

THERMAL DIFFUSIVITY MEASUREMENTS BASED ON LASER INDUCED HEAT TRANSFER IN LOW-CONDUCTIVITY THIN FILMS*

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Original experimental method for evaluation of thermal diffusivity coefficient of vacuum deposited thin films with low thermal conductivity is presented. For this purpose three-layered samples are vacuum deposited onto precleaned glass substrate. Thin film of TeO₂ or NaCl respectively is sandwiched between array of connected in series thin film thermocouples at the bottom and metal layer at the top. Nd:YAG laser radiation ($\lambda=1064\text{nm}$, $\tau=12\text{ns}$) absorbed in the metal layer is used to create heat pulse in the sample. The heat released is transferred to the thermocouple array through the film studied with a delay proportional to thermal diffusivity of the sandwiched material. Further, a simple relation between the thermal diffusivity coefficient, film thickness and time of the thermoelectric response delay is used to estimate the thermal diffusivity of NaCl or TeO₂ thin film. A relationship between the thermal properties and the microstructure of the film studied is revealed. Finally, it is demonstrated that the method applied is appropriate for studying of any thin film material with low thermal conductivity.

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1. Introduction

The thermal properties of solids are intensively investigated since the 19th century, when A.J.Ångström reports for the first time his experimental results on thermal conductivity measurement of metals [1]. Up to now variety of methods for studying thermal characteristics of homogeneous bulk materials are developed [2]. In the very beginning they were applied for basic research of massive metals or binary compounds. Nowadays, the development of new thin-film and nano - structured materials for high-tech application is a field of vivid interest in contemporary material science. This stimulates also the efforts for development of methods [3-6] suitable for studying of the thermal properties of new advanced materials. However, it is well known that in principle the bulk material properties differ substantially from that of the thin films. Therefore, the existing methods applicable for bulk material should be modified or replaced with new suitable experimental solution for measurements of the specific thin film properties.

Usually, the few methods for thermal diffusivity measurements are based on periodic heating and cooling of the sample surface, thus inducing temperature oscillations and distribution of thermal wave within thin film material. In this case, the wave parameters could be used for thermal diffusivity or thermal conductivity evaluation. Another approach for investigation of thermal properties is demonstrated by the so-called transient heat-flow methods that use heat pulse propagation within the material studied. The advantages of these methods are the short measurement time, which leads to limitation of undesirable heat losses via dissipation as well as substantial experimental error. The Kubičár's method [7] is a transient heat-flow method well developed for

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bulk material investigation. It is relatively simple for realization and seems to be applicable for thin-film materials too.

It is the aim of the present work to modify the Kubičár's method in order to be useful for thermal diffusivity measurements of low-conductivity thin films.

2. Experimental

The thermal diffusivity measurements of low-conductive inorganic thin films are carried out using three-layered samples (Fig. 1) vacuum deposited on precleaned Na-Ca-silicate glass substrates by means of thermal evaporation technique. The samples deposition is performed under high vacuum better than $5 \cdot 10^{-4}$ Pa using standard vacuum equipment including both rotary and oil diffusion pumps. An indirectly heated crucible mounted in water-cooled massive silver block is used as a vapor source. This allows to keep the temperature of the melted material very precisely. Besides, the deposition rate, always in the range of 0,1 - 1,0 nm/s, is controlled by means of quartz oscillator. In addition, the substrates are maintained at room temperature during the deposition procedure. The thickness of each layer incorporated in the sample is measured by Talystep profilometer.

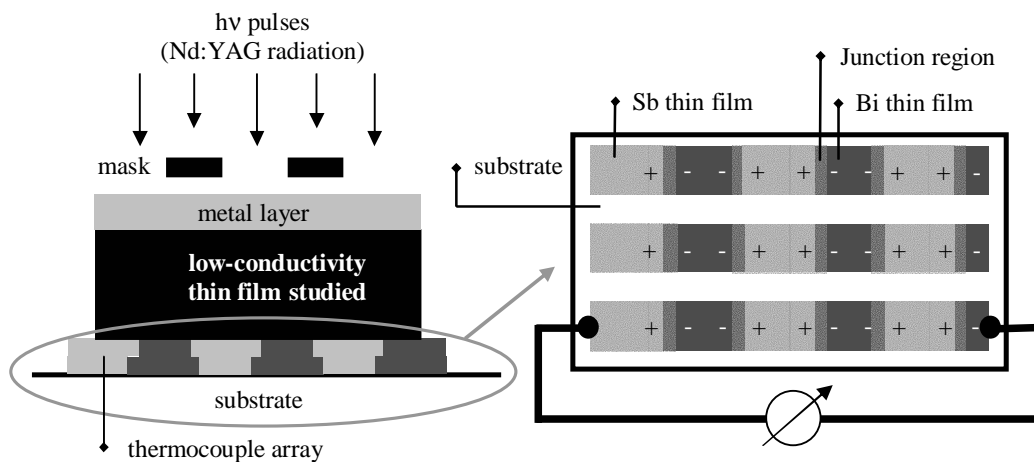


Fig. 1. Scheme of the three-layered samples.

The film studied with thickness in the range 300 – 800 nm is sandwiched between array of connected in series thin-film thermocouples at bottom and top metal layer used as heat source. In the present paper two different low-conductivity thin-film materials are studied – NaCl and TeO₂. The sodium chloride films are used mainly as a model system since in the literature there are reliable data for the thermal properties of NaCl. Therefore, the literature data for the thermal diffusivity of bulk NaCl are used in order to verify the results obtained by the method described. However, the thermal properties of TeO₂ are more interesting for several thin film applications developed in our laboratory [8,9].

An antimony thin film with thickness of about 200 nm is deposited as top metal layer. Its relatively high melting point (630 °C) allows thermal investigations of the samples to be carried out in wide temperature range without Sb film damage. Besides, the good absorption of the antimony in the infrared spectral range is a prerequisite for preparation of metal layer as fast heat supplier using pulsed laser radiation. For this purpose a Q – switched Nd:YAG laser ($\lambda=1064\text{nm}$, $\tau=12\text{ns}$) is used. The Sb thin film heat source thus optimized makes the measured sample flexible to study the thermal properties of any thin-film material under different experimental conditions.

The thermocouples are also important part of the samples. It is well known that two metals in contact induce as higher thermoelectric power as wide separated each other they are in the

Seebeck metals sequence. For that reason Bi and Sb are chosen for preparation of the thin-film thermocouples, which are deposited on the glass substrate by consecutive evaporation of bismuth and antimony. The Sb film partially overlaps the Bi film thus forming a junction region with mean surface area $6 \cdot 10^{-3} \text{ mm}^2$ and total thickness of about 100 nm. The thermocouple thus selected is characterized by rapid thermal response and linear dependence of the thermoelectric power versus temperature (Fig. 2). It should be noted here that the accuracy of the method used increases with the thermoelectric power per degree Celsius. Its value could be multiplied using the array of connected in series thermocouples. However, the latter are inverted each other with respect to the polarity of the potential difference produced. As a result, the total thermoelectric power could be zero. In order to avoid this effect, the sample areas over the unipolarity thin-film thermocouples are heated only, when the top metal layer is irradiated through a suitable mask (Fig. 1).

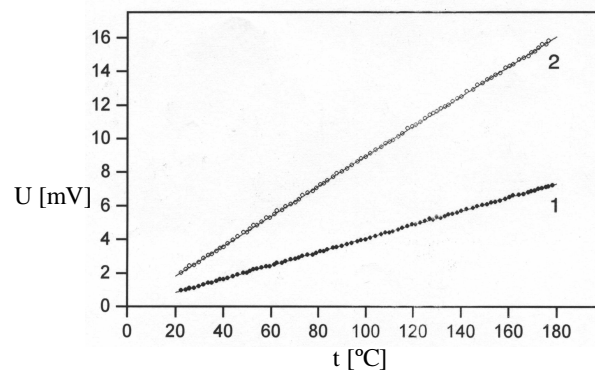


Fig. 2. Thermoelectric power versus temperature of Bi/Sb thin film thermocouple (2) compared to that of bulk chromel-alumel thermocouple (1).

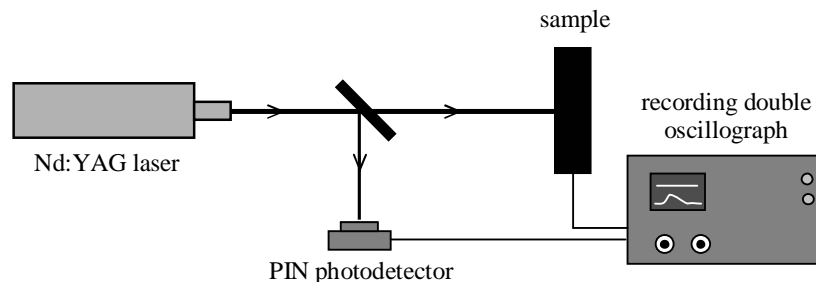


Fig. 3. Scheme of the experimental setup.

During the experiment the Sb metal layer absorbs a short Nd:YAG laser shot thus generating single heat pulse in the samples. The thermal pulse transferred through the thin film studied is detected by the thermocouple array. Further, the total thermoelectric power induced is monitored by means of differential, recording, double oscillograph. A fast PIN photodetector is used for synchronization of the oscillograph with the emitted laser pulse (Fig. 3). The thermal diffusivity coefficient a is evaluated by the simple relation [7]:

$$a = d^2/(2t_m), \quad (1)$$

measuring the film thickness d and the delay time t_m for maximal thermal response of the thermocouple with respect to the initial heat pulse. It should be noted that this relation is obtained, applying the condition for extremum of the thermal equation solution in the case of sample with incorporated planar heat source.

Finally, the microstructure and growth morphology of NaCl and TeO₂ films are studied under scanning electron microscope Philips 515. For this purpose a microfractographic preparation

technique is applied, the details of this experimental procedure being described earlier [10]. Conductive coatings of C and Au, about 10 nm thick, are consecutively deposited on the film surface in order to enhance the contrast of the obtained SEM image of the growth profiles.

3. Results and Discussion

Fig. 4 shows a typical thermal response of thermocouple array after single Nd:YAG pulse irradiation of the three-layered sample. For 300 nm thick NaCl film a delay time t_m of 600 ns is measured. Applying equation (1), the value of the thermal diffusivity coefficient a is evaluated as

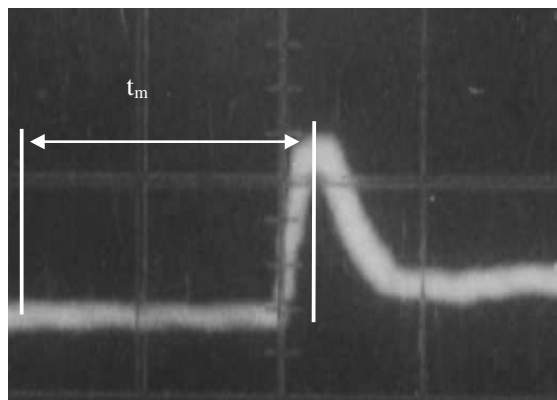


Fig. 4. Thermal response of the thermocouple array.

$7,5 \cdot 10^{-4} \text{ cm}^2/\text{s}$. However, calculating a from the literature data for single crystalline NaCl [2] the value of $3,32 \cdot 10^{-2} \text{ cm}^2/\text{s}$ is obtained. As seen, this value is about two orders of magnitude higher than the experimental data obtained. The discrepancy between both values could be result of two different reasons. The equation (1) is derived, assuming that both the heater and thermometer, in our case – Sb layer and thermocouple array respectively, have a specific heat C_p equal to zero. Besides, the heat source has to generate heat pulses with δ -function shape. The excellent thermal contact between the heat source, material studied and thermocouple is also suggested. The latter seems to be satisfied in the experimental setup described above, having in mind that the vacuum deposition provides in fact interatomic contact at the interface between the different layers in the samples. On the other hand, in the real case the heat losses could not be avoided since C_p of the Sb layer as well as of NaCl is not zero. Therefore, the influence of the heat losses on the experimental data obtained has to be estimated, evaluating an appropriate correction coefficient f_a . Kubičár has published results from the theoretical analysis of the influence of variety of experimental non-idealities on the thermal diffusivity data, measured in bulk materials [7]. Based on this analysis, it is possible to estimate the correction coefficient for the thermal diffusivity of NaCl thin film in the case of real heater, generating pulses with finite, nonzero duration. It is found that the value of f_a is equal to 0,7 using the literature data for material density, specific heat C_p and thermal conductivity k of NaCl. This means that the real measured value of a should be $5,3 \cdot 10^{-4} \text{ cm}^2/\text{s}$. As seen, the theoretical correction made does not reduce the difference between the literature and experimentally obtained thermal diffusivity coefficient. It should be noted, however, that in principal the density of thin-films is quite different than that of the bulk material. Therefore, if the correction coefficient has to be calculated more precisely, the sodium chloride film density has to be evaluated. It is found that measuring both the film thickness and weight of several thin films, the vacuum deposited NaCl has a lower density ($1,9 \text{ g/cm}^3$) compared to that of bulk material ($2,165 \text{ g/cm}^3$). Using this result, the recalculated value of the correction coefficient is 0,6. Obviously, the enormous difference between the thermal diffusivity of single crystalline NaCl and thin films remain approximately the same despite of the theoretical evaluation of the experimental error.

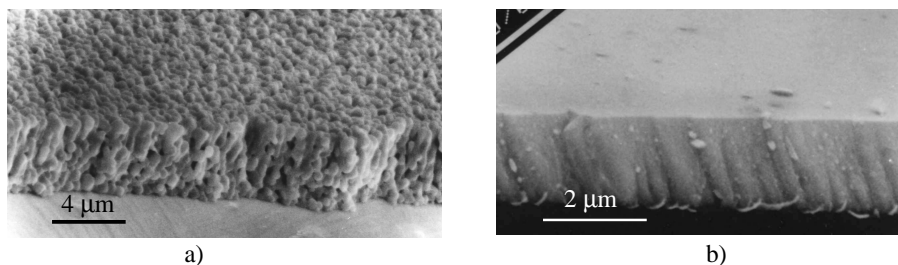


Fig. 5. SEM micrographs of growth profile and surface morphology of 4 μm thick NaCl film (a) and 1,8 μm thick TeO_2 (b) film [9].

It is clear that other factor affects strongly the thermal diffusivity of the thin films than the thermal non-ideality of the samples. Therefore, the microstructure of NaCl thin films is studied. Fig. 5a) shows a scanning electron micrograph of growth profile and surface morphology of the NaCl thin film vacuum deposited on glass substrate. In order to simulate the film structure in the real sample, the sodium chloride is grown on preliminary deposited 100 nm thick Sb film. As clearly seen, the film studied is characterized by a grain-like microstructure with high porosity. Obviously, the film free volume hinders the heat propagation in the sample and is responsible for the lower thermal diffusivity compared to the bulk material. Therefore, the microstructure influences drastically the measured thermal diffusivity of vacuum deposited thin films.

In the present study the modified Kubičár's method is applied also for evaluation of the thermal diffusivity of 800 nm thick TeO_2 film. It is found that in this case $\alpha = 6,4 \cdot 10^{-3} \text{ cm}^2/\text{s}$. As seen from the SEM micrograph on Fig 5b) [9], the visualized growth morphology of the vacuum deposited TeO_2 reveals a typical columnar microstructure. However, this microstructure is more compact and free of voids than that of the NaCl thin film, as could be seen comparing Fig. 5a) and Fig. 5b). Therefore, if the substantially low α value of the thin films is related mainly to the microstructure, the thermal diffusivity of TeO_2 film should be higher than that measured in the NaCl film.

4. Conclusions

In the present study a transient heat-flow method adapted for thermal diffusivity measurements of thin films is demonstrated. The thermal diffusivity coefficient of NaCl and TeO_2 thin films is evaluated, applying the method developed. It is found that the microstructure substantially influences on the thermal properties of the thin film materials. Finally, it should be noted that the method developed is suitable for investigation of other low-conductivity thin films.

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