

Heat conduction in ZnS:SiO₂ composite films

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The thermal conductivity of RF sputtered ZnS:SiO₂ composite film is measured in the temperature range between 50 K and 300 K using the 3ω method. This composite film shows two distinct modes of behavior. One is that, at room temperature, the thermal conductivity of the composite film is lower than the conventionally estimated minimum values for disordered ZnS and SiO₂. The other is that the temperature dependence is weaker than for usual glasslike films. Although the Einstein model could explain values of the conductivity at room temperature, the contribution of phonons cannot be excluded at lower temperatures. The low thermal conductivity is more successfully explained by the presumed thermal boundary resistance between ZnS particles and the SiO₂ matrix.

I. INTRODUCTION

Recent progress in thin-film technology has enabled the fabrication of artificial structures with varying physical properties. The thermal properties of thin films are very different from that of bulk and furthermore depend on growth conditions and resulting microstructures. In particular, the heat conduction mechanisms in composite films have been little studied—ZnS:SiO₂ is an example. This composite film is used as a thermal barrier in digital versatile disk—random access memory (DVD—RAM).¹ It consists of nanometer-sized crystalline ZnS particles dispersed in an amorphous SiO₂ matrix. The macroscopic parallels to this film have been studied extensively by dispersing highly conductive particles into less conducting matrix like epoxies.^{2,3} The thermal conductivity of macroscopic composites was explained theoretically in terms of the thermal boundary resistance.^{4,5} It was suggested that the thermal conductivity of composites can be even smaller than that of the matrix if the thermal boundary resistance between the constituent components is larger than the critical boundary resistance R_c or the size of conducting particles is smaller than the critical size a_c .

However, the validity of the theory is neither tested nor clarified for nanoscale composites. One of the reasons is that the theory is based on the Fourier heat equation involving only macroscopic properties, namely the thermal conductivity and the boundary resistance. The thermal boundary resistance arises from the phonon scattering due to different acoustic properties of the two interfacing materials while the thermal conductivity arises from the phonon scattering inside the material due to imperfections of intrinsic and extrinsic nature. For ZnS:SiO₂ film, since the phonon mean free path of ZnS is expected to be limited to nanometer scales, long-wavelength phonons would be scattered at the ZnS/SiO₂ interface while short-wavelength ones would encounter imper-

fections both inside the composite and at the interface. Therefore, it is evident that the thermal conductivity of ZnS particles in the composite should be considered in a different way from that of the bulk case even though the particles are as crystalline as the bulk crystals.

On the other hand, the thermal boundary resistance has been explained using the acoustic mismatch model or the diffused mismatch model.⁶ At low temperatures, where long-wavelength phonons are the major heat carriers and the interface behaves as the major phonon scatterer, these acoustic models suitably describe the measured boundary resistance. However, at elevated temperatures where high-frequency phonons are the dominant heat carriers, some measurements disagree with the theoretical calculations by an order of magnitude for metal-dielectric interfaces.⁷ The boundary phonon scattering seems to be more complicated and dependent on the anharmonicity of interfacing materials as well as on the interface quality. Recently, there have also been trials to explain the thermal boundary resistance between the solid-solid interface in the filmed structure based on interfacial phonon scattering and the Boltzmann transport equation for phonons.⁸

In this paper, the thermal conductivity of ZnS:SiO₂ composite film is measured. The lower bound of the ‘‘effective’’ thermal boundary resistance is defined to understand the thermal property of the composite film, which is derived from the lower bound theory of thermal conductivity by Torquato and Rintoul.⁴ The effective thermal boundary resistance is compared with the result of the conventional diffused mismatch theory.

II. EXPERIMENT

RF sputtered ZnS:SiO₂ film was deposited on 5-in-Si substrate using a ZnS(80%):SiO₂(20%) composite target. A transmission electron microscope image showed that ZnS

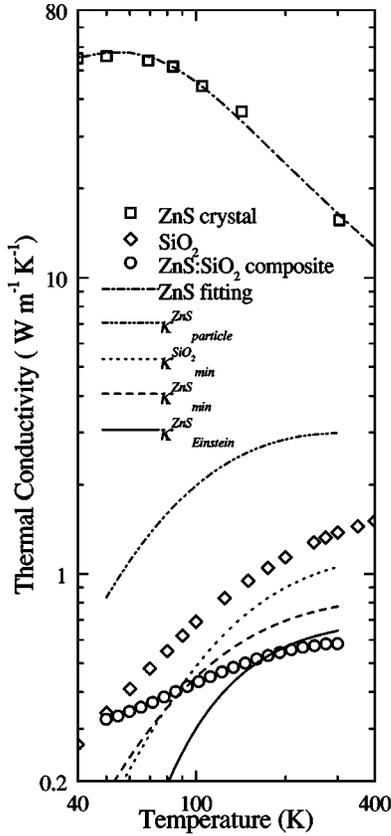


FIG. 1. Thermal conductivity of ZnS:SiO₂ composite film. The size effect of ZnS particle on scattering rate (dashed-dot-dot line) is calculated from Eq. (1). Dotted lines are the calculated minimum thermal conductivity of disordered SiO₂ and ZnS and the solid line is the minimum value derived from the Einstein model. Thermal conductivity of ZnS single crystals (Ref. 14) and SiO₂ amorphous bulk (Ref. 11) are shown for comparison.

was particulate with small-sized particles (average radius: $a \sim 2$ nm) in an SiO₂ matrix.¹ The volume fraction of ZnS particles was estimated to be 63.6% from the bulk density of ZnS and SiO₂. This value is comparable to the randomly closed-packing density (63–64%).⁹ The film thickness was determined by a scanning electron micrograph. The thickness uniformity of the film was found to be better than 4%.

Thermal conductivity of the film was measured using the 3ω method.¹⁰ The gold heater/thermometer line, of 11- μ m width and 1-mm length, with a thin-chromium-adhesion layer was patterned using the lift-off method. The thermometer response appears as a superposition of the temperature oscillation of the substrate and the temperature drop across the film and interfaces. The measurements were carried out on two kinds of films with different thickness (100 nm and 560 nm). From the difference between the apparent thermal conductivity data of the two films, the intrinsic thermal conductivity of ZnS:SiO₂ film was obtained. At each thickness, the data were reproducible for three samples.

III. RESULTS AND DISCUSSION

The measured intrinsic thermal conductivity of ZnS:SiO₂ composite film is given in Fig. 1 as a function of temperature. The data indicate much lower values for the thermal

TABLE I. Parameters for the calculation of minimum thermal conductivity and thermal boundary resistance: n represents atomic number density, ρ the mass density, and v_l and v_t represent longitudinal and transverse sound velocities, respectively.

	ZnS	SiO ₂ ^a
$n(10^{22}/\text{cm}^3)$	5.05	6.61
$\rho(\text{g}/\text{cm}^3)$	4.075 ^b	2.198
$v_l(10^5 \text{ cm/s})$	5.45 ^c	5.8
$v_t(10^5 \text{ cm/s})$	2.92 ^c	3.7

^aReference 11.

^bReference 15.

^cReference 16.

conductivity than those for ZnS single crystal and SiO₂ amorphous bulk. Also, the reported minimum thermal conductivity of SiO₂, $\kappa_{\text{min}}^{\text{SiO}_2}$, which was calculated either by the disordered phonon transport model¹¹ or by the Einstein model,¹² lies well above the measured data at room temperature.

Thus, as a first step, the possibility that ZnS particles may have such a low-heat conductivity is examined from a microscopic point of view based on the phonon-scattering rate. The phonon mean free path l_i in the ZnS single crystal is approximated from fits to the data for the single crystal as follows,

$$l_i = (A/\lambda_i^4 + BT e^{-C/T}/\lambda_i^2 + 1/D)^{-1}, \quad (1)$$

where λ_i is the wavelength of i th mode phonons and A through D are parameters. The three terms in the right-hand side of Eq. (1) are related to the Rayleigh scattering, phonon-phonon scattering, and boundary scattering, respectively. The parameter D is a measure of the maximum phonon mean free path for the single crystal and was about 40 μ m for the data fit. For ZnS particles, the particle size should affect the boundary scattering rate and impose restrictions on the phonon mean free path down to the particle size, $D=4$ nm in Eq. (1). The calculated values for ZnS particles, $\kappa_{\text{particle}}^{\text{ZnS}}$, however, are still much larger than the measured data as shown in Fig. 1.

Next, the data for the composite film are compared with the minimum thermal conductivity, $\kappa_{\text{min}}^{\text{ZnS}}$, which describes successfully the lower limit of the thermal conductivity of single-layer films.¹³ But the minimum thermal conductivities of disordered ZnS and SiO₂, calculated by using the parameters in Table I, are also larger than the thermal conductivity of the composite film at room temperature. At room temperature, the data are rather well explained by the minimum value of the Einstein model for ZnS, $\kappa_{\text{Einstein}}^{\text{ZnS}}$, where the phonon effect is excluded. This value is believed to be the lower limit of the thermal conductivity of ZnS. The difference between the measured data and $\kappa_{\text{Einstein}}^{\text{ZnS}}$ may be attributed to the limitation in accuracy of our measurement, the calculation for the single component of the composite, and incorrect use of the acoustic information; we used the value for the bulk phases. However, at low temperatures, the measured data for ZnS:SiO₂ film show so weak temperature dependence that the value exceeds both the minimum thermal conductivity and the nonphonon transport limit calculations.

These imply that the heat transport in the composite film may be dissimilar to that of normal amorphous films like SiO_2 . Thus, instead of estimating the thermal conductivity *a priori*, the data are analyzed from the phenomenological point of view using the thermal boundary resistance, which reflects the areal scattering at the interface.

Torquato and Rintoul studied the thermal boundary resistance effect on the thermal conductivity of composites where highly heat conductive spheres were randomly dispersed in a less conductive matrix.⁴ They obtained the upper bound κ_{upp} and lower bound κ_{low} of the thermal conductivity based on the energy dissipation theory with the variational method using the trial temperature gradient field and the heat flux field as follows,

$$\kappa_{\text{low}} \leq \kappa_e \leq \kappa_{\text{upp}},$$

$$\left(\frac{\phi_m}{\kappa_m} + \frac{\phi_p}{\kappa_p} + 3 \frac{R}{a} \frac{\phi_p}{\kappa_p} - E \right)^{-1} \leq \kappa_e \leq (\kappa_m \phi_m + \kappa_p \phi_p - F), \quad (2)$$

where κ and ϕ are the thermal conductivity and the volume fraction of particle and matrix ($\phi_m = 1 - \phi_p$), respectively, with the subscript *p* (particle) and *m* (matrix). κ_e is the effective thermal conductivity of composite. Here, *E* and *F* are functions of the thermal conductivity, volume fraction, particle radius *a*, a geometric configuration parameter ζ of the constituent components, and the thermal boundary resistance *R* between them. The simulation result of $\zeta = 0.134$ for $\phi_p = 0.6$ is used in this study.¹⁷ The same calculation was performed based on their model assuming that all the ZnS particles were hard spheres of identical size. If there is no thermal boundary resistance between the particles and the matrix, the results for the effective thermal conductivity of ZnS:SiO₂ composite indicate much larger values than for our data as shown in Fig. 2.

To understand the thermal conductivity of ZnS:SiO₂ composite film, we estimate the thermal boundary resistance between ZnS particles and the SiO₂ matrix by solving the inverse problem of either the lower bound or upper bound side of Eq. (2). In practice, the lower bound corresponds to the case where the temperature gradient is mainly generated by the thermal boundary resistance perpendicular to the heat flow while the upper bound approximates the case where the heat tends to flow along the conducting matrix rather than through the embedded spheres. As Torquato suggested, the lower bound is more reasonable for the resistance case $\kappa_m \ll \kappa_p$.¹⁸ Since there is no evidence to confirm that the nanocrystalline ZnS spheres are less conductive than the SiO₂ matrix, the measured data were considered as the lower bound of the system. The lower bound of the effective thermal boundary resistance R_{LB} was thus obtained by fitting the lower bound of Eq. (2) to the measured data. The upper and lower bounds of thermal conductivity for the case $R = R_{LB}$ are plotted in Fig. 2.

The empirical lower bound of the effective thermal boundary resistance R_{LB} is compared with the prediction of the well-known diffused mismatch model (DMM) for solid-solid semi-infinite interfaces. Although this comparison may not give a self-consistent explanation for the thermal boundary resistance, it is valuable to examine the order of magni-

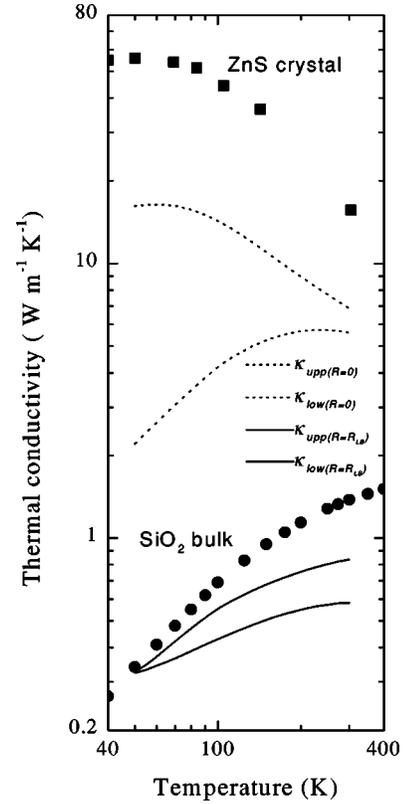


FIG. 2. The upper bound and lower bound of thermal conductivity of the composite in Eq. (2) for the lower bound of empirical thermal boundary resistance (solid line). The calculated thermal conductivity of the composite without boundary resistance is also plotted for comparison (dotted line).

tude of the resistance estimated. The DMM assumes that the phonons scattered at the interface preferentially propagate to the interfacing material having a larger Debye density of state.⁶ The thermal boundary resistance between ZnS and SiO₂ bulk based on DMM, R_{DMM} , is calculated using the bulk parameters in Table I. R_{DMM} is smaller than R_{LB} as shown in Fig. 3. At high temperatures, high-frequency phonons predominantly contribute to the heat conduction and hence the thermal boundary resistance also depends on the quality of the interface.⁷ In composite film, the imperfection at the interface due to the mechanical instability between ZnS and SiO₂ may cause additional phonon scattering resulting in a higher thermal boundary resistance.

It is noted that the temperature dependence of R_{LB} does not follow that of R_{DMM} . Since the long-wavelength phonons are the major heat carriers at low temperatures, the fact indicates peculiar aspects of R_{LB} of this composite; the boundary of the ZnS particle seems more transparent to long-wavelength phonons. Such frequency dependence can be observed from the phonon scattering by point or line defects.¹⁹ Hence we may suggest that some ZnS particles are in contact with strain-/stress-induced defects in that contact region. Then the phonons may be scattered at the contact region with ω^n dependence. To complete the discussion, further study of the thermal boundary resistance by multilayer films of ZnS and SiO₂ is necessary. Unfortunately, however, the lattice mismatch between ZnS and SiO₂ is so large that growth of the stable ZnS/SiO₂ multilayer film is very difficult.¹

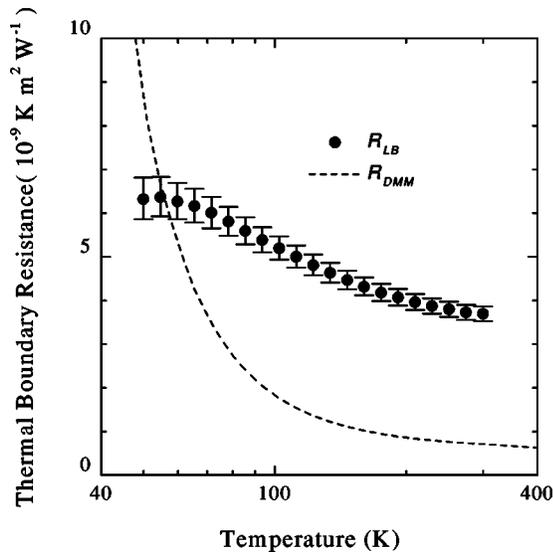


FIG. 3. Temperature dependence of the empirical thermal boundary resistance between ZnS and SiO₂, R_{LB} obtained by fitting the lower bound of the effective thermal conductivity in Eq. (2) to the measured data. The results of DMM are also shown for comparison. The error in R_{LB} is ascribed to the uncertainty, $\sim \pm 5\%$ of the film thickness that is a parameter in determining the thermal conductivity of the film.

At room temperature, the empirical resistance between ZnS and SiO₂, R_{LB} , is smaller than the typical thermal boundary resistance between metals and dielectrics, i.e., $0.5 \sim 3 \times 10^{-8} \text{ Km}^2 \text{ W}^{-1}$,²⁰ while the thermal conductivity of the composite film is smaller than the minimum conductivities of the constituent components. For fixed boundary resistance, the smaller the particle size, the larger the temperature gradient around the particle. Then heat transport through the conducting sphere becomes more difficult than through the less conducting matrix as particles become smaller than the critical size a_c . The critical size of ZnS particles, estimated by $a_c = R_{LB} / (1/\kappa_p - 1/\kappa_m)$, is plotted in Fig. 4. The size of ZnS in this experiment is smaller than the estimated critical size. Hence, the dominant effect on the thermal conductivity of the composite is attributed to the nanosized ZnS particles as well as the thermal boundary resistance.

Finally, we also note that other heat transport mechanisms may be responsible for our observation. This argument is based on the weak temperature dependence of our data. According to the recent work for the thermal conductivity of network forming glass, the increase of the thermal conductivity above the plateau region was attributed to the vibra-

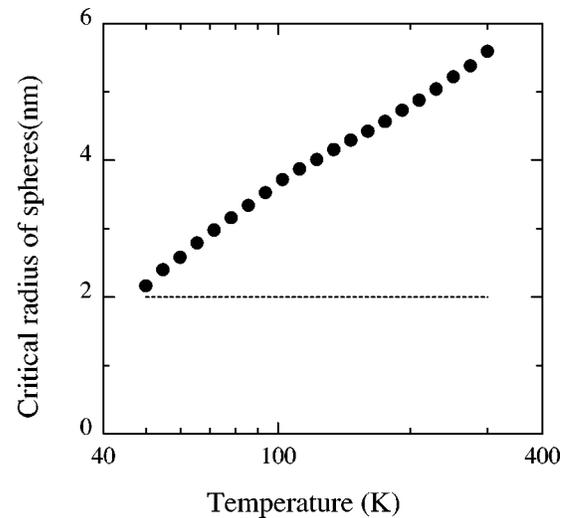


FIG. 4. The critical radius of ZnS particles. The average radius of ZnS in this study, 2 nm, is indicated by the dotted line.

tional hopping motion of the localized modes via extended phonon.²¹ If the hopping process is hindered by some mechanism in the glass system, the plateau region may be extended to higher temperatures. Since the investigated ZnS:SiO₂ is an aperiodic or amorphous mixture system, the observed weak temperature dependence may be explained in the view point of an extended plateau.

In summary, ZnS:SiO₂ composite film shows very low thermal conductivity and weak temperature dependence. Neither the size effect on the scattering rate nor the minimum thermal conductivity of a single component of the disordered materials can explain the low value. At room temperature, the data are as low as the results of the Einstein model. However, at low temperature, the contribution of phonons must be considered. From the phenomenological point of view, we estimated the lower bound of the effective thermal boundary resistance from fitting the lower bound of thermal conductivity to the measured data. The effect of the boundary resistance on thermal conductivity explains our data rather successfully.

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