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SPECTROSCOPIC ELLIPSOMETRY STUDY OF NANOSTRUCTURED PbSe THIN FILMS

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Abstract- Spectroscopic ellipsometry (SE) method has been used to investigate the optical properties of nanostructured PbSe thin films obtained by chemical bath deposition (CBD) method. For a better resolution of the structure of interband transitions and for determination of critical points, the function obtained by numerical differentiation of the experimental data of the dielectric function is used. The theoretical fitting was carried out using the "Graphical Analysis" program. The best fit is obtained with a 2D-critical point line shape (m = 0) for E=2÷3 eV energy region. One critical point corresponding to E_g = 2.5 eV have been determined. This value is attributed to the $L_4 \rightarrow L_6$ transition of the Brillouin zone.

Keywords: Spectroscopic Ellipsometry, Brillouin Zone, Chemical Bath Deposition, Lead Selenide, Dielectric Function, Fitting, Second Derivative.

1. INTRODUCTION

Narrow band gap leads chalcogenides (PbX, X = S, Se, Te), (0.2-0.41 eV), are among the most studied compounds in recent decades, both for their wide technological application and for their interesting and unusual physical properties. The thin films of these compounds are of great interest for their applications in the production of photodiodes [1], solar elements [2], lasers [3], thermoelectric converters [4], and so on. Together with the CdX chalcogenide family (CdS, CdSe, CdTe), the PbX systems are used to obtain heterogeneous nanocrystals with new physical properties [5-7].

One of the reasons for such an extensive study of PbX compounds is that, in contrast to all other semiconductors, the temperature coefficient of their band gap is positive (for example, for PbSe β=5.1×10^{-4} eV/K) [8]. Lead selenide compounds have a direct narrow energy gap (0.28 eV) at the L-point of the Brullion zone, characterized by a high dielectric constant and a high Boron-exciton radius.

Since the band gaps of these semiconductors depend to a large extent on the crystallite sizes, they are considered suitable materials as absorbers in solar cells.

There are reports on the manufacture of solar cells based on PbS [9], PbSe [10] and PbS_xSe_{1-x} [11] nanocrystals and between PbX nanocrystals [12-14].

This work is devoted to the study of the results of the ellipsometric measurements of nanostructured PbSe thin films obtained by chemical bath deposition method on glass substrates.

The determination of the critical points of a semiconductor is the main task in the physics of semiconductors. Spectroscopic ellipsometry is one of the research methods to find these points. One of the key issues in the analysis of the results of these measurements is the fitting of the experimental curves to theoretical functions. To perform the fitting process, many researchers use complex calculations [15], Savitsky-Golay algorithms, SA algorithms [16, 17], etc. Though the "Graphical analysis" program is a very useful program for this purpose, since it is possible to build an experimental curve previously given by the coordinates using this program. The first and second derivatives of this dependence can be very easily obtained, and finally, it is possible to perform the fitting process (in other words, to determine the theoretical dependencies that may coincide with this curve) whole curve or part of its region [18].

As is known, the experimental dates of the energy dependence of the complex dielectric function, obtained as a result of ellipometric measurements are presented in the form of coordinates of the energy dependence of its real and imaginary parts. Using the "Graphical Analysis" program on the basis of these coordinates, it is possible to construct the energy dependence of the real and imaginary parts of a complex dielectric function.

To perform the fitting process of these dependencies or their definite part, their second derivatives are used. All this is carried out by the "Graphic Analysis" program. As a result, the four constants included in these functions are determined. One of these constants is a critical point E, which is a very important quantity for the theory of semiconductors.

Of course, fitting of second derivatives of the real and imaginary parts does not simply mean fitting over two separate additions and finding four separate constants for each. Since these two functions are the real and imaginary parts of the same complex quantity, the four constants that are sought for in the fittings process must be the same.

2. EXPERIMENTAL METHODS

The solution used for the deposition of the of PbSe thin films by CBD method is prepared by mixing of equal (13 ml) volumetric amounts of each of the following solutions: 0,07 M lead acetate ($Pb(CH_3COO)_2$), 0.3 M sodium hydroxide (NaOH), 0.06 M triethanolamine ($C_6H_{15}NO_3$) and 0.17 M sodium selenosulphate (Na_2SSeO_3). Sodium selenosulphate was prepared by refluxing 0.425 gm of selenium powder with 1.245 gm of anhydrous sodium sulphite (Na_2SO_3) in a three round bottom flask containing 100 ml of distilled water for 7 hours at 90°C. Undissolved selenium particles were filtered out after the solution was cooled to room temperature. The resultant product yielded clear sodium selenosulphate solution [19].

The PbSe thin films obtained in a 60 ml beaker on the cleaned in acidic media microscope glass substrate. Glass substrate was dipped into beaker vertically. The mixed solutions were stirred well magnetically. The bath temperature was kept at 40°C. After a deposition period of 20 min. substrates were removed from the beaker, washed with distilled water and dried.

After these processes a deep brown, homogeneous, with good adhesion PbSe thin film was obtained on the glass substrate.

X-ray diffractometric analyzes of PbSe thin films were investigated by "D-8 Advance" diffractometer for values of 2θ ranging from 20° to 70° for CuKα (λ=1.54 A) radiation.

The morphological and microstructural properties of PbSe thin film obtained on glass substrates were investigated using a "TM-3000" Hitachi scanning electron microscope. Optical measurements were carried out by "J.A. Woollam Company - M 2000 Ellipsometer".

The measurements were performed at angles from 60 to 75° with a step of 5° in the spectral range of 0.74-6.45 eV. The angle of 60° was used for modeling; the thin film – semi-infinite substrate system was chosen as the model.

3. ANALYSIS METHODOLOGY AND MAIN EXPRESSIONS

The method consists of fitting the second derivative of the complex dielectric function to standard analytic functions. The analytic expression for the complex dielectric function for $m \neq 0$ is given by

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

where, A is the amplitude, E is it is the critical point, Γ is the broadening and θ is the excitonic phase angle. According to the type of the critical point, the value m in the expression, can get four different prices: $m = \frac{1}{2}$ refers to the type of three-dimensional (3D) critical point; $m = 0$ refers to the type of two-dimensional (2D) critical point; $m = -\frac{1}{2}$ refers to the type of one-dimensional (1D) critical point and $m = -1$ refers to the exciton type critical point [20].

For the case of $m = 0$ the expression (1) is as follows:

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

However, to determine the parameters included in functions (1) and (2) (as well as to remove parameter C), it is necessary to use the function $\frac{d^2\varepsilon}{d\omega^2}$, obtained by numerical differentiation of the experimental data of the dielectric function $\varepsilon(\omega)$.

The corresponding second derivatives of functions (1) and (2) for the case of $m \neq 0$ will be

$$\frac{d^2\varepsilon}{d\omega^2} = -m(m-1)Ae^{i\theta}(\omega - E + i\Gamma)^{m-2} \tag{3}$$

or if we write in trigonometric form

$$\frac{d^2\varepsilon}{d\omega^2} = A^1(\Omega)^{m-2/2}\left\{\cos\left[(m-2)\arg\cos\left(\frac{\omega - E}{\Omega^{\frac{1}{2}}}\right) + \theta\right] + i\sin\left[(m-2)\arg\sin\left(\frac{\omega - E}{\Omega^{\frac{1}{2}}}\right) + \theta\right]\right\} \tag{4}$$

where $A^1 = -m(m-1)A$ and $\Omega = (\omega - E)^2 + \Gamma^2$, and for the case of $m = 0$

$$\frac{d^2\varepsilon}{d\omega^2} = Ae^{i\theta}(\omega - E + i\Gamma)^{-2} \tag{5}$$

or if we write in trigonometric form

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

To perform the fitting process, the real $d^2\varepsilon_1(\omega)/d\omega^2$ and imaginary $d^2\varepsilon_2(\omega)/d\omega^2$ components of the function (4) (for $m \neq 0$) or (6) (for $m = 0$) written in trigonometric form are used.

In other words, the curves $d^2\varepsilon_1(\omega)/d\omega^2$ and $d^2\varepsilon_2(\omega)/d\omega^2$ calculated from the experimental dependence of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ participate to fitting with the curves $d^2\varepsilon_1(\omega)/d\omega^2$ and $d^2\varepsilon_2(\omega)/d\omega^2$ obtained from functions (4) or (6) and A, E, Γ and θ- parameters are determined for a better fitting condition. It should be noted that the "Graphical analysis" program gives these constants as a result.

4. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction spectrum of the thin PbSe layer obtained by chemical bath deposition.

As can be seen from the spectrum, the locations and intensities of all peaks of the PbSe thin film coincide with PbSe standards. Figure 2 presents SEM image of the nanostructured PbSe thin film.

As shown in Figure 2, the PbSe thin film consists of nanorods with a length of 5-6 µm and a width of 150 nm.

Figure 3 shows the principal angles of ellipsometry Ψ and Δ. The experimental data are shown in circles, and the solid line shows the calculated data obtained from the model. As can be seen from the figure, there is good agreement between the experiment and the calculated data, the mean square error MSE = 9.8, when MSE < 20 is considered acceptable in ellipsometry.

From the constructed model, it was found that the thickness of the thin film is 239.36 nm, and the surface roughness is 27.59 nm.

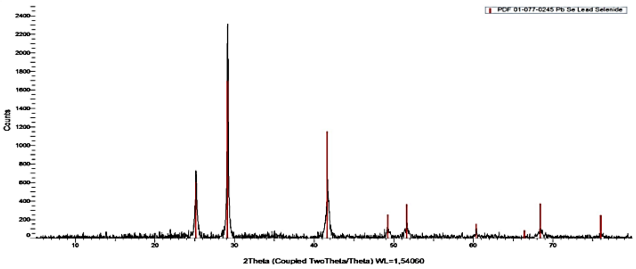

Figure 1. X-ray diffraction spectrum of PbSe thin film

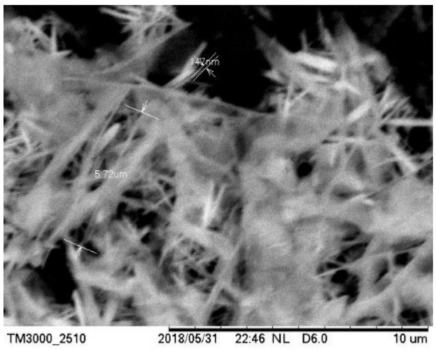

Figure 2. The nanorods observed in the PbSe thin film

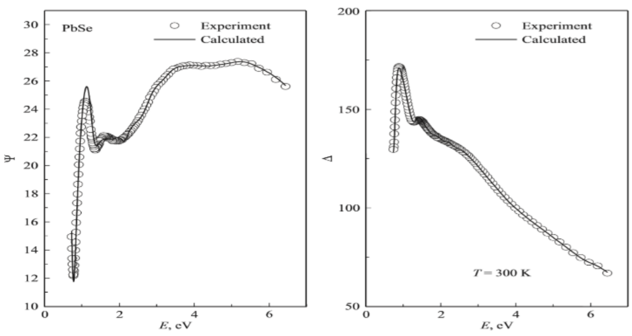

Figure 3. The main angles of ellipsometry Ψ and Δ of the PbSe thin film

Figure 4 shows the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ dependencies constructed by the "Graphical analysis" program in accordance with the experimental data of more than 700 coordinate points obtained as a result of ellipsometric measurements.

To perform the fitting to the theoretical expression the second derivatives of $d^2\varepsilon_1(\omega)/d\omega^2$ and $d^2\varepsilon_2(\omega)/d\omega^2$ of the experimental $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ dependencies were obtained by the "Graphical analysis" program (Figure 5).

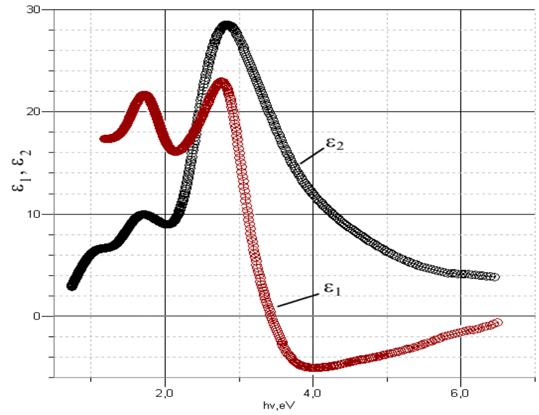

Figure 4. Spectral dependencies of the $\varepsilon_1(\omega)$ is real and $\varepsilon_2(\omega)$ is imaginary parts of the complex dielectric function of the nanostructured PbSe thin film

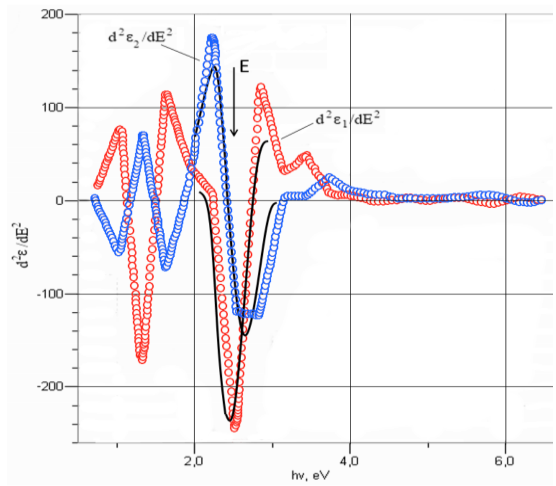

Figure 5. Spectral dependencies of the second derivatives of the $\varepsilon_1(\omega)$ is real and $\varepsilon_2(\omega)$ is imaginary parts of the complex dielectric function (respectively shown in red and blue circles) and the best fittings curves constructed by "Graphical analysis" program for 2÷3 eV energy region (solid lines) of the nanostructured PbSe thin film

If you carefully analyze these curves, then you can easily establish that only in the range 2÷3 eV it is possible to perform a fitting, so it is known that the real and imaginary parts of the dielectric function are related by the Krammers-Croning relation and this condition is satisfied in this area. The best fitting for this region was obtained for the 2D form of the critical point ($m = 0$).

The best fittings were obtained for the values of constants A = 25, E = 2.5, Γ = 0.33, and θ = 0.5 included in theoretical expression.

The value of E = 2.5 eV, found as a critical point for the PbSe thin film as a result of fittings, is very close to the theoretically calculated E = 2.3 eV and corresponds to the two-dimensional (2D) state of the critical point and the $L_4 \rightarrow L_6$ transition of the Brillouin zone [21].

5. CONCLUSIONS

Spectroscopic ellipsometry (SE) method has been used to investigate the optical properties of nanostructured PbSe thin films obtained by chemıcal bath depositıon (CBD) method.

The theoretical fitting was carried out using the "Graphical Analysis" program. The best fit ıs obtained with a 2D-critical point line shape (m = 0) for E=2÷3 eV energy region. One critical point corresponding to E_g = 2.5 eV has been determined. This value is attributed to the $L_4 \rightarrow L_6$ transition of the Brillouin zone.

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