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Reducing Thermal Conductivity of Crystalline Solids at High Temperature Using Embedded Nanostructures

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ABSTRACT

Thermal conductivity of a crystalline solid at high temperature is dominated by the Umklapp process because the number of high frequency phonons increases with temperature. It is challenging to reduce the thermal conductivity of crystalline solids at high temperature although it is widely known that, by increasing the atomic defect concentration, thermal conductivity of crystalline solids can be reduced at low temperature. By increasing the concentration of ErAs nanoparticles in $In_{0.53}Ga_{0.47}As$ up to 6 atom %, we demonstrate a thermal conductivity reduction by almost a factor of 3 below that of $In_{0.53}Ga_{0.47}As$ at high temperature. A theoretical model suggests that the mean free path of the low frequency phonons is suppressed by increasing the ErAs nanoparticle concentration.

Thermal isolation at high temperature is required in many applications such as thermal barriers[1,2] and thermoelectric power generation.[3] For thermoelectric power generation, it is necessary to use a semiconductor with crystalline order to achieve high carrier mobility. Thermal conductivity of crystalline solids at high temperature, higher than the Debye temperature, is dictated mainly by an intrinsic process, that is, the Umklapp process, because of the large number of high frequency phonons at high temperature.[4] Therefore, reducing the thermal conductivity of crystalline solids at high temperatures is challenging, although it is widely known that, by increasing the defect concentration, thermal conductivity of crystalline solids can be reduced at low temperature.[5]

In this paper, we experimentally demonstrate and theoretically explain that it is possible to reduce thermal conductivity of crystalline solids at high temperature by increasing the nanoparticle concentration in a crystalline solid. To do so, we use an $In_{0.53}Ga_{0.47}As$ alloy containing ErAs nanoparticles, 1−5 nm in diameter, which are epitaxially embedded. It has been shown previously that incorporating ErAs nanoparticles effectively reduces thermal conductivity below that of $In_{0.53}Ga_{0.47}As$ alloy because ErAs nanoparticles effectively scatter long and mid-wavelength phonons while atomic substitution in an $In_{0.53}Ga_{0.47}As$ alloy scatters short wavelength phonons.[6] However, the thermal conductivity reduction was evident below and near the Debye temperature of the $In_{0.53}Ga_{0.47}As$ alloy. To reduce thermal conductivity at high temperature, we increase the ErAs nanoparticle concentration while maintaining the mean diameter of ErAs nanoparticles. This implies that the mean free path due to ErAs nanoparticles should be shorter than the mean free path due to the Umklapp process.

A detailed description of the growth method can be found in the literature,[7] and only a brief explanation will be provided here. A sample was grown on an InP substrate with a buffer layer of 100 nm InAlAs and 40 nm of n-type InGaAs doped with 5×10^{18} cm^{-3} silicon using a molecular beam epitaxy (MBE) system at 490 °C. The total thickness of the $In_{0.53}Ga_{0.47}As$ films containing ErAs nanoparticles were 1.0 μm for the 3% ErAs concentration and 2.0 μm for the 6% ErAs concentration. The ErAs nanoparticles are incorporated in the three-dimensional $In_{0.53}Ga_{0.47}As$ matrix. For the purpose of thermal conductivity measurements, a silicon dioxide layer (~0.18 μm) was deposited on top of the samples using plasma-enhanced chemical vapor deposition. The differential 3ω method[8] was used to measure thermal

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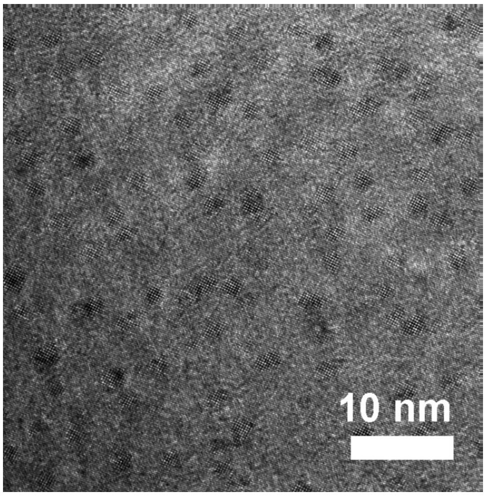

Figure 1. TEM picture of 3% ErAs in $In_{0.53}Ga_{0.47}As$.

conductivity. A platinum (~380 nm in thickness and 30 μm wide) film with chromium (~4 nm thick) as an adhesion layer was deposited and patterned on the top of the silicon dioxide layer for the heater and thermometer.

Figure 1 shows a transmission electron microscope (TEM) image of a sample where the ErAs nanoparticles are incorporated in the $In_{0.53}Ga_{0.47}As$ matrix. The shown image is a cross-sectional TEM image taken along one of the ⟨110⟩ in plane directions of the matrix. TEM sample was prepared by mechanical polishing followed by Ar ion milling at 3 kV in a precision ion polishing system (Gatan). TEM study was carried out using a FEI Tecnai F30UT TEM equipped with a field-emission electron gun operated at 300 kV. The total concentration of ErAs in $In_{0.53}Ga_{0.47}As$ is fixed at 3.0%. The features with higher contrast in the picture correspond to ErAs nanoparticles and the dark gray layer corresponds to $In_{0.53}Ga_{0.47}As$. As shown in Figure 1, ErAs nanoparticles are epitaxially embedded in $In_{0.53}Ga_{0.47}As$, so the overall material remains a single crystal.

Figure 2a plots the thermal conductivity of 6% and 3% ErAs in $In_{0.53}Ga_{0.47}As$. The thermal conductivity of $In_{0.53}Ga_{0.47}As$ and 0.3% ErAs in $In_{0.53}Ga_{0.47}As$ are shown as references.[6] For 0.3% ErAs:$In_{0.53}Ga_{0.47}As$, Umklapp phonon scattering starts to dominate over other scattering processes, thus producing only a marginal reduction over the thermal conductivity of $In_{0.53}Ga_{0.47}As$ at temperatures above 600 K (see Figure 2a). However, the thermal conductivity of 6% and 3% ErAs:$In_{0.53}Ga_{0.47}As$ is lower than those of $In_{0.53}Ga_{0.47}As$ and 0.3% ErAs:$In_{0.53}Ga_{0.47}As$, particularly at temperatures above 600 K. By considering that the Debye temperature of $In_{0.53}Ga_{0.47}As$ is 322 K,[9] this clearly shows that thermal conductivity of crystalline solids at high temperature can be reduced.

To understand the role of ErAs concentration in reducing the thermal conductivity of $In_{0.53}Ga_{0.47}As$ at high temperature, the thermal conductivity is predicted using Callaway's model[10] and shown as the dashed line in Figure 2a. A detailed description of Callaway's model is available in literature,[6,10] so here we are presenting only on the phonon mean free path (MFP) calculation. The MFP, $l(\omega)_{\text{eff}}$, at a certain

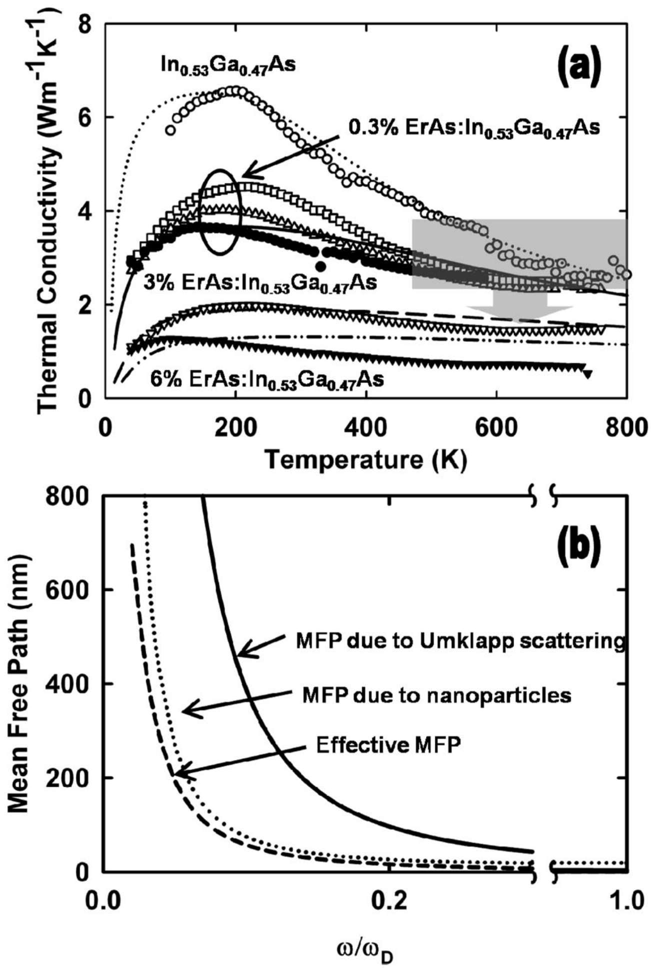

Figure 2. (a) Temperature dependence of thermal conductivity of 6% and 3% ErAs in $In_{0.53}Ga_{0.47}As$ (solid and open downward triangles, respectively). The thermal conductivity of $In_{0.53}Ga_{0.47}As$ (open circles) and 0.3% ErAs in $In_{0.53}Ga_{0.47}As$ [0.4 monolayer thickness with a 40 nm period thickness ErAs/$In_{0.53}Ga_{0.47}As$ superlattice (open squares), 0.1 monolayer thickness with a 10 nm period thickness ErAs/$In_{0.53}Ga_{0.47}As$ superlattice (open upward triangles), and randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ film] are shown as references.[6] Dotted, solid, and dashed lines are based on theoretical analysis. (b) The phonon mean free path (MFP) versus normalized frequency of 3% ErAs in $In_{0.53}Ga_{0.47}As$ at 600 K. The phonon frequency (ω) is normalized as the Debye frequency (ω_D).

frequency, ω, is determined by the Matthiessen's rule[11]

$$l(\omega)_{eff}^{-1} = l(\omega)_B^{-1} + l(\omega)_U^{-1} + l(\omega)_A^{-1} + l(\omega)_{e-ph}^{-1} + l(\omega)_D^{-1} \quad (1)$$

where it is composed of MFP due to boundary scattering, l_B, Umklapp scattering,[12] l_U, defect or alloy scattering,[13] l_A, electron−phonon scattering,[14] $l_{e\text{-}ph}$, and that due to ErAs nanoparticles, l_D. The MFP due to electron−phonon scattering appears because semimetallic ErAs nanoparticles act as dopants[7] and introduce electrons in $In_{0.53}Ga_{0.47}As$. According to Ziman,[15] the electron−phonon scattering rate depends on the electron effective mass, m^*, as $l_{e\text{-}ph} \sim (m^*)^{-3}$. Therefore, considering the low effective mass of ErAs:InGaAs (about $0.043 \times m_e$, where m_e is electron rest mass), electron−phonon scattering is negligible. Introducing charge carriers in $In_{0.53}Ga_{0.47}As$ could increase thermal conductivity of ErAs:$In_{0.53}Ga_{0.47}As$ due to electronic contribution. Comparing thermal conductivity of undoped $In_{0.53}Ga_{0.47}As$ with that of 0.3% ErAs:$In_{0.53}Ga_{0.47}As$ at high temperature indicates electronic contribution may also be negligible.

The MFP due to nanoparticles, l_D, is given by

$$l_D = \frac{V}{\int_0^{\infty} \sigma_{sct}\left(\frac{R^{a-1}e^{-\frac{R}{b}}}{b^a\Gamma(a)}\right)\mathrm{d}R} \quad (2)$$

where V in eq 2 is a mean volume containing one nanoparticle, σ_{sct} denotes scattering cross section, which is based on ref 16. The effect of size distributions of ErAs nanoparticles are incorporated as a gamma distribution[17] which is shown in parenthesis in eq 2. In the parentheses, a is the shape parameter, b is the scale parameter, and $\Gamma(a)$ is the gamma function. The mean diameter of ErAs nanoparticles is equal to ab and the standard deviation is equal to $a^{0.5}b$. On the basis of the TEM image in Figure 1, the mean diameter of the ErAs nanoparticles was found to be 2.4 nm. TEM showed that the particle size was independent of the particle density. To fit the maximum thermal conductivity, a value of 1.5 nm was chosen for the standard deviation.

The agreement between theoretical analysis and experimental data as shown in Figure 2a except for the 6% ErAs in $In_{0.53}Ga_{0.47}As$ suggests that we have a possible explanation of how and why nanoparticles reduce the thermal conductivity of $In_{0.53}Ga_{0.47}As$ at high temperature. Since Umklapp scattering affects high frequency phonons, there should be an additional scattering mechanism which scatters low frequency phonons to reduce thermal conductivity of crystalline solids at high temperature. Conventional atomic scale defects mostly affect high frequency phonons according to the Rayleigh scattering theorem. Recently, it has been shown that nanoparticles scatter low and mid-frequency phonons.[6,18] Therefore, by increasing nanoparticle concentration, as shown clearly in Figure 2b, the MFP due to ErAs nanoparticles is shorter than that of Umklapp scattering mainly at low frequencies. The fact that theoretical analysis of 6% ErAs in $In_{0.53}Ga_{0.47}As$ does not match well with experimental data may be a limitation of our assumption of independent phonon scattering due to nanoparticles.[16] Also, at large concentration of ErAs nanoparticles, the particles showed a strong tendency to order on the {114} planes of the $In_{0.53}Ga_{0.47}As$ matrix.[19] Since our model assumes that particles are evenly distributed, this should also cause some deviation between modeling and experimental data.

In summary, by increasing the concentration of nanoparticles in $In_{0.53}Ga_{0.47}As$, a significant reduction in thermal conductivity over that of $In_{0.53}Ga_{0.47}As$ at high temperature was observed. Theoretical analysis revealed that the MFP due to ErAs nanoparticles is shorter than the MFP due to Umklapp scattering because ErAs nanoparticles scatter low frequency phonons while Umklapp scattering affects high frequency phonons.

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