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Thermal equilibrium changes in diode structures of doped amorphous silicon

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Thermal equilibration processes in diode structures of doped hydrogenated amorphous silicon have been studied. Fast cooling from above the thermal equilibrium temperature (T_E) results in an increase in dark reverse current as well as in forward current. The reverse leakage current and the diode quality factor increase with quenching temperature at above T_E . Therefore, it is concluded that the densities of metastable dangling bonds and active dopants increase upon fast cooling from above T_E . We propose a new model to explain the experimental results.

When doped hydrogenated amorphous silicon (a -Si:H) films are rapidly quenched from above the thermal equilibrium temperature, a nonequilibrium structure is frozen in, which slowly relaxes to the annealed (very slow-cooled) state. Thermal equilibrium temperature (T_E) is the temperature at which the defect structure comes into equilibrium within a few minutes and is $\sim 130^\circ\text{C}$ for n -type and $\sim 80^\circ\text{C}$ for p -type a -Si:H.¹

When doped a -Si:H films are rapidly quenched from above T_E , the room-temperature dark conductivity is higher than the annealed value and slowly relaxes to the annealed one.² This higher conductivity in doped a -Si:H can arise either from the increase of active donors (or acceptors for p -type) or from the decrease of dangling bonds or a combination of the two effects.

Hack *et al.*³ investigated equilibrium changes in n -type a -Si:H by means of capacitance-voltage measurements at varying frequencies and concluded that the density of dangling bonds appears to remain approximately constant, while the dopant density depends on the sample temperature. Stutzmann⁴ has investigated the response of doped a -Si:H to thermal quenching with electron-spin-resonance techniques. He explained the metastable increase of shallow-state electrons by rapid quenching as the reversible decrease of the doping-induced, compensating dangling bond density. Street *et al.*¹ also insisted that the dangling bond density might be reduced by fast cooling through measurements of photoluminescence. On the other hand, it is believed that the dangling bond density increases by fast cooling from above T_E for undoped a -Si:H,⁵ even though T_E is much higher than that for doped a -Si:H.⁶ It is counterintuitive, though not necessarily incorrect, that undoped and doped a -Si:H films behave oppositely when quenched from above T_E .

In this letter we investigated the changes in the current-voltage characteristics for transparent conducting oxide (TCO)/ a -Si:H/ p - p^+ /Al and TCO/ a -Si:H n - n^+ /Al structures by fast cooling from above T_E . Our results indicate that the densities of active dopants and dangling bonds increase upon rapid cooling for a -Si:H.

Samples of a -Si:H are prepared by plasma decomposition of silane mixtures in a glow-discharge deposition system. n -type and p -type a -Si:H films were prepared by the deposition of silane mixtures with PH_3 and B_2H_6 , respectively.

To make diode structures we used SnO_2 -coated glass plates as the substrates. The n^+ - and p^+ - a -Si:H layers were prepared by the deposition of 1.0% PH_3 and B_2H_6 mixed silane, respectively, and these layers were used as ohmic contacts. The thickness of the active layer (p - or n -type a -Si:H) is around $0.6\ \mu\text{m}$. Before measurements, the sample was annealed in vacuum of 10^{-5} Torr. Rapid cooling was performed by flowing water into the substrate holder achieving a rate of $\sim 2^\circ\text{C/s}$. The current-voltage characteristics were measured by a programmable electrometer (Keithley model 617) interfaced to an Apple II microcomputer.

Figure 1 shows the effect of quenching temperature (T_E) on the temperature dependence of the dark conductivity of a film, not a diode, for 1000 ppm boron-doped a -Si:H. The sample was deposited at 170°C and annealed at 250°C for 1 h. The sample was quenched with a cooling rate of $\sim 2^\circ\text{C/s}$, and then the conductivity was measured with increasing temperature. As shown in the figure, the difference between the conductivity of quenched sample and that of a

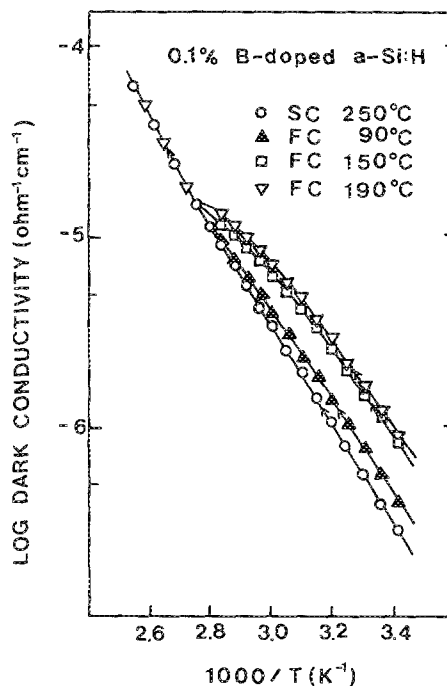


FIG. 1. Effect of quenching temperature on the temperature dependence of dark conductivity for 1000 ppm boron-doped a -Si:H.

slow-cooled one increases with the quenching temperature. T_E is $\sim 90^\circ\text{C}$, which is independent of quenching temperature and is similar to the value published previously.¹

Figure 2 shows the quenching effect for a TCO/*a*-Si:H *p-p*⁺/Al structure using a *p*-layer doping concentration of 100 ppm. The characteristics show a Schottky-like diode behavior because the TCO acts as a metal. The sample was deposited at 150 °C and annealed at 190 °C for 1 h. The diode quality factor is 1.09 for the slow-cooled sample from 190 °C, but it increases slightly with quenching temperature. It is 1.15 after quenching from 90 °C and 1.17 for the device quenched from 110 or 130 °C. The reverse-current density increases with the quenching temperature.

Figure 3 shows the quenching effect on the current-voltage characteristics for a TCO/*a*-Si:H *n-n*⁺ device using an *n*-layer of 10 ppm. The sample was deposited at 150 °C and slow cooled after annealing at 190 °C for 1 h. The diode quality factor of the annealed sample is 1.22, and it increases with quenching temperature. It is 1.37 after quenching from 130 °C, and 1.39 after 150 °C quenching, and 1.40 after 180 °C quenching. The forward as well as the reverse current increases with quenching temperature.

Figure 4 shows the light soaking effect on the current-voltage characteristics for a TCO/*a*-Si:H *n-n*⁺ structure for 30 s under 100 mW/cm². The quenching effect of this sample is shown in Fig. 3. The forward-current density decreases, but the reverse-current density and diode quality factor increase after light soaking.

For undoped *a*-Si:H, the subband-gap optical absorption coefficients determined by photothermal deflection spectroscopy (PDS) increase after rapid quenching and this

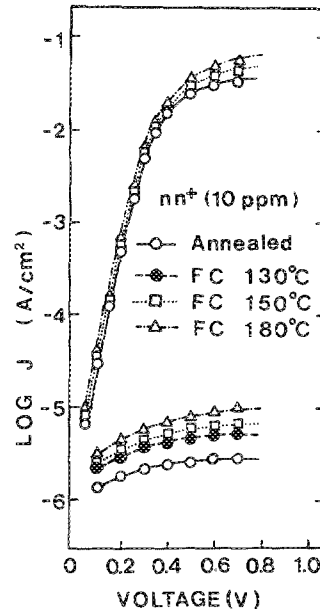


FIG. 3. Effect of quenching temperature on the current-voltage characteristics for a TCO/*a*-Si:H *n-n*⁺ diode using an *n* layer of 10 ppm.

is due to the creation of dangling bonds by electron-hole recombination.⁵ As with the Staebler-Wronski (SW) effect in undoped *a*-Si:H films, the additional dangling bonds lower the dark conductivity because of the shift of the Fermi level toward the midgap.

It is believed that the conductivity and band tail electron density for a doped *a*-Si:H sample is higher for the fast-cooled state than the slow-cooled one. However, it is controversial whether the defect density increases or decreases by rapid quenching. Our results clearly show that the reverse-current density and diode quality factor increase by rapid quenching. The quenching effects on the conductivity of *p*⁺ and *n*⁺ layers were observed to be very small, so that the changes in the characteristics of our devices are probably due to the *p*- or *n*-type *a*-Si:H. We also observed an increase

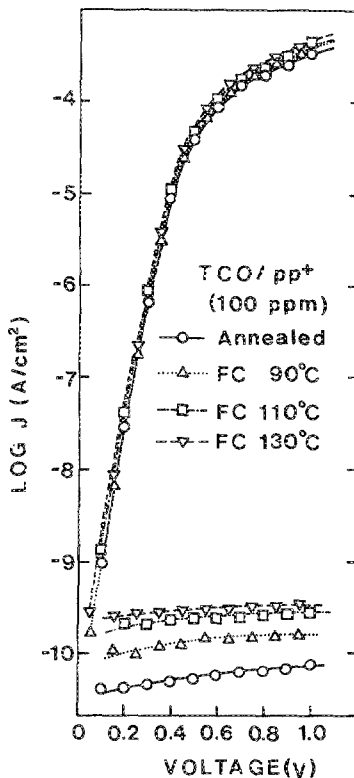


FIG. 2. Effect of quenching temperature on the current-voltage characteristics for a TCO/*a*-Si:H *p-p*⁺ diode using a *p* layer of 100 ppm.

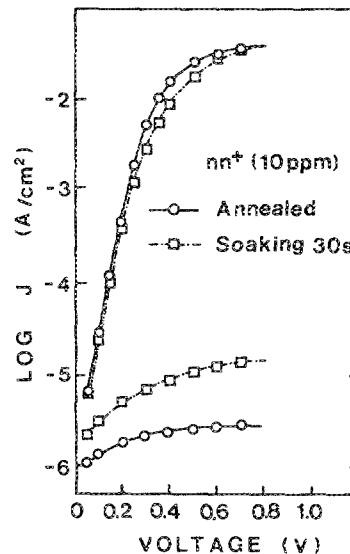


FIG. 4. Effects of light soaking on the current-voltage characteristics for a TCO/*a*-Si:H *n-n*⁺ device using an *n* layer of 10 ppm.

in forward-current density for the investigated devices, and this is due to the increase of conductivity for *n*-type (or *p*-type) *a*-Si:H by rapid quenching.

The increase in reverse current and diode quality factor by rapid quenching is probably due to the increase in dangling bond density. The increase in reverse current may be related to the increase in the effective gap state density whether the transport is through recombination currents in the junction region or through tunneling through the localized states. The change in the diode quality factor by rapid quenching may also be attributed to the increase in the bulk recombination current. We believe the added gap states are dangling bonds, since our observation on lightly doped films can be compared with the reverse-current density and diode quality factor increases observed after light soaking in *a*-Si:H *p-i-n* and Schottky devices.^{7,8} The increases in the lightly doped film are known to be due to the increase in metastable dangling bond density in the intrinsic layer.

We now consider how the metastable active dopants and dangling bonds increase upon rapid cooling. We commonly observe the two-level system for a metastable dangling bond, which is sometimes used to explain the SW effect. In tetrahedral amorphous structures, the energy distribution functions for dangling bonds and dopants are broad. Therefore, multi-metastable structure for the dangling bonds and dopants may exist in the amorphous material. For example, we can assume the two-level system for the metastable dopants as shown in Fig. 5. The upper state in Fig. 5 includes the four-fold coordinated dopant.

One specific reaction for *p*-type *a*-Si:H to illustrate Fig. 5 can be given by



which is proposed by Street to explain the doping mechanism in *a*-Si:H.⁹ The right-hand side in Eq. (1) is the upper state. The reaction to the right shifts the Fermi level toward the valence-band edge, which is the case when we consider the movement of the Fermi level toward the band edge in more highly doped *a*-Si:H.

At high temperatures above T_E , the densities of metastable active dopants and of the compensating, metastable dangling bonds are much higher than those at room temperature. Rapid quenching from above T_E results in higher concentrations of the metastable dangling bonds and of the metastable active dopants compared with the slow-cooled ones. This model also explains that the reverse-current density and diode quality factor increase with quenching temperatures above T_E .

Other specific reactions to illustrate Fig. 5 can also be possible to explain the increases of the metastable active dopants and the dangling bonds. The activation energy of the relaxation time for the metastable active dopants was observed to be ~ 0.2 eV higher than that for the annealing of

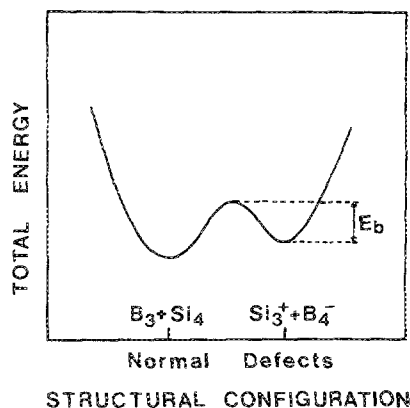


FIG. 5. Schematic diagram of the two-level system controlling the quenching effect. Fast cooling from above T_E results in the increase in both metastable dangling bonds and active dopants.

the created dangling bonds for 100 ppm boron-doped *a*-Si:H.¹⁰ Therefore, two independent reactions, increasing the metastable active dopants and dangling bonds, should be occurring simultaneously during illumination in doped *a*-Si:H. Similarly, it is possible that the metastable active dopant and the dangling bonds are created through independent reactions upon rapid cooling. In this case, the upper state in Fig. 5 may not include the dangling bond and the barrier energy is higher for the metastable active dopants than that for the dangling bonds. Further work is needed to clarify the microscopic reaction during rapid quenching and light soaking in doped *a*-Si:H.

In summary, the reverse current, diode quality factor, and forward current for TCO/*a*-Si:H *n-n⁺* and TCO/*a*-Si:H *p-p⁺* structures increase by rapid quenching from above T_E . The diode quality factor and reverse-current density increase with quenching temperature at above T_E . It is concluded, therefore, that the metastable dangling bonds and active dopants increase upon fast cooling from above T_E .

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