Heat Conduction Below Diffusive Limit in Amorphous Superlattice Structures

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Advanced means to further reduce the thermal conductivity of dense amorphous materials by nanostructuring is important for thermal management in future electronic and optical devices. While the works so far have realized the reduction by scattering propagons, here, we demonstrate that nanostructures can in addition inhibit transport of diffusons, by measuring the thermal conductivity of amorphous-silicon/amorphous-silica superlattices with a periodicity ranging from 4.5 nm to 29.3 nm at room temperature. The measurements show that thermal conductivity of the superlattice with periodicity below 9.5 nm is significantly below the amorphous diffusive limit (~1 W/m K). The measured thermal conductivity can be reproduced using a combination of the phonon-gas kinetics
model and Allen-Feldmann theory without any fitting parameters, with the interfacial transmittance of propagons and diffusons obtained by atomistic Green’s function. In addition to the known reduction of propagon transport, the effective mean free paths of diffusons are reduced from that of the bulk (1–3 nm) to several angstroms or even atomistic by extreme boundary scattering at the interfaces in the superlattice, giving rise to a significant tunability of the amorphous thermal conductivity using truly nanoscale structures. The influence of interface scattering on the diffusion transport can be effectively described by the Boltzmann transport equation, and in this sense, propagons and diffusons do not fundamentally differ.

1. Introduction

A long-standing issue in solid-state physics is elucidating the nature of thermal transport in crystal or amorphous semiconductors and insulators, which is essential for thermal management in modern semiconductor nanodevices. In 1929, by assuming heat carriers (atomic vibrational modes [1, 2]) in crystals as propagating quasiparticles (phonons), Peierls developed the Boltzmann transport equation (BTE) for heat conduction [3]. The Peierls BTE can be solved approximately by linearization [4] or exactly by iterative [5-7], variational [8], or diagonalization methods [9, 10]. With advances in first-principles [4, 6], the Peierls BTE accurately predicts phonon transport in various kinds of bulk and nanostructured crystal materials [7, 11, 12].

In amorphous materials with random atomistic structures, the application of the Peierls BTE requires sufficiently long effective mean free paths (MFPs) of heat carriers so that their wave vectors can be well defined [13]. This condition only occurs for low-frequency modes (propagons) with a limited density of states. A large proportion of the heat carriers in an amorphous material has extremely short
effective MFPs comparable to interatomic spacings (diffusons), leading to ill-defined wave vectors and group velocities. As a result, the Peierls BTE breaks down.

The 100-year-old Einstein’s atomistic vibration theory [14], the minimum thermal conductivity (κ) theory [15], and the fracton theory [16] have all been developed and applied to characterize the transport of diffusons. To date, the most widely accepted theory was first suggested in Hardy’s general velocity operator in 1963 [17], where diagonal elements are the group velocity in the Peierls BTE and the off-diagonal terms can be neglected in crystals. In 1989, Allen and Feldmann (AF) illustrated that these off-diagonal terms are exactly the physical origin of diffusons and dominate heat conduction in amorphous materials [13]. Therefore, the harmonic AF theory was developed to describe the transport of diffusons in bulk amorphous materials. The AF theory neglects propagons in terms of heat transport due to their narrow frequency range and small density of states [18].

However, recent experimental and theoretical works have suggested that propagons in certain amorphous materials such as amorphous silicon (a-Si) [19], amorphous silica (a-SiO₂) [20], and amorphous silicon nitride (a-SiNx) [21] can have extremely long effective MFPs, which exceed tens or even hundreds of nanometers. Consequently, propagons can contribute to a large part of the total κ of bulk amorphous materials despite their small density of states. Hence, the total κ of amorphous materials should be the summation of the contributions of both propagons and diffusons. The “propagon+diffuson” scenario has successfully reproduced the κ of various bulk amorphous materials [22].

The next interesting challenge is to understand the transport of those propagons and diffusons in nanostructured amorphous materials, where boundaries and physical structures at the interface
naturally play an important role. Such an understanding should help control the $\kappa$ of amorphous materials with nanostructures, which is critical for applications that require a reduced $\kappa$ such as thermal barriers and insulators [23-25]. However, previous works are limited to the classical size effect of propagons in amorphous thin films [19] and the band-folding effect in the amorphous superlattices [26], which are only possible for gigahertz modes that have a negligible influence on heat conduction.

In this work, we investigate this interesting topic by measuring the $\kappa$ of a-Si/a-SiO$_2$ superlattices (a-SLs) with a periodicity ranging from 4.5 nm to 29.3 nm at room temperature. Then we analyze the data using a combination of the phonon gas kinetics model and AF theory, which incorporate the transmission/reflection of propagons and diffusons at the a-Si/a-SiO$_2$ interfaces as well as their intrinsic scattering.

2. Results and discussion

The a-SLs used in our study were sets of a-Si/a-SiO$_2$ alternating layers prepared on a single-crystal Si substrate via the sputtering method (deposition pressure: 0.4 Pa, temperature: 300 K, atmosphere gas: argon gas). Table 1 lists the thickness of the a-Si layer ($L_{aSi}$) and that of the a-SiO$_2$ layer ($L_{aSiO}$), the periodicity of the a-SLs ($P_{SL} = L_{aSiO} + L_{aSi}$), and the total thickness of the a-SLs ($L_{aSL}$). Additional samples with a fixed $L_{aSi}$ of 28 nm but various $L_{SiO}$ for doped and non-doped a-Si were also prepared (Table 2). High-resolution transmission electron microscopy (TEM) images (Figs. 1(a)–(f)) clearly show that high-quality superlattice structures with uniform a-Si and a-SiO$_2$ layers are formed for all samples except that with $L_{aSi}$ of 2.7 nm, where the a-Si and a-SiO$_2$ layers are partially interconnected. The amorphous structures of the a-Si and a-SiO$_2$ layers in the a-SLs were identified by electron diffraction measurements (Supplementary Information (SI) Fig. S1 ).
The cross-plane $\kappa$ of the a-SLs ($\kappa_{SL}$) was measured by time-domain thermoreflectance (TDTR), which is a well-established method that operates by a pulse laser and pump-probe technique [27, 28] (Fig. 1(g)) (See SI Section 2 for detail). Figure 2(a) plots $\kappa_{SL}$ of samples with $L_{aSi}$ of 28 nm as a function of $L_{aSiO}$. The error bar shows the standard deviation of five measurements at different positions. Due to the existence of the a-SiO$_2$ layers, the measured $\kappa_{SL}$ for the non-doped case is reduced from 1.87 W/m K (bulk a-Si) to 1.47 W/m K. This suggests that the oxide layers between the a-Si layers can scatter heat carriers in a-SLs and consequently reduce $\kappa$. Moreover, variation of $L_{aSiO}$ (from 0.86 nm to 1.29 nm) has a limited effect on $\kappa_{SL}$, indicating that the $\kappa$ reduction of a-SLs is dominated by a-Si/a-SiO$_2$ interfaces rather than the interior of the a-SiO$_2$ layers. Although doping in the case of bulk a-Si without oxide layers reduces $\kappa_{SL}$, doping does not affect the case with the oxide layers. Doping scatters propagons, but incorporating the oxide layers completely suppresses them. Consequently, dopant scattering has a minimal impact on a further reduction in $\kappa_{SL}$.

To investigate the $\kappa$ reduction that can be achieved by using the a-SL structures, we reduced $L_{aSi}$ so that the interfaces exhibit a stronger scattering of heat carriers in a-SLs. Figure 2(b) plots the measured $\kappa_{SL}$ as a function of $L_{aSi}$. The results show that $\kappa_{SL}$ decreases drastically as $L_{aSi}$ decreases, and can even be significantly below the diffusive limit of both a-Si and a-SiO$_2$ (1 W/m-K [19, 22, 29]) when $L_{aSi}$ is smaller than 12.8 nm. This suggests scattering of diffusons in a-SLs, since otherwise $\kappa_{SL}$ should converge to 1 W/m K as in the works of Braun et al. [19], Kwom et al. [29], and Larkin el al. [22]. As $L_{aSi}$ decreases to the average atomistic spacing (~0.25 nm for a-Si), $\kappa_{SL}$ would recover to $\kappa$ of bulk a-SiO$_2$ due to loss of interfaces. Figure 2(b) plots $\kappa$ of bulk a-SiO$_2$ at $L_{aSi}$ of 0.25 nm to roughly illustrate such a recovery trend. In real fabricated materials, $\kappa$ recovery may also occur for $L_{aSi}$ above 0.25 nm due to reasons such as the interconnections of the a-Si and a-SiO$_2$ layers (Fig. 1 (f)), which are
demonstrated by the measured $\kappa_{SL}$ for $L_{aSi}$ of 2.7 nm. Hence, the existence of continuous a-Si/a-SiO$_2$ interfaces is crucial to control $\kappa$ of amorphous materials.

To gain a microscopic understanding of the $\kappa$ reduction in a-SLs, we first analyzed the transmittance of heat carriers with atomistic Green’s function (AGF). Here, $t_{aSi}$ characterizes the probability of heat carriers in the a-Si layer transmitting through the a-SiO$_2$ layer (Fig. 3(a)), while $t_{aSiO}$ characterizes the probability of the heat carriers in the a-SiO$_2$ layer transmitting through the a-Si layer (Fig. 3(b)). Figure 3(c) plots the calculated results for $t_{aSi}$ and $t_{aSiO}$ (see SI Section 3 for detail). It is shown that $t_{aSi}$ and $t_{aSiO}$ can be clearly identified as two regimes. At high frequencies, $t_{aSi}$ and $t_{aSiO}$ are approximately constant with average values of 0.23 and 0.31, respectively, although the data has some scatter. By contrast, at low frequencies, they clearly depend on the frequency. This frequency dependence can be well fitted with the frequency-dependent transmittance $t(\omega)$ that has been applied to phonons transmitting through the thin amorphous layer at the interface between two crystal silicon leads [12, 23, 30], and is given as

$$t = \frac{1}{\gamma \omega / \omega_{\text{max}} + 1}$$

(1)

where $\omega_{\text{max}}$ is taken as the maximum frequency of the heat carriers in a-Si (16 THz) by assuming elastic transmission dominates in the AGF calculation. This is consistent with experiments [23, 30, 31]. $\gamma$ is the fitting parameter, which is identified as 4.5 and 10.1 for $t_{aSi}$ and $t_{aSiO}$, respectively.

The frequency that divides the two regimes into different transmittance regimes can be approximated by the transition frequency of propagons and diffusons $\omega_t$ [22], indicating that the low-frequency modes below $\omega_t$ are indeed phonon-like propagons. For diffusons, although they exhibit random walks with very short effective MFPs, the force-constant mismatch at the interface still leads
to a strong scattering of diffusons, significantly limiting their transmittance. As a result, in addition to
interface scattering of propagons, a large part of diffusons is scattered by the interfaces. Accordingly,
the $\kappa_{SL}$ is reduced when interfaces are formed (Fig. 2). The origin of the scattering could be a reflection
[23, 30, 31] or localization [32], however, the dominant source remains an open question. Moreover,
tasio is dominated by the a-SiO2/a-Si interface rather than the interior of the a-Si layers (Fig. 3(d)),
indicating that the thermal resistance of the interior of the a-Si layers for heat carriers of a-SiO2 is
much smaller than that of the a-SiO2/a-Si interface. A similar conclusion should also hold for tasii. This
feature clearly explains why $\kappa_{SL}$ is independent of $L_{aSiO}$ (Fig. 2(a)).

The transmittances, tasii and tasio, naturally affect thermal transport in a-SLs by limiting the effective
MFPs of heat carriers. The key issue is whether the transmittances can reproduce the measured $\kappa_{SL}$. We
investigated this in terms of a combination of a phonon gas model and AF theory. First, the total
thermal conductivity ($\kappa_T$) of the bulk amorphous materials includes contributions of both propagons
($\kappa_P$) and diffusons ($\kappa_D$) [13, 22]:

$$\kappa_T = \kappa_P + \kappa_D.$$  \hfill (2)

where $\kappa_P$ from phonon-like propagons follows the phonon gas model [22]

$$\kappa_P = \frac{1}{3} \int_0^{\omega_t} C(\omega)\nu_s(\omega)^2\tau(\omega)d\omega = \frac{1}{3} \int_0^{\omega_t} C(\omega)\nu_s(\omega)\Lambda(\omega)d\omega,$$  \hfill (3)

and $\kappa_D$ from diffusons is evaluated by the AF theory [13] as

$$\kappa_D = \int_{\omega_t}^{\infty} C(\omega)D(\omega)d\omega,$$  \hfill (4)

where $C(\omega)$ is the volumic specific heat capacity including the density of states. $\nu_s$ is the appropriate
sound speed for propagons. $\Lambda$ is the effective MFP and $D(\omega)$ is the AF diffusivity.

Since the eigenvectors of diffusons are randomized [32], the energy of the diffusons diffusively dissipates [17]. As derived in SI Section 5, the $\Lambda$ of diffusons with $\tau$ is taken as the diffuson length of the random walk:

$$\Lambda(\omega) = \sqrt{3D(\omega)\tau(\omega)} = v_D \tau(\omega),$$  \hspace{1cm} (5)

where $v_D$ is the relevant diffusive velocity defined by Eq. (5).

With Eq. (5), $\kappa_D$ expressed by Eq. (4) can be rewritten in the form of Eq. (3). For convenience, $\kappa_T$ in Eq. (2) can be reformatted as:

$$\kappa = \frac{1}{3} \int_0^\infty C(\omega) v(\omega) \Lambda(\omega) d\omega,$$  \hspace{1cm} (6)

where $v$ is $v_s$ or $v_D$, depending on the heat carrier.

Section 4 of the SI provides details of the calculation for the bulk thermal properties of a-Si and a-SiO$_2$ [33]. Figure 2 plots the results of the calculated $\kappa$ of bulk a-Si and a-SiO$_2$. The results agree well with the measured results, and thus verifies our calculation.

Next, we considered $\kappa_{SL}$. The ultra-thin a-SiO$_2$ layer with a thickness ranging from 0.86 nm to 2.19 nm (Tables 1 and 2) is comparable to the $\Lambda$ of diffusons for bulk a-Si and a-SiO$_2$ (0.4–3 nm, Fig. 4). This suggests that thermal transport in the interior of the a-SiO$_2$ layers is ballistic. That is, the thermal resistance is dominated by the interface rather than the interior of the material, which is consistent with the results in Figure. 3 (e). Our AGF analysis (SI Sections 3.2 and 3.3) shows that the typical serial model breaks down when transport is ballistic and the interiors of the a-Si and a-SiO$_2$ layers are
correlated. Instead, thermal transport in a-SLs is described by the parallel model analogous to the thermal radiation of photons, which gives $\kappa_{SL}$ as a combination of those for a-Si ($\kappa_{aSi}$) and a-SiO$_2$ ($\kappa_{aSiO}$):

$$\kappa_{SL} = \kappa_{aSi} + \kappa_{aSiO} = \frac{1}{3} \int_0^\infty C_{aSi} v_{aSi} \Lambda_{aSi} d\omega + \frac{1}{3} \int_0^\infty C_{aSiO} v_{aSiO} \Lambda_{aSiO} d\omega,$$

(7)

where the variables are defined in the same way as those in Eq. (6) with the subscripts denoting those of a-Si and a-SiO$_2$ layers in the a-SLs.

The effect of intrinsic scatterings is included by Matthiessen's rule:

$$\Lambda_{aSi}^{-1} = \Lambda_{aSi,\text{bulk}}^{-1} + \left(\frac{3}{4} \frac{t_{aSi}}{1-t_{aSi}} L_{aSi}\right)^{-1} + L_{aSL}^{-1},$$

(8)

$$\Lambda_{aSiO}^{-1} = \Lambda_{aSiO,\text{bulk}}^{-1} + \left(\frac{3}{4} \frac{t_{aSiO}}{1-t_{aSiO}} L_{aSiO}\right)^{-1} + L_{aSL}^{-1},$$

(9)

where $\Lambda_{aSi,\text{bulk}}$ and $\Lambda_{aSiO,\text{bulk}}$ are the effective MFP for bulk a-Si and a-SiO$_2$, respectively. Note that the $t_{aSi}$ values for samples with $L_{aSi}$ of 12.8 nm and 28 nm are obtained by extrapolation with an exponential function due to the large computation load of AGF (Fig. 3(d)).

The calculated $\kappa_{SL}$ agrees well with the experimental values (Fig. 2). The exception is the sample with $L_{aSi}$ of 2.7 nm in Table 1, where the a-Si and a-SiO$_2$ layers are partially interconnected (39% on average from Fig. 1(f)). Thus, the transmittance should be enhanced by a factor of 1.39. This yields $\kappa_{SL}$ of 0.66 W/m K, with an acceptable error of 19.5% when compared to the measured value (0.82 W/m K). The agreement between the calculations and experiments demonstrates that the drastic reduction of the $\kappa$ in the a-SLs structure can be described in terms of heat carrier scattering by the a-Si/a-SiO$_2$ interfaces.
Now that the calculation has been shown to reproduce the experimental results, we investigated how the transport properties of mode-dependent heat carriers are modulated by the superlattice structures. Figure 4(a) compares the $\Lambda$ of heat carriers of the a-Si and a-SiO$_2$ layers in a-SL and that of bulk a-Si and a-SiO$_2$. The $\Lambda$ of heat carriers in both a-Si and a-SiO$_2$ are drastically suppressed compared to the bulk value. This suppression is apparent for the smallest layer thickness, where $\Lambda$ is only several angstroms for a-Si, which is comparable to atomistic spacings for a-SiO$_2$. A remarkable feature is that $\Lambda$ reduction occurs not only for propagons but also for diffusons, which are believed to have an $\Lambda$ comparable to the atomistic spacing and are unaffected by nanostructures. However, as shown in Figure 4, the $\Lambda$ of diffusons in bulk a-Si and a-SiO$_2$ can exceed 1–3 nm, which is significantly larger than the atomistic spacing and thus can be shortened by nanostructures with a comparable length scale. As a consequence of the scattering of both propagons and diffusons, both $\kappa_P$ and $\kappa_D$ of $\kappa_{SL}$ are dramatically suppressed, as illustrated in Figure 2(b). In the case of a small $L_{aSi}$ such as 3.94 nm and 7.39 nm, propagons are almost completely suppressed, leaving only diffusons to carry the heat in a-SLs. Moreover, $\tilde{\kappa}_{aSiO}$ is small compared with $\tilde{\kappa}_{aSi}$ due to strong interface scattering and the much smaller amount of a-SiO$_2$ than that of a-Si in the a-SLs (Fig. 2(b)).

The agreement of the calculation and experiment results also indicates that transport of diffusons still follows the BTE when their effective diffusive velocity and $\Lambda$ are defined by combining the AF theory and the random walk model (Eq. 5). In this sense, there is no fundamental difference between propagons and diffusons transport.

### 3. Conclusions

In summary, diffuson-mediated thermal transport in amorphous a-Si/a-SiO$_2$ superlattices was
clarified by $\kappa$ measurements and rigorous calculations of the phonon kinetic model and AF theory. The experiments reveal that the $\kappa_{SL}$ with periodicity from 3.94 nm to 29.3 nm is much lower than the bulk value. In fact, it is significantly below the diffusive limit of both bulk a-Si and a-SiO$_2$. Using the frequency-dependent transmittance of the heat carriers across an a-Si/a-SiO$_2$ interface calculated by AGF, the measured $\kappa_{SL}$ can be reproduced by a combination of the phonon gas model and AF theory without any fitting parameters. The analysis reveals that the $\Lambda$ of the diffusons is equivalent to several angstroms or atomistic spacing can be realized by extremely effective interface scattering. The results demonstrate that the $\kappa_{SL}$ can potentially be tuned below the diffusive limit by scattering both propagons and diffusons, offering better thermal solutions in microelectronic devices. Additionally, the transport of diffusons follows the BTE, and in terms of boundary and interface scatterings, there is no fundamental difference between propagons and diffusons.

Acknowledgments

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References


**Figures**

**Figure 1.** (a) TEM image of the cross-section of the 500 nm a-SL sample on a single-crystal Si substrate. (b) a-SLs with $L_{aSiO}$ of 1.29 nm (Table 2). (c), (d), (e), and (f) show TEM images for a-SLs with $L_{aSi}$ of 12.8 nm, 7.29 nm, 3.94 nm and 2.7 nm, respectively (Table 1). (g) Schematics of the TDTR measurements for $\kappa_{SL}$. 
**Figure 2.** Measured and calculated $\kappa$ of a-SLs as a function of $L_{\text{aSiO}}$ (a) and $L_{\text{aSi}}$ (b), with information listed in Table 2 and Table 1, respectively. The filled black circle in (b) represents the calculation with a 1.39 enhancement factor for transmittance.
Figure 3. Structures of a-SiO$_2$ (a) and a-Si (b) interfaces. (c) $t_{\text{aSiO}}$ and $t_{\text{aSi}}$ as functions of frequency. (d) $t_{\text{aSiO}}$ as a function of $L_{\text{aSi}}$. Filled and open dots are the calculated and extrapolated results, respectively.
Figure 4 Effective MFPs of heat carriers in (a) a-Si and (b) a-SiO$_2$ layers of the a-SLs as functions of frequency. Experimental data for relaxation time is taken from previous works using inelastic x-ray scattering (IXS) [34, 35], picosecond optical technique (POT) [36], Brillouin ultraviolet scattering (BUVS) [37, 38], and Brillouin light scattering (BLS) [39]. MFP is obtained using $v_\tau \tau$. 
Table 1 Structures of the non-doped a-SLs and bulk a-Si.

<table>
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<th>Items</th>
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<th>$P_{SL}$ [nm]</th>
<th>$L_{aSL}$ [nm]</th>
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<td>3.94</td>
<td>7.29</td>
<td>12.8</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>28</td>
<td>500</td>
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<tr>
<td>Boron-doped</td>
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<td>1.52</td>
<td>2.16</td>
<td>2.19</td>
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Table 2 Non-doped and Boron-doped a-SLs with $L_{aSi}$ of 28 nm.

<table>
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<td>Boron-doped</td>
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