ISSN 1063-7826, Semiconductors, 2018, Vol. 52, No. 13, pp. 1691–1695. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © E.V. Ivakin, I.G. Kisialiou, L.I. Nykyruy, Y.S. Yavorskyy, 2018, published in Fizika i Tekhnika Poluprovodnikov, 2018, Vol. 52, No. 13, pp. 1584–1588.

SURFACES, INTERFACES, AND THIN FILMS

Optical Studies of Heat Transfer in PbTe:Bi(Sb) Thin Films

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Submitted February 5, 2018; accepted for publication February 12, 2018

Abstract—Electrical and thermal properties of lead-telluride films from 0.3 to 2.4 μm in thickness doped with antimony and bismuth, which were synthesized by thermal evaporation in vacuum, are investigated. Contact-free measurement of the in-plane thermal diffusivity is performed by the excitation of surface transient gratings and it is shown that the developed doping technology leads to a noticeable decrease in this heat-transfer parameter when compared with undoped PbTe.

DOI: 10.1134/S1063782618130067

1. INTRODUCTION

Compounds based on lead chalcogenides are promising for thermoelectric applications because they are characterized by a high carrier concentration, thermal voltage, and relatively low thermal conductivity [1–3]. The doping of lead telluride with antimony and bismuth leads to modification of its electron and phonon subsystems [3, 4]. For example, when doping PbTe with bismuth (the configuration of valent electrons is $6s^26p^3$), its amphoteric properties manifest themselves: when substituting lead in the cation sublattice ($Bi^{3+} \rightarrow Bi^{+}_{Pb}$), it is donor type, and in the anion sublattice ($Bi^{3-} \rightarrow Bi^{-}_{Te}$), it is acceptor type.

To increase the efficiency of thermoelectric conversion, new growth technologies of nanostructured films of lead chalcogenides are developed [5, 6]. When passing from bulk materials to low-dimensional structures, the thermal conductivity decreases and the Seebeck coefficient increases. These parameters can vary due to the influence of the boundaries of nanostructures on phonon and electron scattering. In particular, phonon scattering occurs not only due to the collision with electrons but also at grain boundaries, which leads to a decrease in the thermal conductivity. When varying the structure of low-dimensional objects, we can expect that the electrical conductivity will decrease to a lesser extent when compared with the thermal conductivity. This will result in an increase in the thermoelectric figure of merit.

Thus, the investigation of heat transport in thin-film lead chalcogenides is topical for estimating their thermoelectric properties. In this work, we perform completely contact-free laser-optical measurements of the in-plane thermal diffusivity of thin nanostructured PbTe films with the antimony and bismuth impurity. The investigations are performed by spatial-modulation spectroscopy (the method of transient gratings).

2. FILM PbTe:Bi(Sb) STRUCTURES AND SYNTHESIS TECHNIQUES

To fabricate the films, we used thermal evaporation in vacuum. Synthesized compounds of lead telluride doped with bismuth or antimony (0.1 at %) were used as the charge for evaporation. The compounds were synthesized by the direct fusion of components in sealed quartz ampules. The initial components for synthesis were lead of S-000 grade, tellurium of T-V4 grade, antimony of Su-000 grade, and bismuth of Vi-000 grade. The purity class is 99.999%.

The films were deposited onto glass and fresh muscovite cleavages (0001). The temperature of the evaporator and substrate was 700 and 200°C, respectively. The film thickness was varied within the limits of 0.3–2.4 μm and monitored with the help of an MII-4 microinterferometer. According to our measurements, the specific electrical conductivity and Seebeck coefficient for the PbTe:Bi films were 250 Ω^{-1} cm^{-1} and 200 μV/K, respectively.

Investigations into the charge-transfer phenomena showed that the main contribution to the total carrier mobility of the films PbTe:Bi(Sb) deposited above 200°C is introduced by diffuse scattering at the surface. Additional carrier scattering manifests itself at grain boundaries, which is explained by the rather large crystallite sizes [4, 5].

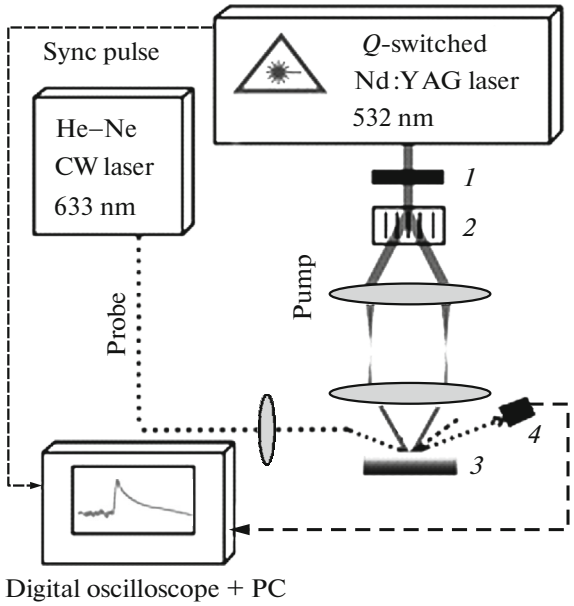

Fig. 1. Layout of the experimental setup. (*1*) Attenuator, (*2*) diffraction light splitter, (*3*) sample, and (*4*) photodetector.

3. PROCEDURE OF THERMAL MEASUREMENTS AND THE EXPERIMENTAL SETUP

Investigations into heat transfer in lead-telluride films are performed by the method of transient gratings, which consists in that the sample absorbing the light is excited by two mutually interfering beams of laser radiation [7, 8]. The spatial-periodic effect on the sample forms a transient diffraction grating in it, which is probed by a continuous laser. The damping kinetics of the diffraction signal is subjected to investigation. The layout of the experimental setup for investigation into the thermal properties of the films is shown in Fig. 1.

The samples were excited by an optical beam from a single-pulse YAG:Nd laser (LOTIS-TII LS-2137U/2, Minsk) at a wavelength of 532 nm with a duration and pulse-repetition frequency of 8 ns and 10 Hz, respectively. The excitation zone was probed by a continuous-wave helium–neon laser with a power of 40 mW at a wavelength of 633 nm. The diffraction signal was measured photometrically by a recording system including a photoelectron multiplier (H6780-20, Hamamatsu) and oscilloscope (TDS 3032B, Tektronix) connected to a computer to process the detected kinetic curves. The full width at half maximum of the function of the pulsed response of the system is 14 ns.

The transmission band of the PbTe-based film thermoelectrics lies in a range larger than 5 μm; therefore, the thermal excitation of the samples has a substantially surface character, while the diffraction signal can be observed only in reflected light. Transient gratings of three types appear on the film surface at the instant of the effect of the laser pulse. These are the profiled grating due to heating and thermal expansion of the material in the near-surface zone of the film, as well as the amplitude and phase gratings of thermal reflection from the surface.

In the general case, the relaxation dynamics of the diffraction signal has a complex character because the thermal response is formed by the sum of contributions of the three mentioned gratings and is determined by heat transfer both along and normal to the surface. This two-dimensional case is considered theoretically [9, 10] as well as implemented experimentally by the example of measurement of the thermal diffusivity of a single-crystal PbTe film grown on the BaF_2 substrate [10].

To simplify the measurement procedure and decrease the errors of the thermal testing of films, we created and used such experimental conditions that the grating of the surface relief played the main role in the formation of the diffraction signal. For this purpose, a weak homodyne beam coherent and collinear with respect to the signal diffraction beam was additionally directed to the photodetector. A permanent grating in contact with the film under study was used to form it. The phase difference between these interfering fields was established such that the diffraction signal from the phase grating of the surface relief would enhance and become considerably larger than the signal from the amplitude grating of thermal reflection. The first application of the homodyne field for interference amplification of the diffraction signal for the transient grating was implemented in [11], where a thin scratch scattering the light towards the photodetector was applied to the sample surface to form it.

The role of the phase grating of the thermal reflection will be described in section 5. Damping diffraction signals accumulated and processed according to a special program were modeled for the additional error function $[\mathrm{erfc}(t/\tau)^{0.5}]^2$ or $\mathrm{erfc}(t/\tau)^{0.5}$ depending on the amplitude-phase parameters of the homodyne field, and the thermal-grating lifetime τ was determined in such a manner. The thermal diffusivity χ was calculated by the measured lattice period Λ and its lifetime from the relationship

$$\chi = \Lambda^2/4\pi^2\tau. \quad (1)$$

4. TESTING OF MODEL SAMPLES

After assembling the setup to investigate the films in reflected light, we performed control measurements of the thermal diffusivity of two reflecting samples, notably, the working reference sample of steel 12Cr18N10T fabricated at the Mendeleev All-Russia Research Institute of Metrology (St. Petersburg) with

a certified value of the thermal diffusivity of $\chi = 0.040 \pm 6\%$ cm^2/s as well as a narrow-gap germanium semiconductor with the reference value of $\chi = 0.35$ cm^2/s. Such selection of the samples was made because of the fact that both materials, similarly to lead telluride, absorb light at a wavelength of 532 nm to a significant degree and, consequently, excited transient gratings have a principally surface character.

Damping kinetic curves of the diffraction signal for two samples are presented in Fig. 2. In both cases, signal oscillations caused by heat treatment into a thin adjoining air layer and the formation of a monochromatic ultrasonic wave overlap the heat kinetics. The oscillation frequency is 10–12 MHz, which is determined by the propagation velocity of ultrasound in air at this temperature. The amplitude of these oscillations for the reference sample is small, and their presence does not complicate the processing of the recorded plots. The first observation and explanation of this photoacoustic effect in air is contained in [12]. On the contrary, this amplitude for germanium is commensurable with the diffraction signal at the thermal grating and, in order to decrease the measurement error, the germanium wafer was placed into a vacuum chamber.

A short but rather power diffraction peak, caused by the formation of free carrier plasma, is seen in Fig. 2b at the beginning of kinetic curves *1* and *2*. Due to the application of a homodyne beam of increased power, two diffraction components are recorded separately in Fig. 2b (see the inset), which facilitates the physical interpretation of the found result. The fact that diffraction signals lie on different sides relative to the homodyne level is related to the fact that the photoinduced variations in the refractive index of an electronic and thermal nature in the surface layer of the sample have opposite signs. We previously found similar results when working with diamond samples [13, 14]. The authors of [15] also observed a two-component diffraction signal when investigating single-crystal silicon. It is natural that the electron-diffraction component is absent in Fig. 2a.

According to the published data, the carrier diffusivity is on the order of 100 cm^2/s. This fact means that the lifetime of the electron diffraction component for a grating period of 25 μm, which is determined by diffusion processes, does not exceed several nanoseconds and, consequently, the decay kinetics of the electron-diffraction component, though it is detected by our equipment, is not time-resolved.

The result of processing several kinetic curves of diffraction found under the excitation of a metallic reference sample (Fig. 2), gave an average thermal diffusivity of 0.038 cm^2/s, which corresponds to the reference value with an error of 5%. The average value of $\chi = 0.41$ cm^2/s is found for the germanium sample. This is 15% higher than the value of χ presented in reference books.

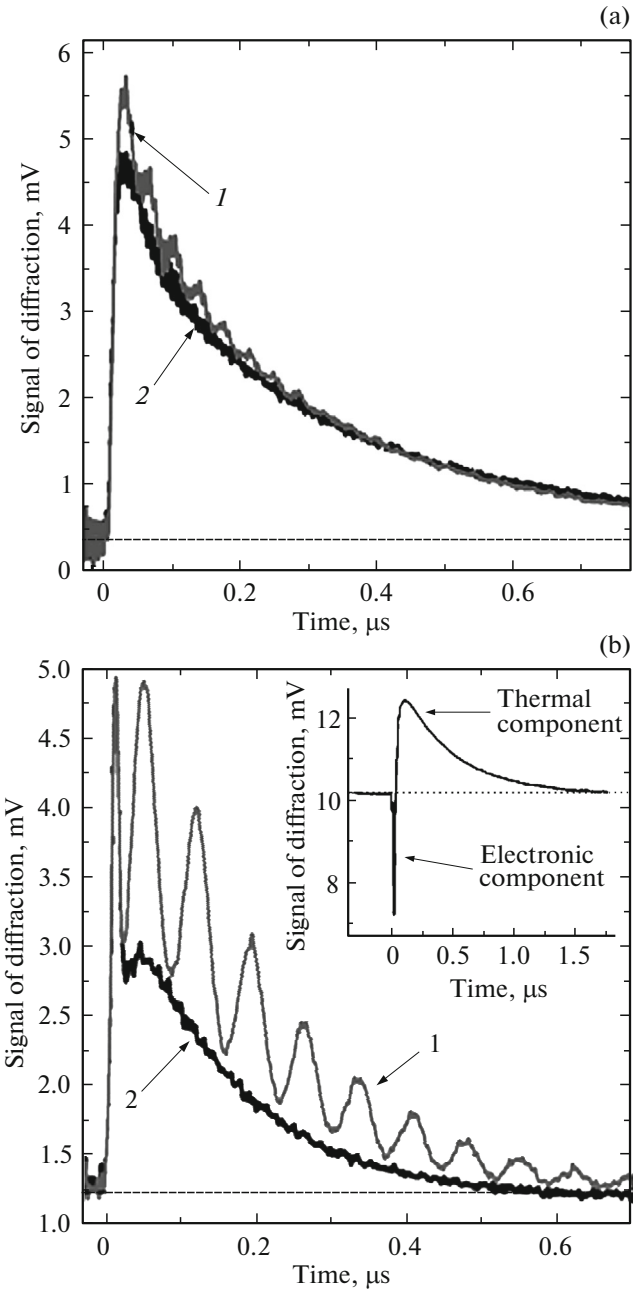

Fig. 2. Kinetic curves of the diffraction signal recorded during laser excitation of the surfaces of (a) the steel reference sample and (b) single-crystal germanium (*1*) in air and (*2*) in vacuum. Transient gratings period $\Lambda = 25.5$ μm. The homodyne power level is denoted by a horizontal dashed line. The inset in Fig. 2b corresponds to germanium in vacuum. In this case, the kinetics is found at an increased homodyne power; therefore, diffraction signals of a thermal and electron nature are recorded simultaneously.

Using the preliminarily calibrated diffraction efficiency of gratings, the height of their surface relief is estimated. It was smaller than 10 Å at this pumping level.

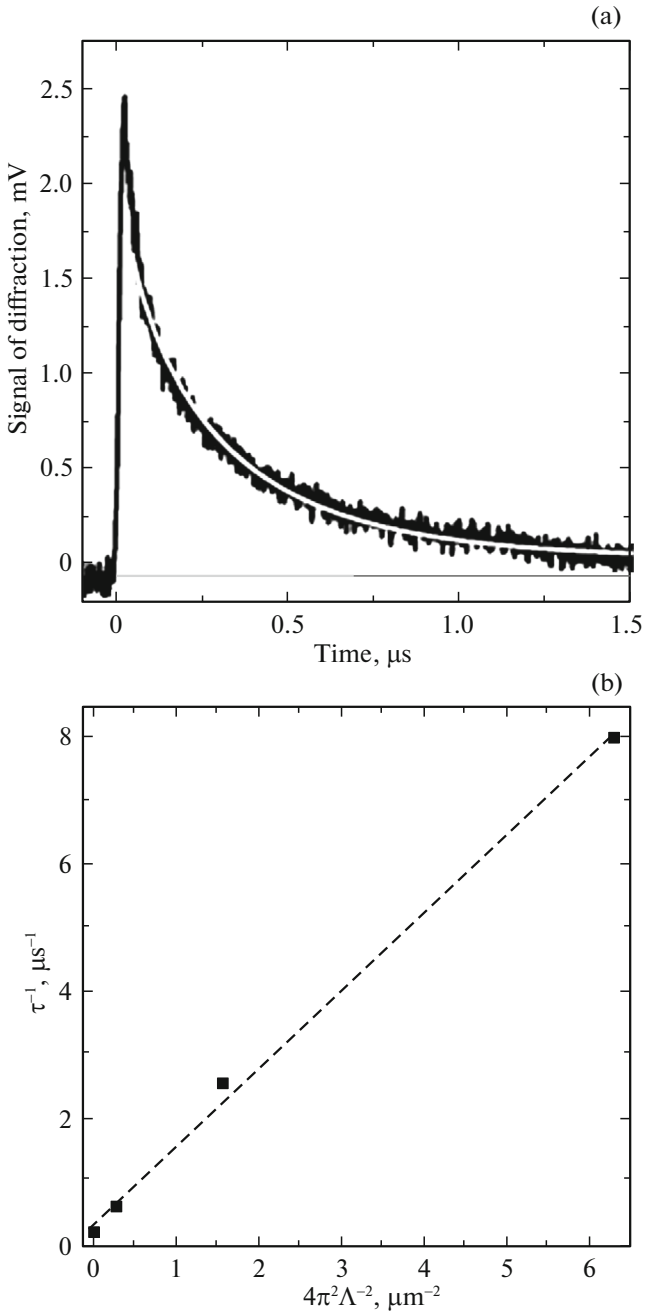

Fig. 3. (a) Diffraction signal in the film of undoped PbTe on glass. While the line in the plot corresponds to the result of modeling to the function $\mathrm{erfc}(t/\tau)^{0.5}$. (b) Final plot plotted according to the results of sequential measurement of the lifetime τ of thermal gratings with periods $\Lambda = 2.5$, 5.0, 11.3, and 25.0 μm in a PbTe:Bi film 2.5 μm in thickness on mica. Points correspond to the experiment and the dashed line corresponds to the linear approximation.

5. INVESTIGATION INTO HEAT TRANSFER IN PbTe-BASED FILMS

When investigating the films, we took into account the following circumstances. First, the three above-mentioned types of diffraction gratings contribute to the diffraction signal in the general case; therefore, the resulting kinetics can have a complex character. Second, according to the results of [10], two-phase gratings—the relief and thermal reflection ones—are in antiphase relative to one another. In this context, the initial kinetics segment should have a smooth signal transition from zero to the maximum at commensurable efficiencies of these gratings. Such a form of the transition is caused by the presence of a damping stage of the phase grating of thermal reflection. This regularity is seen in Fig. 2b, where participation of the electron grating leads to smoothing of the diffraction maximum at the initial instant of formation of the thermal grating. Third, the presence of a substrate can introduce errors into the results of measurements at periods of Λ larger than three thicknesses of the film [9]. However, the input control of the represented samples revealed the peculiarities of the films under study, which considerably decreased the role of the above factors. Analysis of the initial part of the diffraction kinetic curves showed (the typical plot found when working with the films is presented in Fig. 3a) that the diffraction signal has an abrupt transition from zero to the maximum. This fact evidences that the phase grating of thermal reflection has a low efficiency when compared with the efficiency of the grating of the surface relief and, consequently, its influence can be neglected.

Figure 3a shows the damping kinetics of the diffraction signal on a transient gratings with the period $\Lambda = 5$ μm in an undoped PbTe film 1.3 μm in thickness. The measured value of χ was 1.72×10^{-2} cm^2/s with an error smaller than 10%.

It was also established that the mechanical (and, consequently, thermal as well) contact between the film and the substrate for most of the samples turned out to be weak up to complete delamination so that certain parts of the films 2–3 mm in size were in a free state. This made it possible to use transient gratings with not only small but also with a large spatial period for the measurement of χ, which increased the reliability of measurements. The absence of the influence of the substrate on the result of thermal-diffusivity measurement is shown by the plot in Fig. 3b, where the values of the reverse lifetime of the thermal gratings at various spatial periods from 2.5 to 25 μm are presented. According to expression (1), the tangent of the angle between axis x and the approximation line gives an average value of χ of 1.35×10^{-2} cm^2/s with an error of ±6%. Similar plots were plotted by the results of the investigation of other samples. The common result of thermal testing of the films is shown in Fig. 4.

It is seen from Fig. 4 that the largest effect of a decrease in the thermal diffusivity is attained for PbTe:Sb films on glass. Similarly to the case of germanium and the metallic reference sample, ultra-acoustic vibrations, although of an insignificant amplitude,

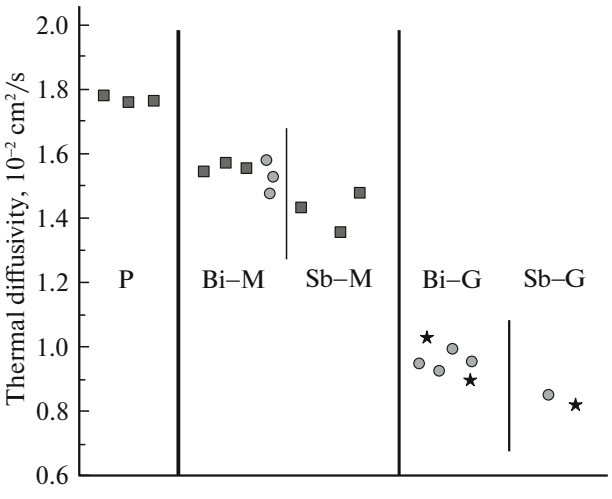

Fig. 4. Results of the thermal-diffusivity measurement of PbTe films doped with bismuth (Bi) and antimony (Sb) on muscovite (M) and glass (G) substrates in comparison with the undoped PbTe film (P).

were recorded at a grating lattice period of 25 μm in addition to the thermal component.

6. CONCLUSION

Our investigations into the temporal and amplitude properties of transient gratings recorded in thin films of doped lead telluride on substrates point to the fact that the main contribution to the diffraction signal is given by the phase relief grating on the film surface caused by thermal expansion of its surface layer. The contribution to the diffraction signal from the gratings formed due to a variation in the refractive index on the surface of doped films is noticeably smaller. This is evidenced by the shape of the initial part of the recorded diffraction signals with an abrupt transition of kinetic curves from excitation to the relaxation stage.

The revealed effect of complete or partial delamination allowed us to consider the film in selected sections as a layer thermally insulated from the substrate and excite transient gratings with an extended range of periods Λ from 2.5 to 25 μm. It is established by performed measurements of the films 1.5–2.5 μm in thickness that the doping of lead-telluride films with bismuth and antimony leads to a noticeable decrease in the thermal diffusivity of the films when compared with undoped PbTe films.

In contrast to single-crystal germanium (Fig. 2b), no diffraction signal from the electron component of semiconductor lead-telluride films to the fundamental absorption band is found. One cause of this is associated with the fact that according to available data of other authors on typical carrier mobilities in PbTe, the electron-grating lifetime conditioned by diffusion processes lies in a range shorter than 1 ns. This is far from the temporal resolution limits of our detection system.

ACKNOWLEDGMENTS

This study was supported by the Belarusian Republican Foundation for Fundamental Research, projects nos. F13K-063 and F16K-054, and by the State Fund for Fundamental Research of Ukraine, project no. F73/38-2017.

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Translated by N. Korovin