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Application of DLC layers in 3-omega thermal conductivity method

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Properties

ABSTRACT

Purpose: The 3-omega method is a unique measuring technique which can be applied for thermal conductivity measurements of bulk materials and layers. In order to measure thermal conductivity of semiconducting and metallic materials (e.g. thermoelectric materials) it is necessary to separate the sensor from the substrate by a dielectric layer. The layer should exhibit thermal conductivity λ_s comparable or greater than thermal conductivity of characterised materials, as well as good, electrically insulating properties.

Design/methodology/approach: The DLC layers were prepared via the magnetron sputtering technique. The reactive sputtering process was carried out in the mixture of Ar and methane (CH_4) work gases at the pressure ranging from 0.3 to 0.7 Pa. The layers were deposited on glass and selected thermoelectric materials. The temperature of substrate was controlled in range from 35 ºC to 500 ºC depending on type of the substrate material. The thickness of received DLC layers was in range from 0.2 to 2 μm.

Findings: In order to estimate the accuracy of the modified 3-omega method thermal conductivity measurement results were compared to results of measurements without additional DLC layers and independent data obtained by the laser-flash method. Analysis of experimental results of test measurements show that application of 300 nm thick DLC insulating films allow for characterization of materials exhibiting $\lambda < 1.2 Wm^{-1}K^{-1}$ with the accuracy better than 9%.

Research limitations/implications: Results of investigations indicate that prepared DLC layers satisfy requirements of 3-omega method and do not influence significantly on precision and accuracy of thermal conductivity measurements.

Originality/value: We have developed the new method of preparation of diamond-like carbon (DLC) layers which satisfy requirements of the 3-omega technique. The layers can be applied for thermal properties measurements of selected thermoelectric materials.

Keywords: Thin layers; 3-omega method; Thermal conductivity; DLC layers

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1. Introduction

The 3-omega method has become a common technique for direct thermal conductivity measurement because of its high accuracy and possibility of application for investigations of thin film as well as substrate properties during a single measurement. The method was originally developed by Cahill [1-3], for characterization of thin films of insulators and was extended later for heat capacity measurements [4].

The technique involves the diffusion of heat into a medium from a periodically oscillating small heater located on the surface. The amplitude of temperature oscillations of the heater itself contains the thermal information of the underlying medium. The 3-omega method has commonly been used to investigate the thermal conductivity of glasses, ceramics, polymers and other non-electrically-conducting materials in a form of thin layers.

However, application of the 3-omega method becomes a challenge for measurements of electrically conductive samples e.g. semiconductors and metals. The main issue in such measurements is electrical separation of metallic heater from the measured electrically conductive sample surface by additional insulating film [5-8]. Such a film should meet many important materials requirements: good thermal conductivity, high resistance for dielectric puncture and good mechanical properties matched to properties of an investigated layer [8]. Consequently, in order to utilize the 3-omega method for a broader range of materials, new approaches associated with sample preparation must be developed.

This paper presents the methodologies involved in adapting the sample preparation for use of the 3-omega method in measurements of materials for thermoelectric applications: especially for characterisation of functional materials (e.g. Bi_2Te_3, $CoSb_3$), as well as, thermal barrier coatings (TBC), and antidiffusion layers. Thermoelectric materials, developed by us, can find wide-ranging application in electronic industry such as in cooling of infrared detectors, computer processors and light emitting diodes, as well as, in energy conversion applications e.g. for construction of thermoelectric generators TEG.

2. Overview of the 3-omega method

This section, presents a brief overview of the 3-omega technique to illustrate better the required changes for accommodating DLC insulating films. The 3-omega method generally proceeds by applying an alternating current of angular frequency ω through a metallic strip that has been directly deposited on an electrically insulating sample (Fig. 1).

The metallic strip acts both as a heater and as a temperature sensor. The electrical current warms up the heater at a frequency of 2ω due to Joule-Lenz effect, producing temperature oscillations also at a frequency of 2ω with the amplitude of $\Delta T_{2\omega}$. Since the resistance of metallic heater increases linearly along with the temperature, the temperature oscillations introduce resistance oscillations in the metallic strip at a frequency of 3ω. Thus, the average temperature rise of the strip can be obtained from the measurement of the third harmonic of the voltage drop $V_{3\omega}$ using e.g. Wheatstone bridge (see Fig. 2).

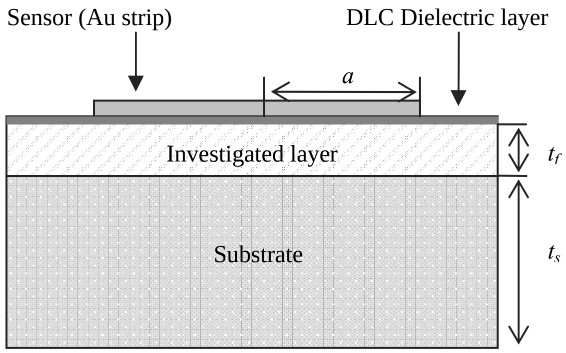

Fig. 1. Scheme of specimen cross-section with a sensor (Au strip) deposited onto an insulating layer

The amplitude of temperature oscillations can be calculated from the equation:

$$\Delta T_{2\omega} = \frac{2V_{3\omega}}{IR\alpha} \qquad (1)$$

where: I – current, R – strip resistivity, α - temperature coefficient of the strip material resistivity, and $V_{3\omega}$ - amplitude of third harmonic component of the measured signal.

Our measuring system consists of an electrical circuit with the Wheatstone bridge (Fig. 2), where the measuring element is installed in one of the arms of the bridge, and in other arms there are high-class resistors and potentiometers, having accuracy better than 0.1%. The specimen with a sensor strip is mounted on a heating panel in a vacuum chamber maintaining nearly adiabatic condition of measurements.

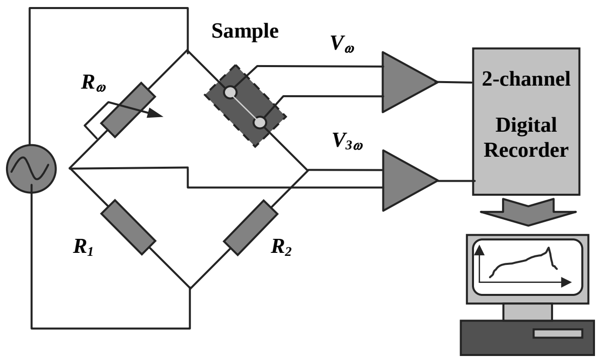

Fig. 2. Arrangement for thermal conductivity measurements by a 3-omega method

The Wheatstone bridge is supplied from a generator with digitally synthesized sinusoidal signal, with a precisely defined frequency (< 0.0001 Hz) and very small contribution of harmonic components (< 0.01%). The differential signal from the bridge contains the preextracted signal $V_{3\omega}$. The signal is amplified by precise analog amplifier and sampled by a dual channel, high-resolution (16-bits) analog-to-digital converter (ADC) with a sampling frequency of 200 kHz. In the second channel, the base line signal, V_{ω}, is recorded. The data collected from at least 8 periods are transmitted to a computer for further numerical processing.

The exact amplitudes V_{ω} and $V_{3\omega}$ are determined using fast Fourier transform (FFT) analysis. The third harmonic voltages amplitude $V_{3\omega}$ is measured by performing a logarithmic frequency sweep typically from 0.1 Hz to 20 kHz. Finally, the thermal conductivity of the sample is evaluated by measuring the frequency ω dependence of the temperature oscillations ΔT_{ω}.

It should be noted that the applied analysis method usually requires the assumptions that the heater should be considered of infinite length and that the sample is effectively semi-infinite. The method requires that the generated thermal waves penetrate deeper into the sample in comparison to the heater width, the film thickness t_f must be far less than the thermal penetration depth in the investigated film, d, and the film must be much thinner than the heater half-width l. Additionally, the thickness of the underlying substrate t_s must be such that the condition $t_s > d > l$ is maintained to avoid back surface reflection and assure the validity of the line source and semi-infinite substrate approximations.

The application of the additional dielectric layer generates additional requirements. In order to avoid the influence of this addition film on experimental results the separating dielectric layer should have thermal conductivity λ_{diel} much greater than thermal conductivities of measured materials, and should have much lower thickness than the investigated underlying layer.

Additional details and issues concerning the 3-omega technique can be found in [9-11] and are therefore not discussed thoroughly here.

3. Experimental details

3.1. Deposition of DLC layers

As one of the tested materials to be used in 3-omega method, layers of insulating DLC (diamond like carbon) were selected. Layers were deposited on cleaned optical glass, silicon and $CoSb_3$ substrates by pulsed magnetron sputtering (PMS) technique. The sputtering process was carried out in the vacuum chamber of 60 dm^3 volume, with WMK-50 magnetron and a target made from graphite foil, in the mixture of CH_4 (0.40 Pa) and Ar (0.10 Pa). The magnetron was supplied by RF DPS power supply with a frequency of 160 kHz. The cathode current was stabilized at a value of 0.15 A and the power was about 70 W. The problem about deposition is to avoid pinholes, cracks, and other defects presumably caused by mechanical stresses. These defects in the dielectric layer can lead to undesirable electrical conductance paths (shortcuts) between the metal strip and the substrate and they are the reason of wrong measurements results. Therefore, in order to minimize amount of defects, the substrates were placed during layer deposition on a ceramic hot-plate which maintained the temperature $T_{subst.}$ from 25 °C to 400 °C. The rate of the deposition process did not exceed 3nm·min^{-1} and the thicknesses of obtained DLC layers were in range from 200 nm to 2 μm. The impedance spectroscopy measurements (ZEHNER IM 5d impedance meter) of the investigated DLC films showed that they had high electrical resistance about 5.0 GΩ, what confirmed their good insulating properties.

3.2. Preparation of 3-omega sensors

Magnetron sputtering technique was also used for preparation of measuring probes (sensors) in the form of thin strips of Au. For that purpose, ceramic shadow masks were applied during deposition process of Au. The sensors had half-width a = 30 μm, length of about 4 mm and were ended with circular pads (Fig. 3). The absolute resistance of obtained sensors at 25 °C was in range from 50 to 100 Ω, and their temperature coefficient of resistance $\alpha = 8.66\cdot10^{-4}$ K^{-1}.

a) b)

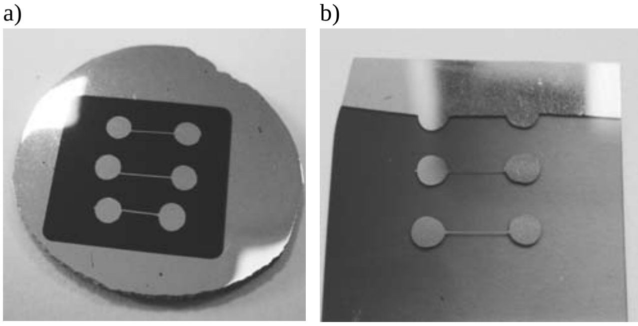

Fig. 3. Sample of Si single-crystal a) and glass b) with DLC insulating film of ~300 nm thick and 3-omega Au sensors

3.3. Thermal conductivity measurements by 3-omega method

The measured values can be plotted in a $\Delta T_{2\omega}$ versus f (frequency) coordinate system, which allows for determination of thermal conductivity λ in selected range of penetration depth $|q^{-1}|$ from the relationship [1-3]:

$$\Delta T_{2\omega} = \frac{-P_l}{2\pi\lambda} \cdot \ln(4\pi \cdot f) + c \qquad (2)$$

where P_l is power produced per unit length and c is a constant parameter. The thermal conductivity value λ is directly determined from the slope of a regression line [1-3]. The above, simple mathematical model can be applied when the thickness of insulating layer and its thermal conductivity λ_s meet specific conditions.

Shin *et al.* [12] analyzed both experimentally and theoretically the influence of separating layers on the precision of 3-omega method. They applied SiO_2 and SiN_x dielectric films with thermal conductivities of about 0.93 $Wm^{-1}K^{-1}$ and 0.96 $Wm^{-1}K^{-1}$, respectively. They found that the measurement error in 3-omega technique is less than 5% for their layers of 360 nm thick, deposited on glass substrates. However, thermal conductivity of typical DLC films obtained by RF technique, with dominating sp^2 form of carbon is slightly larger, and is located in range from 1.4 to 2.1 $Wm^{-1}K^{-1}$ [13]. Taking the above data into consideration, it can be calculated that for DLC layers, with thickness not exceeding 500 nm, the systematic error should be less than 5%. Though, even if the thermophysical properties of the insulating layer are known, several experiments on studied layers are necessary in order to identify influence of additional layer on accuracy of the method.

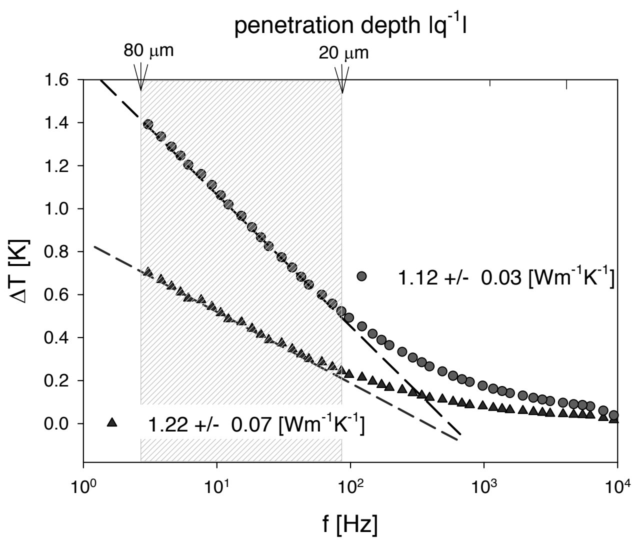

Fig. 4. Examples of analysis of 3-omega mesurement results. Red dots – glass substrate with DLC film (P_l = 1.926 Wm^{-1}); blue triangles – glass substrate without DLC (P_l = 1.114 Wm^{-1}). Analysed thermal wave penetration depth is marked by shadowed region

3.4. Thermal conductivity measurements by laser-flash method

Thermal conductivity of substrate materials was determined by laser-flash technique on LFA 457 MicroFlash Netzsch apparatus [14, 15]. In this method the front side of a sample is heated by a short laser pulse of Nd: YAG laser with pulse energy up to 15J and wavelength of 1061 nm. The heat induced propagates through the sample and causes a temperature increase on the rear surface. The temperature rise on the back surface of the sample is measured versus time using an InSb infrared detector cooled by liquid nitrogen. The measured signal is fitted with the heat radiation model which includes laser pulse correction.

Selected samples for measurements were washed in alcohol, dried in air, and weighted with accuracy of 0.0001g (Sartorius balance). Densities of materials *d* were calculated from average geometrical parameters and mass of samples. Transparent samples (glass) were coated on both sides with thin layer of gold (< 1 μm) by the magnetron sputtering technique and thin layer of sprayed graphite in order to improve absorption of the laser light.

The reference sample (Pyrocerm 9606) and measured samples were placed in holders of LFA 457 apparatus. Measurement was made at the flow of pure nitrogen (20 cm^3min^{-1}). Three laser shots were applied for each sample at given temperature with 0.5 ms laser pulse length.

Because the investigated samples were semi-transparent, heat radiation model including laser pulse correction was applied.

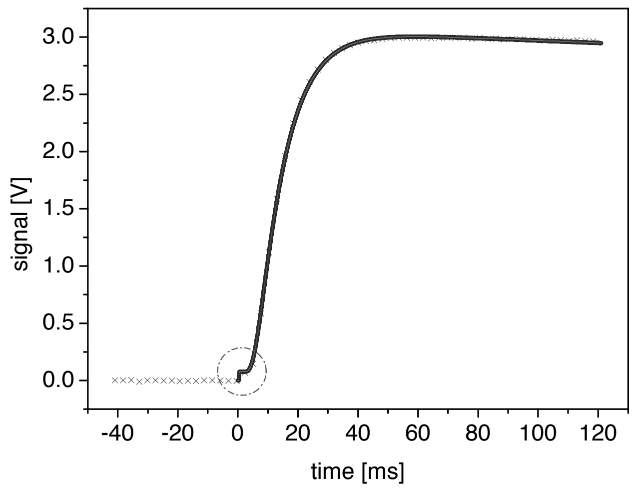

Fig. 5. Output signal measured by the infrared In-Sb detector (green points) and fitting model curve (blue line) for the glass sample (T = 25°C). For semi-transparent samples heat radiation model including laser pulse correction was applied. The signal change due to heat radiation effect is marked by the circle

Figure 5 shows results of fitting data (dots) by applied theoretical model of heat conduction (blue solid line). In result of computations both thermal diffusivity α and specific heat c_p were ascertained.

Thermal conductivity λ in function of temperature T was determined from Eq. (3):

$$\lambda(T) = d(T)c_p(T)a(T) \quad (3)$$

4. Results and discussion

The systematic 3-omega test measurements were made for sets of glass samples with different thickness of DLC layers (~300 to ~700 nm) as well as for various lengths of sensors and applied power density P_l. Figure 4 shows, for illustration, results of analysis for glass samples with and without DLC layer in the same range of $|q^{-1}|$ from 20 to 80 μm.

The thermal conductivity of substrate material (glass) was defined using two independent methods: 3-omega and laser-flash technique (Table 1.). Both results of measurements are in agreement within experimental error for statistical significance level $1-\alpha = 0.95$.

Results of measurements of thermal conductivity λ of glass samples with DLC separating films are presented in Table 2. It contains results of measurements of materials deposited at selected temperature of substrates: 35 °C, 200 °C and 400 °C. The comparison of data shows that discrepancies between results for samples prepared in different temperatures are not statistically significant. The average value of λ for all results is $1.17 \pm 0.08\ Wm^{-1}K^{-1}$.

5. Summary

The 3-omega method allows for measurements of thermal conductivity λ of both layers as well as substrates in a single experiment. The method allows performing in-depth measurements, over a distance up to a few millimetres from the surface depending on properties of investigated material. In order to accommodate the 3-omega method for measurements of conducting materials, we have developed and implemented the sample preparation technique which includes magnetron sputtering of DLC insulating films.

Analysis of experimental results of test measurements shows that 300 nm thick DLC insulating films allow for characterization of materials with the accuracy higher than 9%. The comparison of statistical results shows that developed DLC insulating films have not significant influence on precision of the method.

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Table 1.
Results of measurements of thermal conductivity λ of glass samples by laser-flash and 3-omega method (T = 25 ºC)

Measurement method	Length of heater l [mm]	P_l [Wm^{-1}]	Number of meas.	λ [$Wm^{-1}K^{-1}$]	$\Delta\lambda$ [$Wm^{-1}K^{-1}$]
3-omega	3.904	0.895	5	1.05	0.04
laser-flash (LFA 457)	-	-	3	1.04	0.05

Table 2.
Results of measurements of thermal conductivity λ by 3-omega method (T = 25 ºC) of glass samples with DLC separating films deposited at various temperatures of substrate T_{substr}

Sample	l [mm]	P_l [Wm^{-1}]	Number of meas.	Thermal conductivity λ [$Wm^{-1}K^{-1}$]	$\Delta\lambda$ [$Wm^{-1}K^{-1}$]
Glass with DLC1 $T_{substr.}$ = 35°C	3.959	1.521	5	0.93	0.03
	4.380	1.432	5	0.86	0.03
	4.031	1.453	5	0.97	0.03
Glass with DLC2 $T_{substr.}$ = 200°C	3.407	1.129	5	1.11	0.04
	4.686	0.923	5	1.00	0.04
Glass with DLC4 $T_{substr.}$ = 400°C	3.957	1.551	5	0.98	0.03
	4.610	3.840	5	0.90	0.03
	3.818	0.154	5	0.86	0.04
Statistical analysis for $1-\alpha = 0.95$				0.95	0.09

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