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Thermal properties of *a*-Si:H at low temperatures

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The specific heat and thermal conductivity of bulk samples of *a*-Si:H have been measured in the temperature range 0.1–5 K. A quasilinear temperature dependence of the specific heat and a T^2 thermal conductivity indicates a density of two-level tunneling systems very similar to that in fused silica. A flow of heat from the sample has been observed at low temperatures, with a decay extending over a period of days.

The electrical and optical properties of hydrogenated amorphous silicon have been studied extensively[1] because of the passivating effect of H on the intrinsic gap states of *a*-Si. The thermal properties, on the other hand, have received very little attention, particularly at temperatures below a few kelvins. Low-temperature thermal measurements are important to resolve the question of the existence of two-level atomic tunneling systems (TLS) in tetrahedrally bonded amorphous semiconductors. We report measurements of heat capacity C_p and thermal conductivity κ of plasma-deposited *a*-Si:H in the temperature range 0.1–5 K that reveal a large quasilinear C_p and a roughly T^2 variation of κ. These results for κ are comparable with similar findings[2] in a related material, *a*-Ge, which were attributed to TLS. We show that the present results are not due to unpaired spins[3] at the dangling bonds because of the low number density of spins found in the material. Thus we interpret our data as evidence for a broad spectrum of TLS in a hydrogenated tetrahedrally coordinated amorphous semiconductor, with a density of states which is very similar to that in a typical melt-quenched glass such as fused silica.[4]

We have also observed a flow of heat from the sample to the bath which depends on the thermal history on cooling from 300 K. This slow release of heat does not affect the (transient) heat-capacity measurements.

The samples were prepared by plasma decomposition of silane on an aluminum substrate at an average temperature of 120–180 °C. The plasma was produced from silane with 10 ppm B_2H_6 at an average rf power of 2 W. Irregularly shaped pieces several millimeters in each dimension were obtained by removing them from the supports of the plasma chamber after many runs. The density of spins N_s was measured by ESR to be $4.4\times10^{16}\ \mathrm{cm}^{-3}$. The mass density ρ was 2.00 g/cm^3, i.e., 14% lower than the density of crystalline Si. The concentration of hydrogen as measured by NMR[5] was 17 at.%. The evolution of hydrogen from one 5.7-mg piece was monitored with a mass spectrometer as the sample was heated at the rate of 10 °C/min in a high vacuum. The largest peak occurred at 320 °C, indicating[6] $(\mathrm{SiH}_2)_n$ polysilane material in intercolumnar regions. A second broad peak $\frac{1}{10}$ as large occurred at ~550 °C, indicating bulk SiH and SiH_2. A narrow peak at 630 °C accompanied crystallization. The sample broke into many smaller pieces during the heating process.

A thermal relaxation technique[7] was used to measure C_p with a thin Au wire serving as the thermal link between the calorimeter and a dilution refrigerator. The thermal conductivity was measured with a two-heater one-thermometer technique on a sample roughly in the shape of a circular cylinder of ~2-mm diam and ~4-mm length. Thermal contact to the sample at four places along its length was made by wrapping and gluing several turns of thin Au wire at each location.

The typical cooling procedure from 300 K consisted of a slow cooling (12 h) to ~150 K followed by relatively rapid cooling (2 h) to 4.2 K. On several occasions, however, an extra 24 h was spent cooling to 135 K, resulting in a 10% smaller heat flow from the sample at low temperatures.

Nine pieces of *a*-Si:H totaling 100 mg were used in various combinations in the calorimeter during six separate runs. Typical results for 60 mg are shown in Fig. 1. The heat capacity of the addenda, typically 40% of the *a*-Si:H contribution, has been subtracted from the raw data. A quasilinear regime at the lowest temperatures gradually changes to a T^3 dependence at higher temperatures. The data can be reproduced quite well with the expression

$$C_p = c_1 T^{\alpha} + c_3 T^3 , \tag{1}$$

where

$$\alpha = 1.34 \pm 0.03,\ c_1 = (1.8 \pm 0.1)\times10^{-6}\,\mathrm{J\,K^{-2.34}\,g^{-1}} ,$$

and

$$c_3 = (1.9 \pm 0.1)\times10^{-6}\,\mathrm{J\,K^{-4}\,g^{-1}} .$$

The first term[8] in Eq. (1) is almost identical in magnitude and temperature dependence with that[4] for *a*-SiO_2, for which $\alpha = 1.30$ and $c_1 = 1.5\times10^{-6}\,\mathrm{J\,K^{-2.30}\,g^{-1}}$.

The sample temperature T_S in Fig. 1 did not fall below $T_{\mathrm{min}} \sim 125$ mK even with the refrigerator at ~20 mK. Using this temperature difference and the previously measured temperature-dependent conductance of the thermal link, we calculate a heat flow $\dot{Q}$ of 2.2×10^{-9} W for the 60-mg sample. During one run, $\dot{Q}$ was monitored for four days. $\dot{Q}$ was observed to decrease with time (nonexponentially), requiring ~2 days to reach half of its initial value.[9]

The thermal conductivity of one 15-mg piece of *a*-Si:H is presented in Fig. 2. The κ sample was somewhat better coupled to the refrigerator than the C_p samples were, and the T_{min} is correspondingly lower. We estimate the temperature drop along the sample due to $\dot{Q}$ in the absence of

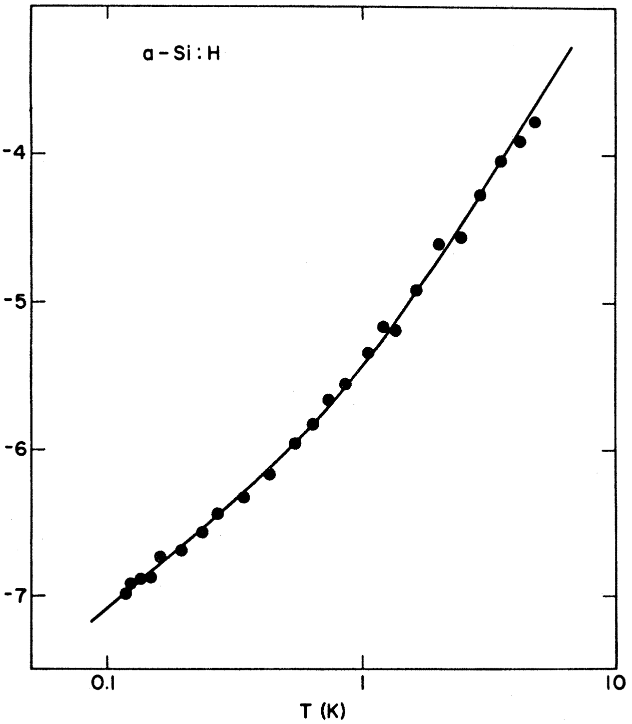

FIG. 1. Heat capacity of bulk a-Si:H. The solid line represents Eq. (1) with parameters given in the text.

applied heat to be ~1 mK at the lowest temperature. The data vary approximately as $T^{1.9}$ below ~1 K and T above. They are similar in magnitude and temperature dependence to κ for a-SiO$_2$ with a less pronounced plateau, at least within our temperature range.

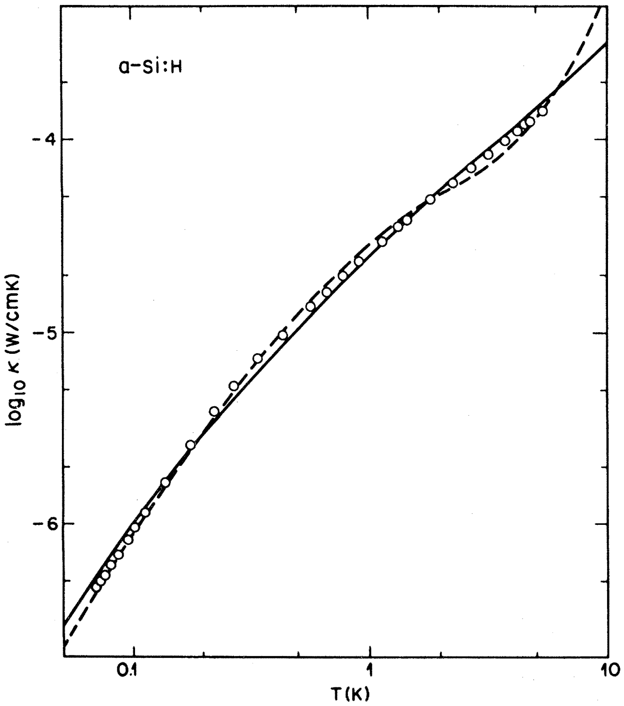

FIG. 2. Thermal conductivity of a-Si:H. The solid and dashed lines represent calculations described in the text.

Considering the small density of free spins in the sample ($< 10^{17}$ cm^{-3}), we argue that the quasilinear specific heat is not due to free spins. The entropy corresponding to the heat capacity, integrated from 0.1–5 K, is 120 ergs/g K. Even if *all* of the N_s spins contributed to the specific heat by being distributed over a band of energy 5 K wide, the available entropy would be only $N_s k_B \ln 2/\rho = 2$ ergs/g K, i.e., a factor of 60 too small to account for the heat capacity.

Because of the similarity between the present results and those of other glasses, we interpret the data in terms of the two-level tunneling theory.[10,11] It is assumed that a glass contains many atoms or groups of atoms that can tunnel between two nearly degenerate configurations. These TLS are widely distributed in energy splittings with a density of states n_0 that is roughly constant in energy, producing a linear heat capacity

$$C_p = \pi^2 k_B^2 n_0 T / 6\rho \ . \tag{2}$$

Most glasses, like the present material, exhibit a superlinear temperature dependence at low temperatures, but if we use $\alpha = 1$ as indicated in Eq. (2), we calculate $n_0 \approx 9 \times 10^{32}$ ergs^{-1}cm^{-3}. This may be compared with a value of 8×10^{32} ergs^{-1}cm^{-3} for a-SiO$_2$.

The inverse scattering length l_t^{-1} due to TLS is related to a scattering strength $\bar{P}M^2$, where $\bar{P}$ is the density of effective scatterers and M their phonon matrix element. An important feature of the tunneling model is a wide distribution in relaxation times, even for TLS of a given energy splitting. n_0 includes all the TLS while $\bar{P}$ includes only the fastest relaxing (most strongly coupled) TLS. $\bar{P}$ thus represents a subset of n_0 with, typically, $\bar{P}/n_0 \sim 0.1$.

To extract a value of $\bar{P}M^2$, we fit the κ data by including[12] two additional scattering mechanisms in the total mean-free path:

$$l = (l_t^{-1} + l_R^{-1})^{-1} + l_m \ . \tag{3}$$

l_R is due to Rayleigh scattering from inhomogeneities and the constant l_m serves as a first approximation to more complicated processes which begin to be important only at our highest temperatures.[2] We use $l_R = B(\hbar\omega/k_B)^{-\mu}$, with $\mu = 2$ or 3, corresponding to planar or cylindrical inhomogeneities, respectively. The plateau above 1 K is not pronounced enough to require $\mu = 4$ (spherical inhomogeneities). The solid (dashed) line in Fig. 2 represents the integration over frequency,[4,13] with $\mu = 2(3)$, $A = 13(8)$ μm K, $B = 7.7$ μm K^2 (18 μm K^3), and $l_m = 1.2 \times 10^{-7}$ (1.6×10^{-6}) cm. Neither $\mu = 2$ nor $\mu = 3$ alone describes the higher-temperature data well. Better agreement can be achieved using a combination of $\mu = 2$ and $\mu = 3$ terms, suggesting a variety of inhomogeneities. From the TLS contribution, which dominates for $T < 0.3$ K, we calculate $\bar{P}M^2 \approx 2 \times 10^8$ ergs cm^{-3} and, assuming $M = 1$ eV, $\bar{P} \approx 0.8 \times 10^{32}$ ergs^{-1}cm^{-3}. Thus $\bar{P}/n_0 \approx 0.1$. These values are all very close to those[4] in a typical glass, a-SiO$_2$.

We suggest several models for TLS in a-Si:H. While the TLS are not directly attributed to spins, they may be associated with tunneling of hydrogen at the dangling bonds. Alternatively, atomic or molecular hydrogen at other sites may constitute TLS.[14] Another possibility, not involving hydrogen, is the type of TLS observed[2] in hydrogen-free a-Ge and associated predominantly with the defect structure because of the correlation of the TLS density of states with the volume fraction of low-density regions. At a density deficit relative to the crystal of 14%, as in the present material, *a*-Ge showed a TLS scattering strength $\bar{P}M^2$ of $\sim 10^8\ \mathrm{ergs\,cm^{-3}}$. This value is only a factor of 2 smaller than what we deduce from the present thermal conductivity.

The data presented here indicate the existence of TLS in a hydrogenated tetrahedrally bonded amorphous semiconductor. Thus we have further evidence that atomic tunneling can indeed take place in materials with nominally tetrahedral bonding.

Note added in proof. Evolution of heat from *a*-Si:H has recently been reported independently by H. v. Löhneysen, H. J. Schink, and W. Beyer, Phys. Rev. Lett. 52, 549 (1984). In addition, J. E. Graebner, B. Golding, L. C. Allen, D. K. Biegelsen, and M. Stutzmann, Phys. Rev. Lett. 52, 553 (1984) have reported a large, time-dependent contribution to C_p in annealed films of *a*-Si:H which they interpret as orientational ordering within clusters of solid H_2. This contribution is not observed in the present measurments on bulk, unannealed *a*-Si:H.

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[7] R. J. Schutz, Rev. Sci. Instrum. 45, 548 (1974).

[8] The T^3 coefficient in the specific heat is a factor of 6.8 times larger in the present material than in pure, crystalline Si. Thus the Debye temperature Θ_D is calculated to be 330 K, which is only 0.52 times the crystalline value of 630 K. By contrast, Θ_D for pure *a*-Ge is 0.84 times the pure crystalline value [see C. N. King, W. A. Phillips, and J. P. deNeufville, Phys. Rev. Lett. 32, 538 (1974), and A. Cruz-Uribe and J. Trefny, in *Amorphous and Liquid Semiconductors,* edited by W. E. Spear (CICL Univ. of Edinburgh, Edinburgh, 1977, p. 175]. The very large reduction in the present case is therefore attributed to the presence of hydrogen in the sample.

[9] To account for the heat released by the *a*-Si:H, we assume that a fraction of the hydrogen is in molecular form and that the heat is due to ortho-para conversion. The dependence on cooling rate is then attributed to the temperature-dependent equilibrium ortho-para population ratio and conversion rate. The time dependence of $\dot{Q}(t)$ at liquid-helium temperatures can be modeled with a bimolecular rate equation. Approximating the initial ortho-para population ratio at low temperatures by its room-temperature value of 3, we obtain a rate constant of $0.010\ \mathrm{h^{-1}}$ and a density of H_2 molecules of $\sim 1.8\times 10^{19}\ \mathrm{cm^{-3}}$, or 0.25% of the hydrogen present in the sample. A similar conversion rate ($0.010\ \mathrm{h^{-1}}$) and fraction of H_2 (up to 700 ppm) have been inferred from NMR measurements in *a*-Si:H films [see W. E. Carlos and P. C. Taylor, Phys. Rev. B 25, 1435 (1982), and Ref. 5].

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[12] J. Jäckle, in *The Physics of Non-Crystalline Solids,* edited by G. H. Frishat (Transtech, Rockport, MA, 1976), p. 568.

[13] The average phonon velocity is calculated from c_3 in Eq. (1) and the density to be 3.6×10^5 cm/sec.

[14] Recent measurements of electron-spin-relaxation times in *a*-Si:H and *a*-Ge:H [M. Stutzmann and D. K. Biegelsen, Phys. Rev. B 28, 6256 (1983)] have been interpreted as being dominated by an interaction with TLS which, however, are not associated with the hydrogen at the dangling bonds.