TOWARD THE ELIMINATION OF LIGHT-INDUCED DEGRADATION OF AMORPHOUS Si BY FLUORINE INCORPORATION

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ABSTRACT

We report on evidence that fluorine, properly incorporated into a-Si, replaces weakly bonded hydrogen and improves the material stability under light soaking. Our fluorinated amorphous silicon (a-Si:H:F) is made by rf glow discharge at high deposition temperatures up to 430 C from a gas mixture of SiH_4 or Si_2H_6 and F_2. These a-Si:H:F films show much lower density of states in the light soaking saturated state than device quality a-Si:H prepared in the same deposition system. It is evident from our results that fluorine incorporated into the network at such high deposition temperature makes for a new configuration which minimizes dangling bonds and other defects.

INTRODUCTION

The photovoltaic application of amorphous Si alloy (a-Si:H) is limited by its light-induced degradation, i.e., the Staebler-Wronski Effect (SWE) [1]. The conversion efficiency of solar cells made with a-Si:H drops about 15-20% after light soaking. Although many models have been proposed [2] to explain the SWE, it is generally believed that SWE is associated with H, which is weakly bonded to Si and has relatively high mobility inside a-Si network [3].

To minimize this problem one needs to replace the part of H that is loosely bonded to Si network with an element that bonds to Si stronger. As Ovshinsky et al. pointed out and demonstrated in 1978 [4], replacing some of the H in a-Si:H by F greatly suppresses the SWE and enhances the material quality.

In this paper we give further evidences to show the improved stability of a-Si by F incorporation which results in a lower density of defect state in the light-soaking saturated state.

SAMPLE PREPARATION

Our fluorinated amorphous silicon samples (a-Si:H:F) in this study were prepared by rf glow discharge in a specially designed diode plasma chamber with a gas mixture of SiH_4 or Si_2H_6 and F_2 in He dilution. In our deposition reactor, the grounded electrode, on which substrates are mounted, is negatively biased with respect to the rf electrode.

Table I. Deposition conditions of a-Si:H:F and a-Si:H representive samples.

Sample	Type	Gas Mixture	Pressue (mTorr)	Ts (C)	Power (Watt)	Bias (Volt)	Time (min.)	Thickness (μm)
F1	a-Si:H:F	Si_2H_6:F_2:He=1:1.7:40	250	430	10	+145	300	2.1
H2	a-Si:H	Si_2H_6:He=2:7	250	430	4	+69	40	1.8
H3	a-Si:H	SiH_4	250	250	2	+16	150	2

To reduce the loosely bonded H during growth, films were deposited at high deposition temperature (T_s) up to 430 C, which is the temperature limit for this chamber. The deposition power is 10 Watt, corresponding to a power density of 0.22 W/cm^2. The total gas flow is 13 sccm. For comparison, we also made films in the same chamber at 430 C without F_2 and typical device quality a-Si:H samples at 250 C. In Table I, we list the deposition parameters for one representative sample of each category as F1, H2 and H3 respectively.

EXPERIMENTAL DETAILS

To conduct the light-induced degradation experiments, we expose our samples with 800 mW/cm^2 heat filtered white light, obtained by focusing the light of a 300 Watt projector lamp with a fresnel lens. Samples were placed on a water cooled stage in air and blown by an air jet during exposure so that they were kept close to ambient temperature.

We measure the density of states of these samples before and after exposure with photothermal deflection spectroscopy (PDS) [5]. In our PDS measurement, sample is mounted on a stainless steel sample holder that fits into the Quevet cell reproducibly. To assure good reproducibility, we keep the sample on the holder all the time, even during exposure. According to our experience [6], PDS measurement can be reproducible within 10% in this way.

Conductivity (σ) is measured in vacuum with ohmic coplaner Ag electrodes. Temperature dependence of σ is measured during slow cooling from 210 C. Photoconductivity (σ_p) is measured also in vacuum, with about 300 mW/cm^2 heat filtered white light at room temperature. IR spectra were measured with a dual beam IR spectrometer on samples grown on Si wafer.

RESULTS

Figure 1 shows the infrared spectra of these three samples described in Table I. In the spectrum of the a-Si:H:F sample F1, peaks at 830, 920 and 1005 cm^{-1} correspond to SiF, SiF_2 and SiF_4 stretching vibration [7]. The peak at 380 cm^{-1} is due to SiF_2 or $(SiF_2)_n$ bending. The peak at 512 cm^{-1} is the Si-Si vibration (Raman peak) that appears since the symmetry of Si-Si is broken when there is highly electronegative F in the back bond. The IR spectrum of sample F1 also shows SiH wagging and stretching mode at 630 and 2000 cm^{-1} [8] From the intensity of 630 cm^{-1} peak we estimated [9] the H concentration of F1 to be 4.1 at. %. The SiH stretching peak has a shoulder at 2100 cm^{-1}, the position of SiH_2 or $(SiH_2)_n$ stretching. Since we do not find any SiH_2 or $(SiH_2)_n$ scissors bending at 845 and 890 cm^{-1}, the 2100 cm^{-1} shoulder is likely due to the existence of F in the back bond of SiH. There is usually a blue shift in the SiH stretch vibration when there is a more electronegative species like F, O

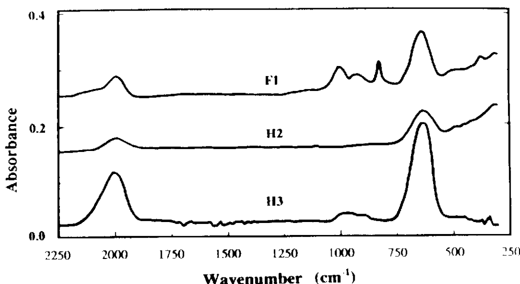

Figure 1. IR absorbance spectra for a-Si:H:F sample F1 and a-Si:H samples H2 and H3. Spectra for F1 and H2 are shifted vertically for clarity.

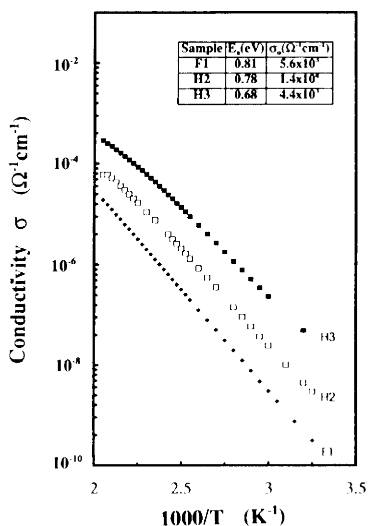

Figure 2. Temperature dependence of dark conductivity for samples F1, H2 and H3. The insert table shows the activation energy and prefactor.

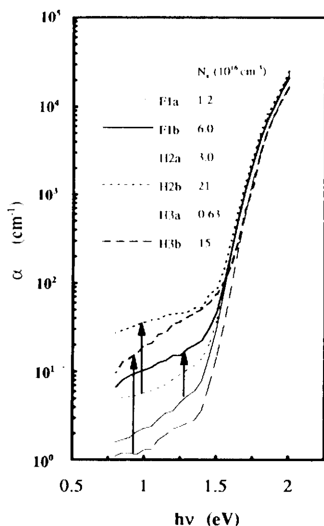

Figure 3. PDS spectra of a-Si:H:F sample F1 and a-Si:H samples H2 and H3 before and after light soaking.

or H in the back bond [10]. We also measured the total amount of F in sample F1 by wavelength dispersive spectroscopy (WDS) and found the total fluorine content to be around 5.9 at. %. In figure 1, the IR spectra of a-Si:H samples H2 and H3 are also shown. They both have SiH wagging and stretching peaks at 630 and 2000 cm^{-1}. The concentrations of H for these two samples, H2 an H3, calculated from 630 cm^{-1} peak intensity are 3.7 at. % and 9.3 at. % respectively. The relatively low H concentration of samples F1 and H2 are due to their high T_s at which H effuses out during deposition.

In figure 2 we plot the temperature dependence of dark conductivity (σ_d) of these three samples. The activation energy (E_a) and prefactor (σ_o) of these curves are listed in the insert. Sample F1 has a higher E_a and a lower room temperature conductivity, indicating that the fluorine incorporation moves the fermi level toward the center of the band gap.

The PDS absorption spectra of these samples before and after light exposure are illustrated in figure 3. Curves F1a, H2a and H3a are the initial states of samples F1, H2 and H3. After PDS measurement, samples are kept on their PDS sample holder and exposed under 800 mW/cm^2 white light for 3 days. If there is any saturation in the degradation [11], we believe that 3 days of light soaking should bring these samples close to their saturation limits. PDS spectra, measured immediately after light soaking, are plotted in figure 3 as F1b, H2b and H3b.

The density of defect states, N_s, calculated [5] from PDS absorption spectrum are also given in the figure 3. Although the density of defect states of sample F1 is higher than that for H3 in the initial state, in the final state the defect density of sample F1 is the lowest among the three samples. The low saturated defect density in a-Si:H:F is due to the strong passivation of dangling bonds and weak bonds by fluorine and not due to the high T_s since the defect density of H2 in the exposed state is much higher. The light induced defect states in a-Si:H:F also have different annealing kinetics from that of a-Si:H. The light induced changes in F1 needs higher temperature or longer time to get

annealed than in sample H3. This is because in sample F1 we do not have much loosely bonded H that diffuses at relatively lower temperature. Our PDS data clearly indicate that fluorine plays a unique structural role in passivating Si dangling bonds due to its special chemical properties that H does not have.

Table II. Photoconductivity before and after 1 hour 300 mW/cm^2 exposure as well as room temperature dark conductivity.

Sample	$\sigma_d(rt)$ $(\Omega^{-1}cm^{-1})$	σ_p $(\Omega^{-1}cm^{-1})$	$\sigma_p/\sigma_d(rt)$	$\sigma_p(after)$ $(\Omega^{-1}cm^{-1})$
F1	2.9×10^{-10}	1.8×10^{-5}	6.2×10^{4}	7.4×10^{-6}
H2	2.8×10^{-9}	9.4×10^{-5}	3.4×10^{4}	3.5×10^{-5}
H3	6.8×10^{-9}	1.9×10^{-4}	2.8×10^{4}	4.6×10^{-5}

From the PDS spectra we also get the information about the band gap, such as E_{03} and E_{04} (α at 10^3 and 10^4 cm^{-1}). The smaller gaps for samples F1 and H2 are consistent with their low H concentrations [12].

Another characteristic of the light-induced degradation is the change in photoconductivity (σ_p). In the light soaking of PDS samples, exposure was done in air to obtain sufficient cooling. A sample left in air usually has water adsorbed on its surface. Such a water contamination layer strongly affects the conductivity measurement [13]. To obtain reliable σ_p study, we measured the σ_p in vacuum in the slowly cooled state after conductivity activation measurement. The sample is subsequently exposed for an hour to 300 mW/cm^2 white light. σ_p for samples F1, H2 and H3 are measured before and after exposure at 25 C. Results are listed in Table II. Also listed in the table are the room temperature σ_d and photosensitivity (σ_p/σ_d) for comparison. The photosensitivity of the a-Si:H:F sample is the highest among the three. Although the relative drop in σ_p after one hour exposure is the lowest in sample F1, the absolute value of σ_p, hence the electron mobility-life time product, is lower than the other two films before and after exposure. The low σ_p of sample F1 may be due to the following two reasons: first, the fermi level of a-Si:H:F sample is deeper in the gap as we see from figure 2, it is possible that there is higher density of state at the fermi level for sample F1; Second, the conduction band tail of sample F1 might be broader than other two a-Si:H samples. The broad conduction band tail suppresses the electron mobility-life time product.

DISCUSSIONS

In the H evolution experiment of conventional a-Si:H [14], two evolution peaks are normally found: one low temperature peak at 370 C and another high temperature peak between 600 and 700 C. H coming out from the low temperature peak has apparently been loosely bonded to Si network. These loose Si-H bonds are responsible for the light induced degradation and most of the intrinsic defects. To improve the quality and eliminate SWE, one has to get rid of these loose Si-H bonds by replacing them with stronger bonding.

Fluorine, being the most electronegative of the elements, bonds to Si almost twice as strong as H [15], hence can replace loose Si-H bonds and passivate dangling and weak bonds more efficiently. Also due to its strong bonding desire, F is less mobile. High deposition temperatures, like 430 C, is therefore important to enhance the mobility of F at the growing surface. Even though some Si atoms are initially loosely bonded to H, at such high T_s, this H would effuse out during growth and leave the site for F for more permanent passivation. In this way, one can reduce or eliminate most of the dangling bonds, as well as the weak bonds, which can be thought of as a reservoir for dangling bonds. In the deposition process, we used F_2 in the gas mixture since we believe F_2 decomposes more efficiently than SiF_4 in the plasma and is better incorporated into a-Si.

Besides F, the presence of H is also necessary in a-Si. Being a small atom and having about the same electronegativity as Si, H bonds to Si network with more flexibility. The existence of H relaxes the strain of the amorphous network, and reduces the density of states. In fact, Janai et al [16] prepared H-free a-Si:F and found a density of state of $2x10^{17}$ cm^{-3}.

Another important advantage of using F_2 in the reactant gas is to use its etching effect. Hydrogen etching has been utilized to grow microcrystalline Si [17], since strong H etching can remove the unfavored Si landed on the growing surface, and leave behind only favored Si-Si bonds. High quality a-Si and a-SiGe alloys are often made with strong H dilution for the same reason. However, due to the need of strong dilution, normally more than 95%, not much active Si species can be put inside the reaction chamber. F_2 has much stronger etching effect than H_2. It removes bad bonds more efficiently during growth. In fact, with more F_2 added in the gas mixture than that in F1, microcrystalline Si has been made, as revealed from Raman spectroscopy. It is believed that amorphous material made in the condition just before crystallization, is much better. Such a concept, is fully utilized in our a-Si:H:F deposition. Also due to the F_2 etching, the surface morphology of sample F1 is much better than that of sample H2, as revealed from scanning electron microscope study.

Due to the proper replacement of loosely bonded H by F, it is likely that doped a-Si:H:F made in similar manner would show higher glass transition temperature and smaller metastable behavior, such as in the quench effect, the bias annealing induced effect and other metastable effect [18].

CONCLUSIONS

Fluorinated a-Si is made with gas mixtures of SiH_4 or Si_2H_6 and F_2, diluted in He, in a specially designed rf glow discharge system at T_s up to 430 C. The incorporation of F in a-Si reduces the defect density, compared to the material made in similar conditions without F_2. a-Si:H:F thus made shows much better stability under light soaking than conventional device quality a-Si:H. It has the lowest defect density in the light soaking saturated state. We believe that further optimization to the deposition and better control to the growth will further improve the F incorporation to a-Si and lead to a high quality material with eliminated light-induced degradation.

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