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SIZE EFFECTS IN *GeTe* THIN FILMS

Dependences of electric conductivity σ, the Seebeck coefficient S, the Hall coefficient R_H, charge carrier mobility μ_H and thermoelectric power $P = S^2\sigma$ on the thickness d (d = 5 – 210 nm) of GeTe thin films grown by thermal evaporation in vacuum of GeTe crystals with subsequent condensation on (001) KCl substrates at temperature $T_S = 520$ K have been studied. For films of different thickness the temperature dependences of σ, R_H and μ_H in the range of 80 – 300 K have been obtained and power coefficient ν in the dependence $\mu_H(T)$ has been determined. Electron microscopy and electron diffraction methods have been used to show that the films possess a rhombohedral structure corresponding to a low-temperature α-modification of GeTe and grow with the preferred orientation (111) and (111) ($\bar{1}11$) || (001) KCl. It has been established that with a growth of film thickness to ~ 100 – 150 nm, the values of σ, μ_H and ν are monotonously increased, the dependences $R_H(d)$, S(d) and P(d) have the form of curves with a peak at ~ 75 nm, and with further increase of d the kinetic coefficients are practically unvaried. The dependence of properties on the thickness of films testifies to manifestation in GeTe films of classical size effect. Theoretical calculation of the dependence $\sigma(d)$ made in the framework of the Fuchs-Sondheimer theory is in good agreement with the experimental data. It has been established that the concentrations of holes in the films are lower, and S and P values are higher than in the bulk crystal. Maximum P values are achieved at d ~ 75 nm.

Key words: germanium telluride, thin films, thickness, temperature, thermoelectric properties, classical size effect.

Introduction

Germanium monotelluride is well known as a promising medium-temperature thermoelectric (TE) material of *p*-type [1-3]. It is a narrow-gap degenerate semiconductor with a multi-valley structure of energy bands and a high degree of deviation from stoichiometry. Within a wide homogeneity range (50.3 – 51.5 at.% *Te*) displaced towards *Te* excess with respect to stoichiometric composition, *GeTe* has three polymorphous modifications, namely high-temperature (β) and two low-temperature (α and γ). At temperatures lower than ~ 670 K the fcc lattice of *NaCl* type in β-*GeTe* is transformed into rhombohedral (α-*GeTe*) or rhombic one (γ-*GeTe*). The low-temperature α- and γ- modifications exist in the range of compositions close to homogeneity region on the side of *Ge* and *Te*, respectively, and in the range of compositions 50.5 – 50.9 at.% *Te* there is an eutectoid decomposition $\beta \rightarrow \alpha + \gamma$. Considerable deviation from stoichiometry determines high concentration of intrinsic defects (for the most part doubly ionized cation vacancies) and *p*-type charge carriers (~ $10^{20} – 10^{21}$ cm^{-3}). Among the disadvantages of *GeTe* as a TE material is too high concentration of holes exceeding the optimal value almost by an order. The problem of *p* reduction is generally solved by doping [1-4].

System dimension is another parameter permitting control of the physical properties, including TE ones [5-7]. For instance, it is known that if film thickness *d* is comparable to mean free path of charge carriers, there is the so-called classical size effect, manifested in the dependence of the kinetic properties of films on their thickness [5, 6]. This effect arises due to the fact that with a reduction of *d* the contribution of surface scattering of charge carriers to the resulting scattering is increased and becomes comparable to the contribution of bulk scattering.

A great many works have been devoted to the study of *GeTe* films. Some works ([8-10]) investigated the mechanism of growth and crystalline structure of *GeTe* films deposited onto glass, mica, (001) *NaCl*, (001) *KCl*, (001) *SnTe*, (111) BaF_2 and other materials at different substrate temperatures T_s. It was shown that depending on substrate temperature the films can be amorphous, textured or epitaxial, and that substrate type does not play a defining role in the determination of structural state of the films. Some works studied the electrical properties of *GeTe* films as a function of various factors (evaporator temperature, substrate type and temperature, thermal treatment, initial substance composition, condensation rate, etc.) [11-18]. It was established that substrate temperature determines not only the structural state of the film, but also the electrophysical and TE parameters. For instance, according to work [13] that investigated *GeTe* films on mica, *Te* content in the charge practically does not affect the electrical properties of the films, and hole concentration *p* in the films is primarily dependent on T_s: at low substrate temperatures *p* in the film is factor of 1.5 – 2 greater than *p* in the initial substance, and at high T_s, – on the contrary, it is reduced by a factor of 3 – 4. The authors of [14] showed that the electrical properties and structure of *GeTe* films are determined not only by substrate temperature, but also by condensation rate, as well as the duration and temperature of annealing, and are practically independent of charge composition. Considerable attention was given to investigation of the character of change in the electrical properties of *GeTe* when going from amorphous to crystalline state [7, 11, 16, 17]. In the interpretation of experimental results, especially the data related to hole concentration in thin films, the majority of explanations was reduced to the assumption of not only quantitative, but also qualitative change in defective structure with a change in technological parameters, as well as to possibility of re-evaporation processes at condensation.

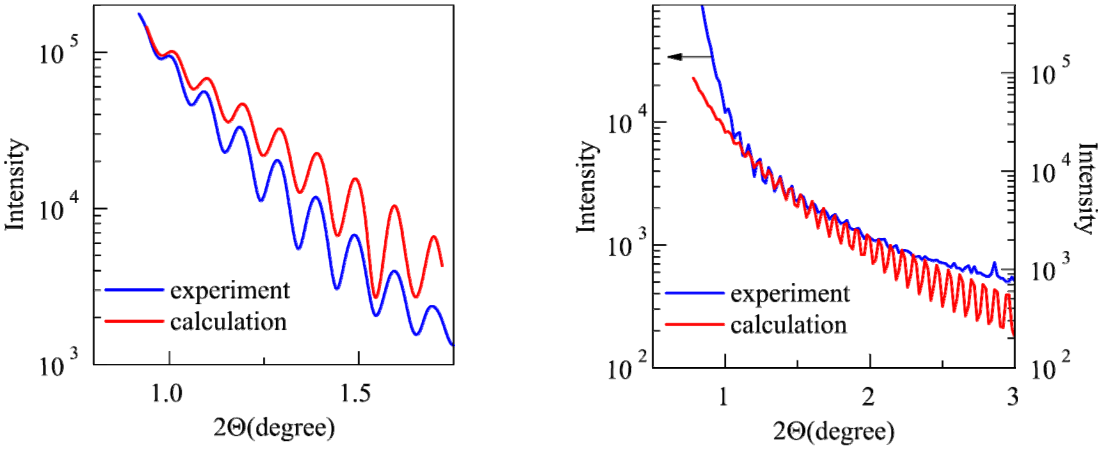
As regards study of the kinetic properties of *GeTe* thin films as a function of thickness *d*, there is work [11] which studies the dependences of resistivity ρ, the Hall coefficient R_H and charge carrier mobility μ_H on the thickness of *GeTe* crystalline films obtained by electron-beam evaporation of *GeTe* crystals with subsequent condensation on the glass at $T_s = 425$ K. In the range of thickness $d = 8 \div 40$ nm the authors of [11] who observed a reduction of ρ and R_H and increase in μ_H with a growth of *d* attributed this fact to structural imperfection of films at low thicknesses. In [19] we reported the observed dependence of electrical conductivity σ and μ_H on the thickness of *GeTe* films obtained by thermal evaporation in vacuum of *GeTe* crystals and subsequent condensation on the surface of (001) *KCl* at 520 K. We attributed the existence of such dependence to classical size effect manifestation.

The purpose of this work is a more detailed study of classical size effect in *GeTe* thin films obtained by thermal evaporation in vacuum through measurement of the galvanomagnetic and TE properties.

Experimental procedure

GeTe thin films of thickness $d = 5 – 210$ nm were prepared by thermal evaporation in vacuum ($\sim 10^{-5} – 10^{-6}$ Pa) of *GeTe* crystals. As a charge for sputtering we used polycrystalline *GeTe* obtained by direct melting of initial components in evacuated quartz ampoules. The rate of films condensation was 0.1 – 0.3 nm/s. As the substrates we used glass at $T_s = 300 \pm 10$ K and *KCl* (001) cleavages at

$T_s = 300 \pm 10$ K and $T_s = 520 \pm 10$ K. To prevent interaction with the air atmosphere, the films were coated with a layer of Al_2O_3 10 – 20 nm thick which was deposited onto the surface of films by electron-beam evaporation method. Film thickness was determined by a pre-calibrated quartz resonator located close to the substrates. Calibration of the resonator for films of $d > 100$ nm was performed by means of interferometer, and for films of $d < 100$ nm – with the use of *X*-ray diffractograms of small-angle scattering for one-layer films by comparison of experimental and calculated diffractograms. In this case, near the primary beam there is *X*-ray diffraction, namely the Kissing oscillations by the period of which one can determine film thickness to an accuracy of 0.1 nm. The calculated film thickness was varied for matching the calculated curve to the experimental one. Diffraction curves were obtained on DRON-2 diffractometer in CuK_α-radiation in $\Theta - 2\Theta$ scanning mode. As an example, Fig. 1 shows calculated and experimental diffraction curves for films with $d = 77$ nm and $d = 105$ nm.



a) *b)*

Fig. 1. Experimental and calculated diffractograms of small-angle X-ray scattering of GeTe films: a) – d = 77 nm, b) – d = 105 nm.

Electron microscope investigations of the films were performed on radiographic electron microscope PEM-125K. The temperature dependences of R_H and σ were obtained by method of direct current through the sample and constant magnetic field with induction 1 T in the temperature range of 80 – 300 K. The measurements of σ and R_H were made in two modes: cooling (300 – 80 K) and heating (80 – 300 K), which prompted a conclusion of practical absence of the temperature hysteresis. The Hall mobility of charge carriers and hole concentration p was calculated by the formulae $\mu_H = \sigma \cdot R_H$ and $p = 1/R_H \cdot e$, respectively, where e is electron charge. The Seebeck coefficient S was measured by compensation method with respect to copper. The error of measurement of R_H, σ and S did not exceed ± 5 %. Measurement of the electrophysical properties of the bulk crystal *GeTe* used as a charge showed that crystal has hole conductivity and the following set of electrophysical parameters: $p = 5.7 \cdot 10^{20}$ cm^{-3}, $\mu = 55$ cm^2/V·s, $\sigma = 5820$ Ω^{-1}cm^{-1}, $S = 32$ μV/K. All the measurements were made on as-prepared films.

Experimental results

Electron-microscopic study of *GeTe* structure has shown that films deposited onto glass and (001) *KCl* surface at $T_s = 300$ K are amorphous. With the investigation in electron microscope they were crystallized under the effect of electron beam. Fig. 2 shows an electron micrograph of crystalline fragment in amorphous die and its microdiffraction pattern. Crystal growth is of dendritic nature.

Crystalline structure of small crystals corresponds to the structure of low-temperature α-modification of *GeTe* (rhombohedrally distorted structure of *NaCl* with parameters $a = 0.5986$ nm, $\alpha = 88.35^{o}$ [3, 4]).

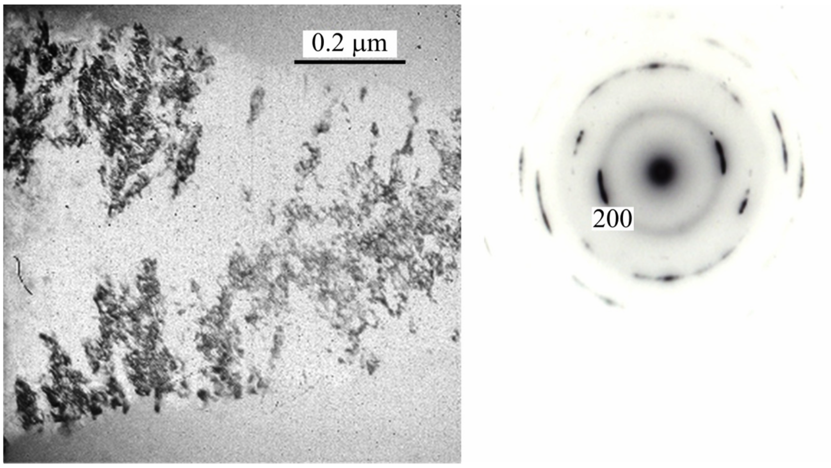


Fig. 2. Crystallization of amorphous GeTe film with d = 40 nm.

According to the results of electron-microscopic study, on (001) *KCl* substrate heated to temperature $T_s = 520$ K, α-*GeTe* film grows by island mechanism with the preferred orientation of (111) and $(\bar{1}11)$ α-*GeTe* || (001) *KCl*, and full healing of the film occurs at $d \approx 20$ nm (Fig. 3). The film with $d = 7$ nm (Fig. 3, *a*) is at the island growth stage, when isolated chips of α-*GeTe* have a distinct crystallographic faceting and grow together mechanically, without a variation of faceting, mutual arrangement and orientation. The angles between the faces of interlocked crystals are practically unrounded. The above described growth form is typical of substance condensation by the mechanism of "vapor-crystal without coalescence of contacting particles" [20]. The α-*GeTe* film with $d = 23$ nm (Fig. 3, *b*) is almost continuous and has plane intercrystalline boundaries faceting the grains. The results obtained are mostly consistent with the data of [7-9].

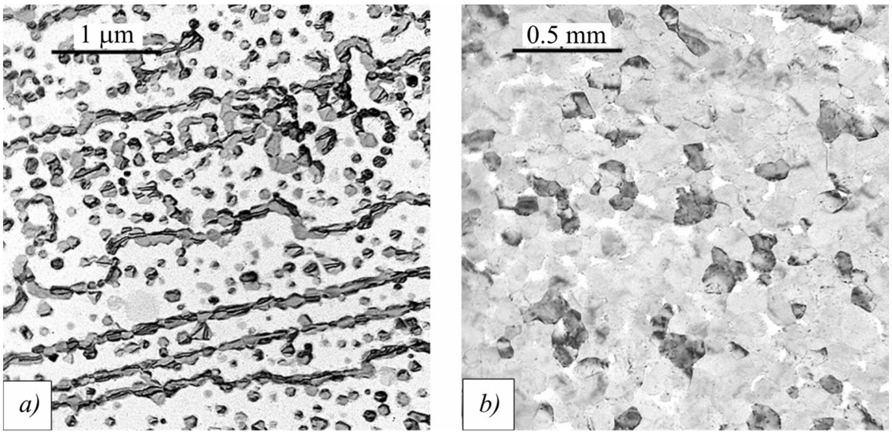


Fig. 3. Electron micrographs of GeTe films deposited onto (001) KCl substrates at temperature T_s = 520 K. Film thicknesses: d = 7 nm (a) and d = 23 nm (b).

Films deposited on (001) *KCl* at $T_s = 520$ K at $d < 25$ nm proved to be nonconducting, which agrees with the presence of island structure with small thicknesses.

Fig. 4, *a* – *d* shows the temperature dependences of σ, μ_H and R_H for *GeTe* polycrystal of which the films were manufactured and for some *GeTe* films ($d = 208$, 170 and 30 nm). For films of other thickness the dependences $\sigma(T)$, $\mu_H(T)$, $R_H(T)$ were of similar type. From Fig. 4, *a* it is clear that the choice of measurement mode (heating-cooling or cooling-heating) does not affect the general type of dependence $\sigma(T)$ and the values of σ. It points to the absence of temperature hysteresis and testifies to sufficiently equilibrium measurement conditions.

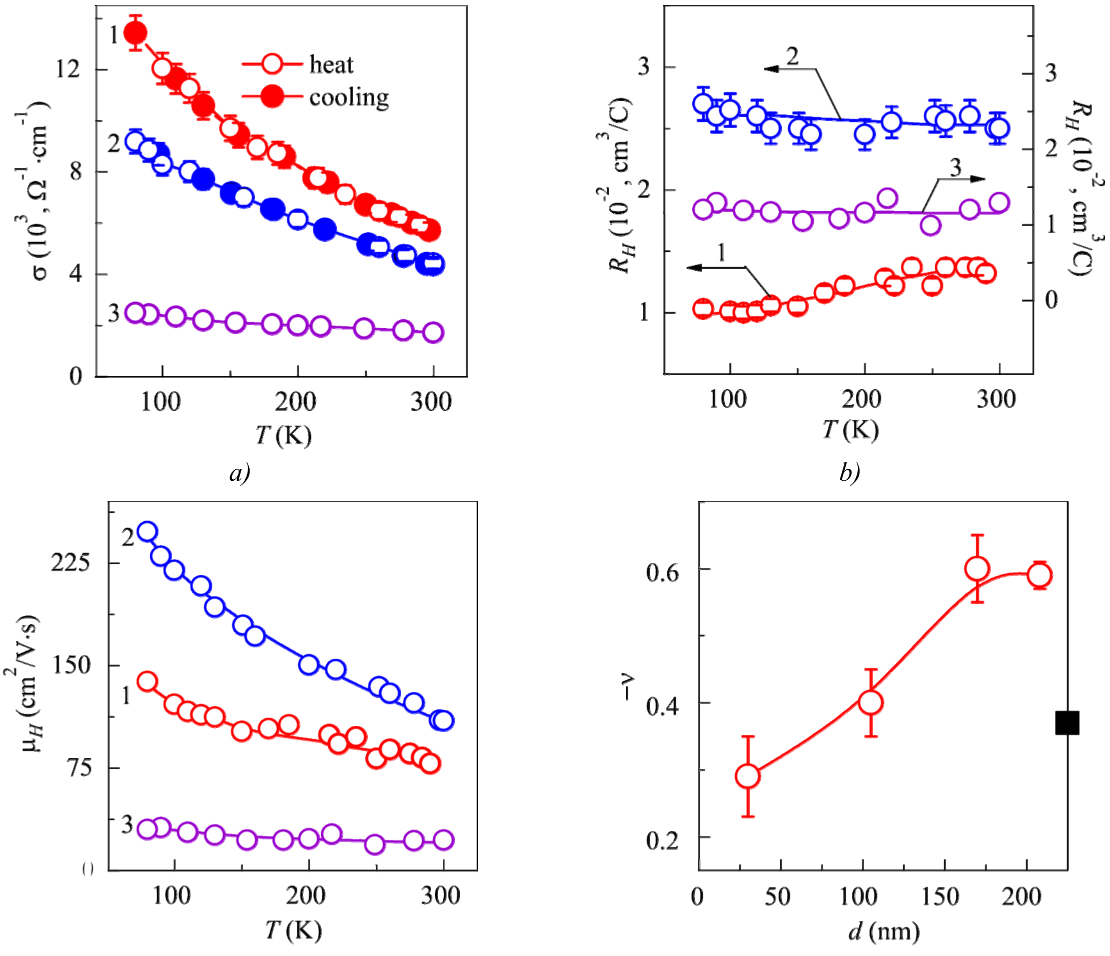
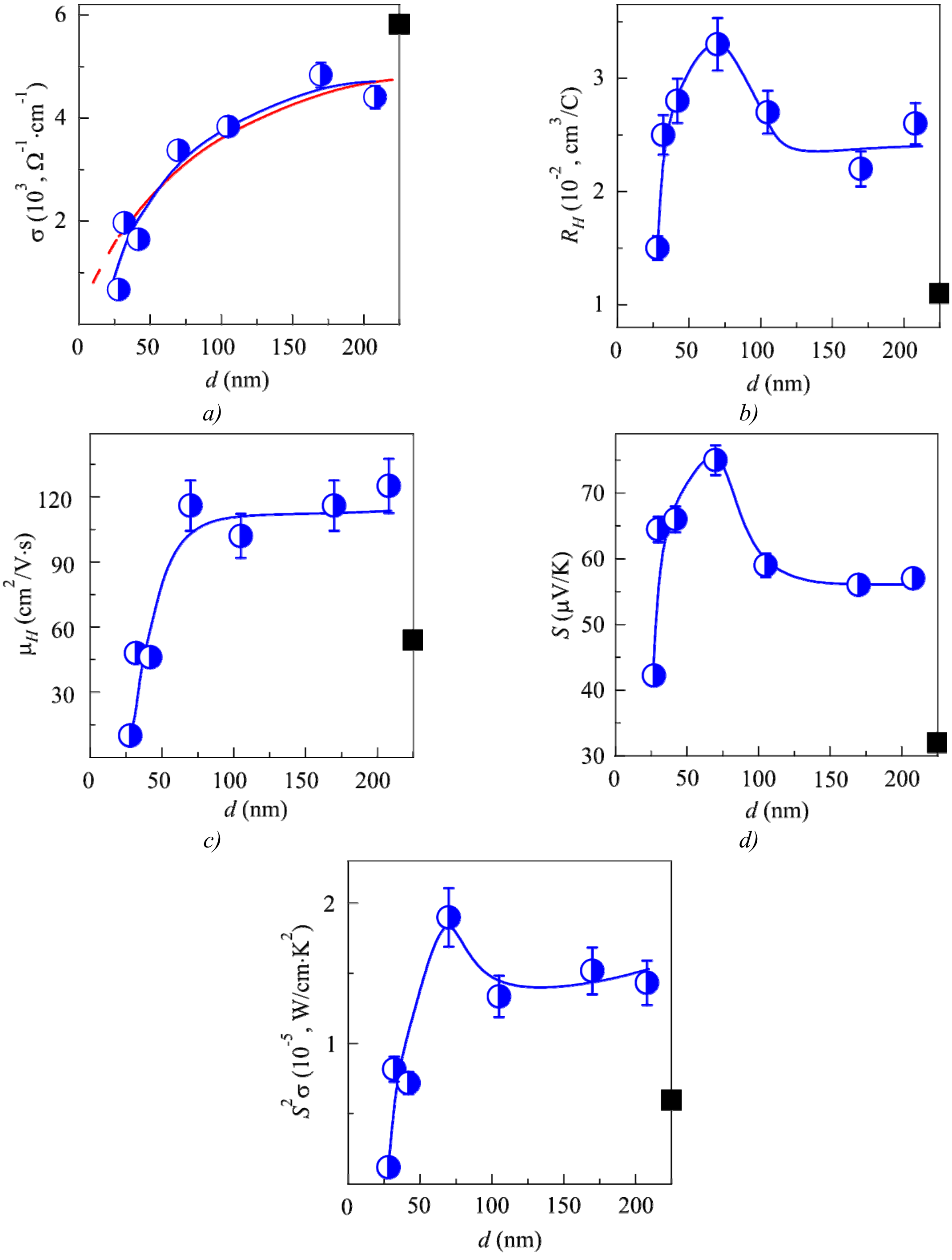


Fig. 4. Temperature dependences of electric conductivity σ (a), the Hall coefficient R_H (b), the Hall mobility of charge carriers μ_H (c) of GeTe thin films and power coefficient ν in the dependence $\mu_H \sim T^{\nu}$ as a function of thickness of GeTe films (d): 1 – polycrystal; 2 – film, d = 208 nm; 3 – film d = 30 nm. (d): Black square on the axis is the value of coefficient ν for polycrystal.

As can be seen, for all investigated samples, with a rise in temperature, the values of σ and μ_H are reduced, and the values of R_H are practically unvaried with temperature for the films and slightly increase for *GeTe* polycrystal. Such type of the temperature dependences of galvanomagnetic properties is characteristic of degenerate semiconductors. The observed R_H increase with temperature for *GeTe* polycrystal is generally related to a complex structure of *GeTe* valence band consisting of two subbands with different density of states and redistribution of holes in the subbands with a rise in temperature [3, 4, 21-24].

On the assumption of the power type of the temperature dependence of charge carrier mobility ($\mu_H \sim T^{\nu}$) based on the experimental data (Fig. 4, *c*) the power coefficients ν were determined by construction of log-log plots ($\ln\mu_H - \ln T$). Fig. 4, *d* shows the dependence of ν on the thickness of films. It is seen that with a growth of *d* the power coefficient increases from $\nu = -0.3 \pm 0.05$ for a film with $d = 30$ nm to $\nu = -0.6 \pm 0.05$ for a film with $d = 170$ nm, following which it is practically unvaried. This testifies to increase with growth of film thickness of phonon scattering contribution (for metals and strongly degenerate semiconductors $\nu = -1.0$) as compared to scattering on crystal lattice defects ($\nu = 0$). For polycrystal $\nu = -0.4 \pm 0.05$, and this indicates that as a result of charge carrier scattering on the grain boundaries polycrystal proves to be more defective than "thick" textured film.



a) *b)* *c)* *d)* *e)*

Fig. 5. Dependences of electric conductivity σ (a), the Hall coefficient R_H (b), the Hall mobility of charge carriers μ_H (c), the Seebeck coefficient S (d) and thermoelectric power $P = S^2 \cdot \sigma$ of GeTe films at 300 K. Black squares are the values of σ, μ_H, R_H, S and P for the bulk polycrystal of GeTe; red line in Fig. 5 (a) – theoretical calculation of $\sigma(d)_{theor}$ using the Fuchs-Sondheimer theory.

Fig. 5 shows the dependences of σ, R_H, μ_H, *S* and TE power $P = S^2\sigma$ on the thickness of films at room temperature. Analysis of the dependences σ(*d*), $R_H(d)$, $\mu_H(d)$, *S*(*d*) and *P*(*d*) shows the following.

1) Over the entire investigated thickness range σ is monotonously increased with a growth of *d*, and charge carrier mobility quickly grows to ~ 100 nm, then being practically unvaried;

2) *S*, R_H and *P* vary with thickness in a more complicated way as compared to σ and μ_H: up to *d* ~ 75 nm there is fast growth of *S*, R_H and *P* with increase of film thickness, then these values drop to *d* ~ 100 nm, following which *S*, R_H and *P* do not vary;

3) the values of the Hall coefficient in the bulk crystal are lower than in the films. For instance, for a film of thickness *d* ~ 75 nm R_H is increased as compared to a crystal by a factor of ~ 3.5. It means that in the films it is possible to get lower charge carrier (hole) concentrations than in polycrystal;

5) the values of the Seebeck coefficient and thermoelectric power in the bulk crystal are considerably lower than in the films. Maximum values of *S* and *P* correspond to films of thickness *d* ~ 75 nm.

Analysis of the results

1. First of all, we should state the fact that in the films under study there is a classical size effect related to increase of the share of charge carriers scattered on the film surfaces, as its thickness is reduced. In the bulk crystals the role of the surface serving as structural imperfection is minor, and free path of charge carriers *l* is mainly determined by scattering of the latter in the bulk of the crystal. As the film thickness is reduced, the contribution of surface scattering is increased, leading to a respective change of properties.

The Fuchs-Sondheimer theory of classical size effect [25-27] which was developed for metals is based on the use of the Boltzmann kinetic equation and the boundary conditions on the film surface. The theory has two independent parameters: 1) relationship *d/l* where *l* is free path of charge carriers, and 2) specularity parameter *R* characterizing the share of electrons elastically reflected from the film surface. The value of *R* lies between 0 (for fully diffuse scattering) and 1 (for fully specular scattering).

According to the Fuchs-Sondheimer theory [25, 26], the formula for calculation of the dependence of electric conductivity σ on film thickness *d* is given by:

$$\sigma(d) = \frac{3}{4}\sigma_\infty \frac{d}{l}\ln\left(\frac{l}{d}\right)\left(\frac{1+p}{1-p}\right),\ \frac{d}{l} << 1, \tag{1}$$

where σ_∞ is infinitely thick sample conductivity and *d* is film thickness.

It should be noted that the theory comprises a number of simplifications (consideration is given to a metal with a spherical Fermi surface and isotropic free path; it is assumed that specularity parameter is a constant equal for both Fermi surfaces and trajectory-independent). However, despite the fact that the theory is rather approximate, in many cases for metals there is a good agreement between theory and experiment, though in very thin films, even if they are continuous, the conductivity is generally reduced much faster than it follows from the theory [25-27].

When establishing the dependence of the kinetic coefficients on the film thickness in semiconductors, we must take into account the availability in them of a near-surface space charge. The authors of a number of works tried to do it (see, for instance, [1]), but up to date the theory of size effect for transport phenomena in semiconductors has not been developed yet.

In this connection, we have performed a theoretical calculation of dependence σ(*d*) using formula (1) of the Fuchs-Sondheimer theory. As σ_∞ value, the electric conductivity value for the bulk polycrystal was taken ($\sigma_\infty = 5820\ \Omega^{-1}\cdot\text{cm}^{-1}$). The resulting theoretical dependence $\sigma(d)_{theor}$ (shown in Fig. 5, *a* as a red line) practically coincides with a line drawn through the experimental points by least-squares method, with the following values of specularity parameter p and hole free path l: $R = 0.5 \pm 0.01$ and $l = (680 \pm 10)$ nm. It is seen, however, that the first point corresponding to the smallest thickness lies below the theoretical curve, which is quite explainable, if, apart from the size effect, we take into account the influence of structural factor on the electric conductivity values. The influence of structural factor is due to the fact that *GeTe* films grow on halide crystals according to island mechanism [20], and with a growth of d there is a transition from the film with isolated islands that are formed as a result of nucleation and growth of individual condensate particles to the structure with channels connecting these islands and determining charge transfer along the entire film. After the formation of a continuous film the influence of structural factor on σ and μ_H is considerably reduced; nevertheless, in the region of small thicknesses it is important to take into account the d-dependence of film structure. Fig. 5 shows d-dependences, starting from the thicknesses, when a continuous film is formed. Therefore, the role of structural factor will not be as important as in the case of ultrathin films. As noted above, with very small thicknesses, even in continuous films, the conductivity is generally reduced much faster than follows from the theory [25-27]. Apparently, for this reason the first point on the dependence $\sigma(d)$ lies below the theoretical curve.

2. Comparing the results of the present work and the data of [11] that studied *GeTe* crystalline films grown on the glass at $T_s = 425$ K, it can be seen that films prepared on (001) *KCl* substrates at $T_s = 520$ K (the present work) have higher values of σ (almost 2 fold) and μ_H (almost 8 fold). This testifies to the fact that with selected type ((001) *KCl*) and temperature ($T_s = 520$ K) the substrates of *GeTe* film are structurally more perfect and this provides considerable opportunities for revealing classical size effect and its theoretical description.

3. The fact that curves $R_H(d)$ and $S(d)$ are practically identical shows that dependences $S(p)$ correspond to a semiconductor with one sort of charge carriers. It is known [3, 4, 21] that dependences of the electrical properties of *GeTe* on hole concentration are of abnormal type, and this is because from the standpoint of present-day ideas of the band structure of *GeTe*, the valence band of the latter consists of two subbands with different density of states divided by the energy gap. With a change of hole concentration in the range of $(1.8 - 7.5)\cdot 10^{20}$ cm^{-3}, the Seebeck coefficient drops with a growth of hole concentration in conformity with the ideas of the band theory of degenerate semiconductors with one sort of charge carriers. In this case the Fermi level is in the zone of light holes which are responsible for crystal conductivity. However, with further increase in hole concentration, the Fermi level goes over to the overlap region of valence subbands, and, alongside with light holes, heavy holes start to participate in conductivity, and their ever increasing contribution results in the growth of S. In the range of thicknesses $d = 30 - 75$ nm the hole concentration is reduced from $p = 4.5\cdot 10^{20}$ cm^{-3} to $p = 1.9\cdot 10^{20}$ cm^{-3} and these p values show that light holes take part in conductivity and dependence $S(p)$ corresponds to the dependence for semiconductors with one sort of carriers. A reduction in carrier concentration results in the growth of the Seebeck coefficient whose maximum value is achieved close to $d = 75$ nm.

There is a good correlation between the values of R_H and S corresponding to dependence $S(p)$ established in [21].

4. It is rather difficult to predict the type of R_H and S dependence on the thickness of *GeTe* films caused by classical size effect, with regard to specific features of *GeTe* band structure and the presence of high concentration of intrinsic defects. The non-monotonous type of dependences $R_H(d)$ and $S(d)$ shows that, apart from the size effect, the type of dependences is evidently affected by other factors,

too. It can be assumed that at the first condensation stages of *GeTe* films there is partial tellurium reevaporation, as a result of which the concentrations of charged cation vacancies and *p*-type charge carriers are reduced (to $p = 1.9 \cdot 10^{20}$ cm^{-3} at $d = 75$ nm). This effect can be due to peculiarities of *GeTe* evaporation, as well as the change in thermodynamic equilibrium conditions (and, accordingly, to the change in equilibrium concentration of vacancies) in thin layers as compared to the bulk crystal. Subsequent reduction of R_H with the variation of *d* from 75 nm to ~ 100 nm shows that some additional factor starts to take effect, increasing the number of *p*-type charge carriers. It can be supposed that close to $d = 75$nm the extreme low value of cation vacancies is achieved, and then, alongside with nonstoichiometrtic vacancies, there appear other acceptor-type defects, such as charged twin boundaries formed in the process of film growth [9]. The relaxation phenomena must not be ruled out, taking into account that measurements were performed on as-prepared films.

5. It should be noted that dependence on the thickness of *GeTe* films of another important TE parameter, namely TE power, which significantly determines the efficiency of TE power converter, also is of a non-monotonous type (Fig. 5, *e*), and it should be taken into account when using films in TE devices.

Conclusions

The method of thermal evaporation in vacuum was used to grow *GeTe* films on (001) *KCl* substrates at temperature $T_s = 520$ K in the range of thicknesses $d = 5 - 210$ nm. The electron microscopy and electron diffraction methods were used to show that the films possess a rhombohedral structure corresponding to low-temperature α-modification of *GeTe* and grow with the preferred orientation (111) and $(\bar{1}11)$ α-*GeTe* || (001) *KCl*.

It is established that with a growth of film thickness to $d \sim 100 - 150$ nm the values of conductivity σ, charge carrier mobility μ_H and power coefficient ν in the temperature dependence μ_H are monotonously increased, and *d*-dependences of the Hall coefficient R_H, the Seebeck coefficient *S* and TE power $P = S^2\sigma$ have the form of curves with a peak at ~ 75 nm; with further growth of *d* the kinetic coefficients are practically unvaried. The dependence of properties on the thickness of films testifies to manifestation of classical size effect in *GeTe* films. There is a good agreement between the experimental dependence σ(*d*) and the results of theoretical calculation in the framework of the Fuchs-Sondheimer theory.

From the resulting data it follows that using the method of thermal evaporation of *GeTe* polycrystals in vacuum with the working technological parameters, one can prepare *GeTe* thin films with the values of hole concentration lower than in the bulk polycrystal and higher values of TE power.

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