The kink in the conductivity characteristics of undoped a-Si:H-a comprehensive picture

The kink in the conductivity characteristics of undoped a-Si: H—a comprehensive picture

Pablo Jensen and Robert Meaudre

Département de Physique des Matériaux, Université Claude Bernard Lyon I,
43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cédex, France

Abstract. We study the well known kink in the Arrhenius plots of the DC conductivity of undoped hydrogenated silicon. The widespread transport model above a mobility edge is assumed and the possible explanations for the kink are reviewed. A careful analysis shows that only thermal-equilibrium processes can account for our present experimental data. Furthermore, we show that the kink temperature is the temperature at which the sample becomes frozen in a non-equilibrium configuration.

1. Introduction

It has been widely [1–4] observed that Arrhenius plots of the DC conductivity of undoped and doped hydrogenated amorphous silicon (a-Si:H) show two linear regions intersecting at T_k, the kink temperature, which usually lies in the range 100–200 °C. Several explanations had been proposed [1–3] for the kinks associated with undoped material until Overhof and Beyer [4–5] having carefully studied the statistical shift of the Fermi level E_F concluded that it could explain the kinks in both doped and undoped samples. This last model was generally accepted and some detailed calculations have been made to reproduce the kinks quantitatively [6, 7]. However, Overhof has admitted recently [8, 9] that, for doped a-Si:H, the statistical shift of E_F could not explain the kink and that the latter must be due to thermal-equilibrium processes as demonstrated by the Xerox group [10, 11]. In addition, we have lately [12] pointed out that the statistical shift model for undoped a-Si:H faces some difficulties in quantitatively reproducing the kink. We have, therefore, suggested [12] that thermal-equilibrium processes could be responsible for the kink, even in undoped material. In this paper we present new experimental data that show that the kink temperature of a given sample depends on the cooling rates used in producing the conductivity Arrhenius plots. More precisely, we show that T_k corresponds to the temperature at which the sample becomes frozen in a non-equilibrium state. This clearly indicates that the kink originates in thermal-equilibrium processes.

2. Experimental results

Undoped a-Si:H samples of thicknesses ~1 μm were grown via the RF glow discharge decomposition of silane in the ARCAM deposition reactor [13]. All thermal treatments
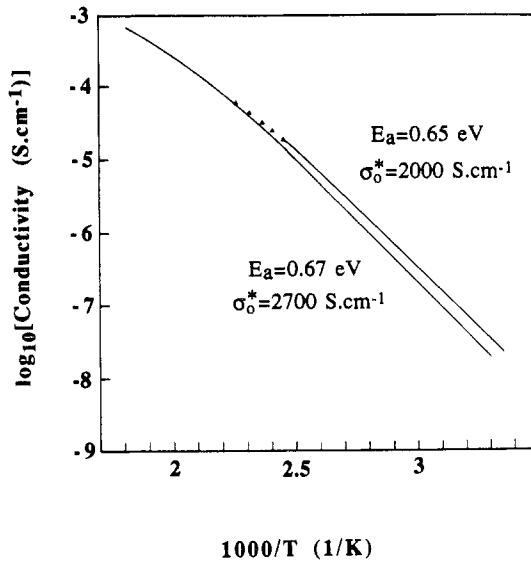
Figure 1. The temperature dependence of the DC conductivity showing the effects of different cooling rates. Lower curve: slow cool (cooling rate 0.04 °C s^{-1}). Upper curve: the temperature was kept constant until equilibrium was reached (triangles) and then a slow cool (0.04 °C s^{-1}, full curve) was performed (see text).

and coplanar conductivity measurements were made in the dark, in vacuum (10^{-6} Torr). The data of figure 1 were obtained as follows: the sample was first annealed at 260 °C (the substrate temperature during deposition) for 30 min to eliminate the effects of any adsorbed gases. A 'standard' (0.04 °C s^{-1}) slow cool was then performed, leading to the well known kink at ~175 °C. The procedure for obtaining the upper curve was slightly more complex. We demonstrated [14, 15] that, owing to thermal-equilibrium processes, the conductivity of undoped a-Si:H was time dependent in the temperature range ~100–200 °C, reaching an equilibrium value after a characteristic relaxation time. This relaxation time rapidly increased with decreasing temperature and passed from a few seconds at 200 °C to about a day at 135 °C. Indeed, the upper curve was obtained by maintaining equilibrium until 135 °C was reached. More precisely, immediately after the preceding slow cool, the sample was heated up to 170 °C and the temperature was kept at this value until equilibrium was reached. The temperature was then fixed at 160 °C until equilibrium was attained and so on down to 135 °C, the total time needed to obtain these five points (T = 170, 160, 150, 143 and 135 °C) being about a week. Finally, a slow cool identical to the preceding one (0.04 °C s^{-1}) was performed from 135 °C to room temperature. It can be seen from figure 1 that this last procedure shifted the kink temperature to about 130 °C. Clearly, this T_k corresponds to the lowest temperature at which the sample was allowed to equilibrate.

We would like to add that, as we have shown in preceding papers [15, 16], adsorbate effects cannot account for the relaxation towards equilibrium which originates from bulk equilibration processes as for doped samples [11].

3. Discussion

We assume that in this temperature range and for our low-defect-density samples, conduction arises from electrons excited above a well defined mobility edge at energy E_c. This assumption immediately leads to

$$\sigma(T) = \sigma_0 \exp[-(E_c - E_F)(T)/kT] \tag{1}$$

where E_F is the Fermi level energy and σ_0 the so-called 'prefactor of conductivity' which is temperature independent and has a value of about 50–150 S cm^{-1} [9, 17, 18]. According to equation (1), a kink is related to the temperature dependence of $E_c - E_F$. More precisely, we can say that a kink necessarily arises from a *sharp change* in the temperature dependence of $E_c - E_F$.

But why should $E_c - E_F$ be temperature dependent? The first reason is that the gap itself is temperature dependent: $E_G(T) = E_G(0) - \gamma_1 kT$, for 200 K $< T <$ 600 K with $\gamma_1 \simeq$ 5–6 [9, 17–19]. Therefore, assuming a uniform scaling of the gap energies, we can approximate the $E_c - E_F$ variation using

$$\frac{d(E_c - E_F)}{dT} \simeq [(E_c - E_F)/E_G] \, dE_G/dT \simeq \tfrac{1}{2} \, dE_G/dT$$

for E_F around mid-gap. But we see immediately that, since $dE_G/dT = -\gamma_1 k$ is constant in the temperature range studied here, the temperature dependence of the gap will not lead to any change in $d(E_c - E_F)/dT$ and thus cannot explain the kink. We will now discuss two other possibilities for an $E_c - E_F$ temperature dependence and will show that one of them will be able to account for the kink.

The Fermi level energy is determined by solving the neutrality equation:

$$n + D^- = p + D^+ \tag{2}$$

where n and p are the electron and hole densities respectively and D^- and D^+ are the densities of charged defects (such as dangling bonds or impurities). Equation (2) can be written as

$$\int g_c(E, T) f(E, E_F, T) \, dE + \int g_D(E, T) f_H^-(E, E_F, T) \, dE$$

$$= \int g_V(E, T)[1 - f(E, E_F, T)] \, dE + \int g_D(E, T) f_H^+(E, E_F, T) \, dE \tag{3}$$

where g_c, g_V and g_D are the densities of states (DOS) for the conduction, the valence and the defect bands respectively, f is the Fermi function and f_H^- and f_H^+ are the distribution functions for correlated states as given by Okamoto *et al* [20]. According to equation (3), the Fermi level can be temperature dependent because:

(i) f and f_H are temperature dependent: that is what is called the 'statistical shift' of the Fermi level. The magnitude of this statistical shift evidently depends on the precise shape of g_c, g_D and g_V (see [9] and [12] for examples);

(ii) g_c, g_D and g_V can be temperature dependent if thermal-equilibrium processes are present in the samples (for example [15], [21], [22]).

Therefore, a kink will appear if there is a (sudden) change in the magnitude of the statistical shift of E_F or a change in the temperature dependence of the density of states.

In a previous paper [12] we investigated both possibilities, the conclusion being that, although a contribution to the kink from the statistical shift of E_F cannot be totally excluded, the observations suggest that thermal-equilibrium processes provide a more natural and preferable explanation. We shall now go back to experimental results of section 2 and demonstrate that the kink is caused by the freezing of the sample in a non-equilibrium configuration.

We first address the upper curve of figure 1. At high temperatures ($T > 135\,°C$) the sample is allowed to equilibrate and then two factors contribute to the shape of the conductivity plot: the statistical shift, of course, but also the temperature dependence of the DOS. These two contributions lead to a slight curvature in the Arrhenius plot for $T > 135\,°C$. For low temperatures ($T < 135\,°C$) the statistical shift is always present but the DOS is *frozen* because the time needed to reach equilibrium is much longer than that allowed by the standard slow cool. There is then a sudden change in the temperature dependence of the DOS at $T = 135\,°C$: this is the very temperature at which the kink is found.

For the lower curve (the 'standard' slow cool) the same reasoning applies. There are, however, two minor differences. First, T_k is higher than for the upper curve because the cooling rate is much higher, leading to freezing at a temperature at which the relaxation time τ is shorter. (As a rule of thumb, the sample freezes for a temperature such as: $\tau(T) \simeq 1\,°C/V$ where V is the cooling rate.) Second, this 'standard' kink is less localized than that at $130\,°C$ because here the transition (allowed to equilibrate)–(frozen) is more gradual (slow cool at a *constant* rate).

We have shown that thermal-equilibrium processes can provide an accurate explanation of the kinks observed. Furthermore, it is clear that a statistical shift explanation of the kink must be abandoned since it would predict a single T_k, regardless of the way in which the sample is cooled.

It could be argued that the different cooling rates lead to different DOS (the freezing T is different) and then to different magnitudes of statistical shift, thus explaining the shift of T_k. However, the changes in the DOS are really very small [15] and cannot account for a $40\,°C$ shift in T_k. Moreover it would be an incredible coincidence if the T_k of the upper curve equalled the last temperature at which the sample was allowed to equilibrate! Before concluding, we would like to add a remark about the magnitude of the statistical shift for $T < 130\,°C$ (the straight part of the plots). A linear Arrhenius plot for σ means, according to equation (1), a linear $E_c - E_F$ temperature dependence:

$$(E_c - E_F)(T) = (E_c - E_F)(0) - \gamma kT. \tag{4}$$

Equations (1) and (4) immediately lead to

$$\sigma(T) = \sigma_0^* \exp(-E_a/kT) \tag{5}$$

where $E_a = (E_c - E_F)(0)$ is the temperature independent activation energy and

$$\sigma_0^* = \sigma_0 \exp(\gamma) \tag{6}$$

is the *measured* pre-exponential factor. Now γ includes the red shift of the gap ($\gamma_1/2$) and the statistical shift of $E_F(\gamma_2)$ (recall that the DOS is frozen):

$$\gamma = \gamma_1/2 + \gamma_2.$$

Taking $\sigma_0 = 100\,S\,cm^{-1}$ and $\gamma_1 \simeq 5.5$, we get

$$\gamma_2 \simeq 0.2 \qquad \text{for the upper curve } (\sigma_0^* \simeq 2000\,S\,cm^{-1})$$

$$\gamma_2 \simeq 0.5 \qquad \text{for the lower curve } (\sigma_0^* \simeq 2700\,S\,cm^{-1}).$$

These values lead to two remarks: first we check that the statistical shift of E_F is not dramatically changed by the different cooling rates; second, these low γ_2 values agree

with earlier calculations and experiments [12, 18] which stated that, at low temperatures, the statistical shift of E_F is very weak.

4. Conclusion

A careful analysis of new experimental data has allowed us to demonstrate that the kink in the conductivity Arrhenius plots of undoped a-Si:H is due to thermal-equilibrium processes. More precisely, it has been shown that the kink temperature corresponds to the temperature at which the sample is 'frozen', that is the time needed to reach equilibrium becomes longer than that allowed by the experimental conditions. T_k can then be varied by changing the cooling rates, which clearly invalidates any statistical-shift explanation of the kink. It would now be interesting to extend our 'freezing' explanation of the kink to other materials like alloys. From consideration of the correlation between the kink curvature and the change in conductivity after a quench [12], it is likely that a-Si:C [23] and a-Si:Ge [24] kinks could be explained by the same freezing arguments.

Acknowledgment

References

[1] Beyer W, Mell H and Overhof H 1977 *Proc. 7th Int. Conf. on Amorphous and Liquid Semiconductors (Edinburgh, 1977)* ed W E Spear (Edinburgh: University of Edinburgh–CICL) p 328
[2] Spear W E, Allan D, Le Comber P and Ghaith A 1980 *J. Non-Cryst. Solids* **35/36** 357
[3] Yang S H and Lee C 1983 *Solid State Commun.* **45** 591
[4] Overhof H and Beyer W 1983 *Phil. Mag.* B **47** 377
[5] Overhof H and Beyer W 1981 *Phys. Status Solidi* b **107** 207
[6] Yoon B G, Lee C and Jang J 1986 *J. Appl. Phys.* **60** (2) 673
[7] Overhof H 1987 *Disordered Semiconductors* ed M A Kastner, G A Thomas and S R Ovshinsky, p 713
[8] Overhof H 1987 *J. Non-Cryst. Solids* **97/98** 539
[9] Overhof H and Thomas P 1989 *Electronic Transport in Hydrogenated Amorphous Semiconductors (Springer Tracts in Modern Physics 114)* (Berlin: Springer) p 143
[10] Kakalios J and Street R A 1986 *Phys. Rev.* B **34** 6014
[11] Street R A, Kakalios J, Tsai C C and Hayes T M 1987 *Phys. Rev.* B **35** 1316
[12] Jensen P, Meaudre R and Meaudre M 1990 *J. Phys.: Condens. Matter* **2** 4785
[13] Roca i Cabarrocas P, Equer B, Huc J, Lhoret A and Schmitt J P M 1987 *Proc. of the 7th Photovoltaic Solar Energy Conference (Sevilla, 1986)* ed A Goetzberger, W Palz and G Willeke (Dordrecht: Reidel) p 533
[14] Meaudre R, Jensen P and Meaudre M 1988 *Phys. Rev.* B **38** 12449
[15] Meaudre M, Jensen P and Meaudre R 1990 *Phil. Mag.* B at press
[16] Meaudre M, Meaudre R and Jensen P 1990 *J. Non-Cryst. Solids* **122** 312
[17] Siebke F, Beyer W, Herion J and Wagner H 1989 *J. Non-Cryst. Solids* **114** 357
[18] Meaudre R, Jensen P, Meaudre M and Godet C 1989 *J. Non-Cryst. Solids* **114** 360
[19] Weiser G and Mell H 1989 *J. Non-Cryst. Solids* **114** 298
[20] Okamoto H and Hamakawa Y 1977 *Solid State Commun.* **24** 23
[21] Smith Z E, Aljishi S, Slobodin D, Chu V, Wagner S, Lenahan P M, Arya R R and Bennett M S 1986 *Phys. Rev. Lett.* **57** 2450
[22] Street R A and Winer K 1989 *Phys. Rev.* B **40** 6236
[23] Xu X, Okumura A, Morimoto A, Kumeda M and Shimizu T 1988 *Phys. Rev.* B **38** 8371
[24] Meaudre R, Meaudre M, Chanel J and Jensen P 1990 *J. Non-Cryst. Solids* at press