ELECTROPHYSICAL PROPERTIES OF PbSe, $Pb_{1-x}Eu_xSe$ THIN FILMS AND HETEROJUNCTIONS ON THEIRS BASE

I.R. NURIYEV[1], A.M. NAZAROV[1], M.S. SADIGOV[1], S.S. FARZALIYEV[1], R.M. SADIGOV[1,2], V.R. ABDULSALAMOVA[1]

[1]Institute of Physics named after G.M. Abdullayev, H.Javid ave., 131, AZ1073 Baku, Azerbaijan

[2]Azerbaijan Technical University, H. Javid ave., 25, AZ1073, Baku, Azerbaijan

afinnazarov@yahoo.com

PbSe, $Pb_{1-x}Eu_xSe$ thin films and PbSe-$Pb_{1-x}Eu_xSe$ heterojunctions were successfully fabricated on ultrasonically cleaned glass substrates using molecular beam deposition technic from a Knudsen cell made of high-purity graphite under a vacuum of 10^{-4} Pa and subsequently investigated.

X-ray diffraction (XRD) patterns revealed that all films exhibited dominant (200) peaks, indicating a highly textured structure. The surface morphology, concentration, and type of charge carriers depended on the substrate temperature, the temperature of the additional compensating selenium source, and the deposition rate. It should be noted that, a transition from *n*-type to *p*-type conductivity occurred at the additional compensating selenium source temperature (T_{Se}) of 450 K. A smooth and uniform surface without clusters was achieved under the following deposition conditions: ϑ_c=8÷9 Å/sec, T_{sub}=620 K.

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INTRODUCTION

A^4B^6 type semiconductors have long attracted scientific interest due to their exceptional properties. These semi-magnetic semiconductor compounds-such as PbS, PbSe, and PbTe-are characterized by a narrow band gap (E_g≈0.1 eV), high carrier mobility, and have been widely used in the fabrication of various infrared (IR) devices. The band gap of these semiconductors can be tuned in several ways: by altering film thickness via the quantum confinement effect, by modifying their chemical composition [1], by adjusting deposition parameters [2,3], and by introducing rare earth elements (e.g., Eu, Mn) to form solid solutions. These modifications expand the application possibilities of the materials. Solid solutions based on A^4 B^6 compounds are widely employed in the development of optoelectronic devices, whose properties can be tuned using external magnetic fields. Among these materials, lead selenide (PbSe) and its solid solution with EuSe have widespread applications in solid-state devices, including mid-infrared (IR) light-emitting and laser diodes, mid-IR sensors, solar cells, optoelectronic devices, and, more recently, as IR emitters and solar control coatings [4]. By adding EuSe (E_g≈3.1 eV) to PbSe (E_g≈0.27 eV), it becomes possible to obtain a $Pb_xEu_{1-x}Se$ solid solution with a tunable band gap ranging from 0.27 to 3.1 eV. This wide tunability significantly expands the range of potential applications for these materials.

So far, a wide range of deposition techniques have been employed to fabricate PbSe films, including chemical bath deposition [5], electrochemical deposition [6], magnetron sputtering, and others. Compared with these methods, molecular beam deposition, which is used in our experiment, is considered one of the most competitive techniques due to its lower cost and ease of handling. This method ensured high quality of the resulting films. In this study, we report on the investigation of the structural and electrophysical properties of PbSe and $Pb_xEu_{1-x}Se$ thin films, as well as PbSe– $Pb_xEu_{1-x}Se$ heterojunctions, deposited by thermal evaporation described above.

EXPERIMENTAL PROCEDURE

High-purity starting materials are essential for obtaining bulk compounds with reproducible properties. Pb, Eu, and Se with a nominal purity of 99.9% were used. To remove surface oxide layers, Pb and Se were etched in CH_3COOH+H_2O_2 (4:1) and in 20% aqueous HCl, respectively. The synthesis crucible, made of clean fused silica with a diameter of approximately 1 cm, was cleaned with nitric and chromic acids, followed by boiling in distilled water. The required amounts of Pb, Eu, and Se were weighed and placed into the crucible, which was then evacuated to 10^{-4} Pa and sealed. The sealed ampoule was placed in a furnace, and the temperature was gradually raised to 1380 K and maintained for 30 h. To ensure uniform mixing of the reactants, the ampoule was slowly vibrated during the synthesis. The melt was then rapidly cooled to room temperature to preserve the homogeneity of the polycrystalline ingot. The resulting materials were used as the source for the deposition of PbSe and $Pb_{1-x}Eu_xSe$ thin films.

Thin films were deposited by thermal evaporation from a Knudsen cell made of high-purity graphite. Regardless of the substrate temperature or deposition rate, the films exhibited n-type conductivity. To achieve conductivity conversion and reduce the electron concentration, the films were co-evaporated with selenium during deposition. Selenium was evaporated from a quartz crucible. During deposition, the temperatures of the Knudsen cell, substrate, and selenium source were maintained at 1230 K, 620 K, and 440-470 K, respectively. Films obtained at selenium source temperatures above 450 K exhibited p-

131, H.Javid ave, AZ-1073, Baku
Institute of Physics
E-mail: jophphysics@gmail.com

type conductivity. After removal from the vacuum chamber, the films were annealed in argon at 420 K for 30 min under 1 atm to improve interfacial quality and reduce point defects. Annealing in argon is known not to change the conductivity type but to increase carrier mobility [7].

The optimized condition for producing n- and p-type PbSe and $Pb_{1-x}Eu_xSe$ films by this method were subsequently used for the fabrication of PbSe - $Pb_{1-x}Eu_xSe$ heterojunctions. PbSe thin films were deposited on ultrasonically cleaned glass substrates using molecular beam deposition technic from a Knudsen cell made of high-purity graphite under a vacuum of 10^{-4} Pa, with the substrate temperature maintained at 620 K. The $Pb_{1-x}Eu_xSe$ film was then deposited on top of the PbSe film under the same vacuum conditions, with selenium co-evaporation applied when p-type $Pb_{1-x}Eu_xSe$ was required. After deposition, the heterostructures were annealed in argon at 420 K for 30 min to improve the interface quality and reduce defect density.

For electrical characterization, circular In contacts (1 mm in diameter) were thermally evaporated onto the top $Pb_{1-x}Eu_xSe$ and PbSe surface through a shadow mask.

To develop the film growth technology, obtain high-quality films, and characterize them, a series of structural and morphological measurements were performed. The structural properties were analyzed by X-ray diffraction (XRD) using a Bruker D2 Phaser (Germany) diffractometer in the θ–2θ scan mode with Ni-filtered CuKα radiation (λ=1.54060 Å). 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, Hitachi S-4800, Japan) equipped with an energy-dispersive X-ray (EDX) analysis system. Film thickness was measured by spectroscopic ellipsometry.

The electrical parameters of the films, including conductivity and Hall voltage, were measured by the potentiometric method in constant electric and magnetic fields. Electrical contacts were formed by vacuum evaporation through a mask of the appropriate configuration, followed by soldering thin copper wires to the ohmic contacts. The carrier concentration and mobility were calculated from the measured conductivity and Hall voltage.

The described synthesis of bulk material, deposition of thin films technik, and characterization procedures provided well-controlled $PbSe-Pb_{1-x}Eu_xSe$ heterostructures suitable for detailed analysis of their structural, morphological, and electrophysical properties, as discussed in the following section.

RESULTS AND DISCUSSION

Fig.1 shows the dependence of the charge carrier concentration on the temperature of the additional selenium vapor source (T_{Se}). Increasing T_{Se} leads to a gradual decrease in electron concentration, which is attributed to the incorporation of excess selenium into the $Pb_{1-x}Eu_xSe$ lattice. This additional selenium compensates for native donor-type defects, such as selenium vacancies, thereby reducing the overall *n*-type carrier density. At T_{Se}=450-460 K, the compensation process becomes sufficient to reverse the dominant carrier type, resulting in *p*-type conductivity.

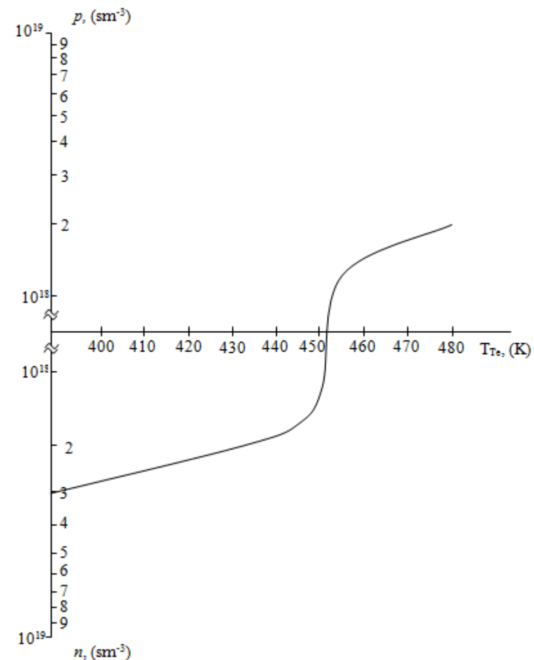

Fig. 1. Dependence of the charge carrier concentration on the temperature of the additional selenium vapor source (T_{Se}).

$PbSe-Pb_{1-x}Eu_xSe$ heterojunctions were fabricated in a single vacuum deposition cycle. First, n-type PbSe was deposited at substrate and selenium source temperatures of 620 K and 400 K, respectively. The selenium source temperature was then increased to 460 K, and p-type $Pb_{1-x}Eu_xSe$ was deposited on top of PbSe film. Indium contacts were thermally evaporated for electrical measurements. The schematic drawing of the $PbSe-Pb_{1-x}Eu_xSe$ heterojunction is presented in Fig.2.

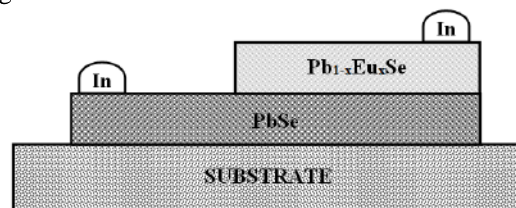

Fig. 2. Schematic diagram of the $PbSe-Pb_{1-x}Eu_xSe$ heterojunction.

The current-voltage (I-V) characteristics of the $PbSe-Pb_{1-x}Eu_xSe$ heterojunction were measured between Ti contacts deposited on the PbSe and $Pb_{1-x}Eu_xSe$ films. It should be noted that the I-V curves for individual n-type PbSe and p-type $Pb_{1-x}Eu_xSe$ films exhibited linear behavior, confirming the ohmic nature of the Ti contacts. Fig.3 presents the room-temperature (T=300 K) I-V characteristic of the $PbSe-Pb_{1-x}Eu_xSe$ *n-p* heterojunction.

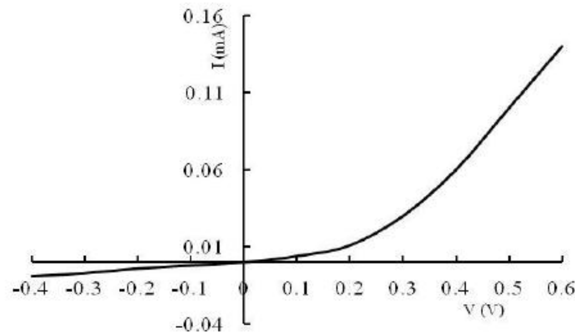

Fig. 3. Current-voltage (I-V) characteristic of the PbSe-$Pb_{1-x}Eu_xSe$ n-p heterojunction at room temperature (300 K).

It is evident from Fig.3 that the heterojunction exhibits pronounced rectifying behavior. The forward current can be described by Shockley's diode equation:

$$J = J_s\left[\exp\left(\frac{eV}{nkT}\right) - 1\right],$$

Where J_s is the saturation current, e is electron charge, n is ideality factor, T is absolute temperature. Analysis of the forward-bias region of the I-V curve yielded an ideality factor of $n \approx 4$, the high value of which is probably associated with a high density of interface states, compositional inhomogeneities, or defect-assisted transport mechanisms at the heterojunction interface.

CONCLUSION

In this work, were synthesized PbSe and $Pb_{1-x}Eu_xSe$ compounds and produced their thin films via thermal evaporation, followed by systematic characterization of their structural and electrophysical properties. XRD analysis revealed that all films exhibited a dominant (200) diffraction peak, indicative of a highly textured crystalline structure. The surface morphology, concentration, and type of charge carriers depended on the substrate temperature, the temperature of the additional compensating selenium source, and the deposition rate. A transition from *n*-type to *p*-type conductivity occurred at the additional compensating selenium source temperature (T_{Se}) of 450 K. The smoothest and most uniform surfaces, free from clusters, were obtained under deposition conditions of ϑ_c=8÷9 Å/sec, T_{sub}=620 K.

PbSe and $Pb_{1-x}Eu_xSe$ thin films, as well as PbSe-$Pb_{1-x}Eu_xSe$ heterojunctions, were successfully fabricated and investigated. The heterojunctions exhibited clear rectifying behavior, and their forward current–voltage characteristics could be described by Shockley's diode equation.

These results demonstrate the potential of PbSe-$Pb_{1-x}Eu_xSe$ heterostructures for applications in mid-infrared optoelectronic devices, where precise control of conductivity type and interface quality is essential.

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