



Theoretical analysis of thermal rectification in a bulk Si/nanoporous Si device

M. Criado-Sancho^a, L.F. del Castillo^b, J. Casas-Vázquez^c, D. Jou^{c,*}

^a Departamento de Ciencias y Técnicas Físicoquímicas, Facultad de Ciencias, UNED, Senda del Rey 9, 20040 Madrid, Spain

^b Departamento de Polímeros, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ap. 70-360 Coyoacán, México DF, 04510, Mexico

^c Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain

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ABSTRACT

We present a theoretical analysis of thermal rectification in a porous Si/bulk Si device, taking into account ballistic effects in phonon-pore collisions when phonon mean free path is much longer than the radius of the pores. Starting from an approximate analytical expression for the effective thermal conductivity of porous Si, we obtain the thermal rectifying coefficient of the device as a function of porosity, pore size, temperature interval, and relative lengths of porous and bulk samples.

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1. Introduction

New possibilities in the accurate control of phonon transport in nanostructures have given a new thrust to the analysis of heat transport [1–4]. In particular, a current topic of interest is the analysis of thermal rectifiers, i.e., devices allowing heat to flow easily in one direction but having a high resistance to heat flow in the reverse direction [5–10]. These devices act in an analogous way as electric rectifiers in electronic circuits, and some combinations of them could even act as the analogous of transistors. The possibility of these sophisticated nonlinear devices has stimulated the relatively new topic of “phononics” in an analogous way as electronics developed in the 1940’s.

One of the main aspects of such an analysis is the search of suitable materials and device configurations allowing for a most efficient heat rectification. The quantity characterizing such rectification is the thermal rectifying coefficient, defined as the ratio of the heat flux in the forward and reverse directions, of easy flux and difficult flux, respectively. Here we provide a theoretical analysis of nanoporous silicon as a possible heat rectifier. Indeed, when the pores are smaller than the phonon mean free path in the bulk, the thermal conductivity of the system becomes very sensitive to the pore size for a given porosity [11–15]. We explore this effect to study the rectifying coefficient of a cylindrical sample of bulk Si

in series with a cylinder of nanoporous Si, in terms of the porosity, the radius of the pores, and the lengths of the two regions.

In Section 2 we discuss the temperature dependence of porous Si, and compare it with that of bulk silicon; in Section 3 we obtain the rectifying coefficient and we discuss the influence of the pore size, the porosity, and the relative size of the regions; and in Section 4 we summarize and discuss the main results.

2. Temperature dependence of nanoporous Si

The transport properties of complex multiphase materials are a topic of much practical and theoretical interest (see for instance [16] for a review of recent progress) in this field. For the analysis in this work, we use for the thermal conductivity of the porous Si the analytical approximate expression obtained in [13,14] by using the so-called phonon hydrodynamics [4,17–22], a thermodynamic description of heat transport based on a generalization of Fourier’s law, incorporating non-local effects and thermal slip along the walls. According to this result, the effective thermal conductivity λ_{eff} of porous Si with porosity ϕ (ratio of the volume of the pores divided by the total volume), pore radius a , and phonon bulk mean free path ℓ is [13,14]

$$\lambda_{eff}(T, \ell/a, \phi) = \frac{\lambda_0(T)(1 - \phi)^3}{1 + \frac{9}{2}\phi(1 - \phi)^3 \frac{(\ell(T)/a)^2}{1 + A'(\ell(T)/a)} (1 + \frac{3}{\sqrt{2}}\sqrt{\phi})} \quad (1)$$

where λ_0 is the thermal conductivity of bulk Si, and $A'(\ell/a)$ is a numerical function comprised between 0.700 for small ℓ/a and 1.164 for high ℓ/a , for which is taken the heuristic form [23]

* Corresponding author. Tel.: +34 93 5811658; fax: +34 93 5812155.

E-mail addresses: mcriado@ccia.uned.es (M. Criado-Sancho), felipe@unam.mx (L.F. del Castillo), Jose.Casas@uab.es (J. Casas-Vázquez), David.Jou@uab.es (D. Jou).

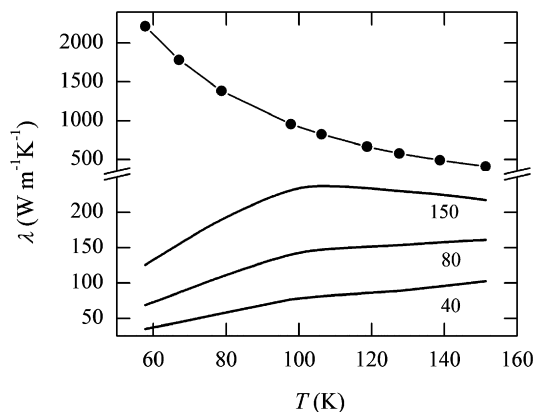


Fig. 1. Heat conductivity of bulk Si (upper line) and of porous Si, for three values of the pore radius a ($a = 150$ nm, 80 nm, and 40 nm) and porosity $\phi = 0.1$, as a function of the temperature, in the range 60 K–150 K. Note the gap of two ranges of values in the vertical axis, because the thermal conductivity of bulk Si is much higher than that of porous Si.

$A'(\ell/a) = 0.864 + 0.290 \exp(-1.25a/\ell)$. According to this expression, the effective thermal conductivity does not depend only on the value of the porosity, but also of the ratio ℓ/a , namely the Knudsen number, as seen in the second term of the denominator, which describes ballistic contributions of phonon collisions against pores, i.e. in the regime where the phonon mean free path is much longer than the radius of the pores. For small values of ℓ/a , (1) reduces to $\lambda_{\text{eff}} = \lambda_0(1 - \phi)^3$, which is the expression used in [11], which yields good approximation to observed values of the effective porosity in this limit. Indeed, the role of the nanopore size is experimentally well known. For instance, in [11,12] it is seen that for a porosity $\phi = 0.4$ and at $T = 300$ K, the effective thermal conductivity of porous Si is $31.2 \text{ W m}^{-1} \text{ K}^{-1}$ for $a = 100$ nm [11] and $1.2 \text{ W m}^{-1} \text{ K}^{-1}$ for $a = 5$ nm [12]. These results are much lower than the heat conductivity of bulk Si at the same temperature, which is $148 \text{ W m}^{-1} \text{ K}^{-1}$. This dependence on the pore size at a given porosity value is also seen in [15]; a different but analogous situation arises, for instance, in the thermal conductivity of carbon nanowires depending on the width of the walls: decreasing the thickness implies decreased values of the thermal conductivity [24].

The phonon mean free path ℓ used in (1) is obtained from the expression for the thermal conductivity in terms the mean free path $\lambda = cv\ell/3$, with c the specific heat per unit volume and v the phonon velocity. Since the bulk phonon mean free path ℓ becomes long and strongly temperature-dependent at low temperatures (for instance, it is of the order of 6680 nm at 50 K, 1430 at 80 K, 700 nm at 100 K, 340 nm at 130 K, and 180 nm at 150 K) the contributions of the pores are expected to be especially relevant at low temperatures and for small pores. Since the phonon mean free path increases when temperature becomes lower, the increase of the denominator for lower temperatures will partially compensate the increase of the numerator in (1).

In Fig. 1, we show the experimental values of heat conductivity of bulk Si [23], and of porous Si, predicted by Eq. (1), in the range between 60 K and 135 K, for three values of the radius of the pores (150 nm, 80 nm, and 40 nm) and porosity $\phi = 0.1$. We have chosen this range of temperature because in it the reduction of thermal conductivity of bulk Si for increasing temperature is most pronounced, and therefore most suitable for heat rectification. In particular, it is seen that whereas the heat conductivity of bulk Si decreases for increasing temperature, that of porous Si slightly increases, for sufficiently small values of the pores. This difference of behavior indicates that a combination of bulk Si and of porous Si could provide a thermal rectifier, because when the hot side is that

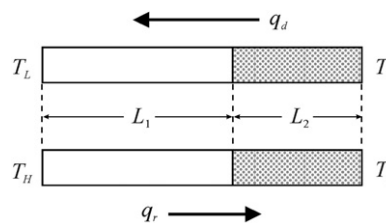


Fig. 2. Sketch of the device being studied, composed of two cylindrical regions of bulk Si (left-hand side) and porous Si (right-hand side). The rectifying effect is shown through the difference of values of the direct and the reverse values of the heat flux between high temperature T_H and low temperature T_L .

of bulk Si (low conductivity) and the cold one is that of porous Si, the thermal conductivity of the device will be lower than in the opposite situation, namely, when the cold side is that of bulk Si (high conductivity) and the hot one is that of porous Si. Note that for $a = 150$ nm the thermal conductivity of the porous Si shows a maximum near $T = 105$ K, and it decreases for higher values of T ; this is because for such values the ballistic contribution in the denominator in (1) becomes smaller than 1, and the effective thermal conductivity decreases with increasing temperature. A similar behavior would be observed for the other two curves but at higher temperatures than those represent in Fig. 1.

3. Thermal rectification coefficient

Here, we study the rectification coefficient of the device shown in Fig. 2, composed of a bulk region and a nanoporous region, in the range between 60 K and 125 K. We take for the length of each region of the device L_1 (bulk Si) and L_2 (porous Si), which could be of the order of a few millimeters, analogous to that considered in [8] and [10]. We consider a cylinder of constant cross section, wide enough in comparison with the value of the bulk phonon mean free path, in order that the collisions with the walls do not contribute to the thermal conductivity. Interfacial effects between bulk and nanoporous Si in the rectification are expected to be small, because there is not a change in the material where phonons are propagating; such effects are expected to be relevant when the average separation between pores becomes comparable to the phonon thermal wavelength, but this would be at much lower temperatures than those being considered. Thus, the role of the interfaces between Si and pores is expected to be globally relevant when all the pores in the porous region are taken into account, but not when only the first layers of the transition region between the bulk region and the porous region are taken into account. In other words, we assume that if the width of the porous regions were much smaller than the size of the phonon mean free path, the reduction of the thermal conductivity and the thermal rectification effects would be negligible. Thus, a full analysis of this problem would require taking into account three sizes: pore radius, phonon mean free path, and phonon wavelength. Our analysis refers to situations in which pore radius is smaller than the mean free path but bigger than phonon thermal wavelength. The classical analyses, instead, are valid when the pore size is much bigger than the mean free path and than the phonon thermal wavelength.

We assume that the cold head of the device is kept at $T_L = 60$ K, and from Fourier's law $q = -\lambda(T, \phi, a)(dT/dx)$, we evaluate the heat flux for a given temperature difference ΔT between both sides; we do so in both directions, and we obtain the thermal rectification coefficient R as the ratio of the direct and reverse heat flux, namely $R = |q_d|/|q_r|$ (in other alternative definitions, the thermal rectification is defined as $R' = (|q_d - q_r|/q_r) \cdot 100$) [7,9]. In Figs. 3 and 4, we show the coefficient R for different values of the temperature difference ΔT , for $T_L = 60$ K, and for different values of the porosity ($\phi = 0.1$ and 0.4, respectively), for two different

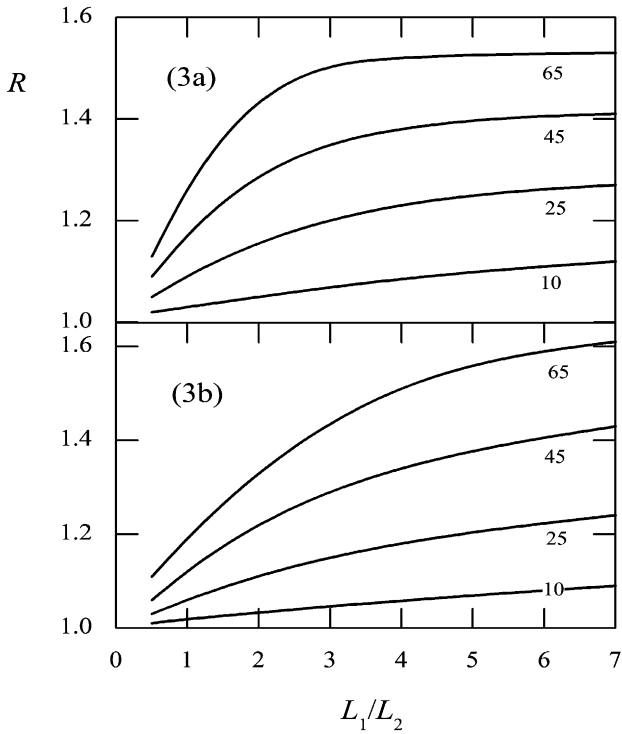


Fig. 3. Rectifying power R of the device shown in Fig. 2 as a function of the ratio L_1/L_2 of the lengths of bulk Si (L_1) and porous Si (L_2) for porosity $\phi = 0.10$, and four different temperature intervals (65 K, 45 K, 25 K and 10 K) for pore radius $a = 150$ nm (3a) and $a = 80$ nm (3b).

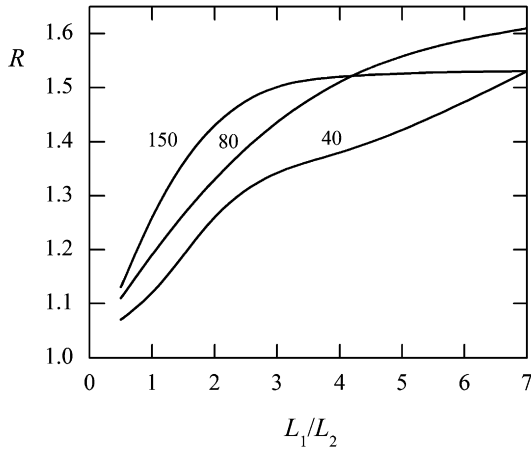


Fig. 4. Rectifying power R of the device shown in Fig. 2 as a function of the ratio L_1/L_2 of the lengths of bulk Si (L_1) and porous Si (L_2) for pore radii $a = 150$ nm, 80 nm, and 40 nm, porosity $\phi = 0.10$, and temperature interval 65 K.

radii of the pores ($a = 150$ nm and 80 nm, respectively), as a function of the ratio L_1/L_2 of the lengths of bulk Si (L_1) and the porous Si (L_2) regions.

Examination of Fig. 3 shows that for $\phi = 0.1$, R as high as 1.52 may be obtained for $a = 150$ nm, and as 1.6 for $a = 80$ nm. Though the results for $a = 40$ nm are lower than those of the other pore size, they would become higher for values of L_1/L_2 higher than those shown in the figure. These theoretical values are slightly higher than the value 1.43 obtained in [8] for an oxide thermal rectifier of LaCoO_3 and $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ for a temperature interval $\Delta T = 60$ K, with lengths 6.3 mm and 6.1 mm respectively for the mentioned materials, between 40 K and 100 K. In our case, since the thermal conductivity of bulk Si is considerably

smaller than that of crystalline Si, we have considered a different length for both materials, in contrast to [8], in which the thermal conductivity of both materials is of the same order (between 5 and 2 $\text{W m}^{-1} \text{K}^{-1}$) for LaCoO_3 and 1 and 2 $\text{W m}^{-1} \text{K}^{-1}$, for $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$. Higher values of porosity yield lesser values for R in this temperature interval because the increase of thermal conductivity with temperature for the porous Si is smaller for higher porosity.

Fig. 4 shows that pore radius $a = 80$ nm leads to higher values of the rectifying coefficient than for $a = 150$ nm, reaching values higher than 1.6, for sufficiently high values of L_1/L_2 . This increase of the value of L_1/L_2 necessary to reach a higher R than for $a = 150$ nm is due to the fact that the thermal conductivity for $a = 80$ nm is lower than for $a = 150$ nm, as it may be understood from Eq. (2). For $a = 40$ nm, the values of R are lower in the regions shown here, but for L_1/L_2 higher than 7 the rectifying coefficient would become higher than that for $a = 150$ nm. The increase of R for lower values of a could be even higher, but it would not be indefinite, because Eq. (1) is valid in the regime when the characteristic phonon wavelength is smaller than the radius of the pores. Since the phonon wavelength at T of the order of 60 K is of the order of 1 nm, Eq. (1) may be safely used for the pore sizes we have considered, and even smaller ones. For higher porosity, as for instance $\phi = 0.4$, the rectifying coefficient is considerably lower than that for $\phi = 0.1$. This is due to the fact that it follows from (1) that the thermal conductivity increase in temperature interval being considered here is smaller for $\phi = 0.4$ than for $\phi = 0.1$, at the same pore radius, and this leads to a lower value for the rectifying coefficient R .

The trends observed here are easily interpreted from the expression for the rectifying coefficient R obtained by integration of Fourier's law, which is

$$R \leq \frac{\lambda_{1H}\lambda_{2L}}{\lambda_{1L}\lambda_{2H}} \left(\frac{\lambda_{2H}L_1 + \lambda_{1L}L_2}{\lambda_{2L}L_1 + \lambda_{1H}L_2} \right), \quad (2)$$

where λ_{iH} and λ_{iL} refer, respectively, to the values of the thermal conductivity of material i (remember that $i = 1$ for bulk Si and $i = 2$ for porous Si) at T_H and T_L , the high and low temperatures at the ends of the device. To have an equality sign, we should use for λ_{iH} and λ_{iL} averages of the thermal conductivity in the interval between at T_H and T_{int} , and T_{int} and T_L , respectively, T_{int} being the temperature in the interface between materials 1 and 2. It follows from here that, for $L_1 = L_2$, the most convenient situation for a high value of R is having a high decrease of thermal conductivity for increasing temperature for material 1 and a high increase for material 2. However, if the thermal conductivity of material 2 is much lower than that of material 1 and if the increase of thermal conductivity of 2 is small (this will happen in our situation when the porosity is high) the coefficient R will be close to 1. Thus, situations with high porosity do not seem very promising for getting high values of R . Even in the case of porosity $\phi = 0.1$, the thermal conductivity of the porous material is considerably lower than that of the bulk material. In this case, to increase the value of R it is convenient to have $L_1 > L_2$. This is the reason why in Figs. 3–4 we consider situations with different values for L_1/L_2 , and explains the trend to increasing R for increasing ratios L_1/L_2 .

4. Conclusions

We have obtained the thermal rectifying coefficient of a device composed of bulk Si and porous Si for two values of the pore size and of porosity coefficient. The results seem promising, as one may get R of the order of 1.7, and even higher. This value is higher than the value 1.43 obtained in [8] in an oxide thermal rectifier, but lower than that of 2.5, calculated for carbon nanocones [9]. Our

analysis suggests one further possible use of porous Si, a system of much interest on its own [11,12,25–27]. Note that the results obtained here are typically ballistic, i.e. they arise because ℓ/a is higher than 1; in contrast, when ℓ/a tends to 0, (1) reduces to $\lambda_{eff} = \lambda_0(1 - \phi)^3$, in which case the behavior of thermal conductivity as a function of temperature will have analogous features to those of crystalline Si, i.e. the thermal conductivity will decrease for increasing temperature in the interval considered here. In such a case, the rectifying power shown here would not appear. We have neglected the possible interface effects at the interface between the porous part and the bulk part because it is the same material in both parts. This kind of device could be achieved by chemically attacking one region of a bulk Si cylinder; however, to ensure in more detail the characteristic of the pores it would be better to make the experiment in two dimensions, namely, on a plate with a continuous region and a perforated region, i.e., combining a continuous regions and a so-called two-dimensional phononic crystal (for experiments on the latter see, for instance, [27]).

Another situation of possible interest would be to consider an inhomogeneous porous system such that the radius of the pores, or the porosity itself, change along the sample. However, since the variation of the thermal conductivity with temperature of porous Si is less pronounced than that for bulk Si, the value for the rectifying coefficient will be smaller than in the situation we have studied here.

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