

STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF Pb_{1-x}Eu_xTe THIN FILMS

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Thin films of Pb_{1-x}Eu_xTe solid solution was grown on freshly cleaved (111) surface of BaF₂ by the method of condensation of molecular beams in a vacuum of 10⁻⁴ Pa. It was shown that as grown film was (200) oriented single crystal. The type of conductivity depends on the temperature of the additional compensating source Te and at 650 K the type of conductivity changes from n to p. The smoother and uniform surface without any clusters was obtained at the deposition condition $\Phi_c=8\div9$ Å/c, $T_{sub}=543\div623$ K. By optical measurements have been established that the produced films are direct band gap semiconductor with $E_g=0.386$ eV, $\alpha=10^4$ cm⁻¹. The energy gap of Pb_{1-x}Eu_xTe (0.386 eV) is larger than that of PbTe (0.320 eV), suggesting that the energy gap can be adjusted by replacing some Te atoms with Eu.

Keywords: thin films, solid solutions, Semiconductor, Pb_{1-x}Eu_xTe, XRD, optical properties.

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INTRODUCTION

In recent years, semi-magnetic semiconductor materials have been widely used and have been in the focus of researchers' attention. Semiconductor compounds of the type A⁴B⁶ (PbS, PbSe and PbTe) are characterized by a narrow band gap ($E_g\sim 0.1$ eV). With the addition of rare earth elements (Eu, Mn) to these compounds, it is possible to regulate the width of the energy gap of solid solutions, which expands the scope of these materials. These solid solutions are widely used in the creation of various optoelectronic devices the properties of which can be controlled by a magnetic field.

Up to now, HgCdTe has been used as predominant material for IR detection due to its high performance [1]. But production of HgCdTe films requires an expensive technique like molecular beam epitaxy and in addition, its yield is limited by the poor mechanical stability. Because of all these, the search for the cheapest materials and technologies has yet to be carried out.

PbTe is one of the important materials with high refractive index in infrared region due to its superior chemical stability and the ease of film deposition. Band gap can be tuned by alloying it with SnTe, EuTe and i.s.

The impurity concentration dependences of the PbTe-based solid solutions parameters are well known [2-7]. By replacing part of the lead with the rare earth element Eu (creating a Pb_{1-x}Eu_xTe ($0\leq x\leq 1$) solid solution), can be smoothly increased its band gap and reduce the refractive index.

Since the basis of the Pb_{1-x}Eu_xTe ($0\leq x\leq 1$) solid solution is the binary compounds PbTe and EuTe, all its properties are, similar to the properties of these compounds. It is natural to assume, and this is

confirmed experimentally, that solid solutions with Eu content close to zero have more similar properties to PbTe. The PbTe and EuTe compounds have the same NaCl structure type and Oh5 - Fm3m symmetry type. They have a face-centered cubic crystal lattice with very close lattice parameters $a_{PbTe}=0.6462$ nm, $a_{EuTe}=0.6595$ nm [2, 8]. Therefore, under normal conditions and at x close to zero, the Pb_{1-x}Eu_xTe ($0\leq x\leq 1$) solid solution retains the structure of PbTe and its thin films can be produced by the method of producing PbTe thin films. For Producing PbTe films have been used a lot of technics, such as evaporation from boat, flash evaporation, hot wall-technique and so on. In this work we used the heater specially made of carbon for evaporation bulk materials with high vapor pressure.

EXPERIMENTAL PROCEDURE

In our experiments 2-5 μm thick Pb_{1-x}Eu_xTe ($x=0.05$) thin films were grown on freshly cleaved BaF₂ (111) surfaces by the condensation method of molecular beams in a vacuum of 10⁻⁴ Pa. During deposition the source and substrate temperatures were kept at $T_{sour}=1000-1100$ K and $T_{sub}=580$ K respectively. As a source materials were used synthesized at 1100 K solid solutions of Pb_{1-x}Eu_xTe ($x=0.05$). For synthesis was used high purity (99.99%) Pb, Te and Eu. The source materials Pb and Te were etched by CH₃COOH+H₂O₂ (4:1) and in 20% aqueous solution of HCl respectively to remove the oxide layer. Then they were placed in quartz ampoule and evacuated to 10⁻⁴ Pa before sealing.

The ampoule was then placed in a furnace. The furnace temperature was raised to 1230 K and kept at this temperature for 30 h. For mixing of the source materials, the ampoule was slowly vibrated. Then the

melt was rapidly cooled down to room temperature to keep homogeneity of polycrystalline ingot.

The evaporator of the starting materials was a Knudsen cell made of especially pure graphite.

To develop the epitaxial growth technology to obtain high-quality single-crystal layers and characterize them, the following measurements were carried out: The structural property was investigated by X-Ray diffraction (XRD) analyses of the films using Bruker D2 Phaser (Germany) diffractometer in θ - 2θ scan mode with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda=1.54060 \text{ \AA}$) source.

Free charge carriers concentration and mobility in the layers was determined by the Keithley Hall effect system;

Topography analysis of the films was performed in Smart SPM 1000 AIST NT (Tokyo Instruments, Japan). Elemental analyses and stoichiometry of the film were carried out using Scanning Electron

Microscopy SEM S-4800 with EDX system (Hitachi Ltd., Japan). Thickness of the film was measured by ellipsometer. The optical properties of the films were studied by Fourier transform spectrometer (FTIR, Nicolet-NEXUS-870) at normal incidence.

RESULTS AND DISCUSSION

Fig.1 shows X-ray diffraction pattern of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ powder (a) and $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ thin film (b) on BaF_2 . All the diffraction peaks of powdered sample correspond to $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ with lattice constant $a=6.463 \text{ \AA}$. We did not observe any peak corresponding to Pb, Eu or Te which conforms that the proper synthesis had been occurred. As XRD of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ thin film contains only one (200) peak we conclude that the obtained in the given conditions films are single crystal by other word on BaF_2 occurred epitaxial growth of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ thin film.

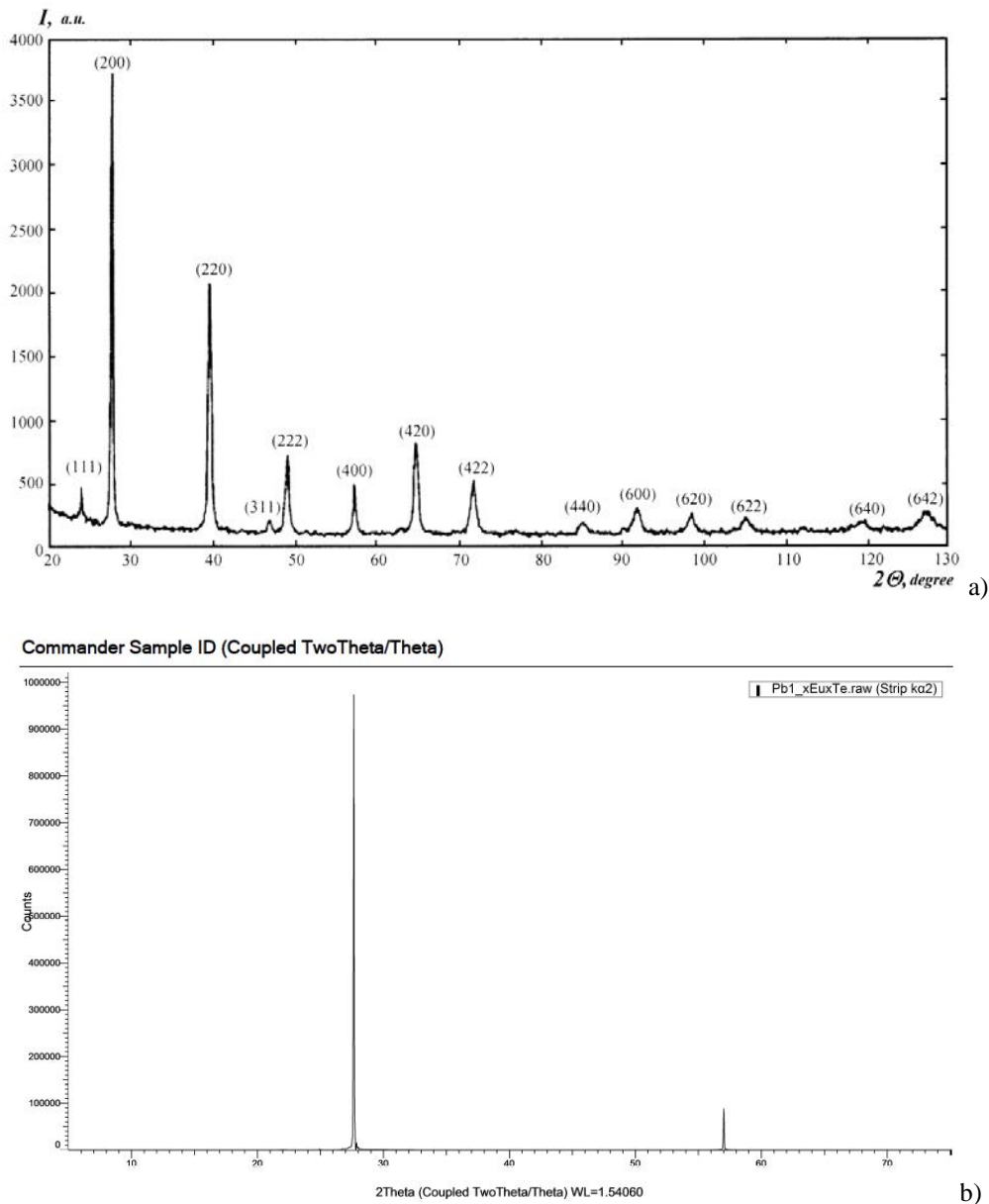


Fig.1. XRD patterns of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ powder (a) and thin film (b).

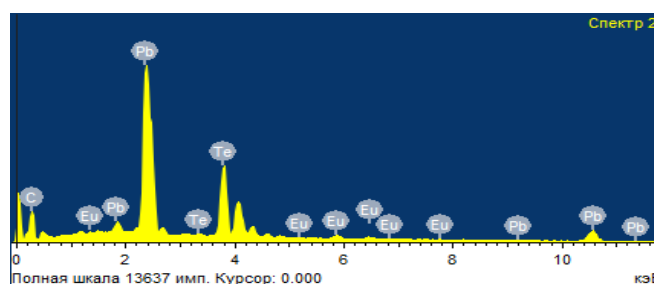
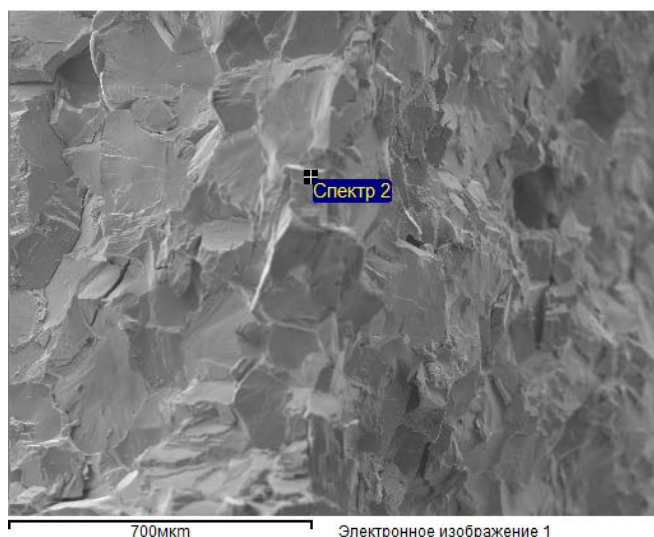


Fig.2. EDS measurement results of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ thin films.

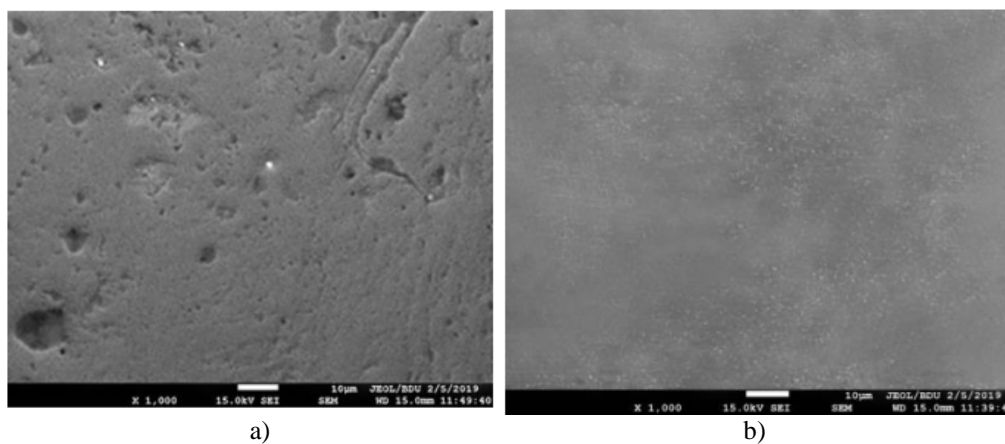


Fig.3. Electron microscopic images of the surface of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ films ($x=0.05$):
a) without, b) with Te compensation.

The elemental composition of the film was determined by EDS spectrum. An illustration of EDS spectrum is given in Fig.2. It shows that only Pb, Eu, and Te are present in the film. The composition is very close to stoichiometry.

The electron microscopic images of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ films without (a) and with Te compensation are shown in Figure 3.

On the electron microscopy images of films without Te compensation, black clusters characteristic for lead chalcogenides [3–5], the number of which increases with a decrease in the condensation rate and an increase in the substrate temperature (Fig.3a). According to the literature, these accumulations are oxides formed due to the capture of

oxygen with excess metal atoms (Pb) during the growth process. Oxygen is captured on the surface of the films by lead atoms. Excess lead atoms are formed as a result of partial decomposition of the starting material during the deposition process. To eliminate the observed accumulations, the films were doped with an additional compensating source of Te vapor during growth. The use of such a source led, along with the disappearance of these clusters, to the production of films with a smoother surface (Fig.3b), a more perfect structure and an increased mobility of charge carriers.

It reveals that by the appearance of the surface, the smoother and uniform surface without any clusters is obtained at the deposition condition $\Theta_k=8\div9 \text{ \AA/c}$,

$T_{\text{sub}}=543\div 623$ K. Here ϑ_k is the rate of thin film deposition.

By adjusting the temperature of the Te compensating source, we succeeded to obtain epitaxial films of n- and p-type conductivity, with low charge carrier concentration ($n, p=2\cdot 10^{18}\text{--}4\cdot 10^{18}\text{ cm}^{-3}$, $T=77$ K) and high mobility ($\mu=2.5\cdot 10^3\text{--}3.0\cdot 10^3\text{ cm}^2/\text{V}\cdot\text{s}$, $T=77$ K). Conductivity inversion occurs at the temperature of the compensating source $T_{\text{cs}}=650$ K.

The optical characterization of a thin film by transmission and reflection measurements is a well-known method. Once the experimental values of R and T are known as a function of wavelength, then it is possible to calculate the absorption coefficient, the

thickness and the value of the band gap width of the film.

In this work, transmission spectra measured at normal incidence were used to calculate the thickness of thin films deposited on transparent substrates. This choice of incidence direction is justified because no polarization effects appear; moreover, most commercial equipment uses this incidence direction.

The beam path in the film is shown in Fig.4. A parallel beam of light is split at both boundaries of the thin film with air and BaF_2 into two beams. This division occurs several times. Then the reflected or transmitted rays, overlapping, give an interference pattern. The optical path difference between the neighboring transmitted beams is $2nd$.

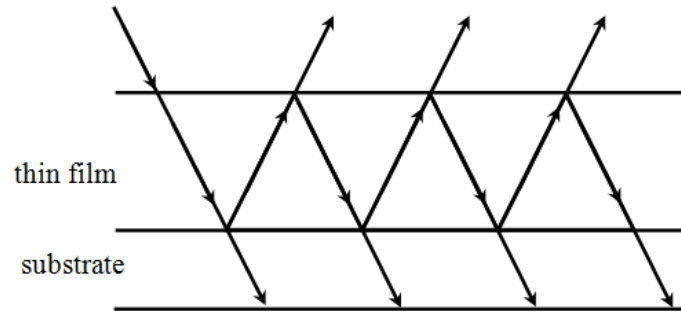


Fig.4. The occurrence of multiple reflections of beam in the film.

For transmitted beams the condition for constructive interference, in the case of normal incidence, is, $2nd=m\lambda_m$, where n is refractive index, $m=1, 2, 3, \dots$, integer numbers is interference fringes order and can be calculated by assuming that the refractive index varies slowly with the wavelength in this region. For two consecutive maximums we can write

$$2nd = m\lambda_m, \quad (1)$$

$$2nd = (m-1)\lambda_{m-1} \quad (2)$$

From these equations we find m as

$$m = \lambda_{m-1} / (\lambda_{m-1} - \lambda_m). \quad (3)$$

Then we calculated d by substituting m in (1) or (2).

In Fig.5 is illustrated the transmittance spectrum of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ thin film in the range of $0\text{--}25\text{ }\mu\text{m}$. From the interference peaks by formula (3) was calculated the thickness of film ($\sim 3\text{ }\mu\text{m}$).

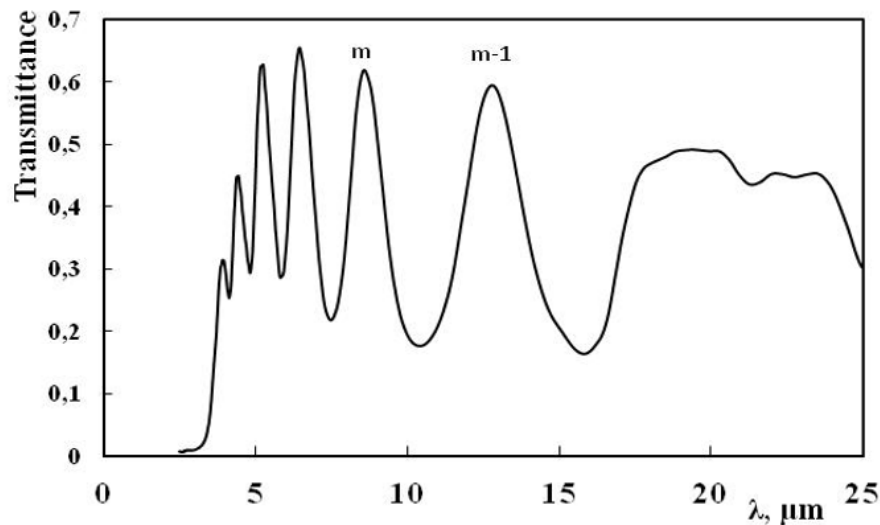


Fig.5. Experimental transmittance spectrum of $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ film with interference fringes.

The absorption coefficients were obtained from the transmission data using the relationship

$$T = T_0 \exp(-\alpha d), \quad (4)$$

where T and T_0 are the intensity of transmitted and incident beam respectively, α the absorption coefficient, and d the sample thickness. From the equation (1) α is calculated as

$$\alpha = \frac{1}{d} \log \frac{T_0}{T} \quad (5)$$

It was observed that the value of absorption coefficient increases rapidly with the increase of photon energy near the fundamental absorption edge.

It is well established that the optical absorption edge in PbTe at 300 K and lower temperatures is connected with direct allowed transition between the nearest band extreme at the point L [9]. It is also known that the electronic transition between valence and conduction bands is given by Tauc's law [10]

$$\alpha h\nu = A(h\nu - E_g)^p \quad (6)$$

Where A is a constant, α the absorption coefficient, E_g the energy gap, ν the frequency of the incident beam and h the Planck's constant. The exponent p is $\frac{1}{2}$ for direct allowed transitions.

We considered that the optical behavior of $Pb_{1-x}Eu_xTe$ must be very similar to that of PbTe and plotted the dependence of $(\alpha h\nu)^2$ on $h\nu$. This plot is shown in Fig.6.

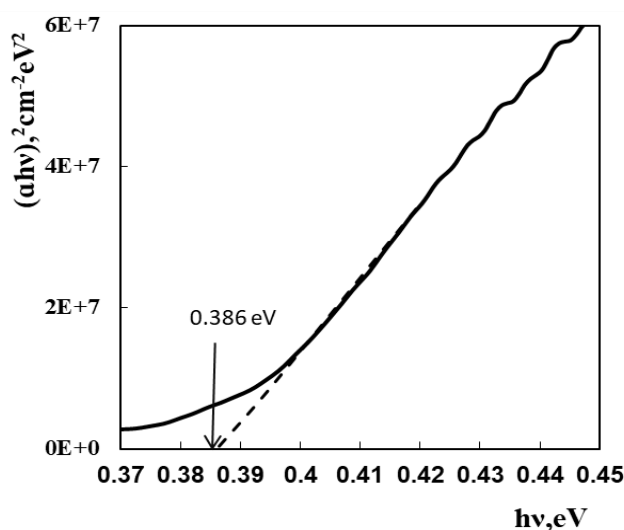


Fig.6. Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for $Pb_{1-x}Eu_xTe$ film.

It is seen that the the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) is linear. By other word in equation (5) the value of $p=1/2$.

The single slope in the curve suggests that the prepared $Pb_{1-x}Eu_xTe$ thin film is single phase in nature and electronic transitions are direct and allowed. That is the obtained film is direct band gap semiconductor with band gap width 0.386 eV and absorption coefficient $\sim 10^4 \text{ cm}^{-1}$.

The found for $Pb_{1-x}Eu_xTe$ band gap (0.386 eV) is larger than that for PbTe (0.320 eV). This result which was expected is probably associated with the presence of Eu.

CONCLUSION

Thus, as a result of the study, the optimal conditions for obtaining $Pb_{1-x}Eu_xTe$ epitaxial films of n- and p-type conductivity with high mobilities were determined. It was found that crystal structure of $Pb_{1-x}Eu_xTe$ is the same cubic as PbTe ($a=6.46 \text{ \AA}$).

It was shown that by replacing some Te atoms with Eu, the energy gap of $Pb_{1-x}Eu_xTe$ can be adjusted. The electronic transitions in $Pb_{1-x}Eu_xTe$ are direct allowed with $E_g=0.386 \text{ eV}$, $\alpha=10^4 \text{ cm}^{-1}$. The energy gap of $Pb_{1-x}Eu_xTe$ (0.386 eV) is larger than that of PbTe (0.320 eV), suggesting that the energy gap can be adjusted by replacing some Te atoms with Eu.

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