DIELECTRIC FUNCTION SPECTRA AND CRITICAL POINTS OF PbSSe THIN FILMS MEASURED BY SPECTROSCOPIC ELLIPSOMETRY

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Abstract- In order to find the critical energy points of PbSSe thin films, the process of fitting the experimental dates of the real $d^2\varepsilon_1/d(hv)^2$ and imaginary $d^2\varepsilon_2/d(hv)^2$ components of these films to the analytical function were carried out. "Graphical analysis" program was used for this purpose. The value of the critical point equal to the energy position E=1.6 eV in the band structure of PbSSe thin films, completely coincides with the theoretically calculated values for both PbS compounds and PbSe compounds and this value of the critical point in these compounds was characterized as $L_5{\rightarrow}L_7$ transition. Therefore, we can assume that the value of the critical point E=1.6 eV in PbSSe thin films also arises due to the $L_5{\rightarrow}L_7$ transition. The second value of critical point $E = 3.2$ eV, which we obtained as a result of fitting for PbSSe thin film, is between $E = 3.5$ eV and $E = 2.9$ eV, which corresponds to the $\Delta_5{\rightarrow}\Delta_6$ transition for PbS and PbSe, respectively, this value can also be attributed to the transition $\Delta_5{\rightarrow}\Delta_6$.

Keywords: Spectroscopic Ellipsometry, Chemical Bath Deposition (CBD), PbSSe, Complex Dielectric Function (CDF), Second-Order Differentiation, Fitting, Band Gap.

1. INTRODUCTION

Chalcogenides of IV elements Group are traditional materials for thermoelectricity, IR optoelectronics and solar cells [1-4]. At the present stage of the development of physics and technology of semiconductors, special attention is paid to the nanostructuring of polycrystalline structures, as well as methods for obtaining and studying nanoparticles, in which the dependence of properties on sizes, the so-called quantum dots, is appears. By changing the sizes of nanoparticles, one can control the value of the effective energy gap. Materials and devices based on them are in demand in many fields of science and technology, including thermoelectricity, solar energy, sensors, medicine, etc. Solar cells have already been developed not only based on PbS [5], PbSe [6] and PbSSe [7] nanocrystals, but also between PbX [8-10] nanocrystals.

As a rule, solar cells of PbSe nanocrystals generate high short-circuit photocurrents, but solar cells of PbS nanocrystals are characterized by higher open-circuit voltage $V_{o,c}$ [7]. This indicates the need to create a ternary PbS$_x$Se$_{1-x}$ for simultaneous optimization of charge transfer and voltage. Therefore, photovoltaic devices fabricated from ternary PbS$_{1-x}$Se$_x$ can provide high efficiency than pure PbS and pure PbSe alone cannot provide [11]. In this work, we study the dielectric properties of PbSSe (PbS$_{0.5}$Se$_{0.5}$) thin films obtained by CBD method, where glass was used as a substrate. The critical point of a semiconductor is its fundamental quantity. These points are determined from ellipsometry measurements. In the process of determining these points, the main procedure is the fitting of empirical data to analytical functions. To perform this procedure, as a rule, authors have used very difficult algorithms and calculations [12-14].

However, it should be noted that there is such a program as "Graphical analysis", which is a very suitable program, mainly due to the fact that with its help it is possible to carry out the fitting (that is, to determine theoretical dependencies that can coincide with experimental dates) of any region of the curve [15]. As a result of ellipsometry measurements the energy dependence of the real and imaginary parts of the complex dielectric function (CDF) is given in a coordinate form (in our measurements there are more than 700 coordinates). Using the "Graphical Analysis" program you can get the first and second derivatives of these dependencies and fit them to the theoretical functions. As a result of the fitting, 4 constants are determined that are included in the theoretical-analytical expression, one of which is the E-critical point. It is important to note, that since $\varepsilon_1(hv)$ and $\varepsilon_2(hv)$ are the real and imaginary components of the same CDF, the 4 parameters resulting from the fitting must be the same in both cases.

2. EXPERIMENTAL DETAILS

A mixture of the following solutions was used to obtain of PbSSe thin films by chemical bath deposition at room temperature: Pb (CH$_3$COO)$_2$ (lead acetate)-0.07 M; NaOH (sodium hydroxide)-0.3 M; C$_6$H$_{15}$NO$_3$ (triethanolamine)-0.06 M and 1:1 mixture of Na$_2$SSeO$_3$ (sodium selenosulfate)-0.17 M with (NH$_2$)$_2$CS (thiourea)-

0.17 M. Glass substrates were used to obtain PbSSe thin films. The prepared as above mixed solution was continuously stirred by a magnetic stirrer during the deposition process. The temperature of the solution was taken at 50^0C. The process was continued for 20 minutes. Then the glass substrates were removed from the solution, washed with distilled water and dried in air.

As a result, on the glass substrate a well-adherent, homogeneous, dark brown PbSSe (PbS$_{0.5}$Se$_{0.5}$) thin film was obtained. "D-8 ADVANCE" diffractometer was used for X-ray spectra analysis of PbSSe thin films (for CuKα, (λ=1.54 A) radiation). For ellipsometry measurements, "J.A. Woollam Company, M2000 Ellipsometer" device was used.

3. THEORETICAL FORMULAS USED IN THE ANALYSIS OF MEASUREMENTS

The theoretical function used for fitting the energy dependence curves of the real and imaginary components of the CDF obtained as a result of ellipsometry measurements can have two different forms depending on the value of the constant k included in it. For values of $k \neq 0$ the theoretical function is as follows:

$$\varepsilon(hv) = C - Ae^{i\theta}(hv - E + i\Gamma)^k \tag{1}$$

where, A, E, Γ and θ denote amplitude, critical point, broadening parameter and excitonic phase angle, respectively. The parameter of k is given as $k = -1$, $k = -0.5$, $k = 0$ and $k = 0.5$ for excitonic, 1-, 2-, and 3-dimensional line-shapes, respectively [16]. For 2-dimensional (2D) line-shape ($k = 0$) the expression (1) looks different:

$$\varepsilon(hv) = C - Ae^{i\theta}\ln(hv - E + i\Gamma) \tag{2}$$

But to determine the Equations (1) and (2) equations constants (In this case, the parameter C will also be eliminated), it is more appropriate to use the $d^2\varepsilon/d(hv)^2$ function, obtained by the second-energy differentiation of the empirical coordinates of the $\varepsilon(hv)$. Respectively, the second-energy differentiation of Equations (1) and (2) functions will be as follows:

$$\frac{d^2\varepsilon}{d(hv)^2} = -k(k-1)Ae^{i\theta}(hv - E + i\Gamma)^{k-2}, \ k \neq 0 \tag{3}$$

$$\frac{d^2\varepsilon}{d(hv)^2} = Ae^{i\theta}(hv - E + i\Gamma)^2, \ k = 0 \tag{4}$$

If we write these equations in trigonometric form, Equations (3) and (4) will be as follows respectively:

$$\frac{d^2\varepsilon}{d(hv)^2} = A^1(\Omega)^{(k-2)/2}\cos\left[(k-2)\arg\cos\left(\frac{hv-E}{\Omega^{\frac{1}{2}}}\right) + \theta\right] +$$
$$+ A^1(\Omega)^{(k-2)/2} i\sin\left[(k-2)\arg\cos\left(\frac{hv-E}{\Omega^{\frac{1}{2}}}\right) + \theta\right] \tag{5}$$

where, $A^1 = -k(k-1)A$ and $\Omega = (hv-E)^2 + \Gamma^2$, and

$$\frac{d^2\varepsilon}{d(hv)^2} = \frac{A}{\Omega}\cos\left[-2\arg\cos\left(\frac{hv-E}{\Omega^{\frac{1}{2}}}\right) + \theta\right] +$$
$$+ \frac{A}{\Omega} i\sin\left[-2\arg\cos\left(\frac{hv-E}{\Omega^{\frac{1}{2}}}\right) + \theta\right] \tag{6}$$

where, performing the fitting, functions (5) (for $k \neq 0$) or (6) (for $k \neq 0$) are used as basic formulas.

As a result, the curves $d^2\varepsilon_1/d(hv)^2$ and $d^2\varepsilon_2/d(hv)^2$ obtained from functions (5) or (6) participate to fitting with the curves $d^2\varepsilon_1/d(hv)^2$ and $d^2\varepsilon_2/d(hv)^2$ calculated from the empirical dependence of $\varepsilon_1(hv)$ and $\varepsilon_2(hv)$, and for a better fitting condition A, E, Γ and θ parameters are determined. After the fitting is completed, the constants are obtained as results from the "Graphical analysis" program automatically.

4. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the PbS$_{0.5}$Se$_{0.5}$ thin film obtained by CBD at 50 °C.
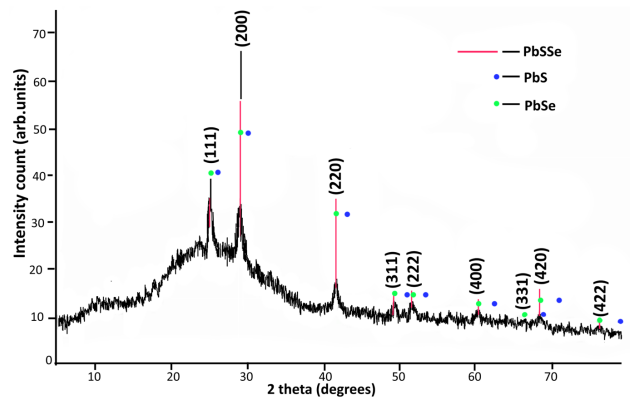

Figure 1. XRD patterns of PbSSe thin film obtained by CBD (green and blue dots are peaks corresponding to PbSe and PbS compounds, respectively)

As can be seen from the figure, a pattern is observed in the spectrum of the PbSSe thin film that corresponds to the peaks belonging to the PbS and PbSe compounds (coincidence of the sequences of peak intensities and similarity of angles), which indicates that the PbSSe thin film crystallizes in the cubic lattice structure. In the figure above each peak, the X-ray reflection planes corresponding to one are shown. The green and blue dots here indicate the position of the peaks belonging to the PbSe and PbS compounds, respectively.

As shown in the figure, the 2θ angles of the X-ray peaks of the PbSSe thin film and the corresponding peaks of the PbSe compound almost completely coincide. And compared to the 2θ angles of the corresponding peaks of the PbS compound, they are shifted towards small angles. For example, if the difference between the angles of the peaks corresponding to the reflection from the (111) planes of the PbSSe thin film and the PbS compound was

2θ=0.9°, this difference gradually increased with increasing angles, and this difference was 2θ=3° for the reflection from the planes (422). Such a shift was found in [17] by comparing PbSSe thin film with PbS and PbSe compounds. Figure 2 shows the experimental curves of the real and imaginary components of the CDF based on more than 700 coordinate points.
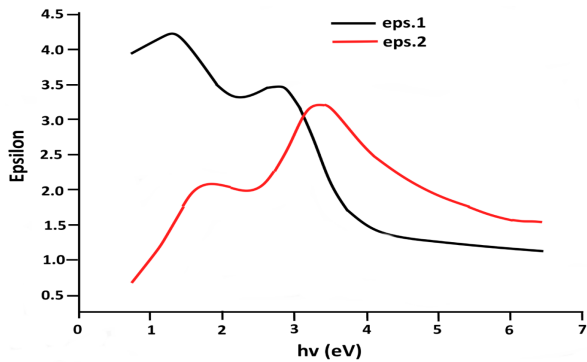

Figure 2. Spectral dependencies of the $\varepsilon_1(hv)$-real and $\varepsilon_2(hv)$, imaginary components of the CDF of PbSSe thin film

In order to fit these dependencies to the theoretical expression $d^2\varepsilon_1/d(hv)^2$ and $d^2\varepsilon_2/d(hv)^2$ obtained by the second-order differentiation of the experimental coordinates of the $\varepsilon_1(hv)$ and $\varepsilon_2(hv)$ dependencies were obtained (Figure 3).
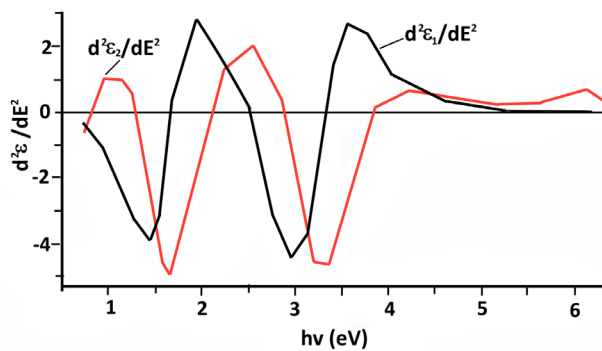

Figure 3. Spectral dependencies of the second-order differentiation of the $\varepsilon_1(hv)$ and $\varepsilon_2(hv)$ components of the CDF of PbSSe thin film

Having carefully considered these dependences, one can see that it is possible to carry out fitting in the ranges E=0.9÷2.4 eV and E=2.5÷3.8 eV.

Since the dependences $d^2\varepsilon_2/d(hv)^2$ and $d^2\varepsilon_1/d(hv)^2$ are the imaginary and real parts of the same complex function, in the laws of their change one should expect sinusoidal and cosine dependences, that is, dependence $d^2\varepsilon_2/d(hv)^2$ must come before in time dependence $d^2\varepsilon_1/d(hv)^2$ by $\pi/2$, and this condition is satisfied in these intervals.

As a result of the fitting performed by "Graphical Analysis" program, the best fit for the region E=0.9÷2.4 eV corresponded to the case of a 2D-shaped critical point ($k=0$) (Figure 4).
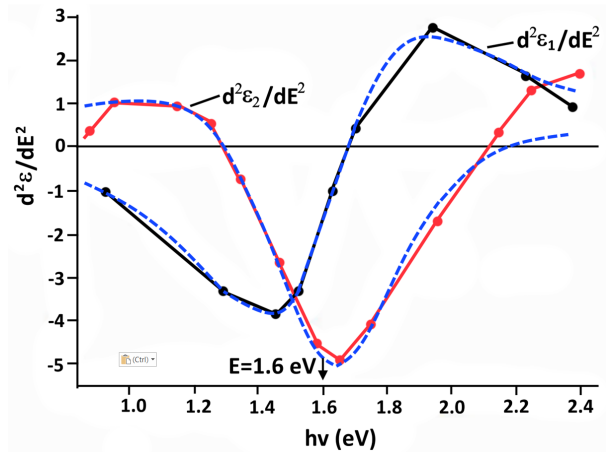

Figure 4. Second-order differentiation (points) of the experimental dependences $\varepsilon_1(hv)$ and $\varepsilon_2(hv)$ (points) and curves of the best fit (dashed lines) for the energy range E=0.9÷2.4 eV of PbSSe thin film using the "Graphical Analysis" program

In this area, the following values of the constants of the analytical function were obtained: A=0.89; E=1.6 eV; Γ=0.42; θ=1.22. The RMSE (Root Mean Square Error) errors were 0.202 for $d^2\varepsilon_1/d(hv)^2$ and 0.846 for $d^2\varepsilon_2/d(hv)^2$. This value of the critical point in the band structure of PbSSe thin films, equal to the energy position E=1.6 eV, completely coincides with the theoretically calculated values for both PbS compounds and PbSe compounds [18] and this value of the critical point in these compounds was characterized as $L_5 \rightarrow L_7$ transition. Therefore, we can assume that the value of the critical point E=1.6 eV in PbSSe thin films also arises due to the $L_5 \rightarrow L_7$ transition.

For the region E=2.5÷3.8 eV, the best fitting was obtained for the 1-dimensional line shape ($k=-0.5$) of the critical point (Figure 5), and the values obtained for the constants of the analytical function in this region were as follows: A=2.5; E=3.2 eV; Γ=0.66; θ=5. The RMSE errors were 0.625 for $d^2\varepsilon_1/d(hv)^2$ and 0.345 for $d^2\varepsilon_2/d(hv)^2$.
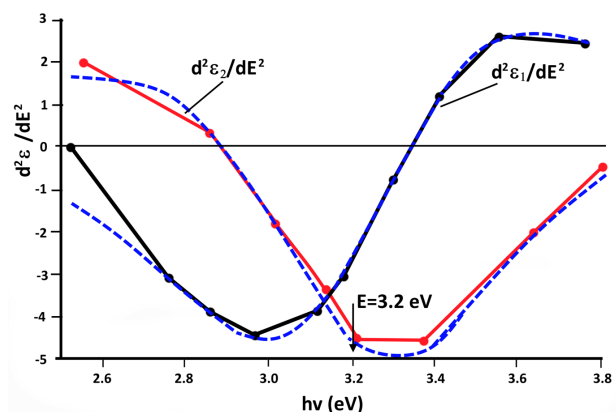

Figure 5. Second-order differentiation (points) of the experimental dependences $\varepsilon_1(hv)$ and $\varepsilon_2(hv)$ and curves of the best fit (dashed lines) for the energy range E=2.5÷3.8 eV of PbSSe thin film using the "Graphical Analysis" program

According to literature data, on the basis of theoretical calculations, the value E=3.5 eV was found for PbS, corresponding to the M2 state, and this value was assigned to the $\Delta_5 \rightarrow \Delta_6$ transition. According to theoretical calculations, was also determined E =2.9 eV, which corresponds to the M2 state and the $\Delta_5 \rightarrow \Delta_6$ transition for PbSe [18].

Since the value of E = 3.2 eV, which we obtained as a result of fitting for PbSSe thin film, is between E = 3.5 eV and E = 2.9 eV, which corresponds to the $\Delta_5 \rightarrow \Delta_6$ transition for PbS and PbSe, respectively, this value can also be attributed to the transition $\Delta_5 \rightarrow \Delta_6$.

5. CONCLUSIONS

$\varepsilon_1(hv)$ and $\varepsilon_2(hv)$ dependencies obtained from spectroscopic ellipsometry measurements were used to determine critical points of PbSSe thin films obtained by chemical bath deposition (CBD). Obtaining the second order derivatives $d^2\varepsilon / d(hv)^2$ of these dependencies and fitting, i.e., the process of determining the theoretical dependences that can overlap with the experimental curve as much as possible, was performed using the "Graphical Analysis" program. Two critical points corresponding to the values of E_1=1.6 eV and E_2=3.2 eV is determined. For the first energy area the best fitting corresponded to the 2D critical point shape case (k=0), and for the second energy area the best fitting corresponded to the 1D ($k = -0.5$) critical point shape case, which can be attributed to the transitions $L_5 \rightarrow L_7$ and $\Delta_5 \rightarrow \Delta_6$ respectively.

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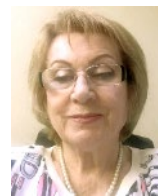
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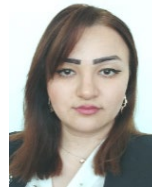
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