current versus voltage of the p-i-n device.

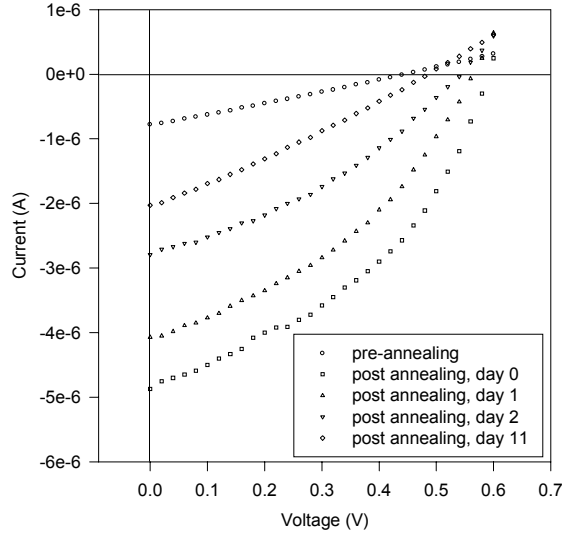


Figure 3. Illuminated current versus voltage of the p-i-n device after annealing.

2. Photoluminescence

In an earlier paper [5] the authors studied the PL of an a-Si:H:T sample and reported a PL peak near 1.6 eV. The photoluminescent intensity was found to decrease with time indicating that fewer electron-hole pairs were recombining radiatively and an increasing fraction of the recombination was non-radiative. The increase in non-radiative recombination was attributed to an increase in the dangling bond concentration from the decay of tritium. These dangling bonds served to enhance the non-radiative recombination rate of electron-hole pairs thus reducing the luminescence.

New data for photoluminescence have been obtained from the same a-Si:H:T sample after it had been in storage for over two years. The increase in the concentration of dangling bonds during this period has been estimated to be over 10^{19} cm^{-3} , corresponding to a loss of nearly 2 % in bonded tritium. The sample showed no luminescent signal, consistent with the presence of a very large number of dangling bonds. The sample was subsequently annealed at 130 °C for 1.5 hours in vacuum. The PL signal was then measured at various intervals after annealing. Figure 4 shows the PL data before annealing and at 3 different times after annealing. It can be seen that the PL signal at 1.55 eV reappears after annealing and that the intensity of the signal decreases with time. One week after the first annealing, the sample was annealed again at the same temperature of 130 °C but for three hours. The PL signal intensity after the second annealing was measured to be 2.5 times stronger than after the first annealing. As previously found, subsequent measurements of photoluminescence showed that the intensity decreased as a function of time.

The mechanism of defect creation and defect annealing of a-Si:H:T is not readily explained by present models used to explain the Stabler-Wronski effect. As pointed out by Crandall [6], most models for the Stabler-Wronski effect fall into either the group of weak-bond

breaking models or charge-trapping models. The weak-bond breaking model requires that Si-Si

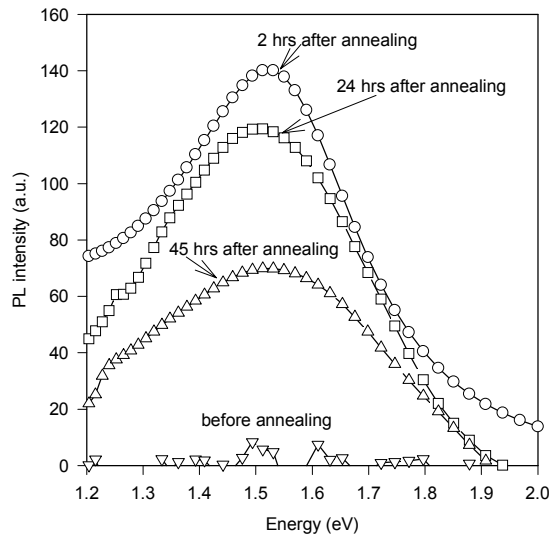


Figure 4. PL measurements of an a-Si:H:T film before and after annealing. We show the raw data for the before annealing. The after annealing data were smoothed.

bonds be broken and, that upon annealing, a neighbouring hydrogen atom be used to passivate one of the dangling bonds thus creating two separated and therefore stable dangling bonds (one at the Si-Si broken bond site, the other at the original Si-H site). Thermal annealing in the weak-bond model would reverse the process. The weak-bond model is not consistent with our observations since the dangling bonds that are created in a-Si:H:T are the consequence of the "removal" of tritium from individual Si-T bonds. Tritium is expected to be uniformly distributed throughout the material and the decay mechanism is random. Therefore, the dangling bonds will not be created in close proximity, as required in the weak-bond model. Furthermore, the motion of hydrogen would not effect the dangling bond concentration.

The charge dangling bond model given by Adler requires that there are at least 10^{17} cm^{-3} existing charged dangling bonds (D^+ and D^-). These charged dangling bonds are thought to be readily available in a-Si:H since they are required to reduce strain in the material. The neutral dangling bond, D^0 , is created during illumination when the generated electrons are trapped at D^+ states and the generated holes are trapped at D^- states. Then a 15° bond angle change would move the defect to the stable D^0 position. Annealing is expected to reverse the above process.

The dangling bond formation in a-Si:T can be summarized using Figure 5. After tritium decays the He^{3+} ion attracts an electron thus becoming a He atom. The He atom then diffuses away leaving behind a positively charged dangling bond (D^+). Given that a beta particle can produce over 1500 electron-hole pairs, the D^+ state can readily attract an electron and through lattice relaxation form a D^0 state. This situation resembles that suggested in the charge-trapping model. It is possible that heating a-Si:H:T may result in exciting the electrons from the D^0 center

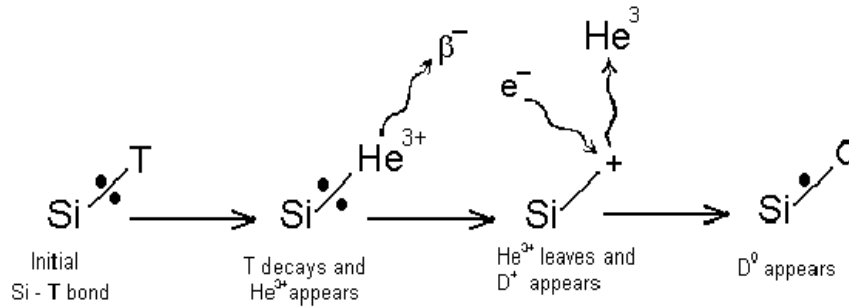


Figure 5. The dangling bond formation after tritium decay.

to form D^+ or D^- states. However, the large number of electron-hole pairs that are being continuously formed in the material as a consequence of β decay should quickly convert the D^+ or D^- states. Also, it is difficult to justify such a large number of stable D^+ and D^- states in the material. Clearly, more work is required to resolve the situation.

CONCLUSIONS

The decay of bonded tritium is an effective method of creating dangling bonds. In a p-i-n diode the dangling bonds significantly reduce the short circuit current and the open-circuit voltage. The decaying tritium also produces states that increase the series resistance of the diode. The diode can be annealed so that most of its photovoltaic properties are recovered. Annealing of an a-Si:H:T film of very large defect density leads to the recovery of its photoluminescent properties.

ACKNOWLEDGEMENTS

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