LETTER TO THE EDITOR

Metastable effects in the DC conductivity of hydrogenated amorphous germanium

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Abstract. We report on the effect of thermal equilibration on the dark conductivity of undoped optimized a-Ge:H with an optical gap of 1.03 eV. The freeze-in temperature T_E is about 160 °C. The isothermal relaxation of the conductivity follows a stretched exponential function. The inverse equilibration time τ^{-1} is thermally activated with an energy E_τ of 1.4–1.5 eV. It is then shown that, as compared with the values for a-Si:H, T_E, τ and E_τ are only slightly different. The results are fully consistent with the model of dispersive diffusion of hydrogen.

Thermal equilibrium processes induced by quenching in undoped a-Si:H have been extensively studied (Street and Winer 1989). The results provide strong support for the idea that hydrogen motion underlies the various metastable effects observed in this material. Such effects have also been studied in hydrogenated amorphous alloys derived from silicon: a-Si, C:H (Xu *et al* 1988), a-Si, N:H (Shimizu *et al* 1989), a-Si, Ge:H, F (Liu *et al* 1990). In contrast, it is surprising that no investigation of a-Ge:H has been undertaken, as similarities exist between parameters that influence metastability in this material (table 1); in fact, the two materials should behave in the same way. We propose to verify this prediction by studying the changes induced in the DC conductivity of a-Ge:H by quenching.

The samples used were grown in the ARCAM reactor (Roca i Cabarrocas *et al* 1987) by using the radiofrequency plasma decomposition of GeH_4 diluted at 1% in H_2 with a high RF power density. The deposition conditions have been shown to give optimized a-Ge:H films (Godet *et al* 1990) with, in particular, an Urbach tail as sharp as the one found in device quality a-Si:H. The deposition conditions and some of the initial properties of the films are given in table 2.

Details concerning all thermal treatments and conductivity measurements are given in a previous paper (Meaudre *et al* 1988), but for a-Ge:H, the temperature is maintained at lower than $\simeq$180 °C to avoid the out-diffusion of hydrogen.

Arrhenius plots of the dark DC conductivity σ are reported in figure 1. The equilibration temperature T_E above which the conductivity is independent of the prior

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Table 1. Binding energy, prefactor D_0 and activation energy E_H of the diffusion coefficients of hydrogen in a-Si:H (Street *et al* 1987) and a-Ge:H (Beyer *et al* 1990).

a-X:H material	X–X binding energy (eV)	X–H binding energy (eV)	D_0 $(10^{-2} \text{cm}^{-2} \text{s}^{-1})$	E_H (eV)
a-Ge:H	1.9	2.9–3	2–5	1.4–1.5
a-Si:H	2.3	3–3.2	0.8	1.5

Table 2. Deposition conditions and properties of the sample. T_S is the substrate temperature, E_G the Tauc gap, E_U the inverse slope of the Urbach tail acquired with photothermal deflection spectroscopy, N_S the EPR dangling bond density and $N(E_F)$ the density of states at the Fermi level derived from transport measurements on Schottky barriers (Kleider *et al* 1989).

T_S (°C)	Gas mixture and flow rate	Power (W cm^{-2})	Pressure (Torr)	H content (at.%)	E_G (eV)	E_U (meV)	N_S (cm^{-3})	$N(E_F)$ (cm^{-3} eV^{-1})
250	GeH$_4$/(GeH$_4$ + H$_2$) = 0.01 120 sccm	0.1	0.2	6.5	1.03	50	4×10^{17}	$\geq 10^{18}$
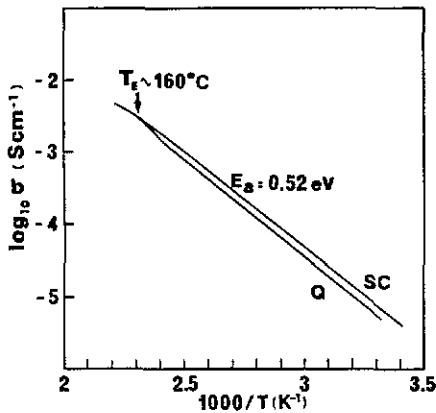
Figure 1. Temperature dependence of the DC conductivity for two cooling rates from 180 °C to room temperature: Q, 10 °C s^{-1}; SC, 0.05 °C s^{-1}.

thermal history of the sample is 160 °C (180 °C–200 °C in undoped a-Si:H), and it is observed that, as in a-Si:H films, the thermal quenching lowers σ. The time dependence of departures from equilibrium dark DC conductivity is well described by a stretched exponential function $\exp(-(t/\tau)^\beta)$ (figure 2) and the inverse relaxation time τ^{-1} is thermally activated with an energy E_τ of about 1.4–1.5 eV (figure 3). a-Ge:H presents a behaviour quite similar to that of a-Si:H, and the values of T_E, τ, E_τ differ only slightly from one material to another.

Let us show that these results agree quite well with the model of dispersive diffusion of hydrogen as proposed by the Xerox group in the case of a-Si:H (Kakalios *et al* 1987, Street *et al* 1988) and just recalled here. At high temperature, thermal equilibrium is
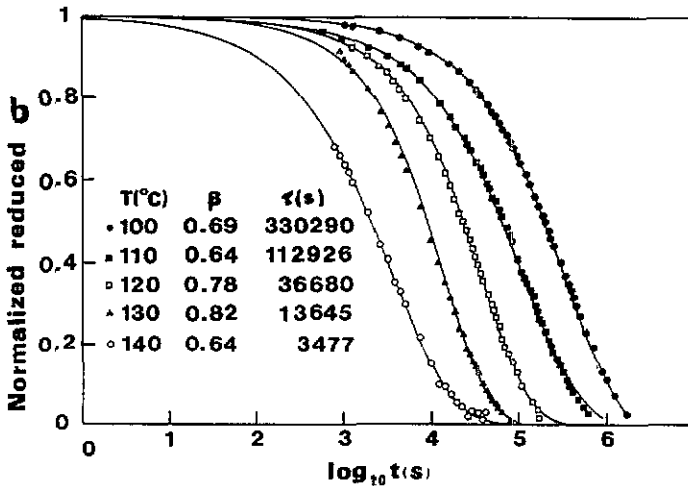
Figure 2. Time dependence of the normalized reduced conductivity at different temperatures. The full curves are fitted to the data using the function $\exp(-(t/\tau)^\beta)$ with values β and τ given in the figure.

reached; when the material is quenched, its structure is frozen in and the return to equilibrium is made via the diffusion of hydrogen, which can be described as follows:

(i) hydrogen is first released from Si–H bonds; then a mechanism whereby interstitial hydrogen is inserted into weak Si–Si bonds, determines the long-range hydrogen motion and the bonding rearrangements;

(ii) hydrogen hops via interstitial sites from one bonded site to another which constitutes the basic diffusion step;

(iii) an exponential distribution of diffusion sites energies leads to a stretched exponential decay of properties that are influenced by hydrogen motion.

The dark conductivity is directly linked to the gap states whose rearrangement is induced by dispersive hydrogen diffusion and then follows a stretched exponential function (Meaudre *et al* 1991).

If thermal relaxation in a-Ge : H is due to the motion of hydrogen, our results show that the diffusion coeficients of hydrogen in a-Si : H and a-Ge : H have nearly equal values. Consequently, that implies similar activation energies of the hydrogen diffusion coefficient and similar distributions of diffusion site energies in the two materials (Jackson *et al* 1989).

Let us first address the activation energy E_H of hydrogen, and consequently E_τ (Jackson *et al* 1989). According to Müller (1988), three contributions to E_H can be identified in the case of a-Si : H: (i) electronic excitation of a weak Si–Si bond requiring an energy E_{ex}; (ii) transfer of a density fluctuation to Si–H sites triggering the H release and requiring an energy E_d; and (iii) interstitial motion of a hydrogen atom requiring an energy E_m, i.e. $E_H = E_{ex} + E_d + E_m$. In a-Ge : H one has $E_{ex} = E_c - E_F \simeq E_F - E_v \simeq$ 0.5–0.55 eV (figure 1), where E_c, E_v and E_F are the conduction band and valence band mobility edges and the Fermi level, respectively. By analogy with crystalline germanium, $E_m \simeq 0.4$ eV (Franck and Thomas 1960). As the slopes of the conduction band and valence band tails of our a-Ge : H are similar to those found for a-Si : H (Godet *et al* 1990,
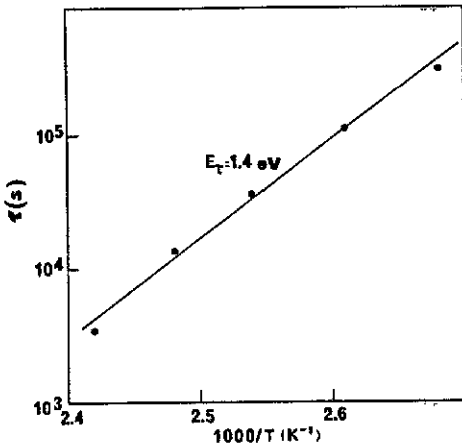
Figure 3. Temperature dependence of the time constant τ.

1991), and taking account of the different values of the energy gap $E_G \simeq 1.03$ eV and effective correlation energy $U \simeq 0.1$ eV (Stutzmann *et al* 1989), E_d is easily obtained from the reaction energy of the bond-breaking reactions given by Müller (1988), i.e. $0 < E_d < 0.3$ eV. The sum of the individual contributions then yields $0.9 < E_H < 1.25$ eV. The same reasoning applied to a-Si:H leads to $1.4 < E_H < 1.8$ eV (Müller 1988). These estimates show that the activation energies of hydrogen diffusion coefficients should not be too different in a-Si:H and a-Ge:H. They are in reasonable agreement with experimentally observed values of E_H and E_τ (table 1, figure 3).

Let us now consider the values of relaxation time τ and equilibrium temperature T_E. According to a model put forward by Street and Winer (1989) in their discussion of defect equilibria in undoped a-Si:H, the distribution of hydrogen bonding energies in Si–Si bonds has the same shape as the valence band tail (except for the doubling of the energy scale) and so will be an exponential of slope $(2\,kT_V)^{-1}$, kT_V being the characteristic energy of the valence band tail which can be assumed to be close to the Urbach energy E_U (Godet *et al* 1990). Applying the same model in the case of weak Ge–Ge bonds, it is clear why a-Ge:H and a-Si:H have roughly the same T_E and τ. Indeed, because of the correspondence between the valence band tail and the hydrogen distribution of trapping sites it is expected that our optimized a-Ge:H with an Urbach tail as sharp as the one found in a-Si:H has roughly the same distribution of trapping sites (providing a similar density of states at E_V) and then similar τ and T_E since equilibration is due to dispersive diffusion in these exponential distributions. As expected from this model, the slightly higher hydrogen diffusion coefficient measured in a-Ge:H (table 1) leads to values of $T_E \simeq 160\,°C$ only slightly lower than those observed in a-Si:H (180–200 °C).

Since we have shown that the values of τ and T_E measured in a-Ge:H and a-Si:H are only slightly different, although in a-Si:H the defect density N_S is two orders of magnitude lower than in a-Ge:H (table 2), we wish to discuss and refine the affirmation sometimes claimed according to which the diffusion coefficient of hydrogen and thus the values of τ and T_E depend strongly on the defect density. The higher defect density measured in a-Ge:H is easily explained (Godet *et al* 1991) in the light of the entropic equilibrium model of Smith and Wagner (1987). According to this model the defect density increases rapidly with E_U or when the dangling bond energy E_D decreases (E_D

is measured with respect to the valence band mobility edge taken as the origin of the energy). If E_U takes similar values in our a-Si:H and a-Ge:H samples, this is not the case for E_D. Indeed if we assume that the Fermi level is pinned between the D^0 and D^- defect state distributions due to Ge dangling bonds and separated by $U \simeq 0.1$ eV, the activation energy of the dark conductivity $E_\sigma \simeq E_c - E_F \simeq 0.52$ eV, is fully consistent with $E_G \simeq 1.03$ eV and $E_D \simeq 0.5$ eV. For a-Si:H one has $E_D \simeq 0.8$ eV; we have then shown (Godet *et al* 1991) that the difference in the energy position E_D allows us to explain the large difference in the dangling bond density quantitatively.

According to the above discussion of the multi-trapping model of diffusion of hydrogen, for samples having the same E_D (and E_F), τ and T_E must increase with E_U and consequently N_S. On the other hand, for samples having different E_D there is no reason for τ and T_E to be correlated with N_S. This is what we have observed in this study.

Finally, although the above-quoted model is quite satisfying in explaining the main experimental features, we wish to make two remarks. First, according to the interpretation of thermal relaxation in terms of dispersive diffusion of hydrogen, the parameter β of the stretched exponential function should be given by $\beta = T/2T_V$. Thus in the temperature range studied and with $T_V = 550$ K, β should be about 0.35–0.4, whereas experimental values are about 0.65–0.82 (figure 2). Secondly, in the case of a-Si:H, Street and Winer (1989) observed that the energy to form mobile hydrogen interstitials (1.5 eV) is close to 2 E_D. Although this feature could be consistent with their model, the authors queried whether or not this is a coincidence. It is clear that in the case a-Ge:H such a relation does not hold.

In conclusion, although having much higher defect densities than a-Si:H, a-Ge:H prepared under optimized conditions shows thermally induced metastable effects quite similar to those observed in a-Si:H. The slight differences observed in the values of T_E, τ and E_τ are fully consistent with the model of dispersive diffusion of hydrogen and the diffusive rearrangement of Ge–H bonds as proposed by the Xerox group and Müller (1988), respectively.

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