Thermal Conductivity and Specific Heat of Thin-Film Amorphous Silicon

B. L. Zink,[1,2,*] R. Pietri,[1] and F. Hellman[1,3]

[1]*Department of Physics, University of California, San Diego, La Jolla, California 92093, USA*
[2]*National Institute of Standards and Technology, 325 Broadway MC 817.03, Boulder, Colorado 80305, USA*
[3]*Department of Physics, University of California, Berkeley, California 94720-7300, USA*
(Received 2 September 2005; published 7 February 2006)

We report the thermal conductivity and specific heat of amorphous silicon thin films measured from 5–300 K using silicon-nitride membrane-based microcalorimeters. Above 50 K the thermal conductivity of thin-film amorphous silicon agrees with values previously reported by other authors. However, our data show no plateau, with a low T suppression of the thermal conductivity that suggests that the scattering of long wavelength, low Q vibrations goes as Q^2. The specific heat shows Debye-like behavior below 15 K, with $\theta_D = 487 \pm 5$ K, and is consistent with a very small contribution of tunneling states in amorphous silicon. Above 15 K, the specific heat deviates less from Debye behavior than does its crystalline allotrope, indicating no significant excess modes (boson peak) in amorphous silicon.

The vibrational spectrum of nearly all amorphous solids contains low-energy excitations which below 1 K cause a linear term in specific heat, C, and a $T^{1.8}$ dependence of the thermal conductivity, k [1]. The standard tunneling model attributes these phenomena to the motion of atoms or groups of atoms between states separated by low tunneling barriers, leading to a constant spectral density of two-level systems (TLS) [2,3]. Despite the success of this model, a complete explanation of the physical mechanism at work is still lacking. These low-energy excitations also cause noise or decoherence which limits the performance of low temperature thin-film devices with amorphous constituents, such as Josephson junctions [4] and superconducting qubits [5]. One route to the improved understanding of these excitations which could lead to reduced $1/f$ noise in Josephson junctions and longer coherence times in qubits is to study amorphous systems with no contribution from two-level systems. Even the earliest work on the tunneling model suggested that tetrahedrally-bonded materials such as amorphous silicon (a-Si) would be free of TLS due to overconstrained atoms which are unable to tunnel [3]. Though few measurements of C and k for a-Si have been reported [6–8], acoustic and internal friction measurements provide strong experimental evidence for the lack of TLS in a-Si [9–11].

In addition to the TLS dominated low T behavior, the higher temperature C and k of a wide range of amorphous solids have common features. Above 1 K, k crosses over to a plateau, followed by a gradual continuing rise. This plateau is typically seen between 10 and 50 K, where excess heat capacity often appears as a broad peak in C/T^3 which is larger than that seen in the analogous crystalline material. The physical mechanism behind these features is also a subject of debate, and it is unclear whether TLS play a role in these higher T phenomena, though there are several theoretical models which attempt to explain the k plateau, the excess heat capacity and the

TLS in a single framework [12–16]. The thermal properties of a-Si have been studied theoretically in some detail, both because of the predicted lack of TLS and because the relative simplicity of the structure enables realistic modeling. Several authors report theoretical predictions based on numerical solution of atomistic models of a-Si [17–20]. Studies by Feldman, Kluge, Allen, and Wooten (FKAW) [17], and by Feldman, Allen, and Bickham (FAB) [18] are particularly relevant to investigations of thermal properties of void-free, pure (not hydrogenated) a-Si above 2 K. These papers also use a clarified terminology for vibrational excitations, where "vibron" is the generic term for a harmonic normal mode, "propagon" describes an extended mode with a well-defined wave vector Q propagating ballistically over a mean free path l long enough for a wavelength to be defined, "diffusons" are neither localized nor extended but contribute to k via an intrinsic diffusivity, and "excess modes" refer to additional states seen in various spectroscopies as a bump in the vibrational density of states and often called a boson peak [21].

In the resulting theoretical picture of a-Si, propagons dominate k below 50 K with large contributions from diffusons seen at higher T. The theory predicts relatively few excess modes and no strong correlation between these modes and the k plateau. In addition, harmonic effects intrinsic to the model are sufficient to eliminate the k plateau, resulting in a glass with a bump in C/T^3 but no plateau in k.

The predictions of these theories have been difficult to test because a-Si is available only in thin-film form, making thermal conductivity and specific heat measurements difficult. An additional complication is a strong dependence of a wide range of the properties of a-Si on the growth method and quality of the sample. Measurements of k and C of a-Si in the temperature range where the k plateau and C/T^3 peak are expected have been limited to one study of k [6] and one of C [7], both on 35–50 μm

thick sputtered a-Si. These results show the plateau and peak occurring at similar temperatures, as expected for amorphous materials. While the resulting k can be explained by the theory [17], the C measurement indicates only qualitative agreement with predicted behavior [18], with a much higher Debye temperature, θ_D.

In this Letter we present the specific heat and thermal conductivity of a-Si thin films, measured from 5–300 K. These measurements are made with Si-N membrane-based microcalorimeters which are optimized for the study of thermal properties of materials in thin-film form. We compare C and k of a-Si to published experimental and theoretical results and discuss the implications for the nature of vibrations in this unique amorphous material.

Thin-film a-Si samples were e-beam evaporated onto microcalorimeters and amorphous Si-N coated Si substrates which were used for profilometry, high resolution cross-section transmission electron microscopy (HR-XTEM), and electron spin resonance (ESR). The HR-XTEM images show no evidence of crystallinity, voids, or other microstructural features. The ESR measurements indicate a dangling bond density of $\sim 10^{19}$ cm^{-3}, typical for evaporated a-Si with no hydrogen passivation. Details of the microcalorimetry techniques such as typical values of background contributions and estimation of error appear elsewhere [22–24].

Figure 1(a) shows k vs T for two a-Si films of different thickness plotted with the available previously published measured a-Si values. Both a-Si films agree well with previous measurements above 50 K, but have significantly lower k below this point, with no plateau. The top axis shows the dominant propagon wavelength, λ_{dom}. This is the wavelength of propagons which carry the most heat [25]. The inset in Fig. 1(a) shows the estimated propagon mean free path, $l = 3k/C_D v_D$. This estimate is reliable below ~ 20 K, where both C and k are dominated by propagons, and gives an upper limit above 70 K, where C is again well described by the Debye function, but k has significant contributions from diffusons. Below 20 K, $l \propto T^{-2}$ suggesting that scattering of vibrations goes as Q^2. In a-Si, at all T the film thickness is $> l > \lambda_{\text{dom}}$ and the contribution of the sample scales as expected with thickness. Though at 5 K the mean free path approaches the thickness of the 1300 Å film, the agreement of k for both films suggests that scattering of vibrons from film surfaces does not significantly modify the thermal transport at these temperatures.

Figure 1(b) compares our data to the two theoretical predictions of k for a-Si which are based on similar models and methods, but treat low-energy modes differently. FKAW uses the expected Rayleigh Q^4 scattering law for small-Q propagons and includes anharmonic effects from TLS to give a predicted k which shows the typical amorphous plateau and agrees well with previous measurements shown in Fig. 1(a). FAB instead does not include anhar-
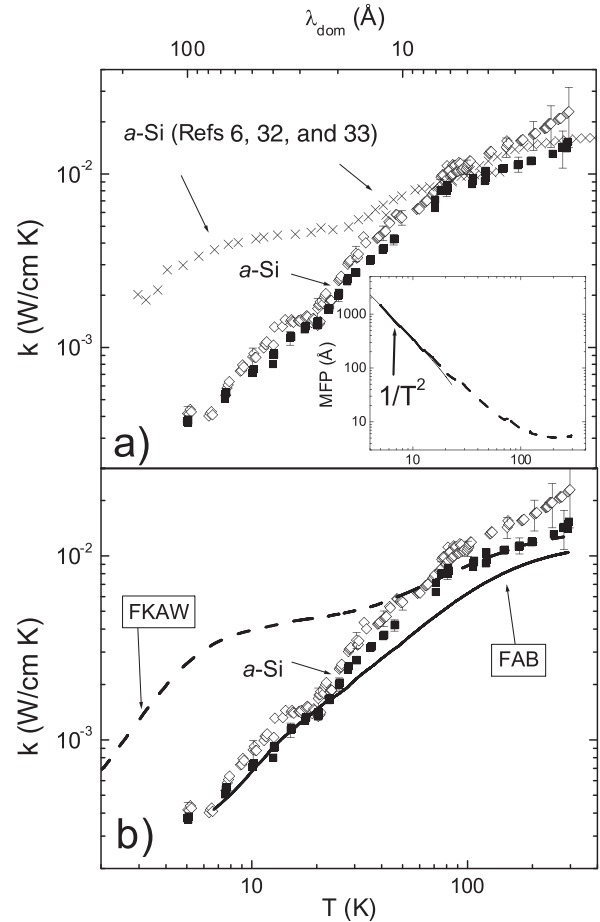

FIG. 1.   (a) k vs T plot shows two thin-film samples (solid square: 2770 Å, open diamond: 1300 Å) compared to previous measurements ($\times$'s) [6,32,33]. Inset: Estimated propagon mean free path vs T. (b) The same data compared to theories of FKAW (dashed line) and FAB (solid line) [17,18].

monic effects such as TLS, and uses the Q^2 law that is predicted by the calculated structure factors of their harmonic model and that agrees with the T dependence of our l. Neither the resulting k nor our data show evidence of a plateau, and the two curves agree quantitatively below 20 K. Note that we have not adjusted any parameter in the theory to match our data.

Turning now to specific heat measurements, Fig. 2 shows C/T vs T^2 for a 4000 Å thick a-Si film at $T \lesssim 17$ K. The data below $T^2 = 200$ K^2 are fit to the form $\gamma + \beta T$, where γ is the linear term in C and $\theta_D = 1944/\beta^{1/3}$. The fit gives γ within error bars of zero and $\theta_D = 487 \pm 5$ K. This lies between Mertig's previously measured value of 528 ± 20 K [7] and the FAB theoretical prediction of 450 K. $\theta_D = 487$ gives a Debye velocity $v_D = 4.47 \times 10^5$ cm/s. This value agrees with the previously measured sound velocity of Young's modulus modes $(4.4 \pm 0.5) \times 10^5$ cm/s [26], and is close to the theoretical value $v_D = [1/3(1/v_L)^3 + 2/3(1/v_T)^3]^{-1/3} = 4.13 \times 10^5$ cm/s, where $v_L = 7.64 \times 10^5$ cm/s and $v_T = 3.67 \times 10^5$ cm/s are
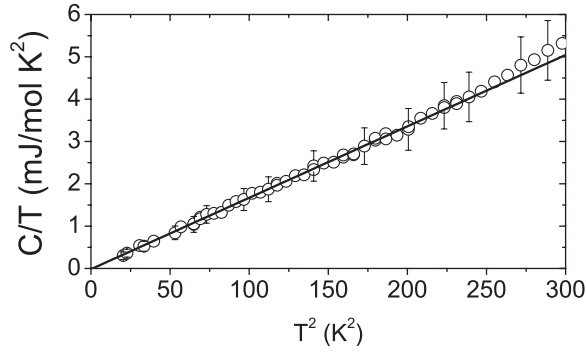
FIG. 2. C/T vs T^2 for a-Si. Open circles indicate data, and the best fit line gives $\theta_D = 487 \pm 5$ K and γ within error bars of 0.

the velocities of longitudinal and transverse excitations, respectively [17]. A recent picosecond ultrasonic measurement [27] of v_L in our film gave $v_L = (7.51 \pm 0.30) \times 10^5$ cm/s which is also within error bars of the theoretical value.

Figure 3 compares C/T^3 vs T (in J/g K^4) of our a-Si (open circles) to data on a 35 μm thick sputtered a-Si film from Mertig *et al.* [7] and values for crystalline Si [28]. The dashed lines show the Debye specific heat function, C_D/T^3, for $\theta_D = 625$ K and $\theta_D = 487$ K (this curve is shown below 20 K, though above 70 K, C/T^3 is again within error bars of the Debye function).

This specific heat data confirms that a-Si deviates significantly from expected behavior in an amorphous insulator in three ways. First, as discussed above, C/T^3 is well described by the Debye model below 15 K, with v_D that agrees with the measured sound velocity. In typical amorphous materials C/T^3 normally exceeds the value suggested by the measured sound velocity by over 50%. Second, as shown in Fig. 2, the fit of C/T vs T^2 for a-Si gives $\gamma \sim 0$. This is in agreement with the small or zero density of TLS reported by other authors, though measure-
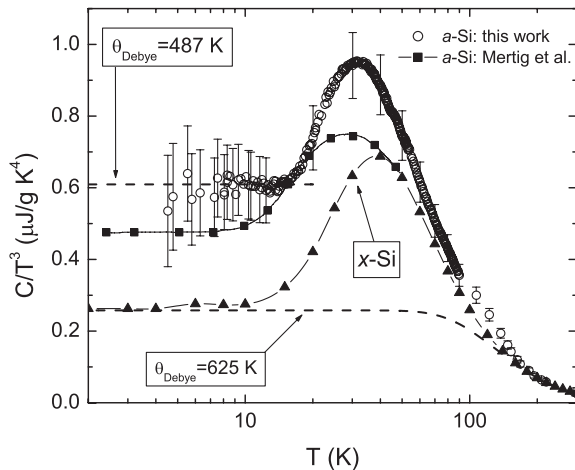

FIG. 3. C/T^3 vs T for a-Si, previously published values [7] and crystalline Si [28].

ments of our sample below 5 K (the lowest T reported here) could still show these contributions. Figure 4 clarifies the third deviation; that our data show few excess modes (i.e., no boson peak) in a-Si, in agreement with Raman spectroscopy [29,30] and FAB's theory. This figure compares the ratio of measured C to the Debye contribution C_D for amorphous and crystalline forms of SiO$_2$ and Si. This is a simple way to quantify how well each material is described by the Debye model and to compare the size of the bump in C/T^3. The amorphous SiO$_2$ in Fig. 4(a) behaves as expected, with a larger deviation from the Debye model than seen in the corresponding crystalline material, which peaks at lower T [31]. In contrast, the a-Si deviates from the Debye model significantly less than does crystalline silicon, leaving little evidence for a large density of excess modes. Note that subtracting the Debye contribution from the measured C gives essentially identical information as the scaling shown here.

Comparing the measured entropy, $S = \int_{T_{\min}}^{T_{\max}} C/T dT$, to that given by the corresponding Debye model in the region dominated by the bump in C/T^3 is another measure of the contribution of excess modes in these materials. In crystalline SiO$_2$ from 5–60 K, the measured entropy exceeds the Debye contribution by 425 mJ/mol K, while in a-SiO$_2$ over the same range, measured entropy exceeds the Debye contribution by 595 mJ/mol K. Both these values repre-
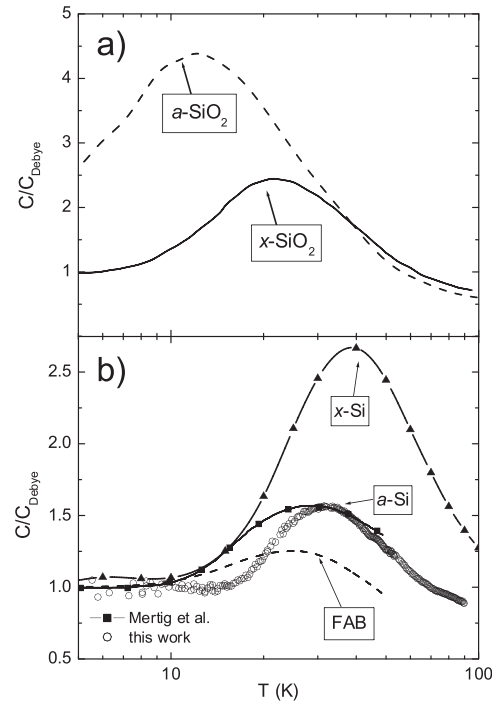

FIG. 4. Ratio of measured C to the Debye contribution for (a) amorphous and crystalline SiO$_2$ [1] and (b) amorphous and crystalline Si [28]. a-SiO$_2$ shows typical behavior for an amorphous insulator, while in a-Si the Debye model is a better description of C than for crystalline silicon. This atypical behavior suggests few excess modes in a-Si, consistent with FAB.

sent $\sim 30\%$ of the total measured entropy in this range. In contrast, crystalline Si from 5–90 K gives excess entropy of 1300 mJ/mol K (41% of the measured entropy) while a-Si shows just 300 mJ/mol K in excess of the Debye model (only 8% of the measured entropy) over the same range. Though the bump in C/T^3 is quite distinct, these comparisons show it is smaller than that expected in the "typical" amorphous solid and consistent with no significant excess modes in a-Si.

In summary, we have measured k and C of e-beam evaporated amorphous silicon thin films over a wide temperature range. k of our a-Si samples shows no plateau and agrees at low T with a model based on Q^2 scattering of harmonic excitations. C of thin-film a-Si matches a Debye model at both low and high T, with smaller overall deviation from Debye behavior than crystalline Si shows, indicating small contributions from TLS and excess modes. Our continuing work focuses on extending our thin-film k and C measurements to lower T.

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*Electronic address: bzink@boulder.nist.gov

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