

ON THE ELECTRICAL AND OPTICAL PROPERTIES OF THE STRATIFIED TELLURIUM THIN FILMS*

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The electrical and optical properties of Te thin films ($d = 90 - 1400$ nm) deposited onto glass substrates by thermal evaporation in vacuum are investigated in relation with the film structure. It is found that the values of the hole concentration and of the optical parameters α , n (in the IR spectral range) decrease with the increase of the film thickness. This dependence is found to be associated with the modification of the film microstructure during the film growth, especially with the change of the crystallite orientation. The results are discussed in correlation with both the specific character of chemical bonds in Te crystal and with their anisotropic properties.

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1. Introduction

In the last years, the interest for the study of the electronic transport and optical properties of tellurium thin films has been intensified due to their importance for various practical applications such as infrared detectors, thermoelectric devices, thin-film transistors, etc. [1 – 4].

The experimental data on the electrical and optical properties of Te films showed an important dependence of these properties both on the thickness and the preparation conditions of the films [5 – 16]. This indicates a strongly correlation between the properties and structure of the film.

In our recent paper [14] on the structure of evaporated Te thin films, we have established that during the growth process, the film crystallites change their orientation with increase of the film thickness. In relatively thin films (100–300 nm) Te crystallites have a preferred orientation with their c -axis (tellurium has a hexagonal structure) parallel to the substrate. As the film thickness increases, the crystallites grow with their c -axis oblique to the substrate. This specific stratified structure of evaporated Te films may have an important role in determining their physical properties.

In this paper some electrical and optical properties of such Te thin films are investigated.

2. Experimental

Tellurium thin films have been deposited onto glass substrates by thermal evaporation in vacuum ($\approx 10^{-5}$ Torr) of polycrystalline tellurium powder (99.99% purity). The evaporation source, consisting in a quartz crucible heated by a Mo spiral, was mounted about 10 cm below the substrate holder assembly. The substrate temperature, T_s , was kept constant during the film growth and its values varied between 290 and 450K. The deposition rate, r_d , ranged from 2 nm/s to 25 nm/s and the incidence angle of the tellurium vapours on the substrate, φ , was within the range $0^\circ - 60^\circ$. By modification of the deposition times, films in the same experimental conditions but having different thicknesses were prepared.

The film thicknesses, d , measured with an interference microscope ranged between 90 and 1400 nm.

The film structures were investigated by standard X-ray diffraction (XRD) technique, using CuK_α radiation.

The carrier concentrations for the studied films were obtained by using the standard d.c. techniques for Hall coefficient measurements. The gold electrodes were used as ohmic contacts, the

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ohmicity being verified by current-voltage characteristics over the all investigated temperature range. For all studied samples, the sign of Hall coefficient was positive, i. e. the Te films have a p-type conduction.

The IR transmission spectra have been recorded at room temperature in the wavelength range of 2-5 μm and the reflection ones within the range 2-25 μm .

The refraction index, n , and extinction coefficient, k , have been determined from transmission and reflection measurements using a computational method [17]. The absorption coefficient α has been determined in accordance with the relation $\alpha = 4\pi k/\lambda$. For the Te films with greater thicknesses (above 1 μm) the absorption coefficient was determined by the relation [18]:

$$\alpha = \frac{1}{d} \ln \frac{(1-R)(1-R')}{T} \quad (1)$$

where R and R' are the reflectivity corresponding to the air-film and film-substrate interfaces respectively and T is the film transmittance.

3. Results and Discussion

3.1. Structural characteristics of the films

In Fig. 1, the typical XRD patterns for the studied samples are presented. The patterns (a) – (c) correspond to the samples having different thicknesses but deposited at the same experimental conditions. The pattern (d) is for a sample deposited in conditions that favour the growth of the film crystallites preponderant oblique oriented to the substrate.

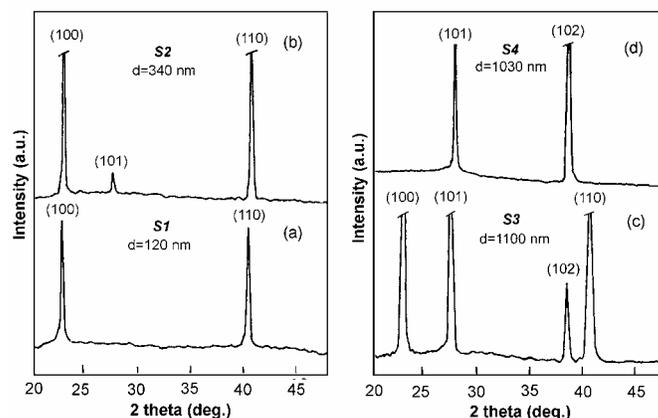


Fig. 1. XRD patterns ($\text{CuK}\alpha$ radiation) of Te thin films with various thicknesses and deposited at different conditions: (a) – (c): $T_s=293\text{ K}$, $r_d=2\text{ nm/s}$, $\varphi=0^\circ$; (d): $T_s=370\text{ K}$, $r_d=22\text{ nm/s}$, $\varphi=45^\circ$;

As it may be seen from Fig.1 (a–c) some structural modifications appear in the films with the increase of the film thickness. In the films with smaller thickness (Fig.1a, b), the crystallites grow with the (100) and (110) planes parallel to the substrate. This fact shows that in these films the crystallites are oriented with their c -axis parallel to the substrate. As the film thickness increases, the XRD patterns exhibit peaks corresponding to X-ray reflections from (101), (102) and (111) planes which are not parallel to c -axis of the crystallites (Fig. 1c). This fact shows that from a certain thickness the crystallites begin to grow obliquely to the substrate.

Depending on the deposition conditions, it is possible to obtain films with about identical thicknesses but having different orientation of their crystallites. As it can be seen from Fig. 1 (c, d), the samples S3 and S4 have about the same thicknesses but in the XRD pattern of sample S4 the peaks corresponding to the X-ray reflections from (100) and (110) planes do not occur. This indicates that in the sample S4 the crystallites are only oblique oriented to the substrate.

The change of the crystallite orientation during film growth as a function of film thickness and deposition conditions indicates that the studied films have a stratified structure formed from two superposed layers: a first layer in which the crystallites are oriented with c -axis parallel to the substrate and a second layer having the crystallites with c -axis oblique oriented to the substrate. The

thicknesses of these sublayers are influenced by deposition conditions so, films with the same total thicknesses may have different thicknesses of each of those two sublayers. Such films may have different electrical and optical properties, as it will be seen in the following paragraphs.

3.2. Electrical properties

Our previous studies revealed that the electrical conductivity of Te thin films deposited onto glass substrates depends on the deposition conditions of the film and decreases as the film thickness increases [14].

In this paper, we have investigated the dependence of the hole concentration on thickness and deposition conditions of the films.

For the studied samples, the hole concentrations were calculated using the relation [19]:

$$p = \frac{3\pi}{8} \cdot \frac{1}{eR_H} \quad , \quad (2)$$

where e is the electron charge and R_H is the Hall coefficient.

The temperature dependence of hole concentration for three representative samples are presented in Fig. 2. Curve (a) is for a film with a small thickness, in which the crystallites are oriented with their c - axis parallel to the substrate. Curve (c) is characteristic for the samples obtained under conditions that favour a structure with the crystallites obliquely oriented to the plane of the substrate. The curve (b) is for a sample having an intermediate structure.

As it may be seen from Fig. 2, the hole concentration decreases as the film thickness increases. Also, p has lower values for the sample having crystallites predominantly oblique oriented. In the whole investigated temperature range these characteristics are maintained.

We consider that these results are determined, in addition to other factors, by the specific orientation of crystallites in the films with different thicknesses. This may be explaining if one takes into account the character of chemical bonds between neighbouring atoms in tellurium crystal.

As is known [19], the crystalline structure of Te consists of helical atomic chains arranged parallel to the c -axis of hexagonal unit cell. Each atom is tightly bonded to two neighbours in a chain with covalent bond. The interaction between atoms in neighbouring chains is much weaker and is of van der Waals type. For this reason, the nucleation process of Te films on the glass substrate starts by disposition of atomic chains in the plane of the substrate. Consequently, the crystallites begin to grow with their c - axis parallel to the substrate. In the growth process, the atomic chains in one crystallite are interrupted at the contact with other crystallites. Therefore, in the intergrain domains there are a great number of unsatisfied chemical bonds, which induce a great number of acceptor states in the band gap. These domains are localised at extremities of the crystallites, situated perpendicular to their c - axis. Thus, in the films having small thickness, the crystallites being predominantly oriented with their c - axis parallel to the substrate, the domains with great concentration of acceptor states appear even in initial phases of film growth. Consequently, in such films, the hole concentration will be great.

When the substrate is completely coated with a continuous assembly of crystallites, the deposition of the atoms from incident beam takes place onto a new "support" formed from previously deposited layer. The crystallites primarily formed onto substrates may include tellurium atoms with unsatisfied covalent bonds that will trap the atoms from incident beam. In this way, atomic chains having an obliquely position on the substrate will start to form. As result, an increasing number of crystallite will grow with their c - axis oblique oriented to the substrate. But in this case, the length of atomic chains is weakly influenced by the presence of neighbours crystallites and therefore the number of unsatisfied chemical bonds in the new sublayer will decrease. Consequently, the concentration of acceptor state and hole concentration in respective films will be lower in comparison with that in thinner films. In this way, the thickness dependence of hole concentration may be explained.

Of course, the deposition parameters such as the substrate temperature and deposition rate also influence the film structure and hence the charge carriers concentrations. But we consider that in the case of the evaporated Te films, the change of crystallite orientation with increasing film thickness may be an important factor, which determine the thickness dependence of electrical properties of these films.

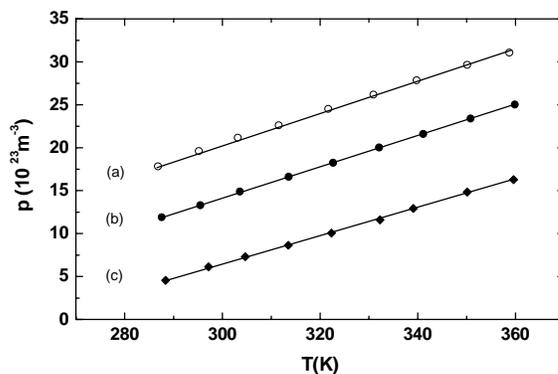


Fig. 2. Temperature dependence of hole concentration in the films deposited at different experimental conditions: (a) $T_s=293$ K, $r_d=2$ nm/s, $d=120$ nm; (b) $T_s=293$ K, $r_d=2$ nm/s, $d=1100$ nm; (c) $T_s=370$ K, $r_d=22$ nm/s, $d=1030$ nm;

3.3. Optical Properties

The optical properties of the studied films are also influenced by the stratified structure of the films. Typical spectral dependences of the absorption coefficient, α , in the photon energy range of the fundamental absorption edge are shown in Fig. 3, for Te films having different orientations of the crystallites. As it can be seen, the absorption curves show a shoulder in the low energy side of the fundamental absorption edge, which is more prominent for the thin film. The occurrence of this shoulder may be related to the existence of a high density of levels within the band gap situated near the top of the valence band. These levels correspond to the electronic states determined at the crystallite boundaries by the discontinuities in the atomic chains. In these intergrain domains there are a great number of unsaturated bonds, which trap electron like the acceptor impurities in a p-type semiconductor. The electronic transitions from respective acceptor levels to the conduction band can be responsible for the occurrence of the above-mentioned shoulder. As it has been showed in the previous paragraph, in the case of textured Te films, the trap density is great and decreases with the increase of the film thickness. This fact explains the high 'shoulder' absorption in the sample *S/* (Fig. 3, curve a).

The influence of the crystallite orientation on the optical properties of the Te films results also from the analysis of reflection spectra in the range 0.08 – 0.20 eV, plotted in Fig. 4. As it seen, in respective spectra, at photon energy of about 0.12 eV a reflection minimum occurs, which is deeper for the thinner film.

This minimum might be connected with the light absorption in the film due to the electronic transitions between the two subbands of the valence band, found out for bulk Te [20]. The thickness dependence of the intensity of these reflection minimums may be related to the infrared dichroic properties of Te crystallites and to the modification of their orientation with thickness increase. As it known, the tellurium crystal is a dichroic semiconductor, its absorption coefficient, α , depends on the polarization of the incident radiation. For electric vector \mathbf{E} parallel to the c -axis the α value is greater than in the case of $\mathbf{E} \perp c$ [21]. It is possible that the microcrystallites from the studied films have such dichroic properties. In this case, the optical absorption in Te thin films will be influenced by the orientation of the crystallites in the film. As for the Te films having the crystallites preponderantly oriented with c -axis parallel to the substrate but randomly oriented in this plane, the absorption of the electric vector component parallel to the c -axis from the normal incidence unpolarised light will be more significant in comparison with those of the \mathbf{E} component $\perp c$. This may explain the deeper minimum observed in reflection spectrum of the thinner Te films.

A dependence of the optical properties on the film thickness is shown in Fig. 5 in which the spectral dependences of the film refraction index are presented. It may be observed that the respective films have a different refraction index although they were deposited in the same conditions. This may be due to the same anisotropic properties of the film crystallites and their orientation. It is known that the values of n for the Te crystal depend on the polarization of incident radiation, being greater for $\mathbf{E} \parallel c$ [21]. If one takes into account this behavior it results that the films with the crystallites having c -axis parallel to the substrate will be have a greater value for refraction index as those of the films with oblique oriented crystallites. The results from Fig. 5 confirm this conclusion.

Therefore, the investigated optical properties revealed that in the infrared wavelength range the studied Te thin films displays some peculiarities similar to those of bulk Te.

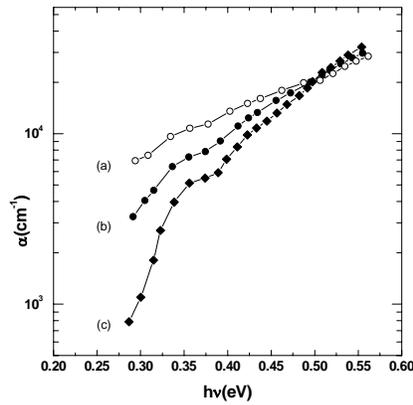


Fig. 3. The absorption spectra at the fundamental absorption edge of films with different crystallite orientation: (a) *c*-axis parallel to the substrate (sample *S1*); (b) intermediate structure (sample *S3*); (c) *c*-axis oblique to the substrate (sample *S4*).

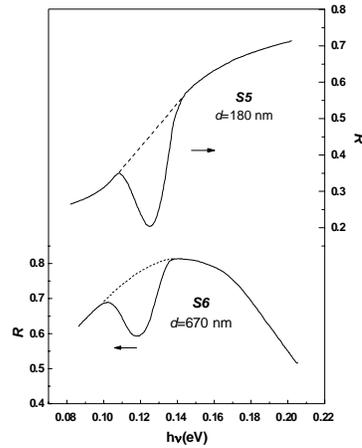


Fig. 4. Spectral dependence of the reflectance from two films with different thickness deposited in the same experimental conditions ($T_s = 293$ K; $r_d = 3$ nm/s).

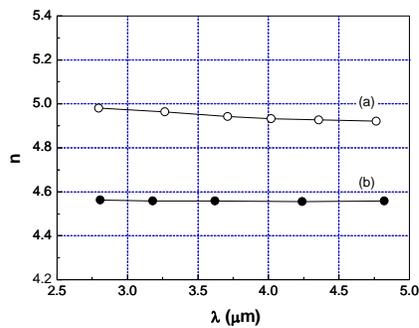


Fig. 5. Spectral dependence of the refractive index of two films with different thickness deposited at the same experimental conditions: ($T_s=293$ K; $r_d=3$ nm/s). (a) sample *S5*; (b) sample *S6*.

4. Conclusions

The Te thin films were deposited onto glass substrates by thermal evaporation in vacuum. The thickness dependence of the absorption coefficient, α , and the refraction index, n , in IR wavelength range and also of the hole concentration, p , in these films have been established. The X-ray diffraction measurements revealed that the studied films have a stratified polycrystalline structure formed by a first layer having a preferred orientation of crystallites with their c -axis parallel to the substrate and a second layer in which the crystallites have the c -axis oblique oriented to the substrate. This modification of the microcrystallite orientation during the film growth influences the values of the above mentioned parameters. In the textured films, the hole concentration, optical absorption and refraction index have greater values in comparison with those of films with preponderantly obliquely oriented crystallites.

It was found that the dichroic behavior of the microcrystallites in Te thin films and the modification of their orientation during film growth plays an important role in determination of the values of the optical parameters.

We concluded that for a correct interpretation of the thickness dependence of physical properties of Te thin films it must be taken into account the modification of the film microstructure during their growth, in addition to other factors.

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