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THE INFLUENCE OF STRUCTURAL INHOMOGENEITY ON THE CONDUCTION BAND TRANSPORT IN a-Si:H ALLOYS

D. A. Anderson† and William Paul

Division of Applied Sciences, Gordon McKay Laboratory
Harvard University
Cambridge, Massachusetts 02138
U.S.A.

We present new data on conductivity and thermopower for rf sputtered a-Si:H having low gap state density and low H-content. The band transport is characterized by $E_s = E_\sigma$, $\sigma_o \sim 5 \times 10^3 \Omega^{-1}\mathrm{cm}^{-1}$, $S_o = -kA/|e| = 0$ mV/K and no high temperature kinks. Data showing $E_s < E_\sigma$, $S_o \sim -0.5$ mV/K and kinks in both σ and S are interpreted in terms of a two-phase model of a-Si:H islands with a H-rich connective tissue. The implications of the large value of σ_o in both types of sample are also considered.

I. Introduction

Transport measurements on a-Si:H, howsoever prepared, have always been interpreted assuming the material is structurally homogeneous although disordered. This has occurred despite evidence of structural inhomogeneity in early studies of evaporated unhydrogenated material, and despite common knowledge that many films nucleated and grew in a manner leading to gross and easily observable inhomogeneities. Recently, Knights and Lujan [1] have pointed out that many films produced by glow discharge possess microstructure on a scale of about 100 Å which is even observable as columns stretching over 1 micron from substrate interface to the free surface. They have also attempted to identify the chemical and structural differences between the columnar material and the intercolumnar tissue, and to correlate these with differences in measured properties. However, the full implications of heterogeneity for the interpretation of transport data have not been explored.

There is an impressive agreement of published experimental results on transport in a-Si:H films prepared under a wide variety of conditions, suggesting that several observations which, at first sight, seem not to accord with current theory are not artifacts of the preparation method or the measurement procedure. Attempts to explain these observations have met with only limited success under rather strained assumptions and only when a subset of the totality of results is considered.

In Section II we survey the principal experimental results which appear to be general, and present pertinent new data. In Section III we suggest that most films studied are structurally inhomogeneous and examine to what extent a model based on film heterogeneity can account for apparent anomalies.

II. Theory of Diffusive Transport and the Experimental Results

We confine our attention to temperatures T where the experimental conductivity σ and thermopower S may be described by

$$\sigma = \sigma_o \exp[-E_\sigma/kT] \quad \text{and} \quad S = [E_s/eT] + S_o \quad . \tag{1}$$

The transport is assumed to occur in a conduction band of delocalized states of density N, independent of energy above E_c. If we suppose that the Fermi level E_f displaces linearly with T as $E_c - E_f = (E_c - E_f)_o + \gamma T$, and that the mobility μ and thermopower S are given by formulae for diffusive transport derived in the random phase approximation [2], then the theoretical σ and S may be written as

$$\sigma = ne\mu = ne(a/kT) = eNa\exp(-\gamma/k)\exp[-(E_c - E_f)_o/kT] \quad , \tag{2}$$

$$S = (k/e)\,[\{(E_c - E_f)/kT\} + A] = [(E_c - E_f)_o/eT] + (Ak/e) \quad . \tag{3}$$

Here a is a T-independent constant, $A \approx 1$, and we identify E_σ and E_s with $(E_c - E_f)_o$, σ_o with $eNa\exp(-\gamma/k)$ and S_o with (Ak/e). For $N = 10^{21} eV^{-1}\text{-}cm^{-3}$, T = 300 K, and plausible choices of other parameters, we calculate $\mu \approx 10\ cm^2\text{-}V^{-1}\text{-}s^{-1}$, $S_o \approx 0.1\ (mV\text{-}K^{-1})$ and $\sigma_o \approx 40 \exp(-\gamma/k)(ohm\text{-}cm)^{-1}$.

Figure (1) shows our typical data for σ and S for undoped a-Si:H of high H-content (>10 at.%), prepared at low substrate temperatures T_s (200°C), and partial pressures p_H greater than 1 mTorr (Samples Type α). We exclude consideration for the moment of the data below $10^3/T = 2.2$ ($T \geq 440$ K) and all data on doped material. Extrapolation of the data to $1/T = 0$ gives $\sigma_o = 5.6 \times 10^3 (ohm\text{-}cm)^{-1}$ and $S_o = -0.59\ mV\ \text{-}K^{-1}$. These values of σ_o and S_o characterize our samples thus-prepared and, significantly, are also typical of those for glow-discharge produced material.

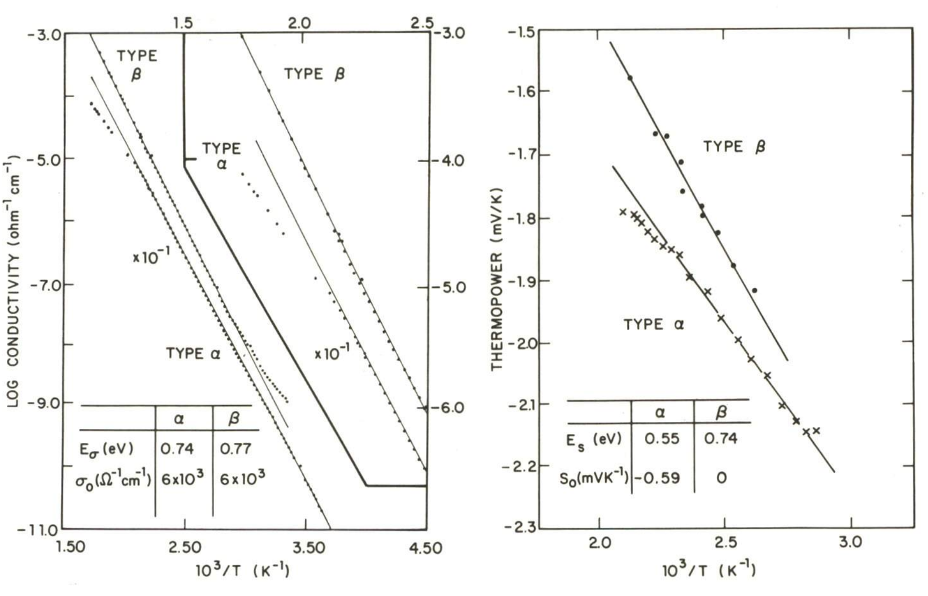

Figure 1 σ and S data for Sample Type α (large c_H) and Type β (small c_H). In the expanded high T region of the inset, the data for Type α show a clear kink not present for those of Type β

The disagreements between theory and experiment may now be identified. (1) Since $\sigma_o(exp) = 6 \times 10^3 (ohm\text{-}cm)^{-1} = 40 \exp(-\gamma/k)$, a high value of $\gamma = -4.3 \times 10^{-4} eV\ \text{-}K^{-1}$ is required to reconcile theory with experiment. While there are insufficient data to discount this value, it appears implausible that it should be consistently high in many sample preparations. (2) Figure (1) and other reports in the literature yield $E_\sigma - E_s$ finite, between 0.1 and 0.2 eV. (3) Figures (1) and (2) illustrate clearly a decrease in the slopes of σ vs 1/T and S vs 1/T for $10^3/T \leq 2.2\ K^{-1}$. Similar data have been reported earlier on sputtered a-Ge:H and SiH_4-derived a-Si:H [3]. These kinks, always observed for Samples Type α, the high values of σ_o and S_o, and the finite $E_\sigma - E_s$ are therefore real properties of many samples, independent of measurement system, electrode geometry or material, method of preparation or laboratory of origin.

The detailed deposition parameters, as much as the final H-content, determine the transport in all a-Si:H. We now discuss a new regime of our preparation not previously reported. Type β films have low H-content (3-10 at.%), and are prepared at low p_H and high T_s ($\geq$ 300°C). <u>All</u> Type β samples, with typical results illustrated in Fig.(1), have σ_o consistently near $5 \times 10^3 (ohm\text{-}cm)^{-1}$, $S_o \approx 0\ mV\ \text{-}K^{-1}$, and $E_s = E_\sigma$ within experimental error. The simplest interpretation is that the transport is single-band, with no activation energy for mobility, and $A \approx 1$ as predicted by all simple transport mechanisms. Because of the similarities in σ_o and E_σ for Sample Type β and Sample Type α below the kink, we identify the transport in Type α for $10^3/T \geq 2.2$ as band transport also.

III. Discussion of Structural Inhomogeneity

We now focus on the likelihood that many a-Si:H films are structurally inhomogeneous on a scale of ~100 Å. When T_s is high (~350°C) and p_H is low (< 1 mTorr), isolated H atoms are postulated to compensate dangling Si bonds and reduce the incidence of long Si-Si bonds. These compensating effects dominate the potential for the increased defect production when the network is forced to grow around the growth termination at a Si-H site. Thus, the film nucleates and grows in islands which successfully knit together with a minimum volume of defected connective tissue. However, when p_H is increased beyond 1 mTorr at any T, the increased creation of network defects near Si-H sites and the increased concentration of multiply bonded SiH_x complexes makes it difficult for growing nuclei to coalesce. The result is essentially a second phase of highly defected, probably H-rich connective tissue with, importantly, a different band structure and conductivity. This model clearly resembles Knights' work [1] on the growth morphology of silane-derived a-Si:H prepared at different T_s. Although we have no evidence from S.E.M. measurements on Type α and β films of columnar growth, we believe the existence of two interlinked phases to be very likely, and have analyzed the changes in transport with p_H on this basis [4]. Here we focus discussion on the anomalies already described.

We refer for convenience to the island material as phase 1 and the connective tissue as phase 2. It seems reasonable that the transport in both is activated, with a different activation energy; guided by experiment, we suppose phase 2 to have the lower activation energy, but that $|\sigma_1| \approx |\sigma_2|$ near $(10^3/T) = 2.2$. For a heterogeneous mixture of the two phases, with neither forming a continuous channel between the electrodes, the conductance will be governed by the phase of <u>lower</u> conductivity, and measured σ vs 1/T with <u>downward</u> kinks like those of Fig.(1) will eventuate. Of course, the relative volumes of the two phases matter, but the rapid variations of σ_1 and σ_2 with T probably ensure that the kinks in σ vs 1/T will all occur near the same T. Although we expect this model for σ to be borne out by percolation calculations, it is not clear what the behavior of S will be. We suppose that the far smaller range in magnitude of S with 1/T means that both phases contribute to S(measured), and that this both reduces the apparent slope E_s and increases the extrapolated $|S_o|$.

We conclude that the data for $10^3/T > 2.2$ in Figs.(1) and (2) represent transport in the conduction band of a-Si. The linear log σ vs 1/T over six orders of magnitude, the equality of E_σ and E_s and the magnitude of σ_o of 5×10^3(ohm-cm)$^{-1}$ all suggest band transport with no mobility activation energy at a sharp density of states edge and no contribution from tail-state hopping. The deduced value of mobility (order of $10^2 cm^2\text{-}V^{-1}\text{-}S^{-1}$) is high even when a plausible value for γ is chosen, and is more appropriate for quasi-free particle motion with occasional scattering than for transport at a mobility edge. Additional experimental and theoretical work is required to reconcile this conclusion with the absence of a Hall effect in undoped homogeneous samples at high T [4].

In summary, many of the apparent anomalies in the transport data for tetrahedral amorphous solids may be accounted for by considering the effects of film inhomogeneity. Clearly a more quantitative test of our model is necessary, and an attempt to correlate directly the observation of kinks in the transport with the existence of microstructure is now underway.

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References

† Present address: R. S. R. E., Malvern, Worcs., U. K.

1) J.C. Knights and R.A. Lujan: Appl. Phys. Lett. 35 (1979) 244.

2) We have followed D. Emin, Solid State Commun. 22 (1977) 409 in omitting a term (γ/e) from the final formula of eq.(3). Inclusion of it would, in fact, strengthen the arguments of this paper.

3) (Ge) A.J. Lewis: Phys. Rev. B 14 (1976) 658; (Si) W.E. Spear, D. Allan, P. LeComber and A. Ghaith: J. Non-Cryst. Solids 35-36 (1980) 357.

4) Unpublished work from this laboratory.