Thermal conductivity across nanostructured porous silicon films

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Abstract. This paper models the effect of pore size, pore arrangement and porosity on room temperature thermal conductivity across low porosity meso-porous silicon (meso-PS) films known as n+ and p+ type PS. Whereas the meso-PS films are simulated using a three-dimensional (3D) pore network generator, the heat conduction is modeled using the Monte Carlo method (MCM) recently developed for simulating steady-state phonon transport in submicron structures. The simulations show that (i) the thermal conductivity across meso-porous films decreases when the pore size decreases or the porosity increases, in accordance with past studies. (ii) The thermal conductivity of n+ type pore network is always greater than that of p+ type due to the difference in pore morphology. Finally, the simulations corresponding to p+ type pore network are shown in good agreement with existing experimental data for low porosity p+ type PS. Such comparison confirms the validity of the current 3D modeling.

1. Introduction
Thermal characterization of porous silicon (PS) has attracted much attention these last years due to their promising use as thermal insulating in sensing devices. In fact, past investigations have pointed out the capability of PS, especially meso-PS (i.e. pore size about 10 nm) with low and moderate porosity, to get low thermal conductivity and useful mechanical solidity [1]. The rapid progress of micro- and nanotechnologies requires the fabrication of nanostructured porous thin films. Moreover, current technological knowledge enables controlling the pore peculiar morphology quite confidently such as pore size in the 1-100 nm range [2]. Previous measurements mainly focus on thermal conductivity of thick layers due to the limit of methods and experimental challenges. Moreover, prior models [1] are based on approximations, thus unable to account for the influence of morphology parameters such as pore size, porosity, pore arrangement, film thickness, and the 3D nature of pore network.

The current study uses for the first time the MCM to investigate the influence of morphology parameters on thermal conduction across meso-PS thin films. First, the material morphologies are simulated using a 3D model derived from past 2D pore network algorithm for PS [3]. Then, the simulation of thermal conduction through the 3D pore-network using the MCM developed especially for steady-state phonon transport [4] is described. Finally, the results are shown and discussed. For illustration, the simulations are compared with experimental data in literature [1, 5].

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2. Porous silicon modeling

Meso-PS layers are obtained by electrochemical etching of the surface of heavy doped (p- and n-type) monocrystalline silicon (Si) in aqueous hydrofluoric acid (HF) solutions [2]. The meso-PS layer exhibits columnar pore structure running perpendicularly to the wafer surface with side pore branches as observed from Scanning electron micrograph (SEM) [2]. To simulate pore formation from etching processes, the Two-scale (TS) [3] model is adopted that explain pore formation from the diffusion of holes or electrons under Brownian motion from the Si wafer to the Si/HF interface. The pore formation is due to particle dissolution when they reach the interface or the aggregate surface. In the TS algorithm, particles are generated randomly above a depletion layer at distance \( dp \) from the interface or surface aggregate then it undergoes random walk. The dissolution process occurs when the particle is at a distance \( dr \) called “drift-length” from a dissolution site (see figure 1). The pore morphology can be controlled by varying the parameters \( dp \) and/or \( dr \).

![Figure 1. 3D illustration of the TS model and configuration of geometry in the MCM.](image)

In this study, the TS algorithm is extended to generate 3D pore network for PS that was not previously performed. The pore network is constituted of connected spherical pores, generated in a 3D simulation box of sizes \( X, Y, \) and \( Z \) as shown in figure 1. The pore growth is in upward direction. In the case of film, \( Z \) is taken greater than 3\( \delta \) while \( X \) and \( Y \) should be infinite. However to limit excessive computation time due to large system dimensions, it is more useful to consider large but finite value of \( X=Y \) but representative of the material. We verified that from the criterion \( X/\delta >5 \), the heat transfer can be treated as 1D. The correspondence between the etching conditions and the TS parameters \( dp \) and \( dr \) are not well clear, therefore they are adjusted so that a qualitative resemblance between the cross-section of 3D pore networks and SEM images [2] is achieved (see figures 2 and 3).

![Figure 2. Typical SEM image of p+ type PS with 38% of porosity [2] (left) and cross-section of 3D pore network with \( dp=2 \) and \( dr=2 \) (right).](image)

![Figure 3. Typical SEM image of n+ type PS with 30% of porosity [2] (left) and cross-section of 3D pore network with \( dp=10 \) and \( dr=2 \) (right).](image)
3. Steady-state heat conduction through 3D pore network using MCM

The numerical model assumes that acoustic phonons, considered as mass-less particles, are the main heat carrier. The phonon confinement and the effect of air entrapped in pores are supposed to be negligible.

The configuration of the simulation is shown in figure 1. The material along the thickness is discretized into juxtaposed 3D cells of size smaller than the phonon mean free path. For each cell is assigned an arbitrary pseudo-temperature which still to be determined. The top and bottom walls are black with fixed temperatures; therefore they can emit and absorb phonons. The flux emitted from each black wall that is related to the wall temperature is divided into a very large number of phonon samples. Then, the following steps that constitute the heart of the MCM are performed.

S1) For each phonon sample is assigned a random position on the emitting boundary area, a random direction in the inward hemispherical space, and random frequency and polarization. Then, the method consists of tracking one by one the samples emitted from the two emitting walls. The phonon moves according to a drift motion while its direction is altered diffusely when it interacts with material imperfection (defect or impurity), pore, or it is scattered specularly by lateral boundary (to mimic 1D heat transfer condition). The track of a phonon is stopped when it is absorbed by an absorbing element (black boundary or cell). Each time a phonon is absorbed, the energy of the absorbing element is incremented by the phonon energy. After tracking all samples emitted from black boundaries, the energy absorbed by each element is computed.

S2) From each cell, a certain number of phonons are emitted so that the cell emitted-energy is equal to the cell absorbed-energy. These newly emitted phonons are tracked again one by one until they are all absorbed according to the reasons mentioned in step S1). After this phonon tracking, the energies absorbed at cells and walls only during this step, referred to as “energies absorbed step by step” are computed.

S3) While the energies absorbed step by step at cells and walls are greater than zero, they are added to the absorbed-energies and the algorithm goes back to step S2). Since the phonons absorbed at boundaries are not reintroduced, the total phonon number in the studied system decreases step by step and becomes equal to zero after a certain number of steps. The necessary information (cell pseudo-temperatures and phonon fluxes) can be extracted from the simulation statistics.

As the initial cell temperatures are unknown, the frequency distribution of phonons in the cells is not correct. Therefore, iteration on the temperatures is required until the temperature profile is unchanged. This consists of repeating steps S1) to S3) using as initial temperatures the latest computed temperatures. Once the convergence is achieved, the thermal conductivity across the simulated film can be deduced using the Fourier law knowing the net heat flux per unit area crossing the film and the local pseudo-temperature gradient. More details about the MCM can be found in [4].

4. Results, discussion and conclusion

4.1. Influence of pore size, pore morphology and porosity on thermal conductivity

In the following, we consider both n+ and p+ type pore networks, two limits of pore size, 10 and 20 nm, as evaluated by Small angle X-ray scattering (SAXS) technique, and porosity values ranging from 15 to 40 %. Note that the effective mean free path of phonons in the studied material ranges from 2 to 15 nm at room temperature. Therefore, the film thickness can be taken about 500 nm for which the diffusion regime prevails (the Knudsen number is always smaller than 0.03) and the thermal conductivity concept is proved. All simulations are running at room temperature with 20 K temperature difference between top (hot) and bottom (cold) boundaries. The MCM described in section 3 is used to simulated phonon transport. Then the thermal conductivity across each porous film is predicted. The result depicted in figure 4 showed that: (i) The conductivity of n+ type pore network is about 1.5 greater than that of p+ type PS for all considered porosities due to difference in pore arrangement. In fact, pore branches of p+ type pore network are much interconnected compared to that of n+ type (figures 2 and 3); therefore it has higher phonon-pore scattering cross-section. (ii) The
effect of pore size is also noticeable. At nanometer scale, the smaller the pores, the lower the thermal conductivity because for an identical porosity, the distance between the surfaces of neighboring pores is shorter for smaller pores (hence the phonon-pore scattering is much more frequent) than larger ones. (iii) The decreasing of thermal conductivity with porosity is far from linear as predicted Dilute-fluid model and Effective-medium theory. Such behavior is due to the nano pore size and pore interconnection that are not taken into account in macroscopic models.

4.2. Comparison of simulations against experimental data in literature.

To perform comparative study with experimental data carried out by Lysenko et al. [1] and more recently by David et al. [5], we consider p+ type meso-PS films having an average pore size of 15 nm, thickness about 500 nm and porosity from 20 to 40 %. Comparison is shown in figure 5. The error bars of the current modeling account for the uncertainty due to the pore size (±5 nm) according to SAXS analysis and the statistical errors inherent to the MCM. We can note that even the experimental data present some disparity; the agreement between the simulation and them for the considered porosities is acceptable confirming the capability of the proposed approach based on 3D MCM.

To conclude, for more realistic modeling of heat conduction in nanostructured materials, better knowledge of morphology parameters is crucial. The MCM is a powerful method enables a multi-dimensional investigation and interpretation of experimental results compared to more approximate models [1]. It is very useful in order to optimize thermally such complex materials. In future work, fine reconstruction of PS will be performed to get eventual multi-scale crystallite size, low and high porosity PS films.

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