ARCHIVES OF METALLURGY AND MATERIALS
Volume 56 2011 Issue 4
DOI: 10.2478/v10172-011-0129-2

R. BURBELO*, D. ANDRUSENKO*, M. ISAIEV*, A. KUZMICH*

LASER PHOTOACOUSTIC DIAGNOSTICS OF ADVANCED MATERIALS WITH DIFFERENT STRUCTURE AND DIMENSIONS

LASEROWA DIAGNOSTYKA FOTOAKUSTYCZNA NOWOCZESNYCH MATERIAŁÓW O RÓŻNEJ STRUKTURZE I GEOMETRII

In the article the results of practical implementation of the PA methods in the study of materials of different structure and dimensions are presented. The features of PA conversion in inhomogeneous semiconductor structures such as porous silicon and doped semiconductor materials are analyzed. To investigate the thermal and elastic properties of porous silicon's based composites gas-microphone and piezoelectric methods registration of PA signal were used.

The results of theoretical and experimental investigation of PA conversion in inhomogeneous silicon-based semiconductor structures under their irradiation by short (~ 10 ns) laser pulse are presented. The influence of thermal parameters distribution of the material structure on the PA signal parameters is shown. Principal possibility of using pulsed radiation for investigation of the modified submicron surface layer is demonstrated.

Keywords: Advanced Materials, Laser Irradiation, Photoacoustic

W pracy zaprezentowano wyniki praktycznej realizacji metod fotoakustycznych do badania materiałów o różnej strukturze i geometrii. Analizowane były aspekty konwersji fotoakustycznej w niejednorodnych strukturach półprzewodnikowych jak porowaty krzem i domieszkowane materiały półprzewodnikowe. Do badania termicznych i elastycznych właściwości kompozytów opartych na porowatym krzemie używano mikrofonowej, piezoelektrycznej metody fotoakustycznej.

Przedstawione zostały wyniki teoretycznych i doświadczalnych badań konwersji fotoakustycznej przy użyciu krótkich impulsów laserowych (około 10 ns). Pokazano wpływ profilu przestrzennego materiałowych parametrów termicznych na sygnał fotoakustyczny. Przedstawiono także możliwości zastosowania metod impulsowych do badania submikronowych warstw powierzchniowych.

1. Introduction

A nowadays development of high technology material science requires an establishing of new methods of characterization and diagnostics, based on new physical principles. Thus up-to-date NDT methods, in particular acoustic ones, can be established only on the base of the researches that provide new scientific data.

Photoacoustic (PA) diagnostics has lately been the rapidly developing field of investigation of various materials properties [1]. The interest here is mainly associated with the successful application of PA methods for investigating the modern materials or their compositions with different structures and dimensions, for which the use of traditional physical methods has significant limitations.

PA effect is the phenomena of generation of elastic fields in material that is irradiated by non-stationary light. It is based on a number of energy conversion processes: light absorption, heating – cooling, the generation of elastic fields. Many factors should be taken into account for an adequate analysis of obtaining the results despite the widespread use of PA effect in science and technology. For example, features of the absorption of optical radiation [2], the temperature distributions formation, the role of electronic subsystem (in the case of semiconductor materials study) and available elastic stresses that exist in the material. So it is clear that the research of PA signal changes depending on various internal and external causes is extremely important.

The results of practical implementation of the PA methods in the study of materials of different structure and dimensions are presented below. The features of PA conversion are analyzed in inhomogeneous semiconductor structures such as porous silicon and doped semiconductor materials. To investigate the thermal and elastic properties of composites based on porous silicon gas-microphone and piezoelectric methods registration of PA signal were used. Radiation with an intensi-

---

* TARAS SHEVCHENKO KYIV NATIONAL UNIVERSITY, FACULTY OF PHYSICS, VOLODIMIRSKA STR., 64, 01601 KYIV, UKRAINE

ty that is modulated by the harmonic law was used in such case. For the analysis of photoacoustic conversion in doped semiconductor structures pulsed laser radiation with pulse duration 10 ns was used. Using a combination of these two techniques allows evaluating thermal and elastic parameters of such materials in different spatial scales.

2. Investigation of porous silicon and composites on its basis by PA technique

PA methods appeared to be effective for the study of objects where the use of traditional experimental approaches is difficult (in particular for porous materials [3]). The interest to the study of porous materials and composites based on it has been increased in recent years. This is due to the fact that such materials are often nanostructured, and substance of the porous matrix and of the filler in the composite is in a state with confinement geometry. Special attention (based on applied applications) is involved by questions of clarifying the features of PA conversion and exploring the possibilities of PA methods usage to obtain the information about the thermal and elastic properties of porous silicon (PSi) and composites (such as composite system "porous matrix – fluid") based on it.

Implementation of classical stationary methods of measuring the large part of thermophysical properties needs a good thermal contact between sample and other parts of the measuring device. In the case of porous samples, especially with open pore morphology, the implementation of such contact without violating the material structure is a challenge.

We shall note that PSi, as the most part of porous materials and powders, scatters good light. Thermal parameters and elastic modules of PSi may differ from the characteristic of the monolithic materials within one – two orders of value [4]. From this point of view the usage of PA methods for the diagnosis of PSi is perspective and effective.

The study of thermal and spectral properties of PSi known in the literature is performed as a rule by classical spectroscopy methods PA (PAS). The main mechanism of signal formation in this case is the mechanism of the so-called "gas piston" [5,6]. In this case the PA signal parameters are sensitive to the optical absorption spectrum of radiation and thermal properties of the sample. At the same time, it is not possible to determine the elastic modules and the coefficient of thermal expansion by PAS methods

One of the possible ways of solving this problem is to use a "membrane" effect at gas-microphone method of forming the signal (so-called geometry of "open window" [7]). It is essential that in some cases PSi parameters are such that the "membrane effect" is significant and well measured in the frequency range of modulation typical for low- frequency PA experiment. This allows you to register thermoelastic component of the PA signal from PSi plate and composites based on it.

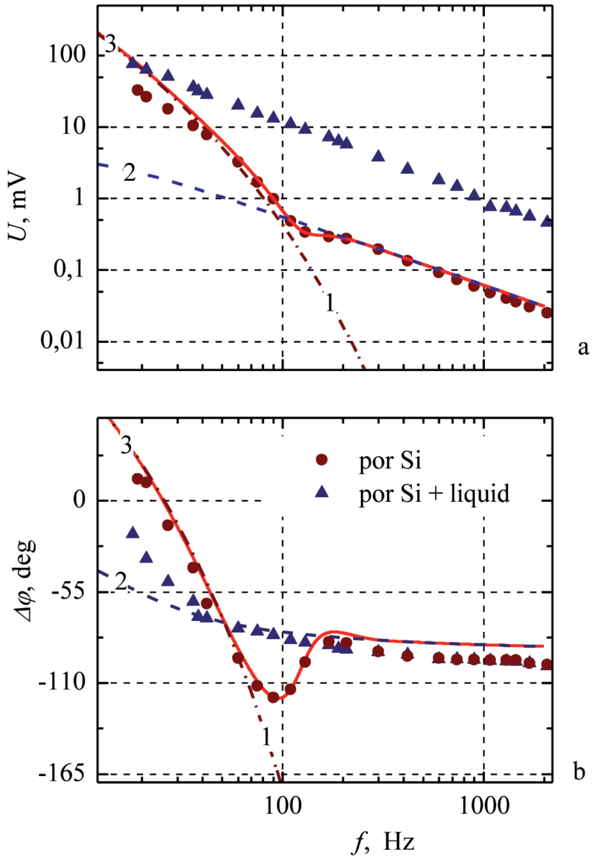

Fig. 1. Dependence of amplitude (a) and phase shift (b) on frequency for samples of PSi. Dashed lines show the calculated dependencies for the component (thermoelastic and thermowave) separately, solid – the result of summation. Experimental data are shown by dot.

In Figure 1b the dependence of the phase shift ($\Delta\phi$) of PA signal on the light modulation frequency from the mesoporous PSi plate thickness of 270 microns is given. The minimum in dependence is caused by mutual influence of different mechanisms of formation of variable pressure component, namely: "membrane" and "gas piston". A similar minimum was observed previously for samples [8,9] that have value of thermal diffusivity corresponding to the value of meso-PSi. Numerical simulation shows that position and depth of the minimum is determined by the values of thermal conductivity and coefficient of thermal expansion of porous silicon.

Experimental dependence of the amplitude (U) of PA signal for composite "PSi – oil" is shown in figure 1a by triangle. It is seen that at high frequency modulation the amplitude of PA signal from the composite significantly (20 times) more than the amplitude from the

PSi sample of the same thickness. This difference may be explained by an increasing of the effective thermal expansion coefficient of the composite compared with thermal expansion coefficient of PSi.

Experiment setting (in geometry ”open window”) has several advantages compared with traditional used in PA spectroscopy of porous silicon. Figure 2 shows dependence of the phase shift of PA signal obtained from samples of nano-porous PSi layer (7mkm) on silicon substrate, with excitation of PA phenomena by light with different wavelengths. It is seen that these dependencies significantly differ among themselves with frequency increasing. This allows using of this PA experiment’s geometry to obtain optical absorption spectra. We shall note that the advantage of this geometry is that the signal amplitude depends little on absorption of porous layer and remains significant at frequencies where a layer of PSi is ”thermally thick” (opposed to [3], where at high frequencies to the red part of the spectrum signal comes up with amplitude of noise).

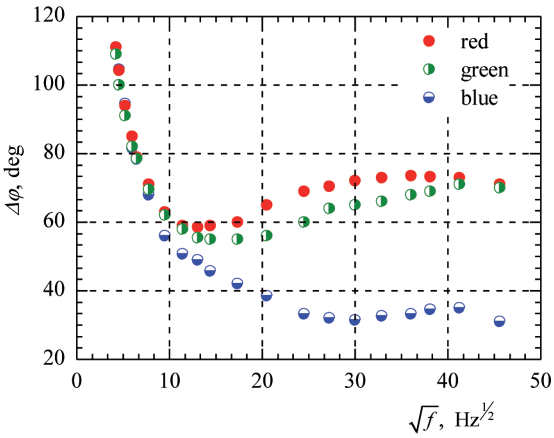

Fig. 2. Dependence of the phase shift of PA signal obtained from samples PSi nanoporous layer (7mkm) on silicon substrate, as exciting was used light with three different wavelengths in the geometry of the experiment ”open window”

Application of PA techniques (including piezoelectric registration) is promising direction for study of the porous medium with liquids transport properties. This problem is relevant in biology, engineering, medicine and other applications. Low frequency registration allows getting a signal proportional to the total value of thermoelastic stresses in the cross section of the sample in selected geometry “sample-Piezoelectric transducer”. Significant difference in values of thermal conductivity PSi and Si allows determining the relaxation time (τ) of thermal induced fluid pressure in pores. Through the value of τ it is possible to identify the characteristics of morphology of porous material or fluid parameters related to the viscous flow in porous system. Oscillogram’ approximation (curve 1) represents by the sum of linear growth (thermoelastic component of PA signal - curve 2,2’) and exponential decay (component associated with relaxation of thermal induced pressures3).

Fig. 3 shows the dependence of PA signal (solid line) on the composite “PSi-ethanol” at a rectangular modulation of excitation light and registration by piezoelectric transducer. We associate the minimum observed on this dependence, to the relaxation of thermo induced fluid pressure in pores. The relaxation of pressure and permeability of porous material by liquid can be determined from the minimum position.

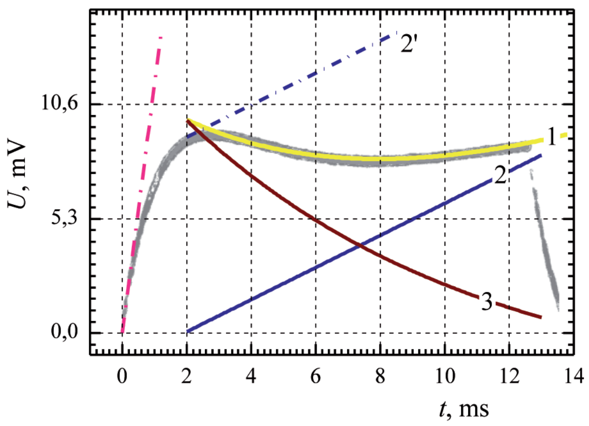

Fig. 3. Oscillogram of PA signal (piezoelectric registration) for the structure ”PSi – ethanol”. Oscillogram’ approximation (curve 1) represents by the sum of linear growth (thermoelasity component of PA signal – curve 2,2) and exponential decay (component associated with relaxation of thermal induced pressures, curve 3)

Basing on the model of quasi-stationary thermoelastic oscillations we have proposed a measurement method and the construction of a multilayer transducer [10], which allows to determine the thermal diffusivity of the porous layer when the latter is on a monolithic substrate [11]. In this case significant difference of the elastic properties of porous and solid layers in these samples is the important. In terms of the proposed model an experiment with samples of mesoporous PSi layer on a monocrystalline substrate was made. Increase in the rate of growth potential after a certain period of time (0.4 ms for the porous layer with thickness 50 microns and a porosity 65%) from the beginning of heating was observed during the experiment. By selecting the parameters of material in the numerical model, we were pursuing the coincidence of the character of the time changes in calculated and experimental dependencies. The obtained value of thermal conductivity of mesoporous layer-layer sample was compared with the experimental value of thermal conductivity of the porous layer, grown under the same anodization regimes but separated from the substrate. The results are in good agreement with each other.

3. Pulse laser techniques for study submicron surface layers

The investigation of structure with a modified surface layer using conventional [6] photoacoustic methods is problematic. This is due to the fact that the study of properties of subsurface layer has a thickness less than one micron, it is necessary to achieve frequency of light modulation more than ten megahertz, which is associated with technical difficulties. The use of pulsed laser radiation (as excitation) is perspective [12] for solving this problem. In this case the use of traditional methods of harmonic analysis (measuring amplitude and phase) for the interpretation of photoacoustic signal is problematic, because the exciting signal has a rather wide range [13].

In [14,15,16] the formation of PA signal in weakly absorbing materials is examined. In this case the main carrier of information about the material' structure is the acoustic wave, and the phenomenon of thermal diffusion practically has no effect on the process of PA conversion. The use of such purely acoustic methods to consider structures with modified subsurface layer (in most cases their experimental and technical realization) is difficult, because the length of the acoustic wave is much larger than the area of modification.

Let's consider the temperature profiles formation in the model inhomogeneous two-layer structure; layers of such structure differ only by thermal diffusivity (χ). In this paper we analyze the case of strong absorption when the excitation beam size is much larger than the light penetration depth. In this case we consider one-dimensional heat equation to simplify the analysis:

$$\frac{\partial T(z,t)}{\partial t} = \frac{\partial}{\partial z}\left(\chi(z)\frac{\partial T(z,t)}{\partial z}\right) + \frac{I_0(1-R)\beta\exp(-\beta z)}{c\rho}g(t), \tag{1}$$

where I_0 – intensity of incident radiation, $g(t)$ – function that characterizes the time distribution of intensity, c, ρ – heat capacity and density of the material, β – optical absorption coefficient, R – reflection coefficient, $\chi(z)$ – function that characterizes thermal diffusivity spatial distribution.

This equation supplemented by boundary conditions (the absence of outflow of heat from the upper surface $(\partial T/\partial z)|_{z=0+0} = 0$, contact the lower surface with thermostat $T|_{z=d} = 0$ (d – thickness of the structure)) can be solved using the finite elements methods.

In Fig. 4 the results of numerical calculation of the surface temperature evolution (a) and thermal profile at the end of the laser pulse (b) for the Si-based two-layer structures are represented. Figure 4 shows that with increasing the thickness of modified layer the surface temperature increases, respectively increasing temperature gradient. I.e. in this case the heat concentration in the material' surface layer phenomenon takes place. Let's note that in case of strong light absorption in material with specified thermophysical properties under their irradiation by short laser pulses (Fig. 4), area of thermal energy localization has the same order that the structure' area modification.

Basing on the boundary conditions the solution of the heat equation (1) can be written in the following form:

$$T(z,t) = \sum_{n=0}^{\infty} b_n(t)\cos(a_n z), \tag{2}$$

where $a_n = \pi(0.5+n)/d$, n is non-negative integer.

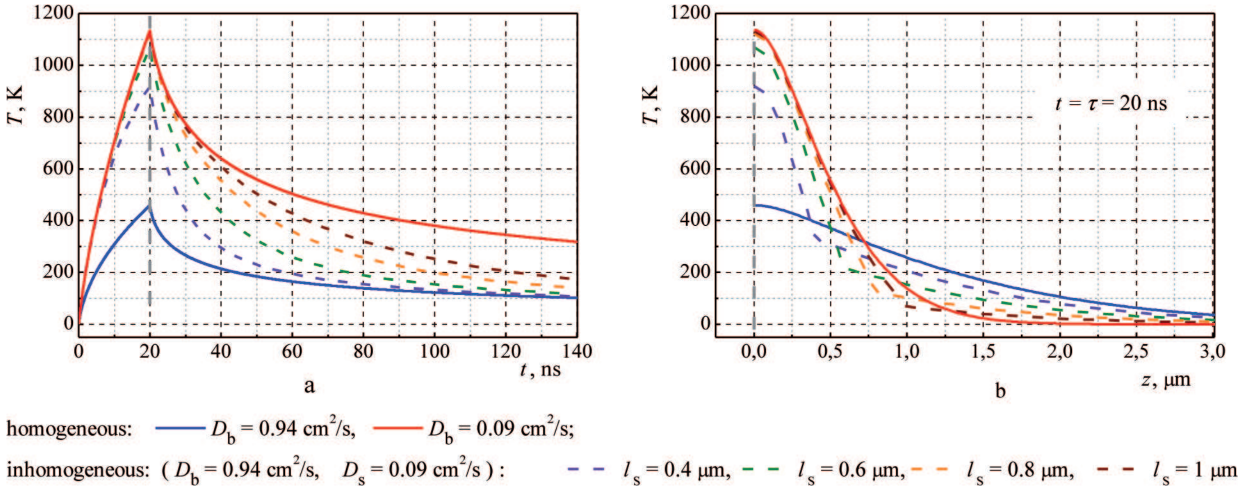

Fig. 4. Surface temperature evolution (a) and temperature profiles (b) at the end of laser pulse for model two layer structures with different thickness of top layer

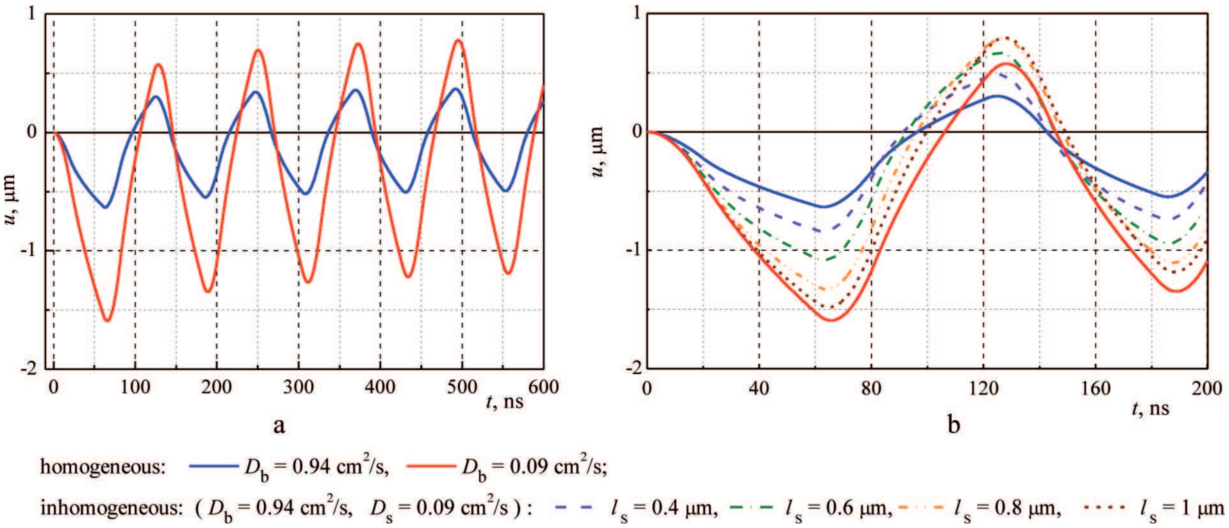

Fig. 5. Surface displacement evolution of homogeneous (a) and inhomogeneous (b) model two layer structures with different thickness of top layer

Let's analyze the fields of elastic displacement formation in the material in the presence of thermal distribution $T(z,t)$. In this case let's consider the thermoelasticity equations [17]. In this paper we consider the model case when there is thermal parameters heterogeneity only along the direction Z. Therefore, to simplify the analysis we consider the one-dimensional case of thermoelasticity equations:

$$\frac{\partial^2 u}{\partial t^2} - v^2 \frac{\partial^2 u}{\partial z^2} = \varepsilon \frac{\partial T}{\partial z}, \qquad \varepsilon = \alpha_T\,(2\lambda + 3\mu)\,/\rho \tag{3}$$

here v – the sound velocity in the environment, λ and μ – Lamé parameters, α_T – thermal expansion coefficient.

We write the boundary conditions for (3) as: $(\partial u/\partial z)|_{z=0+0} = 0,\ u|_{z=d} = 0.$

So

$$u(z,t) = \sum_{m=0}^{\infty} f_m(t)\cos(a_m z) \tag{4}$$

Substituting (2) and (4) in equation (3), taking into account the initial conditions (absence of initial displacements and forces), and solution of (3) can be obtained as:

$$u = \frac{\varepsilon}{v}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} c_{nm}\frac{a_n}{a_m}\int_0^t \sin\left(v a_m(s-t)\right)\cdot b_n(s)ds\times\cos\left(a_m z\right), \tag{5}$$

here

$$c_{nm} = \begin{cases} \dfrac{2}{(m+n+1)\,\pi}, & \text{when } m+n = 2p, \\ & p \text{ is non} - \text{negativ integer} \\ \dfrac{2}{(n-m)\,\pi}, & \text{when } m+n = 2(p+1), \\ & p \text{ is non} - \text{negativ integer} \end{cases}$$

In Figure 5a evolutions of surface displacement of the samples with different values of thermal diffusivity are presented. It is seen that the curve has oscillating character, frequency of oscillation corresponds with the own frequencies of the structure. I.e., if we know the geometrical size of the sample and its elastic parameters, we can estimate in advance the frequency interval in which the PA signal should be analyzed. This is important for the experiment performing. Furthermore, note that the amplitude of this signal will be significantly depended on thermal parameters of investigating samples. Figure 5a shows that with increasing the value of thermal diffusivity the amplitude of the PA signal increases.

Fig. 5b shows the evolutions of surface displacement of the two-layer model samples with different thickness of top layer. It is seen that with increasing of modified layer' thickness changes the parameters of PA response: amplitude and phase shift increases.

In Fig. 6 evolutions of surface displacement of the two-layer model samples with different values of thermal diffusivity of top layer are presented. It is seen that with increasing the surface layer thermal diffusivity the amplitude of PA signal decreases.

Thus, basing on the results obtained above, we can estimate that the thermal properties of structure's surface layer influence the parameters of photoacoustic response. It gives the possibility of the submicron surface layer diagnosis by PA techniques.

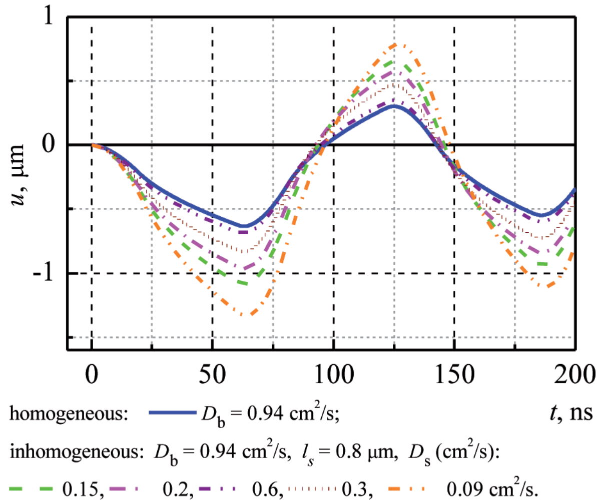

Fig. 6. Surface displacement evolution inhomogeneous (b) model two layer structures with different thermal diffusivity coefficient of top layer

4. Conclusions

In the paper the PA techniques for thermal and elastic properties of advanced materials with different structure and dimensions are presented.

The peculiarities of PA transformation in composite systems based on mesoporous Si are investigated. The results can be applied for study of porous material's morphology and development of sensor systems.

The processes of PA signal formation in inhomogeneous semiconductors structures under their irradiation by short (~ 10 ns) laser pulse was investigated. The case of strong light absorption was analyzed. It was shown that in this case the presence of structural inhomogeneity of submicron surface layer leads to the change of the PA signal parameters (such as amplitude and phase shift). So it gives an opportunity to investigate thermal properties of modified submicron surface layer using pulsed radiation.

Received: 20 March 2011.

REFERENCES

[1] 15th International Conference on Photoacoustic and Photothermal Phenomena (ICPP15) J. Phys. Conf. Ser. **1**, 214 (2010).

[2] G. Mityurich, M. Aleksiejuk, P. Astakhov, A. Serdyukov, Arch. Metall. Mater. **54**, 889-894 (2009).

[3] A.N. Obraztsov, H. Okushi, H. Watanabe, V. Yu. Timoshenko, Fiz.Tekh. Poluprovodn. **31**, 629 (1997) [Semiconductors **31**, 534 (1997)].

[4] O. Bisi, S. Ossicini, L. Pavesi, Sur. Sci. Rep. **38**, 1 (2000).

[5] A. Rosencwaig, A. Gersho, J Appl Phys. **47**, 1, 64-69 (1976).

[6] A. Rosencwaig, in Photoacoustics and Photoacoustic Spectroscopy, Wiley and Sons, N. Y., 850 (1981).

[7] L.F. Perondi, L.C.M. Miranda, J. Appl. Phys. **62** (7), 224 (1987).

[8] P.M. Nikolić, D. Luković, S. Savić, D. Urošević, S. Djurić, Thermal Diffusivity of Sintered 12CaO·$7Al_2O_3$, Science of Sintering **35**, 147-154 (2003).

[9] D. Luković, P.M. Nikolić, S. Vujatović, S. Savić, D. Urošević, Photoacoustic Properties of Single Crystal PbTe(Ni) Science of Sintering **39**, 161-167 (2007).

[10] D.A. Andrusenko, I.Y. Kucherov, Tech. Phys. **44**, 1397 (1999).

[11] S. Alekseev, D. Andrusenko, R. Burbelo, M. Isaiev, A. Kuzmich, Journal of Physics: Conference Series **278**, 012003 (2011).

[12] N. Podymova, A. Karabutov, Journal of Physics: Conference Series **214**, 012054 (2010).

[13] A. Domanowska, R. Bukowski, Int. J. Thermophys **30** (2009), 1536-1556 (2008).

[14] A. Every, W. Sachse, Physical Review B **44**, 13, 6689-6699 (1991).

[15] R. Coulette, E. Lafand, M.-H. Nadal and al., Ultrasonic's **36**, 239-243 (1988).

[16] M. Aleksiejuk, Arch. Acoust. **4**, 30, 103-106 (2005).

[17] G. Rosa, R. Oltra and al., J. Appl. Phys. **10**, 91, 6744-6753 (2002).