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Thermopower and conductivity activation energies in hydrogenated amorphous silicon

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Measurements of the dark conductivity activation energy are compared to that of the thermoelectric effect measured in both open-circuit and short-circuit conditions for doped hydrogenated amorphous silicon. The activation energy of the thermopower is much less than that obtained from the conductance measurements. However, the short-circuit Seebeck-current activation energy agrees exactly with the conductivity activation energy, consistent with the difference in activation energies between conductivity and thermopower arising from long-ranged disorder at the mobility edges. [S0163-1829(96)06535-6]

Despite the loss of long-range order, the transport properties in amorphous semiconductors are fairly similar to those in crystalline semiconductors. However, one striking exception, first observed nearly 20 years ago, is the disagreement between the separation of the mobility edge (E_c for electrons and E_v for holes) and the Fermi energy E_F when measured from the dark conductivity σ and thermopower S. The activation energy ($E_c - E_F$ or $E_F - E_v$) from the dark conductivity E_σ is larger than that of the thermopower E_S by as much as several hundred meV for a wide range of noncrystalline semiconductors, including n-type, p-type, compensated, and lithium implanted hydrogenated amorphous silicon (a-Si:H), amorphous germanium synthesized by both sputtering and glow-discharge deposition techniques, melt-quenched chalcogenide glasses and amorphous alloys of silicon and carbon.[1–4] Several models attempting to explain the difference of E_σ and E_S have been proposed, including polaron transport,[5] charge hopping through localized bandtail states,[6] and two conduction path models.[2,7,8] To account for the similar activation energy differences seen experimentally in rigid tetrahedrally bonded materials like a-Si:H and softer materials like melt-quenched chalcogenide glasses, the polaron transport model requires that the electron-phonon coupling in these different materials be comparable, which is not supported by luminescence data. Hopping through localized bandtail states and two conduction channel models predict a nonlinear temperature dependence for the difference between S and $\ln\sigma$, which is not observed experimentally. These models, therefore, cannot account for the activation energy difference over the wide temperature range for the broad class of disordered materials studied. The model most often invoked to account for the activation energies of conductivity and thermopower attributes their difference to the presence of slowly varying, long-ranged potential fluctuations at the mobility edge.[4,9–11] This paper reports experimental measurements of the conductivity and Seebeck current for doped a-Si:H films which support this model.

Long-ranged potential or compositional fluctuations at the mobility edge, of magnitude several 100 meV and extending over length scales of 10^3–10^4 Å, are believed to arise from the heterogeneous nature of the a-Si:H films.[12] Structural heterogeneities resulting from the nonuniform distribution of hydrogen[13] and any alloying component will cause local variations of the band gap throughout the film. Moreover, the presence of charged dopants and defect centers which are not fully screened by free charges will give rise to Coulombic potential fluctuations at the mobility edge which will be superimposed on the fluctuations of the band gap. Hence even though the Fermi energy is uniform throughout the film, the conductivity can vary locally, which suggests that transport in a-Si:H near the mobility edge may be best described by a percolation process.[14]

In fact, there has been growing evidence that electronic transport in a-Si:H occurs, at least in part, through inhomogeneous current filaments arising from long-range structural modulations or potential fluctuations. The observation of random telegraph switching noise in macroscopic a-Si:H films at and above room temperature has been interpreted as arising from local hydrogen motion altering the conductance of current microchannels.[15] The decrease in the drift mobility in n-type a-Si:H with doping concentration has been shown to accompany an increase in the difference between the conductivity and thermopower activation energies.[10] Optical-absorption measurements in a-SiN$_x$:H alloys[16] and differences in the optical and electrical measurements of the band edge in compensated a-Si:H have also relied on similar explanations.[11] An increase in the difference between E_σ and E_S with light induced defect creation (the Staebler-Wronski effect) may indicate that light soaking increases the disorder at the mobility edges in a-Si:H.[17] Consequently a determination of whether this activation energy difference does indeed reflect long-ranged disorder at the mobility edges and to what extent this disorder affects transport are important issues concerning the nature of electronic conduction in amorphous semiconductors.

Assuming a sharp mobility edge without any long-ranged fluctuations, the thermopower S and conductivity σ for n-type a-Si:H are given by

$$\frac{e}{k_B} S = -\left[\frac{E_C - E_F}{k_B T} + A\right]$$

and

$$\sigma = \sigma_0 \exp\left[\frac{-(E_C - E_F)}{k_B T}\right], \tag{1}$$

respectively, where E_C is the abrupt mobility edge and the heat of transport term A is of order unity.[18] Since local en-

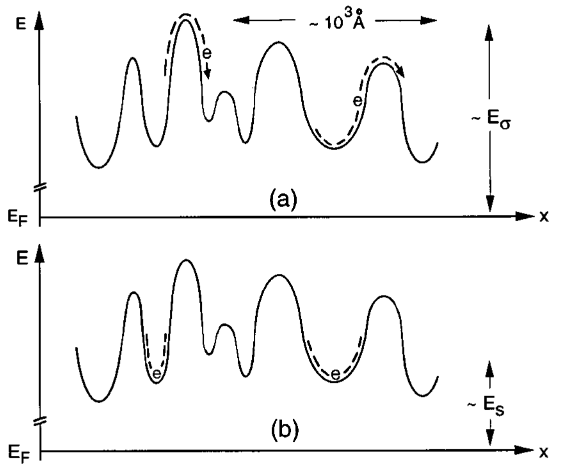

FIG. 1. Sketch of the effect of potential and compositional fluctuations at the conduction-band mobility edge in a conductivity measurement (a) and a thermopower measurement (b). In 1(a) the electrons need to surmount the highest potential barrier in their path while in (b) they come into diffusive equilibrium without necessarily having to overcome the highest potential peak.

ergy variations at the mobility edge are unaccounted for, the activation energies are expected to be equal.

A model for the activation energy difference involving long-ranged fluctuations depends on two complementary factors are argued by Street.[19] Conductivity and thermopower are measured across a macroscopic region of the film, that is over a length scale which is much longer than the average period of the fluctuations at the mobility edge. Hence, the relative weights given to local regions when they are averaged together to give a macroscopic quantity is of crucial importance. Since conductivity and thermopower depend exponentially and linearly, respectively, on $E_C - E_F$, local regions where the potential fluctuations cause a peak act as a ''bottleneck'' and dominate a conductivity measurement, but will contribute more proportionately with other regions in a thermopower measurement.

The other factor that contributes to the difference in the activation energies is that in a conductivity measurement a current necessarily flows across the film, while in a thermopower measurement in an open circuit configuration, no current flows. When the conductivity is measured charge carriers must overcome the highest potential barrier in their path, while this is not necessary in a thermopower measurement. Hence the conductivity activation energy will be the energy difference between the Fermi energy and the energy value of the highest potential peak in the conduction path, as illustrated in Fig. 1(a). Note that it is exactly this local region that is given the heaviest weight by the exponential dependence of the conductivity. On the other hand, as shown in Fig. 1(b), the thermopower activation energy measures the energy difference between the Fermi energy and the mean energy of all the fluctuations along the conduction path. Hence, in this model the activation energy difference is a measure of (though not directly equal to) the amplitude of the fluctuations. In a percolative picture, Fig. 1 would show the energy variations along the least resistive spanning cluster, and the critical energy for conduction is then the energy of the highest potential barrier. In an open circuit (thermopower) measurement, charge carriers move around nearby minima of the potential fluctuations, and do not need to overcome the higher barriers. This continues until a diffusive equilibrium situation is achieved. According to this model,[19] the essential reason for the difference in the activation energies is the passage of a current in the conductivity case, and not in the thermopower case.

The internal thermoelectric voltage generated by a temperature gradient across the film divided by the average temperature of the film gives the thermopower. This thermoelectric voltage can also drive a short circuit current, the Seebeck current, characterized by the Seebeck conductivity σ_s. Normally the conductivity obtained from applying an external voltage is simply called the ''dark conductivity.'' However, since σ_s is also measured in the dark, we will call the ''dark conductivity'' the ''isothermal conductivity'' σ to emphasize the fact that it arises due to the application of an external voltage under nominally uniform temperature conditions, while σ_s is due to an internal bias driven by a temperature gradient. The Seebeck and isothermal conductivities can have different magnitudes since the resistance of the current filaments is temperature dependent. In the model described above, σ_s should have an activation energy comparable to σ. The experimental evidence reported here supports this model and also indicates that the macroscopic conductivity is not highly sensitive to the detailed nature of the current microchannels.

The measurements reported here were made on n-type a-Si:H films with gas-phase doping levels of 10^{-2} and 10^{-5} [PH$_3$]/[SiH$_4$], and p-type a-SiH with 10^{-3} [B$_2$H$_6$]/[SiH$_4$], synthesized in a rf glow-discharge deposition system at Xerox PARC. The films are 1 μm thick and deposited onto Corning 7059 glass at a substrate temperature of 230 °C with an incident rf power of 2 W (electrode area ~50 cm^2). Additional details of the deposition process have been published elsewhere.[20] After deposition of the a-Si:H, coplanar chromium electrodes ~500 Å thick were evaporated onto the films. The chromium and film were then scratched (~0.1 mm wide) with a diamond scribe to yield two regions each having electrodes 1 mm by ~2 mm, with a separation between each electrode of 0.9 mm. These electrodes yield linear current-voltage characteristics for applied voltages in the range ±40 V to less than $\pm 10^{-3}$ V.

The experimental configuration is as follows: two copper blocks with resistive heaters are ~4 mm apart in a shielded vacuum chamber. The sample is mounted across the two heated blocks with the scratch across the sample in a transverse direction in relation to the blocks. Two type T thermocouples, with wire thicknesses of ~0.1 mm measure the temperature of the sample at the chromium electrodes adjacent to each block. The thermoelectric voltage generated when there is a temperature difference across the film is measured with the copper lead from each thermocouple. The two electrodes not involved in the thermopower measurement are used to measure the Seebeck current and the isothermal current (in a different run).

All measurements are taken after the film has been annealed at 470 K for 1 h and then slowly cooled (~1 K/min) to the initial measurement temperature. Thermoelectric voltages and Seebeck currents are measured for temperature dif-

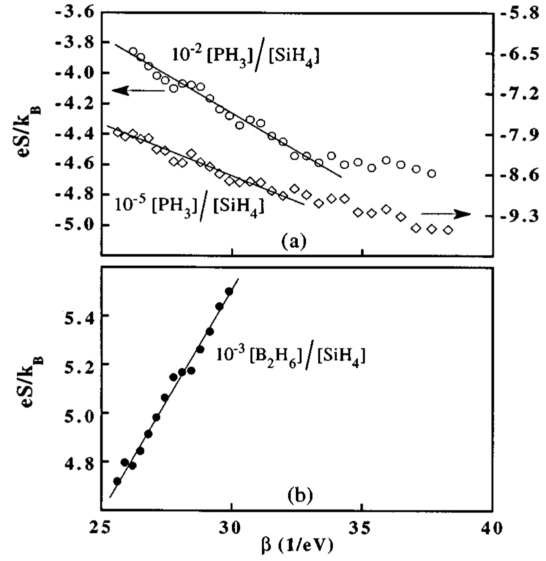

FIG. 2. Thermopower as a function of inverse temperature for a-Si:H doped with (a) 10^4 (○ symbols) and 10 ppm (◇ symbols) PH_3 and (b) a-Si:H doped with 1000 ppm B_2H_6 (symbols).

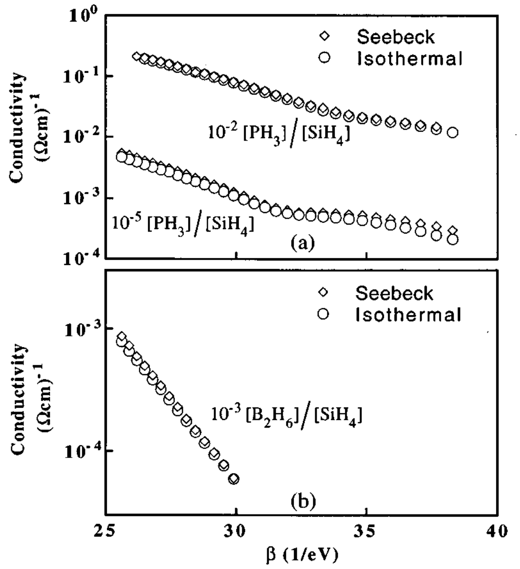

FIG. 3. Seebeck (◇ symbols) and isothermal (○ symbols) conductivities for the a-Si:H films of Fig. 2. The conductivities are equal, with activation energies significantly larger than the thermopower activation energies.

ferences $\Delta T = \pm 6$ K down to ± 1 K, while maintaining a constant average temperature of the film T_{avg}. The thermopower $S(T_{\mathrm{avg}})$ is then obtained by taking the slope of a plot of the thermoelectric voltage against temperature difference, $(\Delta V/\Delta T)_{T_{\mathrm{avg}}}$. The Seebeck conductivity at T_{avg} is given by

$$\sigma_S(T_{\mathrm{avg}}) = g\left(\frac{\Delta I}{\Delta T}\right)_{T_{\mathrm{avg}}} \Bigg/ S(T_{\mathrm{avg}}),$$

where $(\Delta I/\Delta T)_{T_{\mathrm{avg}}}$ is the slope of the plot of Seebeck current against temperature difference and g is a geometrical factor. The isothermal conductance is found in a second run when an external voltage is applied across the film at $\Delta T = 0$ and the resulting current is measured. The Seebeck and isothermal conductivities are obtained by multiplying the corresponding conductance by the same geometrical factor g. The experimental apparatus and measurement procedure are described in detail elsewhere.[4]

Figure 2 shows the thermopower in dimensionless units against reciprocal temperature. The 10^{-2} and 10^{-5} n-type films have high-temperature activation energies $E_S = -0.089$ and -0.16 eV, respectively, while the p-type film has $E_S = +0.18$ eV. Typical error bars for E_S are ~8 meV. The experimental temperature range for the more resistive p-type sample is limited since at lower temperatures the experimental RC time constant does not allow a saturation of the thermoelectric voltage in a reasonable time.

Figure 3 shows σ and σ_s for the n- and p-type a-Si:H films. The change in slopes for the n-type samples at about 80–100 °C indicates the equilibration of the defect structure.[21] The thermopower plot also shows a change of slope at this temperature. The slow rate of cooling after annealing prevents the change of slope to be seen in the p-type sample. The 10^{-2} and 10^{-5} $[PH_3]/[SiH_4]$ n-type films have isothermal conductivity activation energies of 0.29 and 0.34 eV, while the Seebeck conductivity activation energies are 0.28 and 0.35 eV, respectively. The activation energies of σ and σ_s for the p-type sample are 0.60 and 0.62 eV, respectively. Error bars for conductivity activation energies are less than 5 meV. All activation energies cited are measured at high temperature, when the defect structure is in thermal equilibrium, though the agreement between σ and σ_s is also evident in the low temperature ''frozen'' state. In all cases the activation energy of the thermopower is less than one-half that of the isothermal conductivity, while the activation energies for the Seebeck and isothermal conductivities are within 3% of each other. Had the Seebeck conductivity activation energy differed significantly from that of the isothermal conductivity, then a model involving long-ranged fluctuations could not remain a viable explanation for the activation energy difference.

Moreover, the magnitudes of σ and σ_s are identical even though the isothermal current (which is a *drift* current) is more than a factor of 10^3 larger than the Seebeck current (which is *diffusive* in nature), which suggests that in both cases the same states are involved with electronic transport. The agreement of the activation energies of the isothermal and Seebeck conductivities suggests that electronic conduction in amorphous silicon occurs through inhomogeneous current filaments, while the agreement of the magnitudes indicates that these microchannels remain Ohmic for electric fields as low as 0.01 V/cm and thermal gradients of 60 K/cm. In both the isothermal and Seebeck configurations one is measuring the internal bulk resistance of the amorphous silicon film, however the magnitudes of the two conductivities could still differ. For example, it is conceivable that local structural inhomogeneities could create a high resistance region of a current microchannel near one of the electrical contacts. In a Seebeck current measurement this contact can be at a higher temperature than the average temperature of the film, thereby decreasing the resistance of this bottleneck section compared to an isothermal current measurement at the same average temperature. If the high resistance region has a local activation energy of a few tenths of an eV larger than the rest of the filament, then for a thermal gradient of $\Delta T = 6$ K, as used in our experiments, the average resistance will be 15% less than the isothermal resistance, which is certainly within our detection limits. Of course the a-Si:H film will contain a range of high and low resistance regions, in a complex series of parallel and series interconnections, with the most resistive regions not contributing to the average conductance of the film. In the absence of a clear understanding of the microscopic nature of the heterogeneities leading to the filaments, it is nontrivial to determine the averaging procedure under thermal gradient and isothermal conditions.[22]

Disorder at the mobility edge may be due to a combination of both structural and Coulombic potential fluctuations. Assuming that the disorder at the mobility edge arises solely from potential fluctuations, calculations of the magnitude of these variations[10,11,19,23] are significantly less than the experimental values in Figs. 2 and 3, suggesting that fluctuations from structural inhomogeneities must also be considered. Such inhomogeneities are difficult to characterize since they depend sensitively on the microstructure of the films. Nevertheless, general trends may be established, such as alloying a-Si:H should increase the structural disorder. For a series of n-type doped a-SiC$_x$H films with a fixed doping level, but varying carbon content x, we have found a systematic increase in $E_\sigma - E_s$ as the carbon content is increased, reflecting the increasing structural disorder encountered by electrons at the mobility edge.

Finally, we note that long-ranged fluctuations should lead to the coexistence of localized and extended states at the mobility edge, which implies that at $T = 0$ K the differential conductivity $\sigma(E)$ can be both zero and nonzero. However, this is a zero temperature argument, and the relevance of the mobility edge at finite temperatures in the presence of a short (5–10 Å) inelastic scattering length remains open to debate.[24] The experimental results reported here, supporting the influence of long-ranged fluctuations on electronic transport in amorphous semiconductors, would appear to justify a reexamination of the nature of a finite temperature mobility edge.

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