Thermal transport study across interface “nanostructured solid surface / fluid” by photoacoustic technique

K. Voitenko\textsuperscript{1a}, M. Isaiev\textsuperscript{1,2}, A. Pastushenko\textsuperscript{3}, D. Andrusenko\textsuperscript{1}, A. Kuzmich\textsuperscript{1}, V. Lysenko\textsuperscript{3}, and R. Burbelo\textsuperscript{1}

1 Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska Str., Kiev 01601, Ukraine
2 Laboratoire LEMTA, Faculté des Sciences et Technologies, CNRS UMR 7563, Université de Lorraine, BP 70239, 54506 Vandoeuvre les Nancy Cedex, France
3 University of Lyon, Nanotechnology Institute of Lyon, UMR CNRS 5270, INSA de Lyon, F69621, France

\textsuperscript{a} voitenkokateryna@gmail.com

Abstract. In the paper the experimental study of heat transport across the interface “porous silicon/liquid” by photoacoustic technique is reported. Two cases with and without liquid covering of porous silicon surface were considered. Thermal perturbations were excited at the surface of porous silicon as a result of absorption of the light with modulated intensity. The resulting thermal-elastic stresses arising in the system were registered with piezoelectric transducer. The amplitude-frequency dependencies of the voltage on the piezoelectric electrodes were measured. The presence of the liquid film leads to decreasing of the amplitude of photoacoustic signal as a result of the thermal energy evacuation from the porous silicon into the liquid. The experimental dependencies were fitted with the results of simulation that takes into account heat fluxes separation at the porous silicon/liquid interface. With the presented method one can precisely measure heat fluxes transferred from the solid into contacting fluid. Moreover, the presented approach can be easily adopted for the thermal conductivity study of the different nanofluids as well as thermal resistance at the interface nanostructured solid/liquid.

1. Introduction

Interfacial phenomena play a significant role in chemistry, material science, biology etc. In particular, heat, mass and charge transfers across interfaces are crucial for formation of nanostructures [1], functionalization of surfaces [2], in the medicine [3]–[5], and so on. Therefore, the prediction and tuning of the interface properties are essential for the various applied areas.

Photoacoustic technique is an efficient tool for the investigation of the thermal transport properties of different systems. It can be easily applied for the study of materials with different structures and morphologies [6, 7]. This method is nondestructive and requires no special sample preparation procedure since the thermal field excitation is contactless. Moreover, since the parameters of photoacoustic signal depend only on the portion of absorbed energy, it is efficient for the study of highly scattered media such as nanostructured materials and biological tissues [8–11]. It is well-known that there is huge amount of different kinds of photoacoustic setup configurations. However, they
could be classified as direct and non-direct. In non-direct ones the acoustic response is measured in surrounding media. In the direct setups thermoelastic stresses occurring in the sample are detected.

In the paper we discuss the application of photoacoustic phenomena to study the heat transfer across nanostructured solid/liquid interface. Piezoelectric configuration was chosen as a photoacoustic technique with important sensitivity [12, 13]. An experimental configuration where the heat perturbation is excited at the solid/fluid interface was used. As a substrate, the layers of porous silicon with different porosities grown on monocrystalline wafer were chosen as samples with well-defined and well-tuned properties. Since porous silicon surface is hydrophobic, water can be used as a liquid not penetrating in the pores. The experimental measurements of the amplitude-frequency dependencies with/without covering fluid of the nanostructured surface were performed. It allows us to distinguish the heat fluxes passing into solid and, as a result, in the liquid.

2. Experimental details

2.1. Sample preparation

The porous silicon samples were fabricated by electrochemical etching of p+-type monocrystalline Si wafer doped with boron (resistivity about 10-20 mOhm·cm). The etching solution consists the hydrofluoric acid and ethanol (HF (49%):C$_2$H$_5$OH=1:1). The initial thickness of silicon wafer was equal to 500 µm. For obtaining porous silicon with different porosity (45%, 55%, and 65%), different anodic current densities were applied (50 mA/cm$^2$, 100 mA/cm$^2$, 200 mA/cm$^2$, respectively). The time of etching was set to perform the thickness of porous silicon layer to be equal to 50 µm. The morphologies of resulting porous silicon layers were observed via SEM, in particular SEM image of the prepared porous silicon sample with porosity 65% is shown in figure 1b.

2.2. Experimental setup

The photoacoustic signal formation in the porous silicon with/without water film on the sample surface was studied in configuration presented in figure 1a. The thickness of water cover layer was equal to 1 mm. The porous silicon surface was irradiated by square wave modulated light of LED with wavelength $\lambda = 470$ nm. As a result of light absorption the thermal distribution was induced in the sample, thus the thermoelastic stresses were created. The resulting deformations of the system were registered with piezoelectric transducer.

![Figure 1](image)

**Figure 1.** Schematic sketch-view of the geometry of the studied system (a). The SEM image of the prepared porous silicon layer with porosity 65% (b).

The dielectric buffer layer with low thermal conductivity and thermal expansion coefficient values was used to avoid penetration of heat fluxes in piezoelectric transducer (PZT). The thickness of the buffer layer was chosen to be equal to 1 mm to perform the conditions that the total thickness of the
layered structure is much bigger than the thickness of the sample. Amplitude and phase shift of photoacoustic responses (voltage on piezoelectric electrodes) were experimentally measured in the frequency range from 10 Hz to 3000 Hz.

3. Results and discussions

The typical amplitude-frequency dependencies for the cases with/without covering liquid are presented in figure 2. The solid lines present the results of simulations based on the evaluation of the temperature distribution in a multilayered structure with planar periodic heat source located at the interface porous silicon/liquid [14]. In the case of low frequencies (less than 100 Hz), the thermal wavelengths are bigger than the thickness of porous silicon layer and almost all heat energy is transferred into the crystalline silicon. As one can see from the figure, the amplitudes of the signals for the cases with and without water layer are approximately the same for the frequencies <100 Hz. This fact confirms equivalence of the optical conditions for the both cases.

For the treatment of experimental data, we used an approximation of quasi-stationary deformations of the system. In frames of this approximation, voltage difference on the piezoelectric electrodes could be written in the following form [14]

\[ \Delta \phi = \int_{0}^{l} \frac{\alpha_e E}{1 - \nu} \theta(s) g(s) ds \]  

(1)

here \( \alpha_e \) is the thermal expansion coefficient of the material, \( E \) is Young's modulus, \( \nu \) is the Poisson coefficient, \( \theta(s) \) is the temperature distribution in the structure, \( g(s) \) is the function which describes the efficiency of the voltage generation depending on the point \( s \) where the elastic source was applied, \( l \) is the thickness of Si wafer. The spatial distribution of the variable component of temperature \( \theta(s) \) in the layered structure was evaluated by solving the heat conduction equation with the corresponding boundary conditions [15]. The expression (1) was used to fit experimental amplitude–frequency dependencies. Thus, thermal conductivities \( \chi_{PSi} \) of porous silicon samples with different porosity were evaluated (0.50 W/m·K, 0.33 W/m·K, 0.25 W/m·K for porosity 45%, 55%, 65%).

Figure 2. The amplitude–frequency dependencies of the photoacoustic signal measured for porous silicon sample (porosity 55%) for the cases with (circles)/without (squares) presence of the water layer. The results of simulation are presented with continuous lines.

Additionally, the comparison of these the cases with/without water layer shows that in the region of high frequencies (larger than 100 Hz) the amplitude of the signal is bigger for the case of absence of water film. In the case of the presence of water film, the part of the thermal energy is evacuated from the porous silicon into the water.

The dependencies of spatial distribution of ac-temperature component amplitude for the cases with/without water layer for excitation frequencies 100 Hz (a) and 2000 Hz (b) are presented in the figure 3. The evaluation of ac-temperature component was made with the use of Fourier law based heat conduction equation with a planar periodic heat source located at the interface porous silicon/liquid. The system of coordinate was chosen the same as in Fig 1a: origin is located at the interface and abscissa is directed in the depth of porous silicon. As one can see from the figure, for the
case of excitation frequency equal to 100 Hz, the important temperature rise appears in the crystalline silicon. For the higher modulation frequency, the temperature rise in the sample is negligible.

Figure 3. The spatial distribution of the amplitude of ac-temperature component for different frequencies: 100 Hz (a), 2000 Hz (b).

The deformations of the considered system caused by light and amplitude of photoacoustic signal are proportional to the thermal energy in the porous silicon and silicon substrate. Therefore, one can conclude that from the ratio ($\varepsilon$) of amplitudes (figure 4a) of photoacoustic signal with and without water film the portion of the thermal energy transferred in the water from the porous silicon can be define. In particularly, ratio of energy transferred in the water to the energy transferred in the porous silicon ($\gamma$) can be define as follows (fig. 4b):

$$\gamma = (1 - \varepsilon) \frac{e_w}{e_{PSI}}$$

where $e_w = \sqrt{c_w \rho_w \chi_w}$, $e_{PSI} = \sqrt{c_{PSI} \rho_{PSI} \chi_{PSI}}$ are thermal effusivities of water and porous silicon respectively, $c_w$, $\rho_w$, $\chi_w$, $c_{PSI}$, $\rho_{PSI}$, $\chi_{PSI}$ are specific heat capacities, densities and thermal conductivities of water and porous silicon, respectively.

Figure 4. The ratio of photoacoustic signal amplitudes for the cases with/without water film as a function of modulation frequency for different porosities of porous silicon layer (a). Frequency dependencies of $\gamma$ coefficient for samples with different porosities (b).
As one can see from the figure 4, the presence of water film covering the surface leads to increasing of the efficiency of heat transport from the porous silicon into the water at the high frequencies. Moreover, this tendency is more pronounced for porous silicon layers with a high value of porosity due to their lower thermal conductivity.

4. Conclusions

Photoacoustic technique with piezoelectric registration was adopted for the study of heat transport across the interface nanostructured solid/fluid. As a solid substrate porous silicon layer with well-defined and well-tuned properties was chosen. The amplitude-frequency dependencies of the photoacoustic signal were measured for two cases with and without water layer covering solid surface. It was shown that the presence of the liquid layer leads to the decreasing of the amplitude of photoacoustic signal amplitude. Correlation of the experimental results with the result of simulation demonstrates that this decreasing arises because of thermal energy evacuation from the solid into substrate. The heat energy evacuated from the porous silicon increased with porosity, and for the case of the porosity equals to 65% the portion of thermal energy transferred in the water is more than in 3 times bigger the portion transferred in porous silicon. The presented approach can be easily adopted for thermal properties study of different fluids and for thermal resistance of the interfaces nanostructured solid/liquid.

Acknowledgment

Research work described in this paper was partially performed in frames of Marie Sklodowska-Curie Research and Innovation Staff Exchange CARTHER (proposal # 690945). Authors acknowledge European Commission for financial support.

References

[1] Garah M El, Perone R C, Bonilla A S, Haar S, Campitiello M, Gutierrez R, Cuniberti G, Masiero S, Ciesielski A, and Samori P 2015 Chem. Commun. 51 11677.
[2] Goicochea J V, Hu M, Michel B, and Poulikakos D, 2011 J. Heat Transfer 133 082401
[3] Fragneto-Cusani G 2001 J. Phys. Condens. Matter 13 4973
[4] Ge Z, Cahill D G, and Braun P V 2006 Phys. Rev. Lett. 96 18
[5] Dna S P, Van Grinsven B, Vanden Bon N, Strauven H, Grieten L, Murib M, Janssens S D, Haenen K, Scho M J, Jime K L, Vermeerens V, Ameloot M, Michiels L, Thoelen R, De Cuninck W, and Wagner P 2012 ACS Nano 6 2712
[6] Isaiev M, Tutashkonko S, Jean V, Termentzidis K, Nychyporuk T, Andrusenko D, Marty O, Burbelo R M, Lacroix D, Lysenko V 2014 Appl. Phys. Lett. 105 031912
[7] Tytarenko A I, Andrusenko D A, Kuzmich A G, Gavril I V, Skryshevskii V A, Isaiev M V, Burbelo R M 2014 Tech. Phys. Lett. 40 188
[8] Zhong J, Yang S, Zheng X, Zhou T, Xing D 2013 Nanomedicine (Lond) 8 903
[9] Ohl C, Gao F, Feng X, Zheng Y 2014 J. Biomed. Opt. 19 067006
[10] Anees P, Joseph J, Sreejith S, Menon N V, Kang Y, Yu S W-K, Ajayaghosh A, Zhao Y 2016 Chem. Sci. Royal Society of Chemistry 7 4110
[11] Subochev P, Fiks I, Frenz M, Turchin I 2016 Laser Phys. Lett. IOP Publishing 13 25605
[12] Alekseev S, Andrusenko D, Burbelo R, Isaiev M, Kuzmich A 2011 J. Phys. Conf. Ser. 278 012003
[13] Isaiev M, Voitenko K, Doroshchuk V, Andrusenko D, Kuzmich A, Skryshevskii V, Lysenko V, Burbelo R. 2015 Phys. Procedia 70 586
[14] Isaiev M V, Andrusenko D A, Tytarenko A I, Kuzmich A G, Lysenko V V, and Burbelo R M, 2014 Int. J. Thermophys. 35 2341
[15] Andrusenko D, Isaiev M, Kuzmich A, Lysenko V, Burbelo R 2012 Nanoscale Res. Lett. 7 411