Stretched-Exponential Relaxation Arising from Dispersive Diffusion of Hydrogen in Amorphous Silicon

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In this paper we find that the stretched-exponential relaxation commonly observed in disordered systems is explained by time-dependent atomic diffusion. The relaxation is observed in the electronic properties of hydrogenated amorphous silicon (*a*-Si:H), a "hydrogen glass" material, and reflects the equilibrium of localized electronic states. The relaxation is attributed to the motion of bonded hydrogen which exhibits dispersive diffusion with a characteristic power-law time dependence. A quantitative relation between the relaxation and the diffusion is established.

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The results described in this Letter establish a link between two characteristic phenomena of disordered materials. These phenomena are the "stretched-exponential" decay that frequently describes the relaxation of glasses toward equilibrium, and dispersive transport, characterized by a power-law time decay of the mobility or diffusion. The latter, usually associated with electronic transport, is observed for the first time in atomic diffusion.

The stretched-exponential decay, often termed Williams-Watts[1] or Kohlrausch relaxation,[2] is described by the time dependence $\exp[-(t/\tau)^{\beta}]$, where $0<\beta<1$, and is observed in a wide class of disordered systems. In addition to oxide and polymeric glasses, examples include spin correlations in Cu-Mn and Ag-Mn spin-glasses[3]; dielectric relaxation in a charge-density-wave system[4] ($K_{0.3}MoO_3$); specific heat in magnetic glasses[5] (Fe_xZr_{1-x}); and neutron spin-echo measurements of ionic glasses.[6] The interest in the nonexponential decay stems from the observation that for *small* departures Δ from equilibrium, the decay should be given by the linear relation

$$d\Delta/dt = -\nu\Delta \quad (1)$$

irrespective of the detailed microscopic mechanism. Since a single-valued equilibration rate ν yields the conventional Debye relaxation, the nonexponenial decay must be related to the functional form of ν. Two classes of models have been proposed, one of which postulates a distribution of ν values,[7,8] and the other a time dependence of ν. Palmer *et al.*[9] introduced the second alternative and discussed its physical significance in terms of a hierarchy of dynamical constraints. A recent model of the same type by Shlesinger and Montroll[10] is of interest because it involves the concept of a continuous-time random walk with an algebraic pausing-time distribution that is successfully applied to dispersive transport in amorphous semiconductors.

Dispersive transport, widely observed in disordered systems, is also remarkable for its unusual time dependence. The drift mobility of excess carriers in virtually all amorphous photoconductors exhibits a power-law decay, $t^{-\alpha}$. Scher and Montroll[11] first explained this phenomenon using the ideas of a continuous-time random walk. A common origin for the dispersion is an exponential energy distribution of traps, $\exp(-E/k_BT_0)$, where k_BT_0 is the width of the trap distribution and the dispersion parameter α is given by $1-\alpha=T/T_0$.

The material system studied here is doped hydrogenated amorphous silicon (*a*-Si:H). Its localized state structure was recently argued to be in thermal equilibrium, having temperature-dependent densities of dangling bond defects and donor or acceptor states with the following properties.[12,13] The time to reach equilibrium is thermally activated, becoming longer at lower temperatures. When samples are rapidly cooled below a temperature T_E, a nonequilibrium electronic and atomic structure is frozen in, which slowly relaxes with a temperature-dependent time constant. T_E is the temperature at which the defect structure comes into equilibrium within a few minutes and is about 130 °C for *n*-type doped *a*-Si:H and is 80 °C for *p*-type *a*-Si:H. The equilibrium corresponds to the state of relative minimum free energy within the set of accessible structures. The slow relaxation is caused by barriers limiting the transition rate between the accessible states. Present evidence based on diffusion studies indicates that the bonding rearrangements which allow changes in the localized state distribution are associated with the motion of bonded hydrogen.[14] It has been proposed that the bonded hydrogen can be considered as a separate substructure that has properties similar to a glass, distinct from the nonequilibrium amorphous silicon network.[12] In this model the equilibration temperature T_E is equivalent to the glass transition temperature.

Doped *a*-Si:H samples were grown via the rf glow-discharge decomposition of silane (SiH_4) and phosphine (PH_3) for *n*-type doping; or silane and diborane (B_2H_6) for *p*-type doping. The structural relaxation towards equilibrium is conveniently observed through measure-

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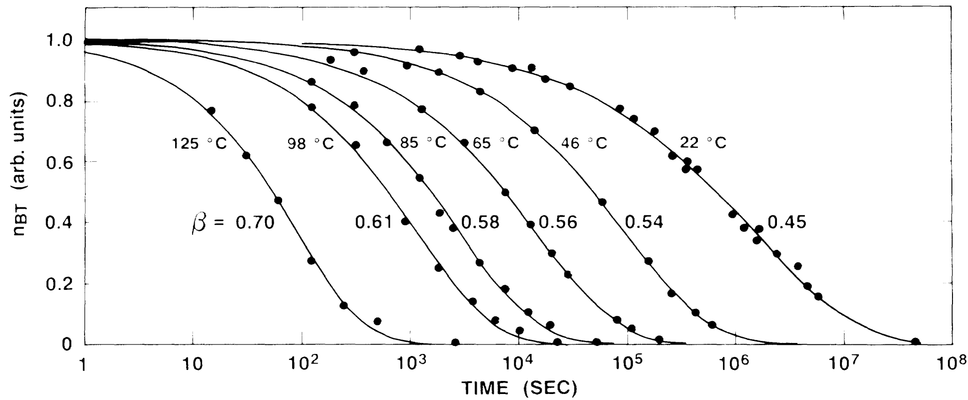

FIG. 1. Time dependence of the density of shallow occupied band-tail states at different temperatures for n-type a-Si:H. The solid lines are fits to the data with use of the function $\exp[-(t/\tau)^\beta]$.

ments of the density of shallow occupied states in the band tail n_{BT}, using the voltage-pulse sweep-out technique.[15] We adopt the model, discussed in detail elsewhere,[13] that dangling bonds are the only deep states in the gap in a-Si:H. n_{BT} is related to the densities of dangling bonds N_{DB} and donors N_{donor} by the charge-neutrality relation

$$n_{BT}=N_{donor}-N_{DB}. \tag{2}$$

Changes in the localized state distribution are therefore reflected in n_{BT}. Equivalent results are also observed in the time dependence of the dc dark conductivity.[13]

Figure 1 shows the time-dependent relaxation of n_{BT} of a 1% PH_3-doped a-Si:H sample when stored in the dark at different temperatures. The sample is first brought into equilibrium by annealing at 210 °C for 10 min and then rapidly cooled (cooling rate $\simeq$2–5 °C/sec) to room temperature to freeze the electronic structure into its nonequilibrium state. The sample is then stored at different temperatures and n_{BT}, measured at room temperature, is monitored as a function of time. The time to reach equilibrium varies from a few minutes at 125 °C up to about one year at room temperature. The time dependence of n_{BT} is well described by the stretched-exponential function

$$\Delta n_{BT}=n_0\exp[-(t/\tau)^\beta], \tag{3}$$

where Δn_{BT} is the departure from the equilibrium value of n_{BT}. The curves are normalized to the same initial value of n_{BT} and the final, steady-state value of each temperature has been subtracted out. The value of β is 0.45 ± 0.05 at room temperature and increases approximately linearly with temperature, as shown in Fig. 2. The time constant τ defined by Eq. (3) obeys an Arrhenius relationship, with an activation energy of 0.95 eV and a preexponential factor of $\tau_0=2\times10^{-10}$ sec. By varying the anneal temperature, we confirm that the decay is independent of the size of Δn_{BT}, although there is a small effect on the value of τ. Similar decays are observed at other doping levels and in p-type material.

We now address the kinetics of the decay of n_{BT}, and seek a relation between the nonexponential decay and the physical relaxation of the structure. While the data in Fig. 1 could be described with either a distribution of relaxation times or a time-dependent relaxation rate, a key point of this paper is that the latter choice yields much greater physical insight into the mechanisms underlying stretched-exponential decay. We therefore consider the possibility that the rate constant ν in Eq. (1) is time dependent,

$$d\Delta n_{BT}/dt=-\nu_E(t)\Delta n_{BT}. \tag{4}$$

Our discussion is based on studies that show that the rate of equilibration of N_{donor} and N_{DB} is related to the

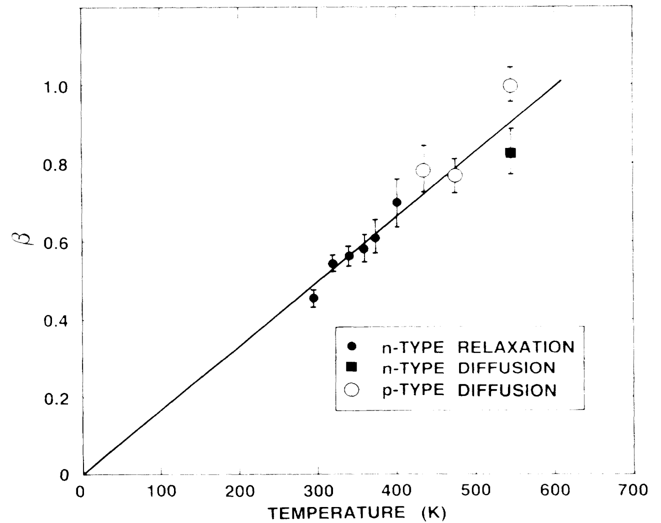

FIG. 2. Temperature dependence of the exponent β for the n-type a-Si:H sample in Fig. 1. The open-circle and solid-square data points are obtained from the time dependence of the hydrogen diffusion coefficient as explained in the text.

diffusion of hydrogen.[13,14] Hydrogen provides the flexibility to rearrange the bonding structure which is difficult to accomplish via the very rigid fourfold-coordinated silicon network. The fact that hydrogen terminates dangling bonds also suggests a link to the electronic structure. According to this model the rate constant $\nu_E(t)$ will be proportional to the hydrogen hopping rate D_H/a^2, where a is a characteristic hopping distance that the hydrogen moves in a single diffusion step and D_H is the diffusion coefficient. Any time dependence of the rate constant must therefore be reflected in D_H.

In order to check this prediction, we have studied the temperature and time dependence of the hydrogen diffusion coefficient in doped a-Si:H. Measurements are made on samples containing a thin deuterated layer sandwiched between layers of doped a-Si:H.[16] The deuterium profile is obtained by secondary-ion mass spectrometry, with the samples being annealed at temperatures between 150 and 300 °C and for varying annealing times at a fixed temperature. Details of the hydrogen diffusion data are published separately.[14]

The results show that, as anticipated, D_H is not uniquely determined at a given temperature but does depend on the annealing time. Figure 3 shows the time dependence of D_H for a 1% B_2H_6-doped a-Si:H sample when annealed at 200 °C. The hydrogen diffusion coefficient decreases by a factor of 5 as the time changes by 3 orders of magnitude. The data in Fig. 3 approximately follow a power law, that is,

$$D_H = D_{H0}(\omega_0 t)^{-\alpha}, \tag{5}$$

where $\alpha \simeq 0.2$–0.25 at 200 °C. D_{H0} is the temperature-dependent diffusion coefficient and ω_0 is an attempt frequency. We have studied the time dependence of D_H from 160 to 270 °C and find that α decreases with increasing temperature. However, the experimental uncertainty is too large to deduce the explicit temperature dependence. A similar power-law decay is also found in n-type samples.

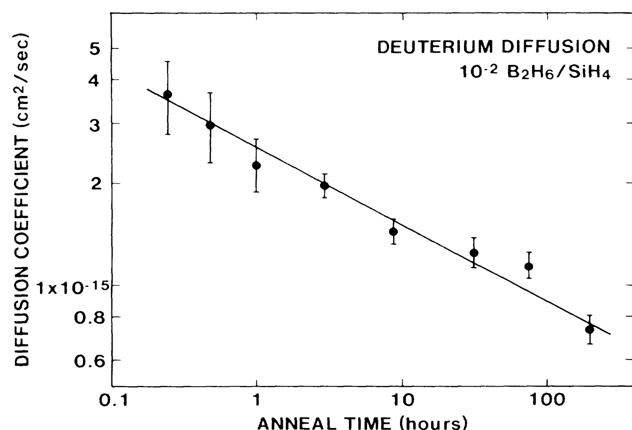

FIG. 3. Time dependence of the hydrogen diffusion coefficient for p-type a-Si:H when annealed at 200 °C.

We now show that the time-dependent diffusion results in a quantitatively correct interpretation of the relaxation. Our analysis is based on the results of Shlesinger and Montroll,[10] who considered the problem of migration of defects which trigger the relaxation of dipoles in polymeric systems. They found that if the diffusion of defects is executed as a continuous-time random walk composed of alternating steps and pauses, and if the pausing-time distribution function has a power-law time dependence, then the relaxation function has the form of a stretched exponential. The same result is obtained from a simple analysis of the rate equation. From the hydrogen diffusion data we set the equilibrium rate as

$$\nu_E = (D_{H0}/a^2)(\omega_0 t)^{-\alpha}. \tag{6}$$

Inserting Eq. (6) into Eq. (4) and integrating immediately yields

$$\Delta n_{BT} - n_0 \exp[-(t/\tau)^\beta], \tag{7}$$

where $\beta = 1-\alpha$. Thus the stretched-exponential decay follows directly from the dispersive diffusion mechanism.

Following the analogy to the dispersive transport of charge carriers, we argue that the dispersive diffusion of hydrogen arises from a broad distribution of release times. Differences in the local atomic configurations should yield a distribution of activation energies for the motion of hydrogen. As the number of sites visited by a hydrogen atom increases with time, so does the probability that it will visit a site in the tail of the energy distribution with a high barrier against release of the hydrogen. When the distribution is broad, D_H will reflect these few sites and the hydrogen motion will become slower at longer times. Furthermore, if the dispersion in D_H arises from an exponential distribution of site energies $\exp(-E/k_B T_0)$, then the theory predicts that

$$1-\alpha = \beta = T/T_0. \tag{8}$$

Figure 2 shows that both the relaxation and the diffusion data do indeed obey a common dependence of this form. From the hydrogen diffusion data in Fig. 3 we obtain the open-circle and solid-square data points in Fig. 2; the solid line in β vs T shown in Fig. 2 is consistent with $T_0 \simeq 600$ K. Moreover the hydrogen diffusion coefficient D_H is thermally activated with activation energies of 1.2–1.3 eV for both n-type and p-type doped a-Si:H. This agrees quite well with the Arrhenius behavior of the time constant τ with an activation energy of 0.95 eV. Thus there is good internal consistency between the hydrogen diffusion measurements and the stretched-exponential relaxation resulting from the equilibration of the defect structure. In addition we suggest that the dispersion probably results from an exponential distribution of bond energies for the release of hydrogen from

Si:H bonds. To summarize the model, we describe the diffusion of hydrogen in terms of a distribution of bond energies, and then relate the time dependence of D_H to the electronic relaxation. In this way the stretched exponential derives from a physically plausible exponential distribution of bond energies, and a direct connection between the structure and the electronic relaxation is found. The fact that *a*-Si:H exhibits this glasslike relaxation which is attributed to hydrogen diffusion supports the recent proposal that the bonded hydrogen can be thought of as a glassy substructure.

We believe the proposed model may have general validity to many material systems, irrespective of the presence of hydrogen, since the relaxation of glassy materials is usually caused by diffusion. The model described above is valid for any disordered material with a distribution of diffusion-site energies. The analogy with dispersive electronic transport suggests that a temperature-dependent β is associated with a distribution of activation energies, whereas a constant β arises from a dispersive tunneling mechanism. Many disordered materials do indeed have a temperature-independent relaxation parameter.

We note that the data in Fig. 1 can of course be fitted by an arbitrary range of relaxation times presumed to originate from a distribution of activation energies E. This procedure yields an asymmetric distribution in E centered at $\simeq 1.0$ eV with a width of $\simeq 0.1$ eV. However, there is no obvious reason why this distribution of relaxation times results in a stretched-exponential decay of electronic properties, nor does it give any insight into the role that hydrogen plays in the structure relaxation. Moreover, unlike the commonly observed exponential distribution of bonding energies, there is no universal or natural connection between this distribution of relaxation times and the observed dispersive hydrogen diffusion.

In conclusion, we have shown that the slow relaxation of the localized-state distribution in doped *a*-Si:H is accurately characterized by a stretched-exponential function. There is quantitative agreement between the stretched-exponential fitting parameters and the measured temperature and time dependence of the hydrogen diffusion coefficient. The exponential distribution of diffusion-site energies leads to a power-law time dependence for hydrogen diffusion. This decrease in D_H at longer times accounts naturally for the slow stretched-exponential decay of properties which are influenced by the hydrogen motion. This paper, for the first time, demonstrates a microscopic mechanism for stretched-exponential decay.

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