ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 21, No. 2. 2015

Dynamical Study of Heat Transport Properties of Porous Silicon

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crossref http://dx.doi.org/10.5755/j01.mm.21.2.5785

Received 25 November 2013; accepted 29 March 2014

A new fast technique to determine thermal conductivity of porous silicon is proposed. Transient thermoelectric voltage is measured after a pulsed laser irradiation, and analysis of the voltage decay time constant and porosity of the structure gives the value of the thermal conductivity. For *n*-type Si of 70 % porosity we show the value of 35 $W\cdot m^{-1}\cdot K^{-1}$. The method can be easily applied for any other porous or otherwise structured low-dimensional media.
Keywords: porous silicon, transient thermoelectric effect, thermal conductivity, thermoelectric material.

1. INTRODUCTION

Porous silicon (por-Si) having unique and interesting properties makes its way into applications of many fields. For instance, por-Si has demonstrated very good features of electroluminescence and photoluminescence in the visible and IR spectra [1, 2], its refractive index and reflection coefficient can be modulated depending on the porosity [3]. These properties make por-Si a promising material for the photonics. Another example of applications of porous Si is in the biological field, such as bio-detector since it is a bio-compatible material [4].

As the world's demand for energy rapidly increases while fossil fuel supplies decrease, it is becoming more important to develop new, inexpensive materials that can supply sustainable and clean energy to meet the needs of the future. One promising approach relies on thermoelectric materials, which interconvert temperature gradients and electricity on a solid-state basis and thus provide a method of cooling and power generation without refrigerant or moving parts. During the past years, nanostructured silicon has been "identified" as high potential thermoelectric material, i. e., as a material with a high thermoelectric figure of merit ZT [5]. The figure of merit is determined by electrical and thermal material properties and given by $ZT = \sigma S^2 T/\kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient, T is the material's temperature, and κ is the thermal conductivity.

One of the ways to boost the material's figure of merit is to lower its thermal conductivity. A lot of works recently have been devoted to the investigations of thermal conductivity of nanostructured silicon. Thermal conductivities of individual single crystalline Si nanowires measured using a microfabricated suspended device were up to two orders of magnitude lower than the bulk value [6]. Strong diameter dependence of thermal conductivity in the nanowires was ascribed to the increased phonon-boundary scattering and possible phonon spectrum modification. Experimental studies using the pulsed-photothermal method revealed that the thermal conductivity of macroporous and mesoporous silicon is two times lower than that of the single crystal silicon (140 $W\cdot m^{-1}\cdot K^{-1}$) [7]. Thermal conductivities of sintered porous silicon films measured at room temperature using a non-contact method based on lock-in thermography ranged from 21 to 2.3 $W\cdot m^{-1}\cdot K^{-1}$) and decreased with increasing porosity [8]. Calculations also indicated that combination of the nanometer size of pores greatly reduces the value of thermal conductivity coefficient [5].

In this paper we demonstrate a handy novel dynamic technique, called the "transient thermoelectric effect (TTE)" method [9], useful to get to know the value of thermal conductivity of a semiconductor layer, and apply it for the porous n-type silicon material.

2. EXPERIMENTAL DETAILS

The (100)-oriented *n*-type 1 $\Omega\cdot$cm silicon 300 μm-thick substrates were cleaned using RCA cleaning method [10] and etched in $HF:C_2H_5OH = 1:1$ for 10 min. at galvanostatic regime at current density 30 mA/cm^2. In-Ga eutectic was deposited onto the backside of the substrate for better electrical contact. During the etching process, the frontside of the substrate was illuminated with 50 W halogen lamp. After the etching process, top nanoporous layer was removed by immersing the porous samples into 1 % KOH solution. The porous layer penetrated to about 10 μm in depth. Top view of the etched surface is presented in Fig. 1. Then the samples were cut into 3 mm × 8 mm strips with porous surface on one side (see Fig. 2). Electric wiring was contacted using silver epoxy CW2400.

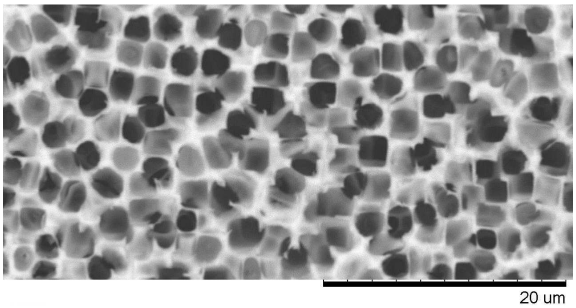

Fig. 1. SEM image (top view) of the etched porous n-Si sample

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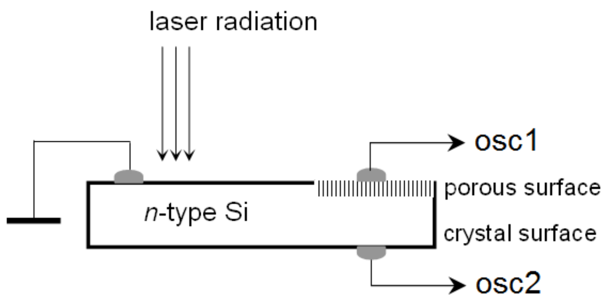

Fig. 2. Schematic side view of the sample and TTE measurement scheme. Dashed area indicates porous surface, grey spots stand for Ag contacts, and OSC points to the oscilloscope

For the TTE measurements the diode pumped solid state Nd:YAG laser producing ~100 ns pulses of 1.064 µm wavelength at 100 Hz repetition rate was used. Maximum laser intensity reached 10 GW·m^{-2} in a focused spot of 0.5 mm diameter. The pulsed laser was irradiated normal to one side of the sample. In order to avoid irradiation near the metal-semiconductor contact, the grounded contact was shielded from the straight laser light (not shown in Fig. 2). Also, to avoid parasitic photovoltages induced by multiple reflections, the intensity was reduced by approximately ten times. The TTE voltages were recorded on digital storage oscilloscope Instek GDS-2202; the one from the etched layer versus grounded left side is indicated in Fig. 2 as OSC1, and the voltage from the non-etched side – as OSC2.

3. RESULTS AND DISCUSSION

The TTE method analyses formation of photoresponse along a similar semiconductor bar exposed to intense laser radiation. Generally, the response consisted of three stages with the characteristic relaxation times. The first one was associated with carrier generation and recombination, the second was considered as the transient Seebeck effect, and the third stage was due to the diffusion of thermal flux or phonons under a temperature gradient generated by a laser pulse.

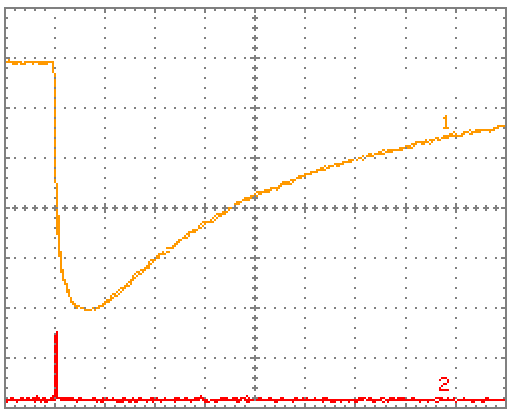

Fig. 3. Oscilloscope trace of TTE voltage for porous *n*-Si sample (orange line, No.1) and short laser pulse (red line, No.2). Vertical scale is 10 mV/div., time scale is 25 µs/div.

In this work we use similar excitation technique but confine and focus the investigation on only the third stage of the photoresponse. Typical long-lasting oscilloscope trace of the TTE voltage for porous *n*-Si sample is shown in Fig. 3. Polarity of the voltage signal, i. e. negative sign of the signal at the upper right contact with respect to the grounded left contact, indicates flow of electrons from the heated side of the sample to the cold one. Similar TTE voltage was detected for the non-etched single-crystal n-Si sample.

According to the TTE model [9], the decay speed of the laser-induced voltage is represented by the time constant which in turn is inversely proportional to the thermal diffusion coefficient defined as

$$D_T = \frac{\kappa}{C_V \rho}, \tag{1}$$

where C_V (J·kg^{-1}·K^{-1}) is the specific heat per mass unit, and ρ (kg·m^{-3}) is the mass density. The values of the volumetric heat capacity of porous silicon (or any porous media) can be calculated taking into account the porosity of the sample by applying a barycentre model [7] according to

$$(C_V \rho)_{\text{por-Si}} = (C_V \rho)_{\text{c-Si}} (1 - \text{porosity}). \tag{2}$$

Using indexes "por-Si" and "c-Si" to mark symbols related to porous and single-crystal sample, respectively, from equations (1) and (2) we obtain the ratio of the voltage decay time constants of the porous and non-etched layers:

$$\frac{\tau_{\text{por-Si}}}{\tau_{\text{c-Si}}} = \frac{D_{T\ \text{c-Si}}}{D_{T\ \text{por-Si}}} = \frac{\kappa_{\text{c-Si}}}{\kappa_{\text{por-Si}}} (1 - \text{porosity}). \tag{3}$$

Or in the other form:

$$\kappa_{\text{por-Si}} = \kappa_{\text{c-Si}} \frac{\tau_{\text{c-Si}}}{\tau_{\text{por-Si}}} (1 - \text{porosity}). \tag{4}$$

Equations (3) and (4) are derived considering that the laser pulse induced thermal flux travels equal paths along the sample for both, por-Si and c-Si, measurement cases. Thus, knowing the values of the both voltage decay time constants and having the porosity number of por-Si, one can evaluate the value of thermal conductivity of the porous layer.

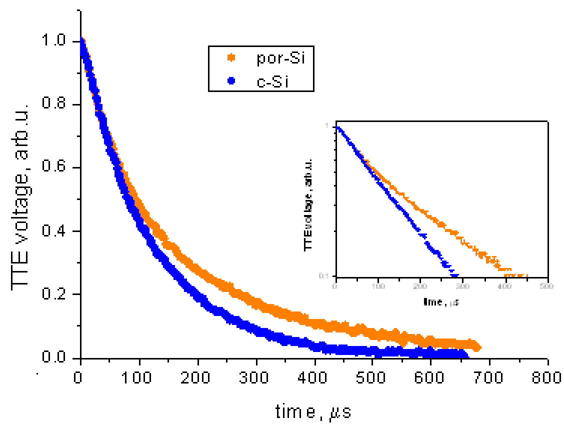

Fig. 4. Time-dependence of normalized to unity TTE voltages for porous n-Si sample (orange dots) and non-etched crystalline Si (blue dots). Inset: the same in semi-log plot

Fig. 4 demonstrates normalized to unity decay traces of the TTE voltage for por-Si (orange trace) and c-Si (blue trace). Visibly, the por-Si voltage relaxes more slowly compared to the one of c-Si. Mathematical approximation of these two relaxation curves revealed them to be of a pure exponential character, and numerical analysis of the exponential decays yielded the values of $\tau_{c\text{-Si}}$ = 117 μs and $\tau_{por\text{-Si}}$ = 140 μs. Since the porosity of the etched layer reached up to 70 % (see Fig. 1), the equation (4) gave us the value of the thermal conductivity $\kappa_{por\text{-Si}} = 35\ W \cdot m^{-1} \cdot K^{-1}$ ($\kappa_{c\text{-Si}} = 140\ W \cdot m^{-1} \cdot K^{-1}$ was taken from [7]).

Table 1 presents a comparison of the values of thermal conductivity for *n*-type porous silicon obtained by different authors and by different methods. It is obvious that the results of our measurements are in reasonable agreement with the results of the other authors. As it was mentioned earlier and is seen from Table 1, higher porosity, i. e. lower dimensions of the residual silicon stem, causes lower values of the thermal conductivity of the structure.

Table 1. Values of thermal conductivity κ for *n*-type porous silicon (PTT and PTA stand for a photothermal and a photoacoustic method, respectively)

κ, $W \cdot m^{-1} \cdot K^{-1}$	Porosity	Method	Source
35	70 %	TTE	Present work
50 – 80	35 % – 15 %	Pulsed-PTT	[7]
13	not indicated	PTA	[11]
31	not indicated	PTT & PTA	[12]

The proposed TTE technique has several undoubted advantages as compared with photothermal and photoacoustic methods. It is faster; it does not require sophisticated apparatus and complicated mathematical analysis of the results of measurement. The measured TTE voltage has relatively high values, much higher than the noise of the equipment, thus excluding possibility of big measurement errors and allowing convenient use and analysis of the results obtained.

It should be also noted that the method presented here is not restricted to the case of *n*-type silicon sample and can be applied equally to the thermal characterization of morphologically related materials. Similar investigations are under way for porous *p*-Si and porous GaAs of our current interest in the field of research of thermoelectric materials.

4. CONCLUSIONS

A new effective and handy model is proposed in this work to evaluate the thermal conductivity of porous materials. The method relies on experimental parallel measurement of transient thermoelectric effect voltage for both porous and non-porous layers and knowledge of the thermal conductivity of bulk material as well as of the sample porosity. The technique is favorable in view of fast evaluation of one of the terms of thermoelectric figure of merit of a material.

Acknowledgments

We express our sincere thanks to Professor Z. Dashevsky from Ben-Gurion University of the Negev for valuable advices and encouragements as well as to O. Žalys for kind technical assistance.

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