

Optical investigations on thermal conductivity in n- and p-type porous silicon

S. Lettieri^{*1}, U. Bernini¹, E. Massera², and P. Maddalena¹

¹ Coherentia-INFM and Dipartimento di Scienze Fisiche, Università di Napoli "Federico II", Complesso Universitario di M. S. Angelo, 80126 Napoli, Italy

² CR-ENEA Portici, Loc. Granatello, Portici (NA), Italy

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Determination of thermal conductivity of top side illuminated n-type and p-type porous silicon (PS) samples have been performed by means of photo-acoustic and optical pump-probe techniques. Concerning the n-type samples, the values found can be explained in the framework of Looyenga effective medium theory, leading to a thermal conductivity of the solid phase of 13 W/mK. This result suggests that n-type thick PS samples formed by top side illumination has a complex multilayer morphology in which mesophases, nanophases and macrophases coexist. The investigation on p-type nanoporous silicon shows that the thermal conductivity does not scale with porosity p as $(1-p)^3$, suggesting that the percolation of the solid phase is more pronounced respect to the case of a regular "Looyenga-like" mesophase.

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1 Introduction

Porous silicon (PS) is a good thermal insulator, as its thermal conductivity can be two or three order of magnitude lower than c-Si one depending on the particular sample morphology and porosity, and it is therefore an useful material for micromachining of differential temperature based sensor element on silicon wafers, realising both a satisfying thermal insulation and a useful mechanical solidity.

In the case of micro- and mesoporous Si, the thermal insulating properties of PS are not only due to the presence of air inside the pores but also to being the mean size of nanocrystals ordinary smaller than the phonon mean free path in bulk silicon (43 nm at room temperature). The values of PS thermal conductivity reported in literature hence scatter significantly one from the other because of the morphological differences: values from 31 W/mK for macroporous n-type [1, 2] to about 0.05 W/mK for high porosity p-type samples have been measured [1–3].

Different techniques have been used to measure PS thermal conductivity, based on the use of microdevices [3, 4] or on optical approaches, such as for instance Raman-scattering based methods [5, 6], photo-acoustic [1, 2, 7] and optical pump-probe [8].

A thermal characterisation based on different optical techniques is shown here of n-type and p-type PS samples. The first set of measurements was performed on n-type front-illuminated PS by means of photo-acoustic (PA) technique, in which one detects the thermal waves generated by surface absorption of an intensity modulated optical beam in a sample, while the second set of measurements was performed on p-type PS by a time-resolved optical pump-probe technique, in which the absorption of the

^{*} Corresponding author: e-mail: stefano.lettieri@na.infn.it, Phone: +00 39-81-676233

pulsed pump beam induces a change of the refractive index of the sample and, in turn, a change of the transmitted fraction of a probe laser.

2 Experimental

A series of n-type PS samples have been fabricated by electrochemical etching n-type 1 Ω cm crystalline silicon <100> oriented. Anodic dissolution was performed during front illumination in a solution of hydrofluoric acid and isopropyl alcohol. Front illumination during anodic etching induces the formation of layers having different morphologies. Usually both mesoporous and nanoporous structures are present into a thick sample and in some cases the thermal properties of such samples cannot be described taking into account a single layer model [1, 2].

Current densities and attack times were chosen in order to have three couples of samples, having 40 %, 57 % and 72 % porosity, respectively. Each couple was made by a sample having a porous layer of a few tens of microns and a thicker one (hundreds of microns) which was used as a reference in the PA measurements. Their characteristics are summarized in Table 1.

Table 1 Sample parameters and measured thermal conductivities of investigated n-type samples. Each couple of samples is made by a thin and a thick PS samples having the same porosity and different thickness.

Couple of samples	Porosity (%)	thickness (μm)	K_{eff} (W/mK)	$K_{\text{eff}}/(1-p)^3$
A	40	45 and 170	2.93	13.6
B	57	60 and 250	1.03	13.0
C	72	40 and 100	0.29	13.2

The PA investigation was performed measuring the PA signal $|\Delta p|$ of a thin sample. The measured signal was normalised to the one $|\Delta p|_R$ obtained from a reference PS sample having the same dimensions and porosity of the sample under investigation but with such a large thickness as to be considered thermally thick. and a reference sample made of the same material but thick with respect to the thermal wave penetration depth.

An expression for the PA signal can be derived using the general formulation of Yasa [9] which takes into account the expansion of the interstitial gas. The general expression for the ratio $|\Delta p|/|\Delta p|_R$ is:

$$\frac{|\Delta p|}{|\Delta p|_R} = B \frac{1}{1 + p(\alpha_s/\alpha_g)^{1/2}} \left| \frac{1 + (E_b/E_s) \tanh[(1+i)d/\mu_s]}{(E_b/E_s) + \tanh[(1+i)d/\mu_s]} + p \left(\frac{\alpha_s}{\alpha_g} \right)^{1/2} \left(1 - \frac{1}{\cosh[(1+i)d/\mu_s]} \right) \right| \quad (1)$$

where I_0 is the incident intensity modulated at frequency ω , R is the reflectance, K , $\alpha = K/\rho C_v$, $E = (K\rho C)^{1/2}$ and $\mu = (2\alpha/\omega)^{1/2}$ are the thermal conductivity, diffusivity, effusivity and diffusion length respectively, d is the PS sample thickness and γ is the thermal expansion coefficient. Suffixes s , g and b refer to the PS sample, coupling gas and crystalline Si backing substrate, respectively. Finally, where $B \approx 1$ is a constant depending on the different values of the incident light intensity. The ratio depends on k and ω only and, hence, in order to determine K it is sufficient a one-parameter fit procedure once the properties of the crystalline substrate and the thickness of the porous layer are known.

In Fig. 1 we reported the ratio $|\Delta p|/|\Delta p|_R$ obtained for the couple of samples A and the best fit curves to the experimental data. Similar experimental curves were obtained for the other couples. In the calculation values reported in literature were used for thermal conductivity and specific heat of c-Si and air. The resulting thermal conductivity values of PS samples are reported in Table 1. It is evident that K decreases for increasing porosity and is about two orders of magnitude less than the one of crystalline silicon. Such low values suggest that some degree of phonon confinement occurs. This results will be discussed in more detail in next section.

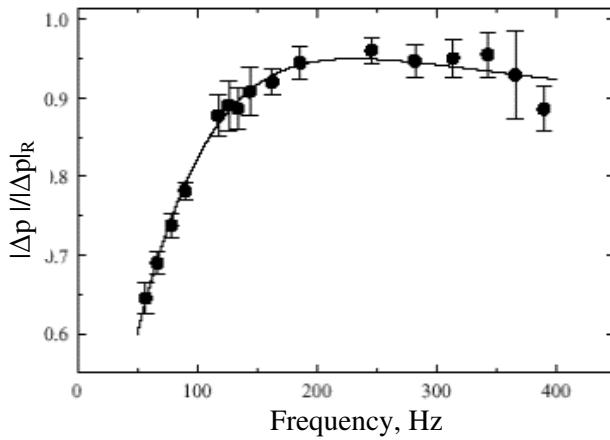


Fig. 1 PA signal (points) and best fit curve (solid line) for n-type 72% porosity sample pair.

Next, we show the results obtained by means of pump-probe technique on p-type PS samples. This technique is based on the change of the local temperature due to pump light absorption. The local temperature change induces, via the thermo-optical effect, a change of refractive index which in turn induces a transient modulation of the probe transmission. The recovery time of this latter modulation depends on the time evolution of the heat in the sample and so involves its heat conductivity. It is possible to demonstrate that the temperature evolution at the optical axis position can be expressed with good approximation as $T(t) = T_0[1 - \exp(-t/\tau_k)]$ where $\tau_k = a^2 \rho C_v / 4K$ [10]. Under a small modulation regime the probe transmission is linearly dependent on the refractive index change, and in turn on the temperature transient modulation. Therefore, one can use the above expression to fit the time-dependent modulation of the probe optical transmission. From the best fit of data one obtains the temperature decay time τ_k and the thermal conductivity K on the spot size of the pump beam a is measured.

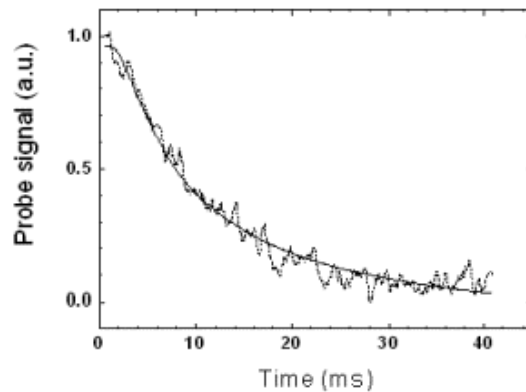


Fig. 2 Thermally-induced non-linear probe transmission (dotted line) and best fit curve (solid line) for p-type 66% porosity sample.

This technique was used in order to investigate free-standing p-type PS samples. The samples were obtained from 0.2 Ωcm <100> oriented silicon wafers and the porous layer was detached by standard lift-off procedure. The pump pulse was obtained from a Q-switched Continuum Nd:YAG laser, whose

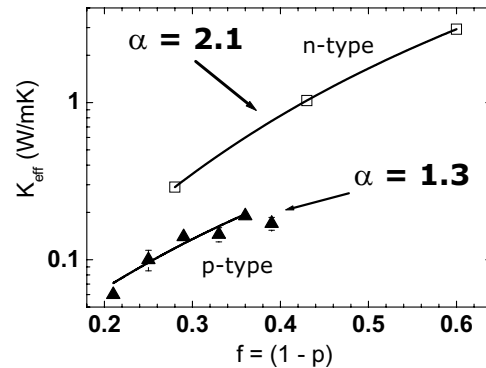


Fig. 3 Measured K values vs. solid phase volume fraction f . Empty squares: n-type samples; full circles: p-type samples.

pulse duration and wavelength are 5 ns and 1064 nm, respectively. A variable attenuator was used in order to avoid damaging of the sample. The probe beam is provided by a Melles-Griot He-Ne 3 mW power laser.

An example of the time-resolved probe transmission corresponding to a sample of porosity $p=61\%$ is shown in Fig. 2, where the best fit curve is also shown. The measured thermal conductivity as a function of the volume fraction $f=(1-p)$ is shown in Fig. 3.

3 Discussion

In order to discuss the low PS thermal conductivity K , three phenomena have to be taken into account. The first is the porosity effect, i.e. the presence of air filling the pores. The air is a thermal insulator ($K_{\text{air}}=0.025$ W/mK at room T) and therefore its presence reduces the thermal conductivity. This effect is purely extensive and therefore it depends linearly scales on the solid fraction parameter $f=1-p$. The degree of percolation inside the structure has also to be considered, as the solid phase which is not interconnected cannot contribute to thermal transport. Therefore, K also depend on a percolation strength parameter g_0 , which is defined as the fraction of interconnected solid phase. Finally, it is to be considered the phonon confinement which occurs when the mean crystallite size is smaller than the phonon mean free path, reducing in such a case the thermal conductivity of the solid phase K_s . Taking into account these consideration and neglecting the low thermal conductivity of air, one can express the effective thermal conductivity of a porous material of porosity p as [3]: $K_{\text{eff}} = f g_0 K_s$, where $f=1-p$, g_0 is the fraction of interconnected solid phase and K_s is the thermal conductivity of the solid phase. In the case of mesoporous silicon, good agreement with the experimental results is found [5] by setting $g_0 = f^2$, as in the Looyenga effective medium model. Concerning our results, the $K \propto (1-p)^3$ behaviour is observed for the n-type samples, as one can see in Table I where K_{eff} and $K_{\text{eff}}/(1-p)^3$ are reported. These latter values are compatible within the experimental uncertainty obtained by the best fit, giving $K_s = K_{\text{eff}}/(1-p)^3 = 13.3 \pm 0.3$ W/mK. This value is one order of magnitude smaller than the bulk silicon thermal conductivity and is consistent with the finding $K_s = 13$ W/mK reported in Ref. [7]. The authors of [7] suggested that this result may be due to the largest of columnar structures in macroporous silicon being made of SiO_2 , whose thermal conductivity is $K_s = 10$ W/mK. As the morphology of front side illuminated thick n-type PS is much more complex, it seems reasonable to guess that both mesoporous and macroporous phases were present in the samples. Therefore phonon confinement as well as the presence of silicon dioxide can both contribute to the low value of thermal conductivity. It is to be noted that our PA results give

porosity scaling rule and values of thermal conductivity which are similar to those well established for p+ type mesoporous silicon, which is known to be well described by the Looyenga model.

Concerning the p-type, one can see that thermal conductivities values are lower than typical ones of n-type and p+-type PS. This phenomenon was clearly observed also in measurements by Gosele and coworkers [3], where the thermal conductivity of p-doped samples was much lower than those measured in p+ samples of equal porosity. Finally, it is very interesting to consider the dependence of thermal conductivity versus porosity for both morphologies and focusing the attention on how the morphology affects the relationship between the percolation strength g_0 and the volume solid fraction f . As a matter of fact, while the Looyenga rule $g_0 = (1-p)^{-2}$ correctly describes regular mesoporous structures, random disorder can in principle affect the correlation between g_0 and f breaking the above rule. Therefore, in Fig. 3 we report the experimental values of the thermal conductivity as a function of the volume fraction f . The experimental data are fitted by means of a power law $K_{\text{eff}} \sim (1-p)^{1+\alpha}$, where $\alpha=2$ gives the Looyenga behaviour. The best fits give $\alpha=2.05 \pm 0.05$ for the n samples, in agreement with the Looyenga model, while in the case of p-type samples is found $\alpha = 1.3 \pm 0.1$. Similar results are obtained using the values of K_{eff} reported for nanoporous samples in refs. [1, 2, 3]. Being $f < 1$, one has $f^{1.3} > f^2$: in other words the experimental results put in evidence that in p-type PS there is a larger amount of percolation than in mesoporous – “Looyenga-like” Si. Therefore, the fact that even at the same porosity p-type PS thermal conductivity is lower than the mesoporous Si one has not to be ascribed by a consequence of percolation effects but to the a reduction of the thermal conductivity of the solid phase K_s itself. This latter reduction is reasonable as one considers that solid phase clusters in microporous silicon are much smaller mesoporous silicon than the ones and therefore higher degree of phonon confinement occurs.

In conclusion, measurements of thermal conductivity in n- and p-type PS samples have been shown by means of different optical techniques. The results obtained for n-type top side illuminated samples show that a mixture of macroporous, mesoporous and nanoporous phases are present, while the overall thermal behaviour can be successfully described by means of Looyenga model. In the case of p-type samples, much lower values are found. This finding can be explained by enhanced phonon confinement within the Si nanocrystals. Moreover, the result obtained for of p-type samples show that the Looyenga scaling rule $g_0 = (1-p)^2$ is not satisfied but an enhanced percolation strength g_0 with respect to mesoporous morphologies manifests.

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