

Thermal equilibration in doped amorphous silicon

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The structure of doped amorphous silicon is shown to be in metastable thermal equilibrium above 130°C, having temperature-dependent densities of dangling bonds and donors. The time to reach equilibrium is thermally activated, so that cooling establishes a slowly relaxing nonequilibrium state resembling a glass. The results are interpreted in terms of the recent defect-compensation model of doping.

Hydrogenated amorphous silicon (*a*-Si:H) is presumed to be far from thermodynamic equilibrium because it cannot be cooled from the melt. Its physical properties are then a direct consequence of the deposition process, which is not true of an equilibrium material. Certainly many properties of *a*-Si:H are determined by the deposition, notably the visible microstructure.¹ On the other hand, some observations suggest equilibrium processes. For example, dangling bonds created by prolonged illumination can be removed by annealing.² Smith and Wagner³ calculate that the dangling-bond density in undoped *a*-Si:H is consistent with the thermal equilibrium value expected at the deposition temperature. Also, the increasing dangling-bond density with doping level is modeled by bonding configurations that are in quasithermal equilibrium at the growing surface.^{4,5} There is no inconsistency in attaining a thermal equilibrium within a set of accessible states which does not include the lowest energy state. However, such a metastable equilibrium is usually associated with melt-cooled glasses above the glass transition, and not with *a*-Si:H.

This paper describes the first experimental evidence that doped *a*-Si:H is indeed in metastable thermal equilibrium. The equilibrium controls the density of gap states and thereby the electronic properties. The equilibration time gets longer at decreasing temperature, freezing in a metastable structure.

Measurements are made of the dark dc conductivity, and of the density of shallow occupied states in the band tail (BT), n_{BT} , using the voltage pulse sweepout technique described elsewhere.^{6,7} By using both planar and transverse electrode structures in the dc conductivity measurements, we eliminate the possibility that the results are due to surface effects. Sweepout is from a thin doped layer entirely contained within undoped *a*-Si:H, thus also eliminating surface effects. n_{BT} is the measured charge divided by the known volume of the doped layer. n_{BT} is related to the densities of donors, N_{donor} , and dangling bonds, N_{DB} . In *n*-type samples there is much evidence that electron transfer from donors results in charged dangling bonds.^{4,5} Electrons therefore occupy the band tail and the overlapping donor states according to the relation

$$n_{BT} \approx N_{donor} - N_{DB} \quad (1)$$

The experiments find that n_{BT} and the conductivity are both time and temperature dependent. Figure 1 illustrates the effects of annealing samples at 220°C for 20 min and

then storing them in the dark at room temperature. Over a period of about two months, n_{BT} decreases slowly by a factor of 2 or more. The decay time increases by a factor 10 when the samples are stored at -10°C . The fractional change $\Delta n_{BT}/n_{BT}$ is similar for all doping levels studied and for both phosphorus and arsenic donors. The dc conductivity has a comparable slow decay after a similar annealing treatment as has been observed by Ast and Brodsky.⁸ Figure 2 shows the temperature dependence of the dc conductivity immediately after annealing and after the sample is also stored in the dark at 25°C for over two months. In these measurements the sample is cooled at the indicated rate and the conductivity is then measured as the sample is slowly warmed from below 250 K. The change in activation energy in the low temperature region indicates that the drop in conductivity arises from a lowering of the Fermi energy, consistent with the reduction in n_{BT} . The time dependence of n_{BT} has also been confirmed by ESR.⁹

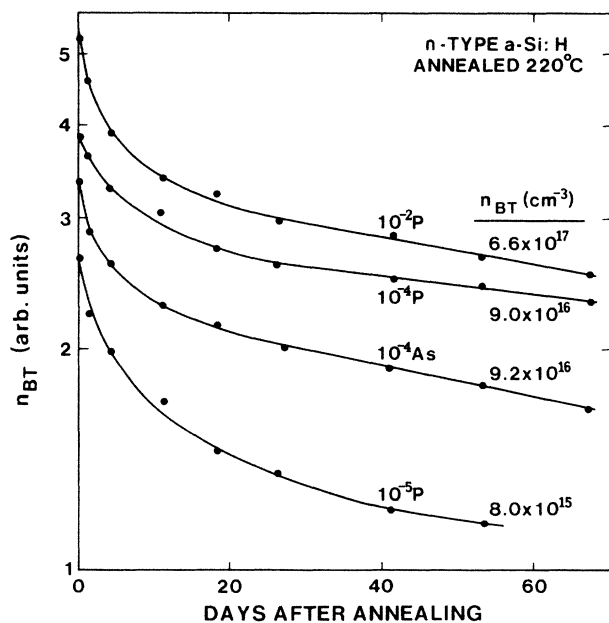


FIG. 1. The time decay of the density of shallow electrons n_{BT} , after annealing at 220°C, for samples doped with P and As. The values of n_{BT} at the end of the decay are shown.

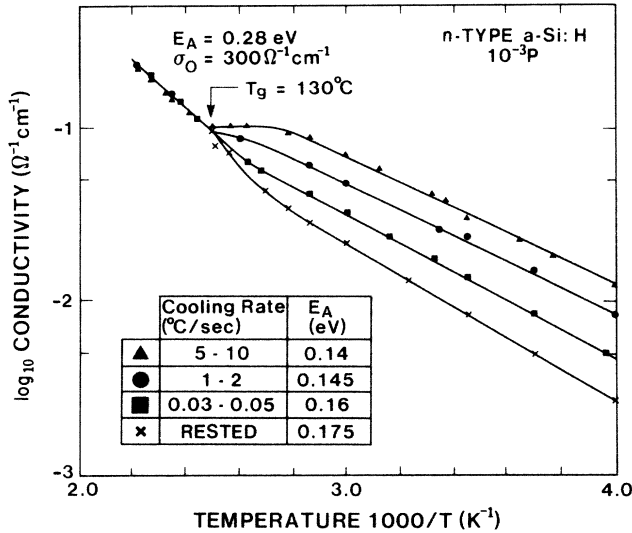


FIG. 2. The temperature dependence of the dc conductivity immediately after annealing for different cooling rates, and after storing at room temperature for 2 months ("RESTED"). E_a is the activation energy. The prefactor σ_0 is $8-10 \Omega^{-1} \text{cm}^{-1}$ for all four sets of data. Note the higher activation energy and prefactor where the data converge.

These changes are reversible by annealing, and the cycle has been repeated several times. However, the annealing behavior is remarkable. Figure 3 shows n_{BT} measured at room temperature immediately after different annealing and cooling conditions. Identical results are found in the dc conductivity. After fast cooling from 250°C ($\sim 5^\circ\text{C}/\text{sec}$), n_{BT} is about three times larger than for similar cooling from 100°C . It is important to note that the results are *not* due to partial annealing that goes to completion at a higher temperature. These experiments are performed by starting at the highest temperature and progressing downward. In fact, the order of the experiments has no influence on n_{BT} when annealing is above 130°C . However, the results do depend on the cooling rate, with slower cooling resulting in a lower n_{BT} (see also Fig. 2). Evidently, n_{BT} reaches a steady-state value within times that are comparable with the cooling times. Indeed, the flattening of the data above 200°C in Fig. 3 is presumably because the limited cooling rate lowers the effective annealing temperature. Below about 130°C , n_{BT} does not decline further because a steady state cannot be reached within the annealing time. Longer annealing results in a lower n_{BT} as shown in Fig. 3. This behavior is consistent with the observations in Fig. 1 that the decay time is very long (weeks) at room temperature. The measured time constant for changes in n_{BT} is thermally activated with an energy of $0.6-0.7 \text{ eV}$. Similar results are obtained for boron-doped *a*-Si:H except that the decay times are shorter ($\sim 1 \text{ h}$ at room temperature).⁹

When annealing occurs above $\sim 130^\circ\text{C}$, n_{BT} quickly reaches a steady state that is independent of the previous treatment. We therefore conclude that thermal equilibrium is established between the densities of dangling bonds and donors that determine n_{BT} . Reversible annealing of

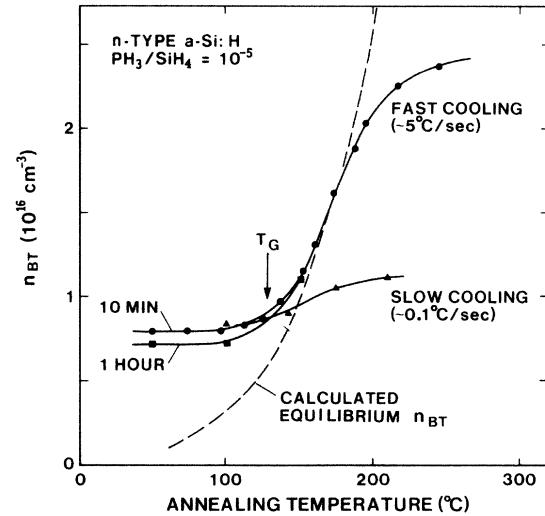


FIG. 3. Values of n_{BT} measured at room temperature after annealing and cooling at different rates. The annealing times are shown. The dashed line is calculated as described in the text.

dangling bonds in *a*-Si:H is, of course, a well known phenomenon.² However, in other cases the samples are first subjected to some external treatment (e.g., illumination, electron bombardment, etc.) that creates extra dangling bonds, so the annealing applies only to these extrinsic defects. In the present experiments the important conclusion is that equilibration must apply to the intrinsic structure formed during the deposition, because there is no such external treatment. Evidently, the thermal equilibrium is such that n_{BT} increases with temperature. Furthermore, the rate at which equilibrium is approached also increases with temperature, requiring weeks at 25°C but only seconds at 200°C , so that a slowly relaxing nonequilibrium structure can be frozen in.

The conclusion that the electronic states are determined by thermal equilibrium structures forces us to take a new look at many properties of *a*-Si:H. For example, it is now evident that the electronic properties are not completely determined by the deposition. In this Rapid Communication we discuss only a few of the consequences. We first focus on the relation between the present results and the defect compensation model of doping, described in detail elsewhere.^{4,5,10,11} According to this model, quasiequilibrium exists during the initial formation of donors (P_4) and dangling bonds (D) at the growing surface. The defect energy is minimized when there are roughly equal densities of charged P_4^+ and D^- states. The Fermi energy E_F will then lie between these states near E_{\min} as shown schematically in Fig. 4. The density of shallow electrons is defined by

$$n_{BT}(T) = \int_{E_{\min}}^{\infty} g(E) \{1 + \exp[(E - E_F)/kT]\}^{-1} dE, \quad (2)$$

where $g(E)$ is the density of states. n_{BT} is also constrained by Eq. (1). During growth n_{BT} is therefore fixed by the condition that E_F is at E_{\min} and T is the deposition temperature (typically $\sim 250^\circ\text{C}$). After the growth is complete two possibilities exist. The first is that structural

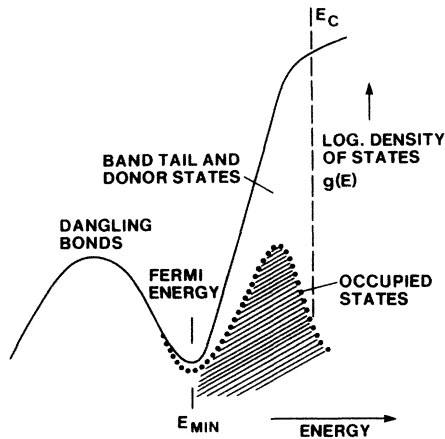


FIG. 4. A schematic diagram of the density of states showing the dangling-bond band, and the band tail that includes the donors. The dotted line indicates the density of occupied states and n_{BT} corresponds to the shaded area.

equilibration continues during cooling. E_F therefore remains at E_{min} and, from Eq. (2), n_{BT} must decrease with T . In order to satisfy Eq. (1), the densities of dangling bonds and/or donors must change. The second possibility is that the structure becomes frozen. In this case, n_{BT} will be constant, and Eq. (2) can only be satisfied if E_F moves closer to the conduction band as T decreases. Clearly this corresponds to a departure from equilibrium.

This description matches our observations. Thermal equilibrium persists down to about 130°C, and the equilibrium structure and n_{BT} are temperature dependent. The model also explains why cooling freezes in a nonequilibrium structure, resulting in the observation of slow relaxation. The observed behavior is therefore a prediction of a doping model which calls for equilibrium in the bulk instead of only at the growing surface. Numerical integrations of Eq. (2) to obtain n_{BT} yield results that are in good agreement with the data, as shown by the dashed line in Fig. 3.⁹ The density of states used in the calculation is taken from Ref. 5, with N_{donor} and N_{DB} scaled to the experimentally determined value^{5,10} for the given doping level. E_F is set 0.41 eV below the mobility edge near the minimum of $g(E)$ to give the equilibrium n_{BT} . For different temperatures N_{DB} is allowed to vary to maintain E_F constant. Comparison of the data and the calculations in Fig. 3 confirms the freezing of the structure at low temperature and the cooling rate effect at high temperature.

These changes in n_{BT} and E_F must be reflected in the electrical transport. Specifically, a change in the conductivity is expected when the structure equilibrates near 130°C. An increase in the activation energy is indeed observed in n -type samples at about this temperature, and its origin has been the source of much speculation.¹² Our results in Fig. 2 clearly show that the change of slope is a direct consequence of the equilibration, and so provides an entirely new explanation of the effect. At low temperatures the structure is frozen, and the conductivity is sensitive to the cooling rate and storage time. The Fermi energy is temperature dependent, maintaining a constant n_{BT} ,

and resulting in a low activation energy and prefactor. At high temperature, thermal equilibration takes place, giving results that are independent of the sample history with a Fermi energy pinned near the minimum of $g(E)$. Calculation again gives good agreement with the experimental results for the two temperature regimes.⁹ At the transition near 130°C the data are time dependent because of the equilibration process. The exact shape of the region below the kink depends on the warming rate. Our observations also provide a natural explanation of the thermally activated increase of doping observed in capacitance measurements.¹³

We next discuss the microscopic structural changes that can lead to thermal equilibration. According to Eq. (1) the changes in n_{BT} can result either from the dangling bonds or the donors,



Our experiments have not yet determined which of these possibilities occurs. However, a change in the dangling-bond density seems a likely mechanism, since those created by extrinsic processes (for example, prolonged illumination) are known to be annealed at 100–200°C.² The annealing is thought to be associated with the motion of hydrogen,² and this mechanism seems likely to apply in the present case. The motion of hydrogen from site to site, and its insertion into weak Si—Si bonds or at other possible configurations,¹⁴ can potentially change the coordination of either Si or the donors, thus allowing these electronic states to attain equilibrium densities. The freezing of the structure at low temperature occurs when the motion of the hydrogen is so slow that the equilibrium cannot be reached within the experimental times.

Finally, we remark that the measured properties of n_{BT} have interesting similarities to those of a glass. At high temperature n_{BT} reaches a metastable thermal equilibrium, as does a glass. During cooling n_{BT} becomes frozen into a nonequilibrium state that depends on the cooling rate. In a glass, these two states are separated by the glass transition temperature. We speculate that there may be a real physical basis to this analogy with a glass, according to the following model. In a -Si:H the silicon random network is essentially fixed during deposition. We propose that the bonded hydrogen can be considered as a separate structural network that becomes increasingly mobile at elevated temperatures. We suggest that the bonded hydrogen may form a glasslike submatrix contained within the fixed matrix of amorphous silicon. The “glass transition” temperature T_g occurs when cooling freezes in the nonequilibrium state, and is indicated in Figs. 2 and 3. According to this mechanism, equilibration should also occur in undoped a -Si:H, although at a higher temperature. Thus the equilibration proposed by Smith and Wagner³ may be a closely related process.

In summary, we find that the structure of doped a -Si:H is in metastable thermal equilibrium, having temperature-dependent densities of dangling bonds and donors. As a result, the density of shallow electrons depends on the annealing history, in turn influencing many experiments. The structure tends to freeze into a nonequilibrium state at

low temperatures because of an increasingly long equilibration time. We propose that the submatrix of bonded hydrogen undergoes a glass transition near 100–150 °C, a new concept in the physics of *a*-Si:H.

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