Optical properties of polycrystalline films of lead telluride with distributed stichiometry

T Akhmedov¹, S M Otajonov¹, Ya Usmonov², M M Khalilov¹, N Yunusov¹ and A K Amonov³

¹Fergana State University, 19, Murabbiylar street, Fergana, 150100, Uzbekistan
²Fergana branch of Tashkent University of Information Technologies named after Mukhammad al-Khwarizmi, 185, Mustaqillik street, Fergana, 150118, Uzbekistan
³Samarkand branch of Tashkent University of information technologies named after Mukhammad al-Khwarizmi, 47A, Sh.Mirzo Street, Samarkand, 140100, Uzbekistan

E-mail: adkham1972@gmail.com

Abstract. In this article, the optical properties of polycrystalline thin films based on PbTe with disturbed stoichiometry are considered. It is shown that in PbTe films with a lead excess of 1.2 wt %, the intrinsic absorption edge is shifted to shorter wavelengths of the spectrum, and this is due to the presence of shallow levels in the forbidden band. It was found that in the band of p-type PbTe spectra with an excess of tellurium of 2.8 and 3.8 wt %, there are additional bands with the cutoff energy \( h\omega = 0.132 \text{ eV} \), which are associated with the presence of free tellurium.

1. Introduction

The study of the optical properties of semiconductors is one of the most important methods for studying the band structure, and also provides information on the frequencies of the optical branches of the phonon spectrum and other parameters of semiconductors [1-3]. In inhomogeneous semiconductors, patterns in the absorption and reflection of an electromagnetic wave can provide information about the influence of these inhomogeneities on the phenomena under consideration [4-6]. As well as some information about their composition [7].

As is known, lead telluride crystallizes with a significant deviation from stoichiometry, which leads to the presence of about \( 10^{18}-10^{19} \text{ cm}^{-3} \) of electrically active intrinsic defects [7]. Therefore, the concentration of current carriers in PbTe crystals will primarily be determined by the deviation of the composition from stoichiometry, i.e. from the excess of one or another component in the sample.

To obtain information on the optical properties of semiconductors based on PbTe with disturbed stoichiometry, in this article, we studied the absorption spectra with excess tellurium and lead, and also studied the effect of shallow levels at the intrinsic absorption edge of lead telluride.

2. Experimental technique

We have obtained PbTe film samples of both n- and p-type conductivity \( \sim 3 \text{ micrometers thick at high vacuum (10}^{-5} \text{ millimeter of mercury column) and investigated the absorption and reflection coefficients of these samples in the IR spectral region at room temperature. In this case, the following tasks were posed: first, the study of the dependence of the position of the edge of the main absorption in PbTe films...
depending on the composition of the initial sprayed charge and determination of the band gap; second, obtaining information on the nature of the scattering mechanism in a wide range of film composition.

When measuring the optical constants of thin films on a substrate, a number of difficulties arise associated with various phenomena in the transmission of light in the film-substrate system. Here it is necessary to take into account the interference of light waves in the film, and multiple reflection in the substrate, and absorption both in the film and in the substrate. To determine the optical constants of thin films in the film-substrate system, the simplest method is the method based on measuring the interference pattern from the transmission spectra when a light beam is incident on a sample. The measurements were carried out on an IKS - 14 infrared spectrometer [8].

3. Results and discussion

To determine the optical constants of the substrate \( n_1 \) and the film \( n = n_2 - ik_2 \), it is necessary to measure the spectral dependence of the transmittance \( T_0 \) of the pure substrate and the film-substrate system \( T \). In the case of a thin film on a transparent substrate, we used the formulas obtained in [3], which the transmission of the film-substrate system is related to the thickness of the film and the optical parameters of the film and substrate. The expression for the extreme values of the transmittance \( T_{extr} \) of the film-substrate system has the form

\[
T_{extr} = 16n^2n_3/p,
\]

where

\[
P = (n + 1)^3(n_3^2 + n_2) - (n - 1)(n_3^2 - n_2) + (-1)^m(n_2 - 1)(n_3^2 - n_2^2);
\]

m-order interference; \( \gamma = \left( \frac{4n}{\lambda} \right)K_2d_2 \); \( \lambda \) - light wavelength; absorption rate; \( d \) is the geometric thickness of the film.

Denoting \( T_{extr} \) the value \( T_{extr} \) at \( \gamma_2 = 0 \) (the case of a non-absorbing substrate), we find

\[
T^o_{extr} = T^o = \frac{2n_3}{n_3^2 + 1} \quad (m\text{- even number})
\]

\[
T^o_{extr} = \frac{4n_3^2n_3}{(n_3^2 + 1)(n_3^2 + n_2^2)} \quad (m\text{- odd number})
\]

Expressions (2) and (3) mean that for even \( m \) \( T_{extr} \) is equal to the transmittance of the transparent substrate \( T_0 \) and for odd \( m \) is different from it. Expanding \( e^{+ix^2} \) in a series up to terms of the second order in \( \gamma_2 \), for odd \( m \), (1) can be represented in the form

\[
T_{extr} = T^o_{extr}[1 - A\gamma_2 + (A^2 - B/2)\gamma_2^2]
\]

where \( T^o_{extr} \) is determined by expression (2), and \( A \) and \( B \) have the form

\[
A = \frac{(n_3^2 + n_2)(n_2 + 1)^3 + (n_3^2 - n_2)(n_2 - 1)^3}{4(n_3^2 - 1)(n_3^2 + n_2^2)}
\]

\[
B = \frac{(n_3^2 + n_2)(n_2 + 1)^3 - (n_3^2 - n_2)(n_2 - 1)^3}{4(n_3^2 - 1)(n_3^2 + n_2^2)}
\]

The optical parameters of PbTe films of variable compositions \( x \) and \( e \) at a given wavelength were determined on a computer by the successive approximation method. The described method for determining the optical parameters is very sensitive and makes it possible to detect small changes. \( x \) \( n \) and \( e \) are at least 1%. The \( T_0 \) values corresponding to the position of the extrema \( \lambda_m \) (m-even) on.
interference fringe system substrate-film and from formula (2) calculated the value of \(n_3\). The order of interference \(m\) was calculated from the relation

\[
m = \frac{\lambda_{m+1}}{\lambda_{m} + \lambda_{m+1}}
\]

where \(\lambda_{m+1}\) and \(\lambda_m\) are the wavelengths of two adjacent extremums. If the calculation gave a fractional value, then the nearest integer was taken for \(m\). At the first stage of the calculation, by substituting the transparency values at an odd extremum into formula (3), we found \(n_2\). Substituting the value of \(n_2\) into formula (1), the first approximation \(T\) was determined, the values of \(n_3, n_2\) and \(\gamma_2\) were worn in (4) and found \(T_{\text{extr}}\). The calculated transparency at the odd extremum was again substituted into (1), the value \(\gamma_2\) was found, etc. When \(n_2\) and \(\gamma_2\) were finally found, the absorption index (coefficient) of the film was calculated from the formula.

\[
K_2 = \frac{n_2 \gamma_2}{m \pi}
\]

Any changes in the films during their production can change the shape and position of the absorption band, the dispersion of the refractive index, which in turn will affect the reflection spectrum.

When the film thickness changes, the reflection spectrum is also affected by the interference of light in this layer. Therefore, all the films under study were obtained under strictly identical conditions and all had the same thickness.

In figure 1 shows the absorption spectra at room temperature, obtained on the basis of measuring the transparency of PbTe film samples with an excess of tellurium and lead, respectively. As can be seen from the figures, there are several bands in the absorption spectra of all the studied films.

![Figure 1. Absorption spectra of PbTe films with excess Te wt%: 1-0; 2-0.8; 3-1.8; 4-2.8; 5-3.8.](image-url)
The spectra of the films, although they have a general character, differ in the position of the absorption bands. These bands experience a shift in scale (hw) and small changes in intensity. The observed changes indicate some differences in the structure and composition of the films, which is in agreement with the data of measurements of other properties of such films.

Comparison of the experimental absorption curves of lead telluride films of variable composition and single-crystal PbTe samples shows that the latter have bands that are similar in position on the energy scale to similar film bands. Based on the foregoing, we can say that the existence of bands in the absorption spectra of films of variable composition, which are related to PbTe single crystals, is determined by the presence of PbTe in the composition of the films.

It can be seen from the figures that at the energy hw = E_g, a sharp increase in absorption is observed due to the transition of carriers between bands.

The spectral dependence of the absorption coefficient £(ω) for direct allowed transitions occurring with absorption of a photon is given by the expression:

\[ \alpha \sim (hw = E_g)^{1/2} \]  

In figures 3, 4 shows the dependence \( \alpha^2(w) \propto hw \) for PbTe films of various compositions; it is seen that the experimental points fit well into straight lines.

For PbTe - Te films with an excess of tellurium, the points cut off by the continuation of straight sections \( \alpha^2(w) \) on the abscissa axis are in the range 0.29: 0.33 eV depending on ΔTe. In PbTe - Pb films, 0.2 and 2.2 wt.% \( \alpha^2(w) \) cuts off on the abscissa axis hw≈0.32 eV, which coincides with the optical width of the forbidden zone of lead telluride single crystals [9]. With an excess of lead of 1.2 wt%, the intrinsic absorption edge shifts to shorter wavelengths.
An excess of lead and tellurium atoms leads to the formation of an appropriate (not always coinciding with the concentration of excess atoms) number of donor or acceptor centers. When a large number of impurity atoms are introduced into the condensate, an impurity band is formed, which for shallow levels merges with the edge of the main band. The tail of the density of states function appears in the band gap. Figure 5a shows a possible band diagram for the formation of an impurity band near the edge of the valence band due to doping with excess tellurium. If the energy width of the tellurium impurity band $\Delta E$, then the intrinsic absorption in the films begins at $h\nu > E_g - \Delta E$ and the edge of the intrinsic absorption will shift by $\Delta E$ to the long-wavelength region of the spectrum, since In this case, the generation of carriers into the conduction band will begin not from the edge of the valence band, but from the edge of the impurity band. Therefore, the data in figure 3 most likely indicate the appearance of an impurity band with an excess of Te in the PbTe films, which shifts the intrinsic absorption edge towards lower $h\nu$ than in PbTe single crystals [10].

In the case of PbTe films with a lead excess of 1.2 wt%, as noted above (figure 4), the intrinsic absorption edge is shifted to shorter wavelengths. This can apparently be explained by the fact that when the films are doped with excess lead, the electron gas in the film partially degenerates (according to [12-13], in PbTe with an excess of Pb, the electron concentration can reach $10^{19}$ cm$^{-3}$) and the Fermi level is in the conduction band (figure 5b). Intrinsic absorption begins at the photon energy $h\nu > E_g + E_F - E_c$ ($E_c$ is the bottom of the conduction band, $E_F$ is the Fermi energy). Since the states below the Fermi level are occupied, the transition of carriers is carried out to states with energies higher than the Fermi energy. The same situation was observed in heavily doped n-PbTe samples [14] (the Burstein-Moss effect).

According to [15], the sections on the $\alpha (w)$ curves corresponding to absorption by free carriers can be used to judge the mechanism of carrier scattering and their concentration. It is known [15] that in PbTe upon absorption of light by free carriers, the absorption coefficient obeys the $\alpha \sim w^n$ dependence.

At the same time, if the concentration of carriers in PbTe is $n < 5 \times 10^{18}$ cm$^{-3}$, then the predominant scattering mechanism is scattering by optical vibrations of the lattice and in the dependence $\alpha \sim w^n$ $n \approx 3$. At $n < 5 \times 10^{18}$ cm$^{-3}$, carriers are scattered by acoustic phonons and $n \approx 1.5$. In the absorption spectra of PbTe films with an excess of Te for all samples, $n \approx 3$, which agrees with the data of Hall measurements: the hole concentration in these samples is less than $5 \times 10^{18}$ cm$^{-3}$. 

Figure 3. Dependence $\alpha^2 (h\nu)$ of the same films as in figure 1.
Figure 4. Dependence $\alpha^2(h\nu)$ for the same films as in figure 2.

Figure 5. PbTe band diagram in the case of doping with an excess of Te with the formation of an impurity band of width $\Delta E$ near the valence band (a) and in the case of degeneracy upon doping with excess lead (b). The arrows show the transitions near the absorption edge.

The absorption spectra on free carriers for PbTe films with an excess of Pb are shown in figure 6. It is seen that for samples 1 and 3 $n$ in the dependence $\alpha - w - n$ is close to 3, and for sample 2 - to 1.5. Consequently, according to [16], the concentration of carriers in this sample exceeds $5 \times 10^{18}$ cm$^{-3}$. This is in complete agreement with the data in figure 4, where, as noted above, the main absorption edge of
samples 1, 3 coincides with the main absorption edge of nondegenerate single crystals, and for film 2, the edge is shifted to shorter wavelengths. Consequently, the set of experimental results in figures 4 and 6 for the sample can be explained by the high concentration of electrons (the Burstein-Moss effect).

In the absorption spectra of PbTe films with an excess of tellurium, an absorption band is observed near $\hbar w = 0.1$ eV. For the PbTe - Te samples, which are hole, the long-wavelength band observed in the $\alpha(\hbar w)$ spectra can be explained in terms of optical transitions between nonequivalent valleys of the PbTe valence band, since the energy gap between the heavy and light branches of the PbTe valence band is 0.1 - 0.12 eV ($T = 300 ^\circ K$) [15]. With an increase in the content of Te in the films, the intensity of this band increases, because with an increase in the carrier concentration, the filling of the heavy subband increases.

The origin of the maxima located near $\hbar w = (0.24 \pm 0.02)$ eV in the absorption spectra of PbTe films with both an excess of lead and an excess of tellurium (figures 1, 2) can apparently be explained by the presence of oxygen in the films. In single-crystal PbTe, the maximum at $\hbar w \approx 0.24$ eV [12,14] is explained by the presence of oxygen in it.

4. Conclusion

According to the results of the study, it can be said that bands in the spectra of samples of p-type conductivity with an excess of tellurium of 2.8 and 3.8 wt%, there are additional bands with the boundary energy $\hbar w \approx 0.13$ eV.

The origin of these maxima is apparently due to the presence of free tellurium. As shown in the absorption spectra of tellurium, in the energy region $\hbar w \approx 0.12$ eV, an absorption band is observed due to the complex structure of the valence band.
The appearance of free tellurium is due to the fact that in the films, $\Delta\text{Te} \geq 2.8$ wt.%, Undissolved over stoichiometric Te precipitates as a second phase along the crystallite boundaries. About the fact that free tellurium can be released in PbTe films. As seen from figures 1-6, the bands corresponding to samples of various compositions are different in intensity. The transparency of the samples depends significantly on the concentration of current carriers. Samples of the n-type have a high absorption coefficient, and with an increase in the amount of lead additives, the intensity of absorption bands increases.

References

[1] Ravich Yu I, Efimova B A and Smirnov I A 1968 Research methods of semiconductors in application and lead chalcogenides PbTe PbSe PbS (Moscow: Science)
[2] Umesh Kh, Sulakshana B and Panjabrao P 2012 Optical Properties of Polycrystalline Zinc Selenide Thin films Materials Sciences and Applications 3 36-40
[3] Manifacier Y C, De Murcia M and Fillad J P 1976 J.Phys. 9 1002-4
[4] Heini S, Tapio K, Mikko R and Markku L 1998 J.Thin Solid films 326(1) 78-82
[5] Rogacheva E I, Tavrina T V, Nashchekina O N, Volobuev V V, Fedorov A G, Sipatov A Yu and Dresselhaus M S 2003 J. Thin Solid films 423(2) 257-61
[6] Egerton R F and Juhasz C 1969 J Thin Solid films 4(4) 239-53
[7] Dashevsky Z, Shufer E, Kasiyan V, Flitsiyan E and Chernyak L 2010 J. Physica B: Condensed Matter. 405(10) 2380-4
[8] Otazhonov S M, Onorkulov M K, Botirov K A, Yunusov N, Mamadzhonov K and Kakhkharova B A 2020 International journal "Universum" technical science 2(71) 56-8
[9] Shufer E, Dashevsky Z, Kasiyan V, Flitsiyan E, Chernyak L and Gartsman K 2010 J. Physica B: Condensed Matter. 405(4) 1058-61
[10] Mallory E, DeCoster, Xin Ch et al. 2019 Thermal Conductivity and Phonon Scattering Processes of ALD Grown PbTe-PbSe Thermoelectric Thin films Advanced Functional Materials 11-3 doi: 10.1002/adfm.201904073
[11] Freik D M, Zapukhlyak R I, Lopjanka M A, Mateik G D and Mikhailonka R Ya 1999 J. Semiconductor Physics Quantum Electronics and Optoelectronics 3 62-5
[12] Axmedova G A, Bagiyeva G Z, Agueev A F and Abdinov J Sh 2009 J. Semiconductor physics and technology 43(11) 1456-9
[13] Urinov Kh O, Jumanov Kh A, Amonov A K Makhmudiv F Dj and Urinov J O 2020 IOP Publishing Journal of Physics: Conference Series 1679 022003 doi:10.1088/1742-6596/1679/2/022003
[14] Atakulov Sh B, Zaynopbidineva S M, Otajonov S M and Tukhtamatov O A 2010 J. PSE, 8(4) 365-70
[15] Praveen T, Amrish K P, Sukhvir S and Srivatava A K 2020 J. Thin Solid films 693(1) doi.org/10.1016/j.tsf.2019.137708
[16] Shamshad A Kh, Zishan H Kh, El-Sebaii A A, Al-Marzouki F M and Al-Ghamdi A A 2010 J. Physica B: Condensed Matter. 405(10) 3384-90