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Abstract: The majority of the silicon devices contain amorphous phase and amorphous/crystalline interfaces which both considerably affect the transport of energy carriers as phonons and electrons. In this article, we investigate the impact of amorphous phases (both amorphous silicon and amorphous SiO_2) of silicon nanoporous membranes on their thermal properties via molecular dynamics simulations. We show that a small fraction of amorphous phase reduces dramatically the thermal transport. One can even create nanostructured materials with subamorphous thermal conductivity, while keeping an important crystalline fraction. In general, the a-SiO_2 shell around the pores reduces the thermal conductivity by a factor of five to ten compared to a-Si shell. The phonon density of states for several systems is also given to give the impact of the amorphisation on the phonon modes.

Keywords: Amorphous Shells; Molecular Dynamics; Pores; Silicon Nanostructured Membranes; Thermal Conductivity.

PACS numbers: 47.11.Mn; 74.25.Fy; 74.78.Fk.

1 Introduction

During the past 10 years, there has been an increased interest on thermal transport properties in nanostructures and nanostructured materials as the thermal conductivity can be tuned with several fabrication strategies. Control the thermal transport is important for several applications as for thermoelectrics, thermal management at the nanoscale, and even for biomedical applications.

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Free surfaces, interfaces and their roughness, nanoinclusions, nanoconstrictions, point, or extended defects reduce the phonon transport and their impact is getting more pronounced as one reduces the characteristic size of nanostructures.

Advances in elaboration methods made possible the fabrication of 3D, 2D, and 1D nanostructures and nanostructured materials. A lot of efforts have been devoted to silicon membranes and to nanoporous phononic-like membranes [1, 2]. The thickness of the membranes achieved up today is of the order of 10 nm and the holes of some nanometre [3]. At such scales, the existence or not of amorphous silicon or amorphous silicon oxide phase on the free surfaces of the pores might play a very important role on the heat transport and might deteriorate the performances of phononic-like crystals. Several theoretical studies are devoted the past years in this direction. Neogi et al. [3] studied the amorphisation impact on silicon membranes (without pores), France-Lanord et al. [4] studied the amorphisation impact on amorphous/crystalline superlattices, and Blandre et al. [5] on silicon nanowires with constrictions. A very recent work of our group on the impact of amorphous silicon shells of nanoporous silicon on thermal conductivity [6] revealed that there are two key parameters that seem to control the behaviour of the thermal conductivity for these systems: the noncrystalline fraction and the surface to volume ratio. In all above cases, the surface effects of nanostructures are the main scattering source for phonons, and physical insights are still necessary to understand how heat carriers interact with perfect, reconstructed, or amorphised free surfaces.

Mesoscopic models such as Monte Carlo resolution of the Boltzmann transport equation for phonons, which use bulk phonon properties fail to describe nanostructured materials with features of some nanometres. Molecular dynamics is a very useful tool for modelling nanostructures and studying their thermal properties. In this article, we explore the impact of amorphisation on the thermal properties of nanoporous silicon membranes. We model nanoporous membranes with pores covered by an amorphous silicon and silicon oxide shells. The impact of the shell thickness is also examined and this reveals interesting results for the role of the two amorphous materials.

2 Simulation Method

2.1 Modelling the Structures

We modelled nanoporous silicon membranes using the methodology described in France-Lanord et al. [7] and which is fully reproducible. The nanopores in the current study have cylindrical shape with the axis of cylinders vertical to the free surfaces of the membranes. We modelled pores without and with shells of amorphous Si (a-Si) or SiO₂ (Fig. 1). The system is relaxed at $T=300$ K with an NVT ensemble during 200 ps. At the end of this procedure, the pressure was 0 Pa. Five cases are studied: nanoporous crystalline Silicon (c-Si) without shell around the pores (Fig. 1a), nanoporous c-Si with a-Si shell (Fig. 1b and c), and nanoporous c-Si with amorphous SiO₂ shell (Fig. 1d and e). The axes of the cylinders are along z -axis. Periodic boundary conditions are set in x and y directions, while the conditions on z are fix. The dimensions of the simulation box for all configurations were set to $10a_0 \times 10a_0 \times 10a_0$ with $a_0 = 5.43$ Å.

2.2 Molecular Dynamics and Thermal Conductivity

Molecular dynamics simulations are performed with *LAMMPS* [8]. Equilibrium molecular dynamics (EMD) method is used to determine the TC via the Green-Kubo formula:

$$k_{xy} = \frac{\mathcal{V}}{k_B T^2} \int_0^{+\infty} \langle J_x(t) J_y(0) \rangle dt \quad (1)$$

where x and y subscripts denote directions, \mathcal{V} the system's volume, J the heat flux, t the time, T the system's temperature, and k_B the Boltzmann constant. With this formula, the TC can be obtained for all directions. In our study, we

give the results for only the in-plane thermal conductivity (averaged in x and y directions).

The time step is set to 0.5 fs. At the beginning of the simulation, the system is relaxed at $T=300$ K with an NVT ensemble during 200 ps. Then the computation of the TC is performed every 40 ps under an NVT ensemble, estimating the flux fluctuations correlation every 10 fs, for a total duration of 10 ns. The TC is averaged over the second half of the simulation, when the steady state is established, in order to reduce the uncertainty on the results [6]. Moreover, each simulation is repeated 10 times with different initial seeds and the TC is averaged. Periodic boundary conditions are applied on surfaces perpendicular to the directions of interest (x and y directions), while nonperiodic and shrink-wrapped boundary conditions are applied on the free surfaces (z direction for membranes).

For systems containing only Silicon atoms, their interactions are described with the Stillinger–Weber potential [9] with modified coefficients by Vink et al. [10] as the latest parameterisation is able to describe thermal transport in silicon, in both crystalline and amorphous phases. When the system contains oxygen (in SiO₂ shells), the interatomic potential is Tersoff SiO [11]. In the bulk crystalline silicon case, the TC obtained with Stillinger–Weber potential is $k=164 \pm 21$ W/m K. That is in good agreement with reported experimental values $k=148$ W/m K at 300 K (EL-CAT Inc.). The consistence of our study has been checked by computing the TC of one of our systems with both potentials and the results are reasonably in agreement (difference less than 5 %).

2.3 DOS

With molecular dynamics, the phonon's density of states (DOS) of the system can also be extracted from the trajectory of the atoms. Indeed, the displacement of the atoms can be decomposed by Fourier transform to find

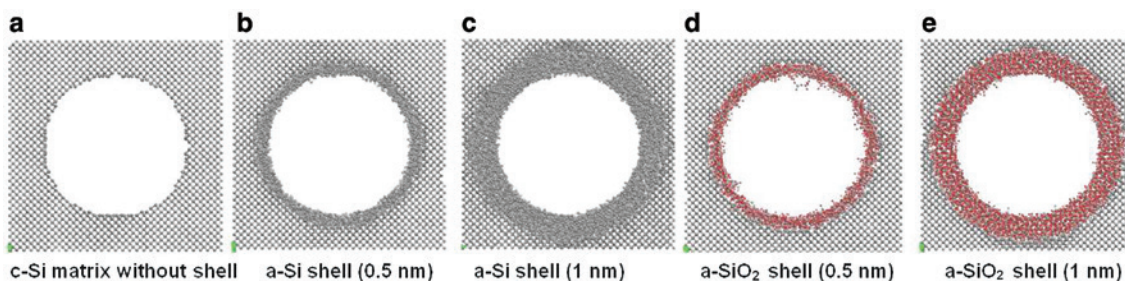


Figure 1: Cross sections of Si membranes with cylindrical pores without and with shells: (a) no shell, (b) amorphous Silicon shell with 0.5 nm thickness, (c) amorphous Silicon shell with 1 nm thickness, (d) amorphous SiO₂ shell with 0.5 nm thickness, and (e) amorphous SiO₂ shell with 1 nm thickness. Grey atoms represent silicon and red the oxygen.

the density of frequencies of phonons. In this article, the *specden* plugin of the *VMD Signal Processing Plugin Package* was used to calculate the phonon DOS of the porous membranes.

3 Results

3.1 Impact of Thickness and Amorphous Material Shells on Thermal Conductivity

In this section, the TC of Si membranes with cylindrical nanopores with different kind of shells as showed in the previous section is investigated with molecular dynamics. The periodicity of the structure is set to $a = 15 a_0$ and the diameter of the pore is $d = 10 a_0$ (8.145 and 5.43 nm, respectively). The thickness of membranes is set to $h = 15 a_0$. The shell thickness e is 0.5 or 1 nm. The thermal conductivity is computed in the inplane direction of the membranes (perpendicular to the axis of the cylinder). For comparison, the thermal conductivity of a silica membrane of thickness of 8 nm measured experimentally is 0.7 W/mK [Goodson et al., J. Heat Transfer 116, 317 (1994)] and for bulk amorphous silicon reported values are in the range 1–1.8 W/mK [Wada, Japanese J.A.P. 35, 5B (1996)].

The thermal conductivity of the modelled structures is shown in Figure 2. The TC of the thin crystalline silicon membrane with pores is only 3.5 W/mK, which is lower than the bulk silicon by a factor of 40. This reduction is

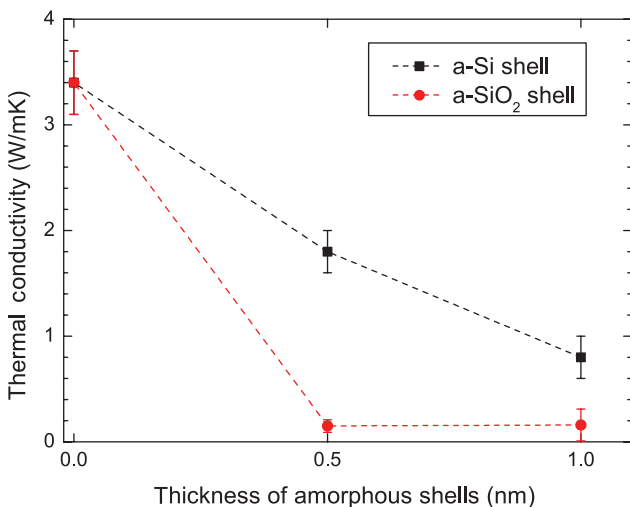


Figure 2: Thermal conductivity of nanoporous silicon membranes and the influence of amorphous shell around the pores depending on the amorphous material and the thickness of the shell. The black squares is for a-Si and the red circles for the a-SiO₂ around the pores. Two shell thickness are studied: 0.5 and 1.0 nm.

first due to the decreasing of dimensions (from 3D to 2D) and also due to the pores that increase considerably the scattering rate of phonons on the free surfaces.

When there is an a-Si shell around the pores, the thermal conductivity reduces rapidly and quite linearly. In increasing the thickness of the amorphous shell around the pores, the thermal conductivity reduces further and can reach subamorphous thermal conduction keeping an important ratio of crystalline material. For a shell thickness of 0.5 nm, the TC is divided by 2 compared to the system without shell. This reduction is more pronounced when the shell thickness is increased. Subamorphous TCs are even reached for $e = 1$ nm. So the presence of an amorphous shell around the pore contributes to lower thermal transport, as has been observed in spherical pores [6]. In fact, the TC is reduced as if the diameter of the pore was the crystalline/amorphous interface. This is an evidence that the a-Si have the same effect as void on the thermal conductivity.

The impact of a-SiO₂ is different than this of a-Si. The TC is again lowered by the presence of an amorphous phase around the pore, but this time the reduction is striking. Comparing same thicknesses of shell with a-Si or a-SiO₂, we can see that their relative reduction is of the rate of 5–12. Another important difference between the two amorphous materials as shells is the in the case of silica the TC does not depend on the shell thickness anymore (this will be explained later with DOS). The thermal conductivity reached by nanostructuring and oxidation can be lower than the bulk amorphous SiO₂ TC (about 1.4 W/m.K).

3.2 Density of States

In order to understand the behaviour of the TC of the precedent structures, their phonon densities of states (DOS) have been computed. Figures 3 and 4 show the impact of the nanostructuring and thickness of amorphous shells on the phonon DOS. Figure 3 shows the effect of the a-Si shell on the DOS. We note that when the shell thickness increases, the DOS becomes closer to the one of bulk amorphous Silicon. This gives a large decrease in the TO peak, a red shift of all the phonons (offset towards lower frequencies), and a smoothing of the two peaks in the middle, which correspond to LA and LO polarisations. All these modifications can explain the reduction of the thermal transport and the more or less linear dependence of the TC with the thickness of shells for the case of a-Si.

Figure 4 shows the influence of a SiO₂ shell on the DOS of the structure. The DOS of bulk SiO₂ is also depicted to help the comparison. As for the a-Si shell, the presence

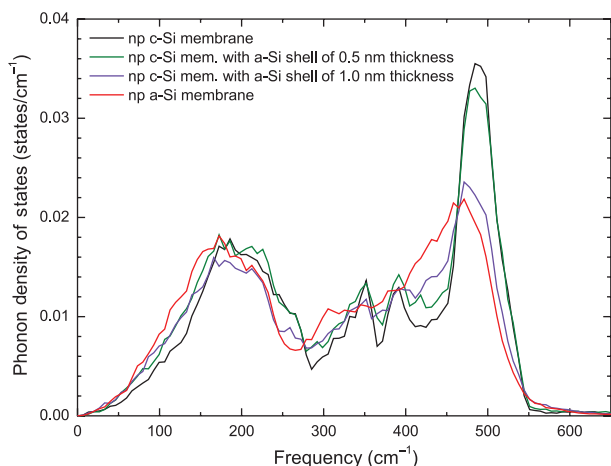


Figure 3: Comparison of the phonon density of states of several nanoporous systems with and without a-Si shells around the pores.

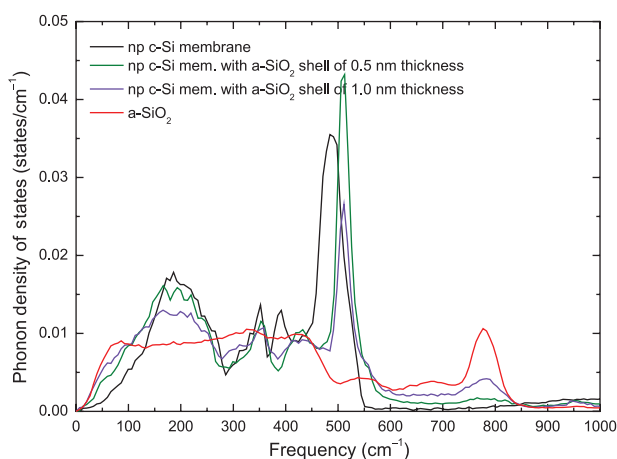


Figure 4: Comparison of the phonon density of states of several nanoporous systems with and without a-SiO₂ shells around the pores.

of a-SiO₂ shell moves the DOS of the system towards the one of bulk SiO₂. Thus, the three lower frequency peaks are smoothed and red shifted, whereas the TO peak is decreased and blue shifted (towards higher frequencies). Because of the presence of oxygen, three high-frequency peaks appear with the SiO₂ shell. This might explain why the TC of systems with SiO₂ shells seems independent from the thickness of the shell: increasing the shell thickness reduces the low-frequency population but increases the number of very high frequency phonons and this two effects might be balanced out. We have to add here that the large DOS mismatch between the crystalline silicon and the amorphous silica should yield large interfacial thermal resistance between the two materials. The DOS mismatch for the case of crystalline/amorphous silicon is not so pronounced as here and this might explain partially

the differences between the effective thermal conductivities of the two systems with amorphous silicon and amorphous silica shells.

4 Conclusion

In this article, we studied the influence of amorphous shells around the pores in nanoporous silicon membranes. The amorphisation reduces rapidly the thermal conduction through membranes. The thickness of the amorphous shell is an important parameter for a-Si but not for a-SiO₂ shells, in which the thermal conductivity reduces dramatically and it is independent of the thickness of the amorphous shell. The phonon density of states might explain this discrepancy. These results show that it is important to consider the amorphous shells that are created during the elaboration method (creation of holes in silicon membranes) or after their exposure to not protecting environments. Further studies are important to be conducted in this direction, specially for systems with nanopores with their between distances greater than the systems studied here.

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