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Band tails and deep-defect density of states in hydrogenated amorphous germanium

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A correlation between the midgap-defect-state density and the Urbach energy is experimentally observed in undoped hydrogenated amorphous germanium (a-Ge:H) thin films prepared by the glow-discharge technique under different conditions. Since these samples show thermally induced metastable effects, the data are analyzed with a thermal-equilibration model recently proposed for a-Si:H. This yields a neutral Ge dangling-bond (D^0) energy at 0.50–0.55 eV above the valence-band edge.

I. INTRODUCTION

The pseudogap density of states (DOS) in covalent tetrahedrally coordinated amorphous materials, such as hydrogenated amorphous silicon (a-Si:H) or germanium (a-Ge:H), is generally described by two exponential-tail-state distributions at the valence and conduction-band edges (with characteristic energies E_v^0 and E_c^0) and a deep-defect-state density. These localized states are respectively attributed to distorted bonds with a weak bonding energy and to broken bonds. The optical-absorption spectra for energies lower than the optical gap provide useful information about the pseudogap DOS. On one hand, the inverse slope of the exponential part of the edge, E^0 (Urbach energy), can be considered equal to E_v^0, which is larger than E_c^0 in a-Si:H and probably also in a-Ge:H (Ref. 1); E^0 is a parameter characteristic of the disorder. On the other hand, the level of absorption at energies below the Urbach tail is determined by the deep-gap-state density N_D, which can be estimated, either by a suitable deconvolution of the optical-absorption spectra,[2] or by some calibration procedure.[3,4]

It is expected that E^0 and N_D are not independent. The experimentally observed correlation between these two parameters in a-Si:H films has been described by different models with a common basis, namely the breaking of the least stable weak bonds into two dangling bonds (D^0). It has been suggested that a thermodynamic equilibrium may be reached between the weak- and dangling-bond distributions, the energy required to break the weak Si—Si bonds being compensated by the mixing entropy gain of the dangling bonds in the network.[5] This model accounts for the results of various thermal-equilibrium measurements performed on a-Si:H and a-Si-Ge:H alloys.[6,7]

On the other hand, the exponential increase of the relaxation time for the creation or the annealing of the dangling bonds with decreasing temperature has been successfully described by a model of hydrogen-diffusion-mediated bond breaking[8] for both doped and undoped a-Si:H.[9,10] The a-Si:H is thus considered a H glass with thermally activated H diffusion in the rigid Si matrix, with nearly identical activation energies for H diffusion and defect equilibration. Experimentally, a convenient way to deduce the glass-transition temperature T_F consists in determining the critical temperature T_E below which the dark conductivity becomes dependent on the cooling rate from an annealing temperature T_A higher than T_E.[10] According to this model, the defect density measured at ambient temperature for a film deposited at $T_s \gtrsim T_F$ is a frozen-in defect density, corresponding to the glass temperature $T_F \simeq T_E$ (weakly dependent on the cooling rate) if the sample has been slowly cooled down after deposition, or to a temperature closer to T_s if the sample has, on the contrary, been rapidly quenched.

We have recently shown that a-Ge:H films with an Urbach tail as sharp as the one found in device-quality a-Si:H ($E^0 \simeq 50$ meV) can be prepared by using the rf plasma decomposition of GeH_4 diluted at 1% in H_2, with a high rf power density of 0.1 W cm^{-2}. However, the sub-band-gap absorption in these a-Ge:H films ($\alpha \simeq 10-20$ cm^{-1} at a photon energy of 0.6 eV)[11] is higher than in a-Si:H by more than an order of magnitude. In order to understand this difference between the deep-defect density in optimized a-Ge:H and a-Si:H, we investigate the possible correlation between the two parameters E^0 and N_D in a large number of a-Ge:H samples prepared under different conditions, and we analyze our data in terms of the equilibrium models proposed for a-Si:H.

II. EXPERIMENTAL RESULTS

The *a*-Ge:H films, with thicknesses ranging from 0.5 to 3 μm, were deposited by the rf (13.56 MHz) plasma decomposition of GeH_4 diluted in H_2 in a capacitively coupled reactor. Different gas compositions, from 1% to 10% GeH_4 in H_2, were used. The rf power density was varied between 0.05 and 0.10 W cm^{-2}, and the substrate temperature between 150 °C and 280 °C.[11] The optical-absorption spectra were accurately determined down to 0.6 eV by a combination of standard optical transmission measurements and photothermal deflection spectroscopy (PDS) experiments performed on the same samples deposited on Corning 7059 glass substrates. By comparing the data obtained on series of films deposited under the same conditions but with different thicknesses, we checked that in all cases surface effects were negligible for thicknesses in the 1–3-μm range; for thicknesses of the order of 0.5'μm, the increase of the apparent sub-band-gap absorption was at most of the order of 50%. The electron-spin-resonance (ESR) experiments were performed at 20 K with a Brucker ESR 300 spectrometer fitted with an Oxford cryostat. We used powders ($\simeq 30$ mg) obtained from samples deposited on Al foils after dissolving the substrates in HCl. The ESR signals were calibrated with a P-doped Si crystal.

In order to estimate the deep-density N_D, we applied to the optical-absorption spectra of a few samples a deconvolution procedure based on the following assumptions: (i) a Gaussian distribution for the deep-gap states and exponential distributions for the band-tail states, and (ii) constant momentum-matrix element for all the optical transitions involved.[2] Good fits to the data could be obtained with a Gaussian distribution centered at $E_D = 0.50 \pm 0.02$ eV above the valence-band mobility edge, with a full width at half height equal to 0.35 ± 0.02 eV. The scatter of the N_D values determined with E_D varying over the reported energy range did not exceed 20%. These "optical" N_D values were then compared to the spin-density values N_s deduced with a 50% uncertainty from ESR experiments on simultaneously deposited samples. A good agreement was found between these two sets of values; for example, for optimized samples, $N_D = (2.5 \pm 0.5) \times 10^{17} cm^{-3}$ compared to $N_s = (4 \pm 2) \times 10^{17} cm^{-3}$.[12] This result suggests that, in *a*-Ge:H as in *a*-Si:H, the paramagnetic dangling-bond states D^0 are responsible for the sub-band-gap absorption. For several samples with quite different properties, a good linear correlation was also observed between the optical-absorption coefficient at a photon energy of 0.6 eV (i.e., around midgap), α_D, and the corresponding optical-defect density N_D or spin density N_s. For simplicity, we thus calibrated the α_D values measured at 0.6 eV by using the relation[12]

$$N_D \simeq N_s = 3.3 \times 10^{16} [\alpha_D (cm^{-1})] \ cm^{-3} .$$

Figure 1 shows the variation of N_D versus E^0 for all the investigated *a*-Ge:H films. The E^0 values given in this figure are "apparent" values determined directly from the slope of the exponential part of the optical-absorption spectra. These values may be influenced by the contribution from the deep-gap-state absorption in the Urbach-tail range. We verified by our deconvolution procedure that the "true" E^0 values are indeed smaller than the "apparent" ones. However, they differ by 2 meV only for the optimized samples, and by at most 10 meV for the worst samples (with the highest deep-state absorption). Figure 1 shows that N_D increases systematically with increasing E^0 as in *a*-Si:H. This result suggests that the thermal-equilibration models proposed for *a*-Si:H may also apply to *a*-Ge:H.

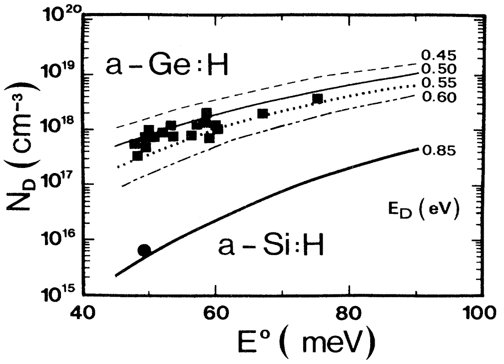

FIG. 1. Experimental dangling-bond density N_D vs valence-band-tail parameter E^0 for *a*-Ge:H samples deposited under different conditions (squares). A typical result for device-quality *a*-Si:H is shown for comparison (circle). The upper curves are obtained from the equilibrium model (Ref. 5) with a constant equilibrium temperature $T_F = 160$ °C and different values of the dangling-bond energy E_D above the valence-band mobility edge; the lower curve is obtained from the same model with $T_F = 190$ °C and $E_D = 0.85$ eV, which corresponds to *a*-Si:H.

In order to verify this assumption, quenching experiments were performed on *a*-Ge:H samples prepared under optimized plasma conditions ($W = 0.1$ W cm^{-2}, H_2 dilution of 1%) at high substrate temperature $T_s = 250$ °C, which have a low H content ($C_H = 6.5$ at. %). The dark-conductivity measurements show thermally induced metastable effects very similar to the ones observed in *a*-Si:H.[13] The freeze-in temperature T_E is of the order of 160 °C, i.e., slightly lower than in *a*-Si:H. This temperature is slightly higher than the lowest substrate temperature used in the present work, 150 °C. However, since the relaxation time of *a*-Ge:H at 150 °C determined from the quenching experiments is much smaller than the deposition times (typically 50 min as compared to 10 h or more), it can be admitted that all the investigated *a*-Ge:H samples have reached equilibrium during deposition.

III. DISCUSSION

In the following, we compare the data reported in Fig. 1 to the predictions of the thermal-equilibrium model proposed by Smith and Wagner for *a*-Si:H.[5] This model minimizes the total free energy of weak and broken bonds, the energy cost of the bond-breaking reaction being partially compensated by the entropy of mixing of the two separated dangling bonds. All the weakest bonds in the valence-band-tail distribution located above a threshold energy E_T are assumed to be broken into two dangling bonds; the resulting N_D is thus the integral above E_T of the valence-band-tail distribution described by

$$N(E)=N_v\exp[-(E/E^0)] \tag{1}$$

(N_v being the density of states at the valence-band mobility edge E_v taken as the origin of energies), so that

$$E_T=E^0\ln(N_vE^0/N_D)\ . \tag{2}$$

N_D is then related to E^0 through

$$(kT_F+2E^0)\ln(N_D)=kT_F\ln(4N_{\mathrm{at}}/e)-2E_D+2E^0\ln(N_vE^0)\ , \tag{3}$$

E_D being the energy of the defect states above the valence-band mobility edge E_v. The $N_D(E^0)$ theoretical curves in Fig. 1 were calculated with the dangling-bond energy E_D as a parameter. A density of states at E_v of $N_v=4\times10^{21}$ $\mathrm{eV^{-1}\,cm^{-3}}$, an atomic density $N_{\mathrm{at}}=5\times10^{22}$ atoms $\mathrm{cm^{-3}}$, and a freeze-in temperature $T_F=160\,^\circ\mathrm{C}$ (as suggested by the quenching experiments) were assumed in the calculations.

It can be seen that the full set of experimental data is consistent with the predictions of the model, with a constant defect energy E_D (corresponding to the Ge D^0) ranging from 0.50 to 0.55 eV above the valence-band mobility edge. The agreement is even better if only the thickest films are considered. Furthermore, these E_D values are very close to those giving the best fit to the optical-absorption edge in our deconvolution procedure ($E_D=0.50\pm0.02$ eV). Through relations (2) and (3), one can deduce the value of the threshold energy for the weak-bond to dangling-bond conversion $E_T=0.31$ eV, and of the bond-breaking energy, $U_B=2(E_D-E_T)=0.44$ eV.

The energy of the neutral dangling-bond states with respect to the valence-band mobility edge is hence much lower in *a*-Ge:H (0.50–0.55 eV) than in *a*-Si:H (0.85 eV) (the curve computed for *a*-Si:H with the same model, with a freeze-in temperature of 190 °C, as well as a typical data point for device-quality *a*-Si:H, are reported in Fig. 1 for comparison). This value is in good agreement with the results of the ESR determination of the D^0 (and D^-) energy positions in *n* and *p*-type doped *a*-Ge:H (and *a*-Si:H),[1] and with those of photoelectron yield spectroscopy experiments on *a*-Ge:H.[7] The low E_D value obtained for *a*-Ge:H explains why the deep-gap-state density in optimized *a*-Ge:H remains higher by more than an order of magnitude in comparison to optimized *a*-Si:H. It must be emphasized that the overlap of the valence- and conduction-band tails in *a*-Ge:H contributes very little to the midgap density; if one assumes $E_v^0\simeq50$ meV and $E_c^0\simeq30$ meV, one obtains a midgap DOS level close to 2×10^{16} $\mathrm{eV^{-1}\,cm^{-3}}$, which has to be compared to the experimental value of 1×10^{18} $\mathrm{eV^{-1}\,cm^{-3}}$.

With the help of other experimental results obtained on the same samples, a consistent picture of the DOS distribution in the pseudogap of *a*-Ge:H can now be proposed. It is first assumed that the Fermi level is pinned between the D^0 and D^- defect-state distributions, which are separated by an effective correlation energy of 0.1 eV.[1] It can then be deduced from the position of the D^0 states with respect to E_v ($E_D=0.50$–0.55 eV) and from the measured activation energy of the dark conductivity ($E_\sigma=E_c-E_F=0.45$–0.50 eV, E_F lying slightly above midgap) that the energy separation between the valence- and conduction-band mobility edges, E_c-E_v, must be of the order of 1.0–1.10 eV. This is in good agreement with the Tauc optical gap $E_T=1.03$–1.06 eV, as well as with the mobility gap obtained by the deconvolution procedure applied to the optical-absorption edge, $E_c-E_v\simeq1.10$ eV.[11,12]

As emphasized in the Introduction, the freeze-in temperature T_F entering expression (3) depends on the cooling rate after decomposition. For the analysis of our data (Fig. 1), we have chosen the same T_F equal to the value deduced from the dark-conductivity quenching experiments performed on our best samples after suitable annealing.[13] This would imply that all the samples deposited above T_F were cooled down to T_F slowly enough to reach equilibrium at T_F. Figure 2 illustrates the influence of T_F on the predictions of the model. It shows the variation with T_F of the calculated dangling-bond density for two values of $E^0=48$ and 50 meV, and for two values of $E_D=0.50$ and 0.53 eV. For a defect energy E_D of 0.53 eV, the model predicts an increase by a factor of 2 of the deep-state density for T_F ranging from 150 °C to 250 °C. As shown in Fig. 2, these predictions are in good agreement with the experimental data obtained for two 2-μm-thick samples deposited at $T_s=150\,^\circ\mathrm{C}$ and 250 °C, respectively, and annealed *in situ* for 25 h, at the deposition temperature; we assume here that the freeze-in temperature in the model is of the order of T_s. This is a general result; the N_D values are indeed systematically larger by a factor of about 2 for the films deposited at $T_s=250\,^\circ\mathrm{C}$ than for those deposited at $T_s=150\,^\circ\mathrm{C}$, irrespective of the

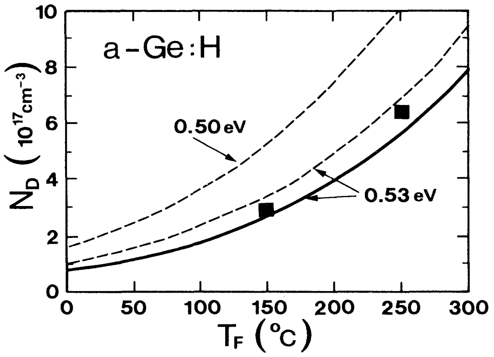

FIG. 2. Variations with the equilibrium temperature T_F of the *a*-Ge:H dangling-bond density calculated for slightly different positions of the dangling-bond states in the gap, $E_D=0.50$ and 0.53 eV; the valence-band-tail parameter E^0 is set to 48 meV (solid line) or 50 meV (dashed lines). The experimental data (squares) correspond to *a*-Ge:H samples deposited at $T_s=150\,^\circ\mathrm{C}$ and 250 °C and annealed for 25 h at T_s; T_F has been taken equal to T_s in each case.

E^0 values. Decreasing the deep-gap-state energy from 0.53 to 0.50 eV results in a homothetic increase of the calculated defect density by a factor of 1.5, which is the typical uncertainty of our data. The error on the E_D determination is therefore estimated at 0.03 eV.

The preceding results show that the equilibrium theory proposed by Smith and Wagner[5] accounts very well for our optical data on *a*-Ge:H. However, alternative models may be considered. A more realistic picture of the threshold energy for the weak-to dangling-bond conversion may be given by assuming a bond-breaking probability equal to unity for weak-bond energies above a certain critical energy E_T^*, and to a Boltzmann factor below E_T^*. As a consequence, the weak bonds with energy below E_T^* should provide the dominant contribution to the weak- to dangling-bond conversion, due to the sharp increase of the valence-band-tail distribution. A simple calculation yields the following total dangling-bond density:

$$N_D = N_v E^0 [E^0/(E^0 - kT_F)] \exp[-(E_T^*/E^0)] \ . \tag{4}$$

The threshold value $E_T^* = 0.39$ eV estimated in this way is now deeper in the pseudogap than in the first model ($E_T = 0.31$ eV). On the other hand, the energy difference between E_D and E_T^* may be derived from the H-diffusion-mediated bond-breaking model proposed by Street *et al.*:[8] $E_D - E_T^* = 0.5kT \ln([\mathrm{H}]/N_D)$. One obtains 0.18 eV for a typical H atomic density of 3.2×10^{21} cm^{-3}, which corresponds to a 6.5% H content.[11] This value is in reasonable agreement with the result $E_D - E_T = 0.22$ eV, deduced above from the Smith-Wagner model.[6]

Let us now consider a different approach suggested by Müller, who proposed a charge-induced bond-breaking process;[14] the width of the mobility gap and the Fermi-level position are the main parameters of this model, which yields a defect density of 1×10^{18} cm^{-3} at 500 K for an optical gap of $\simeq 1$ eV. The predicted equilibrium temperature is $T_E \simeq 430$ K ($\simeq 160$ °C) for an activation energy of 0.45 eV.[14] This is the experimentally observed value for our optimized *a*-Ge:H samples. This value is lower than those obtained by the same method for *a*-Si:H [$T_E = 190$ °C–200 °C (Refs. 10 and 15)], but higher than the T_E values (125 °C–140 °C) reported for *a*-Si-Ge:H alloys.[15,16] These results seem to rule out a simple correlation between T_E and the optical gap.[15] The location of the Fermi level is also expected to be a relevant parameter.

IV. CONCLUSIONS

We have found that the neutral dangling-bond states D^0 are located near midgap in undoped *a*-Ge:H as in undoped *a*-Si:H. The Urbach parameter E^0, considered as indicative of the disorder, is the same ($\simeq 50$ meV) in both optimized materials. However, the deep-gap-state density N_D is higher in optimized *a*-Ge:H than in *a*-Si:H by more than an order of magnitude, which is consistent with a decrease of the photoconductivity yield by a factor of 100.[11] This large difference in the dangling-bond density can be quantitatively explained within the equilibrium theory proposed by Smith and Wagner,[5] in which the fundamental parameter is the energy position E_D of the dangling-bond states above the valence-band edge.

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