The Influence of Technological Factors of Production on the Surface Morphology and Electrical Properties of PbTe Films Doped with Bi

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The influence of technological factors of production, namely, time and the evaporator and substrate temperatures on the surface morphology and electrical properties of Bi-doped PbTe films deposited from the vapor in vacuum on glass ceramic substrates is studied. The atomic-force microscopy, image processing methods and Hall measurements are used. The effect of the shape parameters of surface crystallites on the mobility of free charge carriers is analyzed.

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1. INTRODUCTION

Films based on A\textsuperscript{IV}B\textsuperscript{VI} compounds are promising for the production of active elements of micro- and optoelectronics, such as detectors and sources of infrared radiation of the optical spectrum [1], thermoelectric energy converters [2]. Properties of thin polycrystalline films to a large extent depend on the surface morphology, electronic processes occurring at the interphase boundaries. Here, in particular, it is necessary to take into account phase and grain boundary scattering, as well as other growth defects [3-9]. Among other issues, the problem of stability over time of the electrical parameters remains still unresolved. Moreover, with the exposure of the films to air due to the acceptor action of oxygen, a layer enriched with p-type conductivity carriers is formed on the surface that prevents the production of a stable n-type material based on pure lead telluride.

Doping with donor impurities of the main matrix allows to obtain a stable n-type material based on PbTe.

The influence of technological factors of production on the surface morphology and electrical properties of Bi-doped PbTe films deposited on glass ceramic substrates is investigated in this paper.

2. EXPERIMENTAL

Films for the study were obtained by deposition of the vapor in vacuum on glass ceramic substrates of pre-synthesized Bi-doped lead telluride. During the deposition, the evaporator temperature was \( T_E = 650-750 \) °C and the substrate temperature was \( T_S = 150-250 \) °C that provided different deposition rates and allowed to produce films with different surface morphology. The film thickness was specified by the deposition time in the range of 3-120 s and measured using a micro-interferometer MII-4.

The measurements of the electrical parameters of the films were performed in air at room temperature in constant magnetic and electric fields. The measured sample had four Hall and two current contacts. Silver films were used as ohmic contacts. The current through the samples was equal to \( \sim 1 \) mA. A magnetic field with induction of 1.5 T was directed perpendicular to the film surface. The obtained samples are studied by atomic-force microscopy (AFM) methods Nanoscope 3a Dimension 3000 (Digital Instruments USA) in the periodic contact mode. The measurements are carried out in the central part of the samples using serial silicon probes NSG-11 with a nominal curvature radius of the probe tip up to 10 nm (NT0MDT, Russia). According to the results of AFM studies, in addition to the surface morphology, the sizes of individual nanocrystals in the lateral direction and their heights are determined by the watershed method using the Gwyddion program.

3. SURFACE MORPHOLOGY

AFM-images of PbTe : Bi structures are illustrated in Fig. 1. As seen, the structures obtained are composed of nanosized crystallites of a pyramidal shape. Using the Gwyddion program by the watershed method, it is established that the average crystallite sizes for thin films in the direction perpendicular to the surface are equal to 5-10 nm and in the lateral direction - 30-40 nm (Fig. 1a) and are much less than those for thick films of the sizes of 30-40 nm and 60-100 nm, respectively; moreover, the objects on the surface of thin films are characterized by flatter peaks.

In Fig. 2 we present the dependence of the film thickness \( d \) on the time \( t \) and substrate temperature \( T_S \).

The film thickness increases in proportion to time. The thickness rate is determined by the proportionality factor.

The growth rate of the film thickness \( \text{d}t \) increases with increasing substrate temperature. The dependence has an activation character (Fig. 3, the inset), and the activation energy is 0.17 eV. This energy corresponds to the barrier height, which should be overcome in order the PbTe molecule is attached to the film condensate. So, with increasing temperature, the interaction of the molecule incident on the condensate becomes less elastic.
Fig. 1 – AFM-images of the surface of PbTe:Bi films obtained on glass ceramic substrates under the following technological conditions $T_s$, °C, t, s: 150, 15 (a); 150, 120 (b); 200, 15 (c); 200, 120 (d); 250, 15 (e); 250, 120 (f). Evaporator temperature $T_e = 700$ °C.
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Fig. 2 – Dependence of the grain size in the lateral (curves 1, 2) and normal (curve 3) directions on the thickness of PbTe : Bi films obtained on glass ceramic substrates at different substrate temperatures \( T_S \), °C: 250 (○); 200 (●, □); 150 (●, ■). Evaporator temperature \( T_E \) = 700 °C

Fig. 3 – Dependence of the film thickness on the growth time at different substrate temperatures \( T_S \), °C: 150 (●); 175 (○); 200 (●, □); 250 (□). On the inset: dependence of the film thickness rate on the inverse substrate temperature

Fig. 4 – Dependence of the film thickness on the growth time at different evaporator temperatures: 650 and 700 °C (the lower and upper straight lines, respectively). On the inset: dependence of the film thickness rate on the evaporator temperature

The change in the film thickness versus the time and evaporator temperature \( T_E \) is shown in Fig. 4. The film thickness also increases in proportion to time. The film thickness rate depending on the evaporator temperature increases by the activation dependence (Fig. 4, the inset), and the activation energy is 1.66 eV. This energy corresponds to the height of the barrier to be overcome, so that the PbTe molecule is detached from the charge condensate in the evaporator.

Fig. 5 – Dependence of the form factor of the figures on the film surface versus the square root of the growth time for different evaporator temperature \( T_E \), °C: 650 (●); 700 (▲); 750 (○). On the inset: dependence of the rate of the coefficient of proportionality of the form factor on the substrate temperature

Fig. 6 – The change in the form factor of the figures on the film surface vs the time and substrate temperature \( T_S \), °C: 150 (●); 175 (○); 200 (●, □); 250 (▲). On the inset: dependence of the rate of the form factor on the substrate temperature

Let us establish how the shape of objects changes on the film surface. To describe the shape, we will use the form factor of the figure \( r \) – the height-to-diameter ratio of the figure base \( (r = h/D) \). It turned out that over time, \( r \) varies faster with increasing evaporator temperature, and the dependence itself is approximated by the power function, the exponent of which is \( \sim 0.5 \). In Fig. 5 we show the directional dependence. The square root of time is on the abscissa axis. Thus, \( r = v t^{1/2} \), the dependence on the evaporator temperature is presented on the inset. This dependence has an activation character, and the activation energy is 0.99 eV. By order of magnitude, this energy corresponds to the molecule binding energy [10].

The directional time dependence of the form factor for different substrate temperatures is illustrated in Fig. 6, and the temperature dependence of the proportionality coefficient \( v_r \) is shown on the inset. As seen, \( v_r^{-1} \) has an activation character, and the activation energy is equal to 0.19 eV. This value is close to the activation energy of the film thickness growth rate depending on the substrate temperature.

4. ANALYSIS OF THE ELECTRICAL PROPERTIES

The thickness dependences of the electrical parameters of the vapor-phase condensates are reduced to the following. With increasing thickness \( d \) (decreasing 1/\( d \)), the electrical conductivity \( \sigma \) slightly increases for all
investigated structures grown at a fixed substrate temperature (Fig. 7). However, with increasing deposition temperature for all condensate thicknesses, the electrical conductivity increases significantly (Fig. 7). The concentration of charge carriers also depends weakly on the film thickness; for the growth temperatures of 150, 200, and 250 °C, the concentrations are, respectively, equal to 2, 4 and 8 × 10^19 cm\(^{-3}\).

The thickness dependence of the carrier mobility \(\mu\) of PbTe : Bi films (see Fig. 8) correlates well with the behavior of the crystallite sizes (Fig. 2) and is also approximated by the power dependence, and the exponents practically coincide, that implies the implementation of not only the surface scattering mechanism, but also a significant effect on scattering of intercrystalline boundaries. It should also be noted a substantial increase in the carrier mobility with increasing deposition temperature that is associated with the growth mechanisms and the higher structural perfection of the films obtained at the substrate temperatures of 200-250 °C.

Let us separate the influence of the surface between phases and grains on the electrical properties of the film. In particular, under the condition of the predominance of carrier scattering by the phase surface \(P_s\) and the grain boundaries \(P_g\) and also the constancy of the concentration and effective carrier mass, the total carrier mobility \(\mu\) of the films is determined by the Matissen rule [5]:

\[
\frac{1}{\mu} = \frac{1}{\mu_s} + \frac{1}{\mu_g}. \tag{1}
\]

The mobility associated with the scattering by grain boundaries is defined according to [4]:

\[
\mu_g = \frac{2d}{h} R \left( \frac{3n}{\pi} \right)^{1/3}, \tag{2}
\]

where \(R\) is the average grain size, \(q\) is the carrier charge, \(n\) is the carrier concentration, \(h\) is the Planck constant.

The carrier mobility in the case of diffuse scattering on the surface is determined as [11]:

\[
\mu_s = \mu_e (1 + \lambda/d)^{-1}, \tag{3}
\]

here \(\lambda\) is the carrier mean free path, \(\mu_e\) is the mobility of bulk material.

According to the Taylor model [6], the carrier scattering by grain boundaries is described by the relaxation time \(\tau_g\) in such a way that \(\lambda = \tau_g d\), here \(\lambda\) is the effective carrier mean free path in an infinitely thick film. Then

\[
\sigma = \sigma_0 \left[ 1 - \frac{3\lambda}{8} \left( \frac{1-P}{d} \right) \right]. \tag{4}
\]

where \(\sigma_0\) is the specific electrical conductivity in an infinitely thick film, \(P\) is the fraction of diffuse scattering. Relation (4) describes the linear dependence of \(\sigma\) on \(d^{-1}\).

For room temperature, according to the experimental dependences of the specific electrical conductivity \(\sigma\) on the inverse thickness \(d^{-1}\) of the condensates (Fig. 7),
the carrier mean free path $\lambda$ calculated in accordance with the Taylor model for thin films based on PbTe : Bi is approximately equal to 41, 70, 91 nm for the films obtained at a temperature of $T_S$: 150, 200, and 250 ºC, respectively (Fig. 7). This is caused by the higher structural perfection of the films obtained at higher substrate temperatures. We note that the calculated free path was found to be comparable to the grain size in the lateral direction. Thus, this size determines scattering by the interphase boundaries; we will take $\lambda = D$ to calculate the mobility component.

In order to determine the effect of grain boundaries on the carrier mobility, as a grain size $R$ we will use the size in the direction $h$ normal to the surface, i.e. $R = h$.

The calculated values of mobility for each scattering mechanism separately and summarily are illustrated in Fig. 8. The mobility associated with surface scattering (curve 2, Fig. 8) is an order of magnitude lower than the mobility associated with grain boundary scattering (curve 1, Fig. 8).

It should be noted that accounting of the influence of carrier scattering on the surface and grain boundaries describes well the experimental data. When the current passes along the film surface, the contribution of surface scattering will be determined by the lateral grain size and of grain boundary scattering – by the normal sizes, and their ratio will be determined by the form factors.

5. CONCLUSIONS

1. The influence of the substrate temperature, time, and deposition rate on the surface morphology and electrical properties of thin Bi-doped PbTe films obtained on glass ceramic substrates has been studied.

2. The square root dependence of the form factor of surface objects and the linear dependence of the film thickness on the deposition time have been revealed. The activation energies calculated from the experimental plots correlate with each other and the literature data.

3. The carrier mean free path in the films obtained under different technological conditions has been determined. The carrier mobilities during surface and grain boundary scattering have been associated with the form factors of crystallites.

4. It has been shown that surface scattering is the dominant mechanism, which influences the carrier mobility, and its contribution to the mobility is defined by the lateral size of surface objects.

REFERENCES