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Thermal-equilibrium processes in undoped amorphous-silicon alloys

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We have studied the effect of the rate of cooling from an elevated temperature on the defect distribution in undoped amorphous-silicon alloys. Three different techniques have been used: namely, photothermal deflection spectroscopy, solar-cell performance, and space-charge-limited conduction. We find that the rate of cooling has no effect on the solar-cell performance or the sub-band-gap absorption as measured by photothermal deflection spectroscopy. The density of states at the Fermi level as measured by space-charge-limited conduction shows a small increase (~20%) if the sample is quenched from a temperature of ~220 °C.

The hydrogenated amorphous-silicon alloy (*a*-Si:H) is believed to be structurally far from equilibrium since it cannot be prepared by cooling from the melt. Early evidence for an equilibrium state of these materials came from the experiments of Ast and Brodsky[1] who showed that fast cooling from temperatures above 200 °C increases the dark room-temperature conductivity by a factor of 2 in both undoped and P-doped material. The results were obtained using both planar and sandwich structures. Recently, Street, Kakalios, and Hayes[2] have shown that a substantial part of the atomic structure of doped materials is in thermal equilibrium above ~130 °C in *n*-type, and ~80 °C in *p*-type *a*-Si:H. The existence of thermal equilibrium is readily observable through changes in the material's electronic properties. In particular, the density of band-tail electrons is found to be higher if the material is rapidly quenched from above the equilibrium temperature. The results were interpreted by assuming an increase at high temperature in donor density and/or a decrease in the number of dangling bonds which are "frozen in" as a result of quenching. Later experiments[3] indicated a decrease in dangling-bond density of about 20%–30%.

Experimental evidence for a thermal-equilibrium defect density at elevated temperatures in undoped samples was recently presented by Smith *et al.*[4] In contrast with the experimental results on doped samples, they found an increase in dangling-bond density if the material is quenched from a temperature above ~200 °C. Working on the basis of recombination-induced creation of dangling-bond centers,[5] they argued that there is a dark generation of dangling-bond centers at higher temperatures and most of these defects would be frozen during quenching. The number of defects remaining, of course, will also depend on how fast these defects are annealed out.

We have studied the defect distribution in undoped *a*-Si:H in the slow cooled and quenched state using three different techniques. Information about the density of states above the Fermi level was obtained from space-charge-limited conduction studies in *n*-*i*-*n* diodes. Photothermal deflection spectroscopy measurement and study of *p*-*i*-*n* solar-cell performance were used to obtain information about the deep states. The results are reported in this paper.

a-Si:H films were grown by radio-frequency glow discharge of silane-hydrogen gas mixtures at a substrate temperature of 260 °C. Details of deposition conditions for the samples for space-charge-limited conduction,[6] photothermal deflection,[7] and the solar cells[8] are given elsewhere. Annealing of the samples was carried out in a vacuum and cooling at different rates was done *in situ*.

The sub-band-gap absorption results for a 2-μm-thick intrinsic film after cooling at two different rates are shown in Fig. 1. No change in absorption is found up to annealing temperature of 240 °C. When the films are annealed to 260 °C or above the sub-band-gap absorption increases. Infrared results on annealing of samples deposited on crystalline silicon substrates in the same run show that

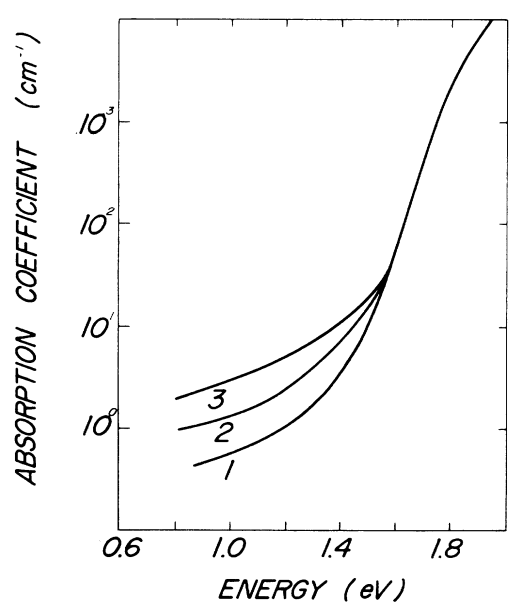

FIG. 1. Sub-band-gap absorption as measured by photothermal deflection spectroscopy of intrinsic *a*-Si alloy after (1) slow (1 °C/min) and fast (10 °C/sec) cooling from 220 °C, (2) subsequent fast cooling from 260 °C, and (3) subsequent slow cooling from 260 °C.

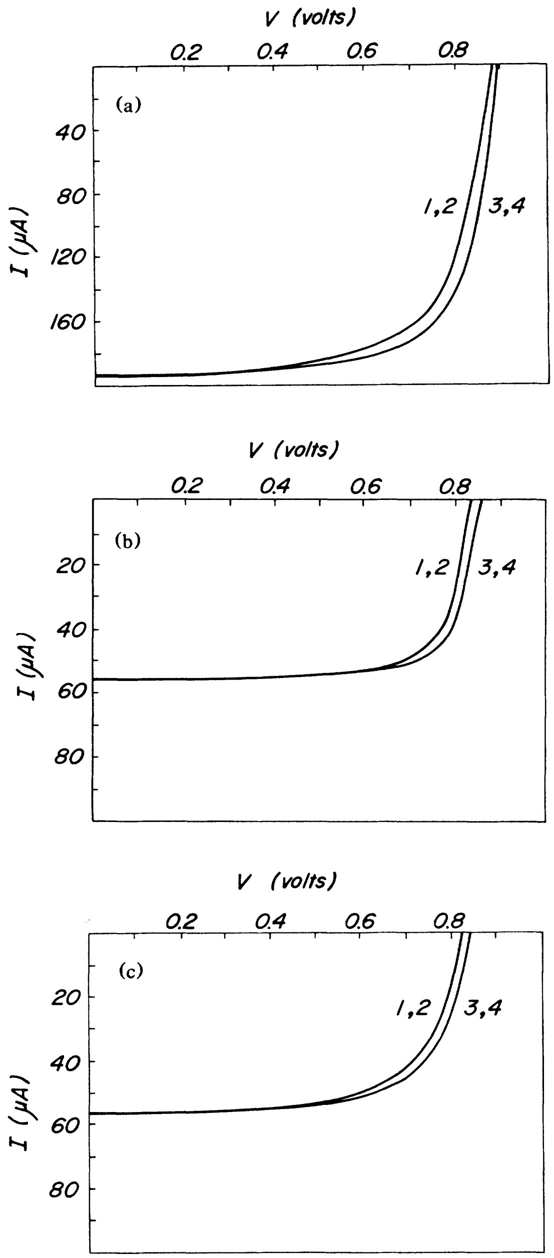

FIG. 2. Lighted current-voltage characteristics of a solar cell under (a) AM1, (b) blue, and (c) red illumination. 1 and 2 refer to the characteristics after slow (1 °C/min) and fast (10 °C/sec) cooling from 220 °C under zero bias. 3 and 4 show corresponding curves when a reverse bias of 5 V was applied to the cell during the annealing and cooling cycles.

there is loss of hydrogen at these temperatures. These effects are irreversible.

In Fig. 2, we show the current-voltage characteristics for AM1, red, and blue illumination for different cooling rates. We find no difference in the characteristics between slow cooling and fast quenching. In agreement with earlier published results,[9] the cell quality improves if a reverse bias is applied to the sample during annealing. In Table I, the values of the fill factor of the cell under different illumination conditions and after different cycles of cooling are shown. We clearly see that only in the case of slow cooling under reverse bias is there a significant improvement in the fill factor.

TABLE I. Fill factor of solar cell under different conditions of cooling rate from 220 °C.

	Zero bias Fast cool	Zero bias Slow cool	Reverse bias Slow cool	Reverse bias Fast cool
AM1	0.67	0.67	0.72	0.69
RED	0.64	0.65	0.70	0.67
BLUE	0.73	0.72	0.74	0.74

In Fig. 3, the distribution of the density of states calculated from the space-charge-limited conduction through a *n-i-n* device with a 2-μm-thick intrinsic layer is shown. We find that the density of states in the region from the Fermi level to 0.1 eV above the Fermi level increases by about 20% when the sample is cooled fast from 200 °C. The change is reversible; i.e., slow cooling restores the original values.

Thus, we find that rapid cooling from temperatures of around 220 °C causes very little change in the gap state density of *a*-Si:H alloys. The change detected by space-charge-limited conduction is only about 20%; such a small change will not affect the sub-band-gap absorption or the solar-cell performance within the resolution of the experiments. Our results are in disagreement with those of Smith *et al.*[4] who found a change of about a factor of 3 in the integrated sub-band-gap absorption for two different rates of cooling. The same authors, however, found only a 27% change in spin density as measured by electron-spin

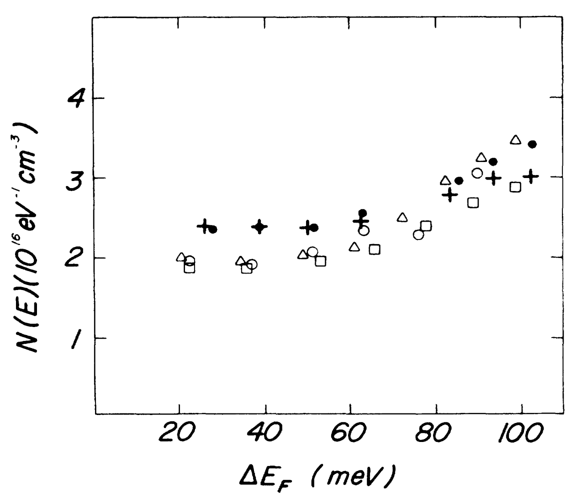

FIG. 3. Gap state density as measured by space-charge-limited conduction as a function of energy for slow (1 °C/min) and fast (10 °C/sec) cooling rate from 220 °C. The symbols denote □, as deposited; ●, subsequent fast cool; ○, subsequent slow cool; + subsequent fast cool; and △, subsequent slow cool.

resonance (ESR). They argued that the ESR measurements may be affected by surface dangling bonds and that the sub-band-gap absorption as measured by the constant photocurrent method reflects the bulk defect density. Our measurements of space-charge-limited conduction and solar-cell performance also are not affected by surface states and should reflect changes in bulk density. Moreover, although sub-band absorptions could be affected by surface states, it has been shown recently[10] that, for high-quality films with thicknesses of $1 \mu m$ and above, it is possible to obtain bulk defect density from photothermal deflection measurements. It is interesting to point out that the sub-band-gap absorption characteristics of our sample, as measured by photothermal deflection spectroscopy, and those measured by Smith *et al.*[4] using the constant photocurrent method are very similar. Therefore, the difference in the equilibration behavior of the sample using the two experiments is not easily understood.

As we have mentioned earlier, when a sample is quenched from a temperature higher than the equilibration temperature, two opposing effects take place. The recombination-induced defect generation model as proposed by Smith *et al.*[4] will give an increase in the dangling-bond density. On the basis of the structural model of Street, Kakalios, Tsai, and Hayes,[3] as originally developed for doped material, we expect a reduction in dangling-bond density. The situation is further complicated by the fact that the magnitude of the increase in dangling-bond density predicted from the first model will depend on (a) the recombination-induced creation of the dangling bonds at the elevated temperature and (b) annealing of the dangling bonds at that temperature. If the equilibrium density of dangling bonds at the elevated temperature is low,[11] one would not expect to see any increase in dangling-bond density after quenching.

In conclusion, we have studied the effect of rate of cooling from a high temperature on the defect distribution in *a*-Si alloys. Three different techniques have been used: namely, photothermal deflection spectroscopy, solar-cell performance, and space-charge-limited conduction. We find that the rate of cooling has no effect on the solar-cell performance or the sub-band-gap absorption as measured by photothermal deflection spectroscopy. The density of states at the Fermi level as measured by space-charge-limited conduction shows a small increase if the sample is quenched from the high temperature

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