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Electric field and infrared-induced recovery of metastability in amorphous hydrogenated silicon

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In this letter we investigate the difference between the bond breaking and the charge trapping model of the light-induced effect in amorphous hydrogenated silicon (*a*-Si:H). We also report the partial recovery from the light-induced effect in *p-i-n* solar cells by infrared illumination in the presence of an electric field.

Currently there are two primary models to explain the occurrence of the light-induced effect in amorphous hydrogenated silicon (*a*-Si:H). The bond breaking model first proposed by Pankove and Berkeyheiser[1] and later demonstrated by Dersch *et al.*[2] has been developed in great detail by Stutzmann *et al.*[3] According to this model the nonradiative recombination of photogenerated electrons and holes releases enough energy to break a weak Si–Si bond thus increasing the dangling bond density in the material. Stutzmann has recently proposed that bond breaking can occur even in the presence of only one type of excess carriers without recombination.[4] The other model first proposed by Adler[5] involves a redistribution of charges in the dangling bonds resulting in a larger concentration of neutral paramagnetic D^0 states in the light-soaked material. A charge trapping model has also been proposed by Nakamura *et al.*,[6] Crandall,[7] and Tanaka *et al.*[8] Yamagishi *et al.*[9] have also explained the light-induced effect in *a*-Si:H by invoking both positively correlated dangling bonds as well as charge trapping in negatively correlated D^* centers. In this letter we report our attempts to distinguish between the bond breaking and the charge trapping models. We report also our results on the partial recovery of the light-induced effect in *p-i-n* cells by infrared illumination in the presence of an electric field.

If the light-induced effect is due to charge trapping alone, it should be possible to re-emit the trapped charges by developing a high electric field in the sample. While a high field cannot reconstruct a broken bond, it can tilt the bands enough to cause field-assisted tunneling. Since maximum tunneling distances are of the order of 10 nm, for a trap depth of 1 eV, a field of 10^5–10^6 V/cm is needed for the field-assisted tunneling to take place.

Measurements were carried out on both *p-i-n* as well as *m-i-m* structures. The *m-i-m* structures were made by glow discharge deposition of *a*-Si:H on Cr on 7059 glass. Cr fingers were then deposited on the *a*-Si:H through metal masks. Dark current-voltage [$I(V)$] characteristics were measured and the breakdown voltages were determined. The samples were light soaked at 100 mW/cm^2 using a calibrated tungsten halogen (ELH) lamp for 12 h. The dark currents dropped by about a factor of 4. A voltage of 10 V was applied across the sample which was typically 0.5–1 μm thick. No change in the $I(V)$ characteristic was found even after leaving the reverse bias on for hours. The samples recovered to state *A* after thermal annealing at 160 °C. Standard solar cells were also light soaked using either the ELH lamp or an Ar laser. There was a drop in open circuit voltage, short circuit current, and fill factor. The sample was then left with a reverse bias of 9 V for a period of a few minutes to a few hours. No recovery of the solar cell characteristics was seen after this treatment.

It is interesting to examine the conditions under which we would or would not expect to see a recovery by applying a high field, see Fig. 1. Supposing the electric field removed the single electron from the D^0 state converting it into a D^+ state and/or added an electron from the valence band to the D^0 states converting it into a D^- state, the material would be left with fewer D^0 states and its properties would be closer to the annealed state. Now, if the sample had a positive correlation energy, so that the D^+ centers were lying close to the valence band, then, in the presence of a high electric field an electron from the valence band would be able to tunnel into a D^+ state converting it back into a D^0 state. Similarly, the electron from the D^- state now close to the conduction band, would tunnel out converting D^- back to D^0. Then we would not see any field-induced recovery. However, if the correlation energy is negative so that the D^+ center is closer to the conduction band no such D^+ to D^0 or D^- to D^0 conversion will be possible and the material will have recovered its prelight-soaked properties. Hence this experiment will distinguish between a charge trapping model and a bond breaking model only if the dangling bonds have a negative correlation energy. Also if the light-induced effect were due to trapping of charges in shallow states as suggested for example by Yamagishi *et al.*[9] we should be able to see an effect of the electric field. Hence, from our measurements we conclude that the light-induced metastability is not due to charge trapping in either shallow states or in states with a negative correlation energy. From this experiment it is not possible to distinguish between the case of charge trapping and bond breaking for dangling bonds with a positive correlation energy. Note that all the arguments in this paragraph

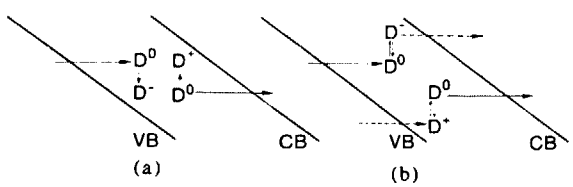

FIG. 1. Field-assisted tunneling paths for (a) negatively correlated and (b) positively correlated dangling bonds.

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apply also to the case of charge exchange between the intimate dangling bonds resulting from the breaking of weak Si–Si bonds.[10]

We now report our result of infrared (IR) illumination on light-soaked *p-i-n* cells. The measurements were done on standard *p-i-n* solar cells grown on textured thermal conducting oxide. The samples were light soaked using either the ELH lamp or the output of an Ar laser. The samples showed considerable light-induced effect which caused a drop in V_{oc}, I_{sc}, and the fill factor. We then irradiated the sample with IR radiation from an ELH lamp focused through a crystalline silicon filter which would transmit only photons with energies less than 1.1 eV. The IR intensity on the sample was 90 mW/cm^2 as measured by a thermopile. Two high-velocity blowers cooled the sample mounted on a brass plate. A thermocouple mounted close to the sample showed a temperature rise of no more than 5 °C. IR illumination alone did not lead to any recovery of the solar cell. However, after applying a high reverse bias to generate a field on the order of 10^4–10^5 V/cm in the *i* layer during the IR illumination many of the samples showed partial recovery in the values of V_{oc}, I_{sc}, and fill factor. The samples were illuminated for a period of 5–10 min. After the initial recovery they did not show any further change even when the IR and reverse bias were kept on for 30 min. Figure 2 shows the $I(V)$ characteristic under AM1 illumination in the as-grown state, after light degradation and IR and reverse bias treatment. Table I gives the J_{sc}, V_{oc}, fill factor, and efficiency values of some of the cells at different stages of measurement. We do not think that the effect we are reporting is due to a change in temperature induced by the IR as we do not see this recovery in all the samples even though we use the same IR intensity. Also, IR irradiation without reverse bias does not have any effect on the cell characteristics. As we reported above, the field without IR also does not cause any recovery. Although we did not see this partial recovery in all the samples we measured, it should be mentioned that many of the cells had low breakdown voltages and may not have sustained a sufficiently high field. However, in some cases even when we were able to apply a reverse bias of 9 V no recovery was observed.

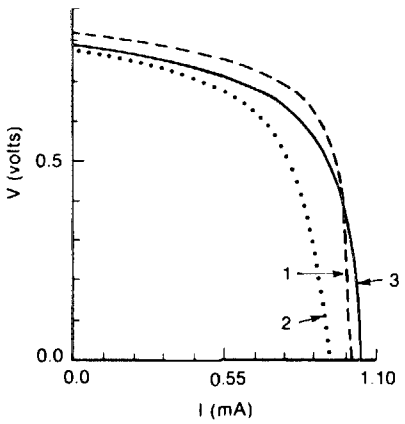

FIG. 2. $I(V)$ characteristic under AM1 illumination for a *p-i-n* diode in (1) As grown, (2) light soaked @ 2.5 suns for 1 h, and (3) after IR and reverse bias treatment.

TABLE I. J_{sc}, V_{oc}, fill factor (FF), and efficiency (η) of some *p-i-n* diodes after different treatments.

Sample	State	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
I	As grown	12.71	0.835	0.64	6.8
Glow discharge	2.5 suns for 1h	11.68	0.784	0.57	5.2
	IR at -6 V for 10 min	13.16	0.805	0.59	6.2
II	As grown	8.12	0.873	0.71	5.02
Glow discharge	Ar laser at $\simeq$ 700 mW/cm^2 for 5 min	7.53	0.84	0.56	3.53
	IR at -9V for 5 min	8.71	0.85	0.58	4.3
III	Annealed	11.5	0.86	0.67	6.6
Photo-CVD	4 suns for 2.5 h	9.47	0.78	0.44	3.3
	IR at -2 V for 10 min	12.5	0.83	0.54	5.6

The tentative model by which we propose to explain the IR + reverse bias recovery is that the IR excites an electron from the valence band to the D^0 center converting it into a D^- center. The resulting hole in the valence band is swept out by the high electric field. Because of the paucity of free holes in intrinsic *a*-Si:H, the D^- center will not capture a hole and convert it back to D^0 on removing both IR and field. It is also possible that the IR excites an electron from a D^0 center to the conduction band converting it into a D^+ center. But since a D^+ center has a high capture cross section for electrons it can easily capture an electron when the field and IR are removed and become a D^0 center again. Thus, hole emission rather than electron emission appears to be responsible for the recovery. This is also consistent with the fact that the presence of excess holes in the material is more detrimental than that of excess electrons.[6,9]

Fathallah *et al.*[11] have reported the creation of light-induced defects even with photons of energy down to 0.7 eV. We have applied IR and reverse bias to samples in the annealed state and have not seen any degradation. The degradation may be inhibited by the presence of the electric field which prevents electrons and holes from recombining. Improvement in solar cell characteristics has been reported by Delahoy and Tonon[12] after light soaking at $\geqslant$20 suns in the presence of a reverse bias. The recovery of the light-induced effect by IR illumination has been reported by Tomozane *et al.*[13] as an improvement in the photoluminescence peak intensity at 1.15 eV when they illuminated the sample with IR radiation after light degradation. The measurements were done at 77 K and the sample was mounted on a temperature controlled table. No field was present during the illumination. They explain their results in terms of absence of hydrogen motion at 77 K.

It is not clear why the effect is not seen in all the samples. Although the effect was not correlated with deposition conditions, it has been seen in both glow discharge and photochemical vapor deposition samples.

In conclusion, we do not see any field-assisted recovery

of the light-induced effect, which rules out charge trapping in shallow traps or in dangling bonds with a negative correlation energy as the cause of light-induced metastability in *a*-Si:H. We see partial recovery from metastability in *p-i-n* cells by IR illumination in the presence of a high field which can be explained in terms of excitation of charge carriers from neutral dangling bonds and their subsequent extraction from the material by the high field leaving only charged dangling bonds in the material.

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