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Thermal equilibrium behavior in inhomogeneous, undoped amorphous silicon

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We report a new thermal equilibrium behavior in inhomogeneous, undoped amorphous silicon. The room-temperature conductivity increases by two orders of magnitude compared with the annealed value just after fast cooling from above 180 °C. The decay of the excess conductivity follows $(\text{time})^{-1}$ behavior, which is independent of the temperature. We suggest a possible explanation based on the material inhomogeneity.

Recently, there has been much interest in the thermal equilibration behavior in doped and undoped hydrogenated amorphous silicon (*a*-Si:H) films. In doped *a*-Si:H films, the conductivity continues to decrease with time even at room temperature when it is measured after rapid cooling from above the thermal equilibrium temperature (Te).[1] The Te for *n*-type *a*-Si:H is 120 °C and 90 °C for *p*-type *a*-Si:H in glow discharge samples.[1]

The thermal equilibrium behavior for undoped *a*-Si:H films is quite different. The room-temperature conductivity decreases by a factor of about 2 (Ref. 2) or does not change just after rapid cooling from above the Te. The Te for undoped *a*-Si:H film is around 190 °C.[3] Meaudre *et al.*,[4] however, have measured a factor of two or more increase of conductivity upon rapid cooling for undoped, sputtered *a*-Si:H films and they claimed that the increase of the conductivity is not due to the incorporation of dopants in the film. This increasing behavior is observed for doped *a*-Si:H films deposited by glow discharge decomposition.[1]

The influence of columnar microstructure on the thermal equilibrium effects in doped *a*-Si:H has been previously reported.[5–7] The columnar materials are grown with SiH_4 diluted in argon, or at a high rf power level. Even though the columnar structure greatly enhances the diffusion of hydrogen,[6] the thermal equilibrium processes are qualitatively similar to those in samples prepared under optimal conditions.[5] Therefore, it is concluded that the thermal equilibrium processes in doped, glow discharged samples proceed in a similar manner regardless of the film's microstructure.

In the present work, we report a new thermal equilibration behavior for undoped *a*-Si:H films deposited by a new deposition technique. The room-temperature conductivity increases by two orders of magnitude compared with the annealed value just after rapid cooling from above 180 °C. The time dependence of conductivity shows t^{-1} decay. We suggest a possible interpretation based on the material inhomogeneity.

The undoped *a*-Si:H films studied in the present work were fabricated by a new deposition technique, called filament-assisted chemical vapor deposition (FACVD), in which the filament chamber generating hydrogen radicals is connected upstream of a remote deposition chamber. The hydrogen radicals are formed by passing hydrogen gas through the hot tungsten filament heated to around 2300 °C. The silane is introduced just above the substrate holder, and is decomposed by the long-lived hydrogen radicals. The total gas pressure during the deposition is 20 Torr and the substrate temperature is around 300 °C (Ref. 8).

To measure the conductivity the sample was heated in vacuum of 10^{-6} Torr for 2 h at 200 °C to remove the surface adsorbates and the effect of prior light exposure. The conductivity was measured by an electrometer (Keithley model 617) interfaced with an Apple II microcomputer.

Figure 1 shows the representative scanning electron micrograph for an undoped *a*-Si:H film deposited at a substrate to filament distance of 2.5 cm. As can be seen from this picture, the microstructural pattern is apparent, while the microstructural pattern decreases as the filament to substrate distance is increased. We could prepare a homogeneous *a*-Si:H film at the filament to substrate distance of 10 cm, whose microstructure is similar to that of the glow discharge produced sample.

Figure 2 shows the effect of cooling rate on the temperature dependence of conductivity. All measurements were done in vacuum just after annealing at 180 °C for 2 h. The sample was heated to 180 °C and annealed for 2 h and then

FIG. 1. Scanning electron micrograph of inhomogeneous, undoped *a*-Si:H film studied in the present work.

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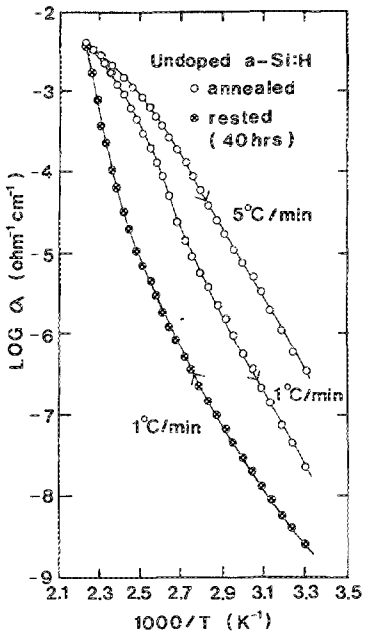

FIG. 2. Temperature dependence of conductivity measured during cooling the undoped a-Si:H film after annealing for 2 h at 180 °C.

the conductivity was measured with decreasing temperature. During the measurements, the sample was cooled down to the measurement temperature with the indicated cooling rate along the solid line. Even at room temperature the conductivity continues to decrease and we could not observe a saturation behavior. The room-temperature conductivity increases with cooling rate and the variation of the change in room-temperature conductivity is very large. Above about 170 °C the low-temperature conductivity curves merge, becoming independent of thermal history. This is a signature of the thermal equilibrium.

Figure 3 shows the time dependence of conductivity at various temperatures. The sample was cooled to the measurement temperature with a cooling rate of 5 °C/min just after annealing the sample at 180 °C for 2 h. We can see a

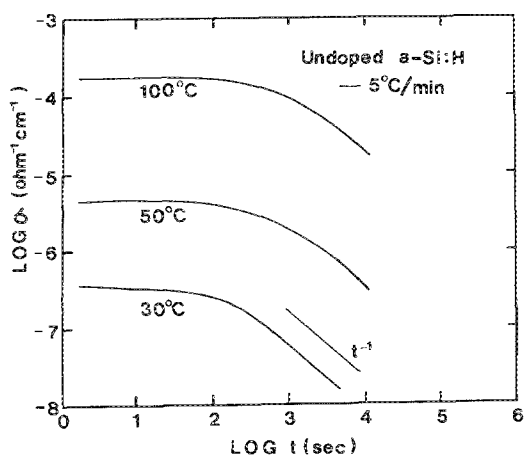

FIG. 3. Decay of the conductivity at various temperatures for undoped a-Si:H film. The sample was cooled to the measurement temperature after annealing for 2 h at 180 °C.

kink in each curve; the conductivity is nearly constant at earlier time than about 100 s and then decay with t^{-1}. This time dependence is nearly independent of the measurement temperature and extends to $\sim 10^5$ s as shown in Fig. 3.

We clearly pointed out that the room-temperature conductivity increases with increasing cooling rate from 180 °C. This behavior is similar to that of the doped a-Si:H film, so that it can be claimed that our samples may be contaminated with n-type or p-type dopants. However, our samples could not be contaminated because of the following three facts: (1) our deposition chamber has been used so far for the deposition of undoped a-Si:H films from the first time; (2) the room-temperature conductivity is extremely low (10^{-9} Ω^{-1} cm^{-1}) compared with that for doped a-Si:H; (3) our undoped a-Si:H film deposited by glow discharge decomposition in the same reaction chamber using the same silane gas shows little thermal equilibrium change.

We should note the close relationship between the material inhomogeneity and the thermal equilibrium behavior in undoped a-Si:H. The anomalous data shown in this letter were obtained from very inhomogeneous a-Si:H films. The homogeneous, undoped a-Si:H film deposited by the FACVD method at the large (10 cm) substrate to filament distance shows little thermal equilibrium behavior.

The reason why the heterogeneous a-Si:H sample shows a large amount of metastability is not clear now, but it is the case that the metastability arises from the inhomogeneous properties of a-Si:H.

The inhomogeneous a-Si:H film studied in the present work shows only Si-H_2 vibrational modes, detected by a Fourier transform infrared spectrophotometer. It should be noted that device-quality, homogeneous a-Si:H films show only Si-H modes.

Next, we want to address the possible origin of the thermal equilibrium behavior in our heterogeneous a-Si:H sample. The hydrogen distribution in inhomogeneous a-Si:H is not homogeneous, so that the materials consist of a high-band-gap, hydrogen-rich region (tissue) and a low-band-gap, less-hydrogen region (island). The interface between the two regions may consist of a high-band-gap, less-density region. Figure 4 shows a schematic band structure denoting the two regions.[9] The transfer of electrons from one (B) to the other (A) region requires activation over the potential barrier (E_b). At high temperatures above Te, the Fermi level is constant through regions A and B. But rapid cooling can result in excess charge in region B if some charges are transferred to the B region at high temperatures because of the difference in the work function between the two regions.

The transfer of carriers from one region (B) to the other (A) is possible during the measurements. The region with small E_b and thus short relaxation time reaches equilibrium faster than the measurement time t so that the change cannot be observed. Therefore, the observable transfer at time t arises from the barrier height given by $E_b = kT\ln(\nu o t)$, where νo is the attempt to escape frequency, k is the Boltzmann constant, and T is absolute temperature. Similar argument has successfully been applied to dispersive transport.[10] In the latter case the emission rate of the trapped carriers varies exponentially with the difference between the conduc-

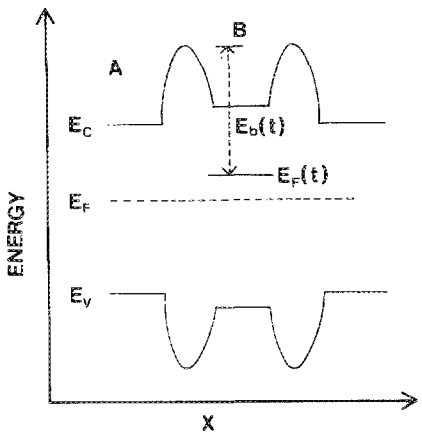

FIG. 4. Schematic two-dimensional band structure of a two-well system caused by material inhomogeneity. E_F, thermal equilibrium Fermi level; $E_F(t)$, Fermi level at time t in region B after rapid cooling from above Te.

tion-band edge and the trap level.

If we assume that the measured conductivity arises from the percolation through the B regions, our results can be explained. In a strongly heterogeneous material, the conduction pass through the tissue can be possible.[11]

The rate equation for the concentration of electrons, n, in conduction band can be given by

$$\frac{dn}{dt} = -n^* vo \exp\left(\frac{-E_b}{kT}\right),$$

giving rise to the solution $n = not^{-1}$, where no is the initial carrier concentration. We can see a t^{-1} dependence of conductivity in Fig. 3. The flat region in Fig. 3 is due to the transfer of carriers in the B region during the cooling of the sample to the measurement temperature.

In some undoped a-Si:H films deposited by glow discharge decomposition, the room-temperature conductivity decreases by a factor of about 2 upon rapid cooling from above 200 °C and the conductivity can be reversed by thermal annealing.[2] The electrical conduction through the region A can give rise to the decrease in conductivity upon rapid cooling. This behavior is related with the material inhomogeneity, and little change in conductivity can be expected for extremely homogeneous a-Si:H. The thermal equilibrium behavior in doped a-Si:H is quite different, so that the interpretation suggested above can be applied only to undoped a-Si:H.

We can consider another explanation for the observed results: the decrease in conductivity can be accompanied by some changes in the density of states. For example, the dangling bonds are created by the motion of hydrogen during the measurement and give rise to the shift of the Fermi level toward the midgap. It is perhaps not obvious that the variation in conductivity represents structural changes. More work is needed to clarify this point.

In summary, we report a new thermal equilibrium behavior in an inhomogeneous, undoped a-Si:H film. The room-temperature conductivity increases by two orders of magnitude just after fast cooling from 180 °C. The decay of the excess conductivity follows t^{-1} behavior. The experimental results are explained on the basis of the material inhomogeneity.

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