TRANSPORT PROPERTIES OF COMPENSATED a-Si FILMS
W. Beyer, H. Mell, H. Overhof

To cite this version:
W. Beyer, H. Mell, H. Overhof. TRANSPORT PROPERTIES OF COMPENSATED a-Si FILMS. Journal de Physique Colloques, 1981, 42 (C4), pp.C4-103-C4-106. <10.1051/jphyscol:1981418>. <jpa-00220805>

HAL Id: jpa-00220805
https://hal.archives-ouvertes.fr/jpa-00220805
Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
TRANSPORT PROPERTIES OF COMPENSATED a-Si FILMS

W. Beyer, H. Mehl* and H. Overhof**

IGF, Kernforschungsanlage Jülich, D-517 Jülich, F.R.G.
* Fachbereich Physik, Univ. Marburg, D-355 Marburg, F.R.G.
** Fachbereich Physik, Univ. Paderborn, D-4700 Paderborn, F.R.G.

Abstract.- The temperature dependence of conductivity and thermopower has been measured for a series of compensated a-Si:H films prepared by glow-discharge decomposition of SiH₄-PH₃-B₂H₆ mixtures. The discussion of the data in terms of current transport models points to extended states conduction with weak fluctuations of the mobility edges due to inhomogeneities. For boron doping levels [B₂H₆] ≥ 100 ppm a perceptible contribution of hopping conduction near Eᵥ is likely to be present. The electronic transport gap is found to be 2.174 eV, and the conductivity prefactors σ₀ for electrons and holes are inferred to be equal within a factor of two.

Introduction.- Although the electronic transport properties of both n- and p-type amorphous silicon films have been studied rather extensively (1-3) the knowledge of parameters which involve both sides of the electronic gap, like the width of the transport gap or the ratio of electron and hole mobilities in the bands is still rather limited. Information on such parameters is expected from the investigation of compensated films where due to the addition of acceptors and donors the Fermi level can be held close to midgap, so that both electrons and holes contribute to the electronic transport. Furthermore, the investigation of compensated a-Si films allows the study of transport parameters as a function of dopant concentration without moving the Fermi level considerably. A discrimination between different mechanisms proposed for the electronic transport in a-Si may thus be possible.

In this article we present conductivity and thermopower data from two compensated systems where the transition from n- to p-type conduction was monitored. In system A, the boron concentration during the glow-discharge deposition process was kept constant at [B₂H₆] = 1000 ppm and the phosphine concentration was varied from 0 to 3000 ppm. In system B, the phosphorus concentration is fixed at [PH₃] = 1000 ppm and the boron content varies.

Experimental.- The a-Si:H films were prepared in an inductively coupled glow-discharge apparatus at an rf power of ≤ 5 W, a pressure of 0.4 mbar and a flow rate of 6 sccm. The deposition rate was ≈1.5 Å/s at a substrate temperature of 300°C. Substrate material was fused silica and sapphire. In order to increase the accuracy of the thermopower measurements, each data point was determined by a least square fit using about 10 values of thermovoltage AV and temperature gradient AT, taken at a given average temperature.

Results and Discussion.- The experimental results for a series of films belonging to system A are shown in Fig.1. Plotted is the conductivity σ (Fig.1a) and the thermopower S (Fig.1b) as a function of reciprocal temperature. Up to 700 ppm PH₃ (curves 1-3) the films are p-type. The conductivity at 300K decreases with increasing PH₃-concentration from σ ≈ 10⁻⁶(Ωcm)⁻¹ for 3 ppm PH₃ to below 10⁻⁸(Ωcm)⁻¹ for 700 ppm. Simultaneously, the positive thermopower increases. Between 700 and 1000 ppm PH₃ the dominant contribution to σ changes from holes to electrons. With further increase of the PH₃-concentration (curves 4-6) the conductivity increases again, and slope as well as absolute value of the negative thermopower decrease. The maximum activation
energy of the conductivity observed in this system is $E_\sigma \approx 0.8$ eV at 500K (curve 4). According to the thermopower, however, even for this sample single-band conduction prevails since in case of ambipolar transport $S$ should be close to zero.

For single-band transport, a plot of $Q = \ln\sigma |(e/k)S|$ versus $1/T$ yields meaningful information on the transport process since this quantity is independent of the position of the Fermi level. In Fig. 2, $Q$ is plotted as a function of $1/T$ for the films shown in Fig. 1. Except for the film doped with $[\text{PH}_3] = 1000$ ppm, where the results indicate a slight contribution of holes to the predominant electron transport, all data points can be fitted by a single line: $Q = Q_0 - E/kT$ with $Q_0 \approx 11$ and $E \approx 0.2$ eV. This value of $E_\sigma$ is approximately by a factor of two larger than for undoped and phosphorus-doped films ($[\text{PH}_3] \leq 1000$ ppm) (5). As is shown in Fig. 3, where $E_\sigma$ is plotted as a function of dopant concentration for both systems A and B, $E_\sigma$ clearly depends on the boron concentration but is almost independent of the phosphorus content (5). The experimental results point to $E_\sigma \approx 0.1$ eV for low boron concentrations ($\leq 100$ ppm) and $E_\sigma \approx 0.2$ eV for high boron contents ($\geq 1000$ ppm) independent of whether the charge transport is dominated by electrons or holes. The insensitivity of $Q$ in system A of doping (Fig. 2) shows that conduction in impurity bands (2) does not contribute significantly to the transport. Hence, the slope $E_\sigma$ cannot be interpreted as a hopping energy. A mixed conduction process in extended states and in an impurity band can also be excluded since in this case a step-like temperature dependence of $Q(T)$ is expected which we do not observe.

In the following, we discuss three physically plausible models which can account for a non-zero $E_\sigma$ rising with increasing boron concentration.

a) $E_\sigma$ is caused entirely by long-range fluctuations of the mobility edges. These fluctuations may be due to spatial variations in the composition of the films as well as to inhomogeneously distributed charges. A random distribution of charges, discussed in a previous paper (6), solely cannot account for the effects observed since the concentration of charged centers should be independent of the type of dopant. A possible explanation for the increase of potential fluctu-
ations upon boron-doping could come from our hydrogen evolution data (7). These, namely, provide evidence for the presence of microstructural inhomogeneities in boron-doped a-Si:H films, in contrast to phosphorus-doped and undoped samples.

b) $E_Q$ is caused, at least in part, by a non-zero slope of the density of states distribution $g(E)$ above the mobility edges. In this case, the kinetic term $A$ of the thermopower becomes larger than unity and temperature dependent. The Kubo-Greenwood formalism (4) yields $E_Q = (A-1)kT + kT^2(\partial g/\partial E)$ and, if $g(E) = g_0 + g^*kT$ and $\mu(E) = \text{const.}$ is assumed, $A = 1 + g^*kT/(g^*kT + g_0)$. The experimental result of an equal increase of $E_Q$ (i.e. A) for electrons and holes with increasing boron concentration could be related to our finding (7) that boron-doped films evolve considerable amounts of hydrogen already during deposition. This may cause additional disorder resulting in tailing effects at the mobility edges. It appears unlikely, however, that $E_Q$ is caused entirely by this effect since the constant $E_Q$ as a function of temperature and phosphorus doping level (system A; Fig.2) would require a rather specific $g(E)$ beyond the mobility edges, independent of doping. A separation of $E_Q$ into terms due to potential fluctuations and due to $A>1$ may be accomplished by a plot of $E_Q - eST$ as a function of temperature. If the influence of potential fluctuations can be described in terms of a formally activated mobility $\mu = (\mu_0/kT) \exp(-E_{EF}/kT)$ the Kubo-Greenwood formalism, if applicable, yields (4)

$$E_Q - |eST| = E_{\mu} - (\delta e^2kT).$$

Here, the shift of the Fermi level $E_{\mu}$ with respect to the local mobility edge is taken to be $(E_C - E_F) = (E_G - E_F) + \delta T$. $E_Q$ becomes:

$$E_Q = E_{\mu} + f(A>1).$$

Analyzing our data by means of eqn. (1), we obtain for $E_Q$ the values shown also in Fig.3. Although this analysis is rather crude involving the differentiation of the conductivity data and an extrapolation to $T=0$, the result of $E_Q \approx 0.1$ eV almost independent of doping appears physically not unreasonable. The number of charged donor and acceptor centers in the compensated systems is almost constant. The increase of $E_Q$ upon boron doping, according to this analysis, could be due to an increase in the kinetic thermopower term $A$, i.e. to tailing effects at both band edges.

c) $E_Q$ is caused in part by a hopping contribution at or near the Fermi level. This conduction path has a small thermopower and a weaker temperature dependence of $\sigma$ than band transport. For phosphorus-doped films we have observed $E_Q \approx 0.1$ eV over a temperature range of 500K (8) which shows that the major part of $E_Q$ cannot be explained in this way and which points rather to long-range potential fluctuations (6). For boron-doped samples, on the other hand, the $\sigma$ versus $1/T$ curves exhibit a kink for $[B_2H_6] = 1000$ ppm (8). Model calculations assuming $\sigma = \sigma_0 \exp(-T_0/T)^{1/4}$ with $T_0 = 10^5$K and using $\sigma_0$ as a free parameter, show that this kink disappears if a proper value of $\sigma_0$ is assumed. At the same time, $E_Q$ is reduced by $\approx 0.05$ eV in system A. In system B, a similar change of $E_Q$ is found for high boron concentrations while there is no indication for a hopping path for samples doped by phosphorus only.

A discrimination between models (a)-(c) can possibly be obtained from the determination of the width of the transport gap. In Fig.4a,b the conductivity and the Peltier heat $eST$ are plotted as a function of $1/T$ and $T$, respectively, for a series of films from system B with $E_Q$ close to midgap. For $[B_2H_6] = 1200$ ppm, one of the four films investigated shows $eST = 0$ over a range of 150K, implying that electrons and holes contribute equally to the electronic transport, i.e. the Fermi level lies at midgap $E_F$. The conductivity of this film has an activation energy $E_{\sigma} \approx 0.87$ eV at 300K, corresponding to a transport gap (extrapolated to $T=0$) of

$$E_{g,0} = 1.74 \text{ eV}.$$  

The optical absorption of our films indicates a gap $E_{opt} = 1.58$ eV at 300K inferred from a Tauc-plot. Using a temperature coefficient of the optical gap, $\gamma = -4.3 \times 10^{-4}$ eV/K (3), and extrapolating to $T=0$, we obtain
which agrees excellently with $E_{\text{tr}}$. Yet, according to Mott and Davis, $E_{\text{opt}}$ does not give the mobility gap but rather the distance between the valence band edge $E_v$ and the conduction band mobility edge $E_c$. Since $(E_v - E_c) \sim 0.2$ eV (2), the optical results indicate a mobility gap of

$$(E_v - E_c) = 1.90 \text{ eV},$$

i.e. larger than $E_{\text{tr}}$. This result is at variance with $g_{\text{opt}}$, models (a) and (b) according to which

$$E_{\text{tr}} > (E_v - E_c)$$

is expected. In model (c), on the other hand, $E_v$ is slightly reduced by a contribution of hopping conduction, so the transport gap is underestimated by the relation $E_{g_{\text{opt}}} = 2E_v$ or $E_M$ and

$$2E_v (E_v - E_{g_{\text{opt}}}) < (E_v - E_c)$$

is easily understood.

Apart from the information on the width of the transport gap, the results of Fig. 4 also show that the conductivity prefactors of electrons, $\sigma_e$, and holes, $\sigma_h$, are equal within a factor of two. This is demonstrated in Fig. 5 where the thermopower data of Fig. 4 are fitted by a model of ambipolar transport in extended states with $E_v = 0.1$ eV and $A = 1$ for both electrons and holes, using $E_{g_{\text{opt}}} = E_F - E_{g_{\text{opt}}}$ as a correlation between electron and hole conductivity activation energies. In Fig. 5a, $\sigma_e / \sigma_h = 1$ gives a surprisingly good agreement with the experimental data whereas for $\sigma_e / \sigma_h = 2$ (Fig. 5b) the fit becomes rather unsatisfactory. We note that equal prefactors for electron and hole conductivities are in agreement with the concept of extended states conduction (1).

References.

(4) BEYER, W., OVERHOF, H., Solid State Comm. 31 (1979) 1.