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PbS films doped with Er^{3+} obtained by the Chemical Bath technique

Películas de PbS dopadas con Er^{3+} obtenido por técnica de Baño Químico

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Abstract

PbS films doped with Er^{3+} are grown by chemical bath technique of Er^{3+}: 3, 5 and 7mLs, deposited on cubic phase, the film doped with 7mLs reflects 45%-70% in 900-1110nm. The reflectivity visible spectra: 1.34eV, 1.62eV, 1.7eV, 1.94eV, 2.02eV, 2.27eV, 2.63eV. The dark conductivity increased by ~4 orders of magnitude, and the concentration of carrier charge increases 3.64×10^{16} cm^{-3}-3.85×10^{17} cm^{-3}. The different changes of Gibbs free energy were calculated to obtain information from the spontaneity of reactions.

Keywords: dopant, Erbium, thin solid films, interplanar distance, dark conductivity.

Resumen

Películas de PbS dopado con Er^{3+} crecidas mediante la técnica Depósito por Baño Químico dopadas con 3, 5, 7mLs de Er^{3+}, depositan en fase cúbica la película dopada con 7mls, refleja 45%-70% en 900-1110nm Los espectros de Reflectividad muestran transiciones: 1.34eV, 1.62eV, 1.7eV, 1.94eV, 2.02eV, 2.27eV, 2.63eV. La conductividad en lo oscuro se incrementa ~4 ordenes de magnitud, comparada con la no dopada, la concentración de portadores de carga se incrementa 3.64×10^{16}cm^{-3} - 3.85×10^{17} cm^{-3}.

Palabras clave: Dopante, Erbio, películas delgadas, distancia interplanar.

1. Introduction

Lead sulphide (PbS) is a direct band semiconductor, this is obtained by combining the elements of the groups IIB and VIA of the periodic table, introduced covalent bond and crystallize in NaCl type cubic phase with the lattice parameter a = 5.936Å determined at T = 300° K [1]. The ionic radii are: Pb^{+2} = 1.21Å, S^{-2} = 1.84Å and Er^{3+} = 0.88Å. It has been reported for PbS deviation from stoichiometry by introduction of donor and acceptor impurities, the doping with excess metals may produce donor levels; however the introduction of acceptor levels caused nonmetals [2]. Some electrical properties such as mobility and Hall effect are reported from the past like monocrystals [3]. Kitaev reported the use of PbS, obtained by the chemical bath technique (CB), as base material in the construction of sensing devices in the region of infrared (IR) [4]. This material absorbs in the far infrared region of the electromagnetic spectrum. There are studies reported on the PbS that present results of research interest in this semiconductor for introducing quantum confinement effects [5, 6, 7]. Doping of optical materials by using rare earth elements has been subject of interest for many years in order to modify their physical properties of important applications. But there are no reports of PbS doped with Er^{3+} obtained by the CB technique. At present, most works in rare earth doped semiconductor direction are mainly focused to Si and III-IV compound semiconductors, but in the past, the research on rare earth doped II-IV compounds was abundant because of the purpose of production of multicolour both cathode-ray tubes and electroluminescent display [8, 9]. In this work the objectives is focused on production of PbS systematically doped with Er^{3+} with three different levels of dopant using the CB technique and also observe the structural changes reflected in morphological, optical and electrical properties. The PbS is interesting because of its high absorption coefficient useful for application in devices for IR detectors and also due to its reflectivity, valuable property applied as a reflective surface in the visible region [6] the purpose of this work is change the optical and electrics properties of PbS for possible applications in the nanotechnology. Doping was carried out chemically during the growth process, and an efficient introduction of Er atoms into semiconductor, without sensitive damage of the lattice, was produced.

2. Experimental details

PbS films are obtained using the chemical bath deposition technique (CBD), the value of pH was 11.0 and the constant temperature is 23 ± 2 °C. The doping parameters reported for this technique are: proportion of volumes of solutions of the dopant, concentrations of reagents, substrate, pH and mechanical agitation of the mixture [10]. The glass substrates were previously immersed in $K_2Cr_2O_7/HCl/H_2O$, 3g of $K_2Cr_2O_7$ in a 0.5 L 100mls, HCl ; after they were rinsed in distilled water and dried in clean hot-air flow. The undoped PbS is deposited in aqueous solution, the solutions are prepared with 18.2 MΩ deionized water with the following concentrations: KOH 0.5M, $Pb(CH_3COO)_2•3H_2O$ 0.01M, NH_4NO_3 1.5M and $SC(NH_2)_2$ 0.2M, these are mixed at normal temperature and pressure. The optimal concentration of the doping solution $Er(NO_3)_3•3H_2O$ was determined after several trial, the concentration appropriate was 0.03M. Structural characterization was performed using a SIEMENS D500 diffractometer using copper K_α line. The UV-VIS spectra, using a UNICAM 8700 spectrometer. The Dark conductivity (CD) is measured in the range 100-500 K, using conventional equipment GMW model 3472-50. An atomic force microscopy (AFM) unit (digital unit) was used to study the surface morphology and surface roughness of the films.

2.1. Analysis of chemical equilibrium thermodynamics

The reactions for the deposition of PbS films doped with Er^{3+} are investigated by changing Gibbs free energy in basic media reported in the used the numerical value of cell potential literature [12]. The Gibbs free energy are related by the Nernst equation: $\Delta G^o = n\tau\varepsilon^0$, here τ is the Faraday constant (96500V/equiv.), n represents the number of equivalent and ε^0 the cell potential. We emphasize the importance of coordination complex $[Pb(NH_3)_4]^{2+}$ formation, which is determinant for the release the Pb^{2+} ions, and their slow recombination with S^{2-} ions. In these conditions the spontaneous formation of the PbS precipitate is a controlled process, in this conditions are obtained films of reflectivity like a mirror , adherent, stoichiometric and crystalline quality. The solutions used to prepare the PbS undoping (A-g) and doped with Er^{3+} are mixed at room temperature. The solution containing the ion Er^{3+} is added routinely to the mix of growth during deposition, for three different levels of Er^{3+} these are labelled: PbSEr03, PbSEr05, PbSEr07, where 03, 05, 07 is the volume of doped solution containing the Er^{3+} ion, the film without doped is labelled as PbSA-g. All films are deposited at pH 11.0; this does not change significantly by adding the respective volume of Er^{3+} . The growing-time was two hours. In our working conditions the coordination complex $[Pb(NH_3)_4]^{2+}$ is formed indirectly by mixing solutions: $Pb(CH_3COO)_2$, NH_4NO_3, KOH and finally thiourea is added and the mixture was kept at constant temperature: T = 23 ± 2°C during the deposit. The stages in obtaining these indirect training films with ion coordination complex $[Pb(NH_3)_4]^{2+}$and the respective free energy changes Gibbs (ΔG^0) are:

Lead acetate is mixed, Potassium hydroxide ion generating $HPbO_2^-$, it´s a white suspension

$HPbO_2^- + H_2O + 2e^- \Leftrightarrow Pb + 3OH^-$ $\Delta G^0 = +104.2$ KJ (1)

The HS^- ion is obtained indirectly, and this is generated by decomposition of thiourea in alkaline medium [13]

$SC(NH_2)_2 + 3H_2O + OH^- \Leftrightarrow CH_2N_2 + CO_3^{2-} + HS^- + 3H^+ + H_2\uparrow$ (2)

The half cell reaction of PbS in which it generates the S^{2-} ion and elemental Pb is

$PbS + 2e \Leftrightarrow Pb + S^{2-}$ $\Delta G^0 = +179.4$ KJ (3)

Reversing the direction of the reaction (3), ΔG^0 changes its sign.

$Pb + S^{2-} \Leftrightarrow PbS + 2e$ $\Delta G^0 = -179.4$ KJ (4)

For the sulphide ion

$S^{2-} \Leftrightarrow S + 2e$ $\Delta G^0 = +86.272$ KJ (5)

$S + 2e + H^+ \Leftrightarrow H_2S$ $\Delta G^0 = -27.40$ KJ (6)

adding (4), (5) and (6), we have the formation of PbS

$Pb + 2S^{2-} + H^+ \Leftrightarrow PbS + HS^-$ $\Delta G^0 = -120.50$ KJ (7)

the reduction of lead is

$Pb^{2+} + 2e \Leftrightarrow Pb \qquad \Delta G^0 = + 24.31\ KJ$ (8) On the other hand

$PbS + 2e + 2H^+ \Leftrightarrow Pb + H_2S \qquad \Delta G^0 = + 177.66\ KJ$ (9)

Reversing the direction of the reaction (9), the sign of ΔG^0 also changes

$Pb + H_2S \Leftrightarrow PbS + 2H^+ + 2e \qquad \Delta G^0 = - 177.66\ KJ$ (10)

The half cell potential for Er^{3+}

$Er + 3OH^- \Leftrightarrow Er(OH)_3 + 3e \qquad \Delta G^0 = - 133.9\ KJ$ (11)

$Er^{3+} + 3e^- \Leftrightarrow Er \qquad \Delta G^0 = + 664.69\ KJ$ (12)

adding (11) y (12), and reversing the direction of the resulting reaction, we have

$Er(OH)_3 \Leftrightarrow Er^{3+} + 3OH^- \qquad \Delta G^0 = - 535.79\ KJ$ (13)

adding (10) y (13)

$PbS + H_2S + Er(OH)_3 \Leftrightarrow PbS + Er^{3+} + 3OH^- + 2H^+ + 2e \qquad \Delta G^0 = - 441.87\ KJ$ (14)

adding (8) y (14)

$Pb^{2+} + H_2S + Er(OH)_3 \Leftrightarrow PbS + Er^{3+} + 3OH^- + 2H^+ \qquad \Delta G^0 = -519.48\ KJ$ (15)

adding (1) y (8).

$HPbO_2^- + H_2O \Leftrightarrow Pb^{2+} + 3OH^- \qquad \Delta G^0 = + 79.84\ KJ$ (16)

Adding (15) y (16).

$HPbO_2^- + H_2S + Er(OH)_3 + H_2O \Leftrightarrow PbS + Er^{3+} + 6OH^- + 2H^+$

$\Delta G^0 = - 439.64\ KJ$ (17)

in the left side of this equation, $Er(OH)_3$ is decoupled and thermodynamic calculations favour the formation of PbS and the Er^{3+} ion is incorporated in the form with ΔG0 < 0, thus the reaction is spontaneous. The compact form of expressing (17) considering the species that give rise to $PbSEr^{3+}$ is

$HPbO_2^{2-} + S^{2-} + Er(OH)_3 \Leftrightarrow PbS + Er^{3+} \qquad \Delta G^0 = - 439.64\ KJ$ (18)

From Equation (18) the free energy change is negative Gibbs ($\Delta G^0 = - 439.64$ KJ), so this reaction is spontaneous and enhances the incorporation of Er in ionic form and not as Erbium hydroxide.

3. Results .

Figure 1 shows the XRD patterns of PbS films undoped and doped with Er. These diffractograms show the peaks corresponding to crystal planes [111], [200], [220], [311], [222], [004]; located in the angular positions: 2θ = [26.00, 30.07, 43.10, 51.00, 53.48, 62.58], these belong to the cubic phase under the standard JCPDS 05-0592 [14]. The film undoped (PbSA-g) shows the plane preferential orientation [200] and doped films PbSEr05, PbSEr03 shows preferential orientation in the plane [111] [200] [311] [222] [004], remain without significant change. The effect of preferential orientation has been observed by other authors in the synthesis of ZnO by the effect of microwave treatment time by hydrothermal technique [15].

In Figure 1, there are no peaks associated with the existence of some other material different from PbS, eg. $Er(OH)_3$ or other complex Er as has been reported to incorporate Er^{3+} in matrix of ZnO, in the reaction (17) shows the dissociation of Nitrato de Erbio in Er^{3+} and OH^-, in our working conditions according to changes in the Gibbs free energy in the reaction steps is probable that this ion could be incorporated in the crystal lattice during a controlled process. This reduces the likelihood of incorporation of $Er(OH)_3$ in PbS or other complex oxides such as (Er_2O_3). In our working conditions according to the XRD spectra is not observed another compound.

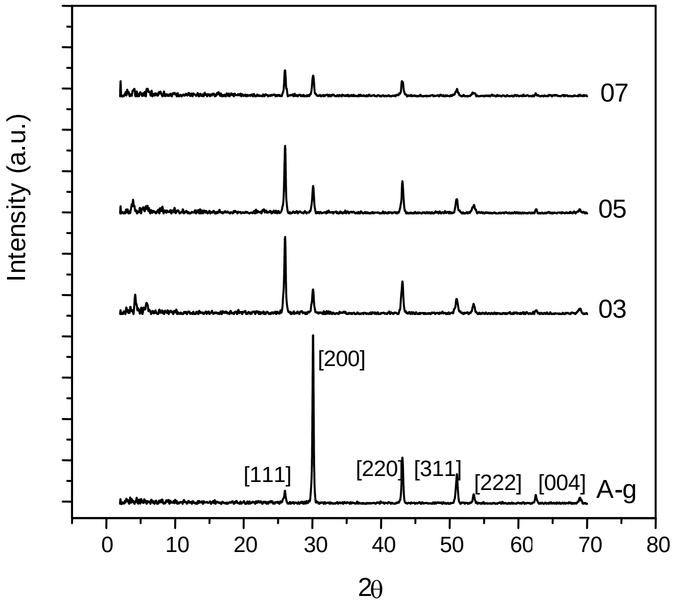

Figure 1. X-ray diffraction for the films doped and non doped (PbSA-g).

Figures 2-5 show the reflectivity spectra of the film undoped and doped in the visible region, the reflected intensities are compared with a pattern that reflects the 100% (silver mirror). This analysis is performed in the visible region, because there is great interest in reflective surfaces in this region of the spectrum.

The graphs show the behaviour of the reflectivity at different angles of the incident beam 10, 20, 30,..., 70º. In these spectra there are differences in both the doped films and the non-doped. The film PbSA-g shows a maximum signal located at 800 nm in wavelength with an angle of 20 degrees. PbSEr03 and PbSEr05 have a maximum reflectivity at around 700-750 nm and the film has higher reflectivity is the film doped PbSEr07 with 70% at 20° incidence, the wavelength of 900nm-1100nm, the reflectivity is increased compared with that of the PbSA-g.

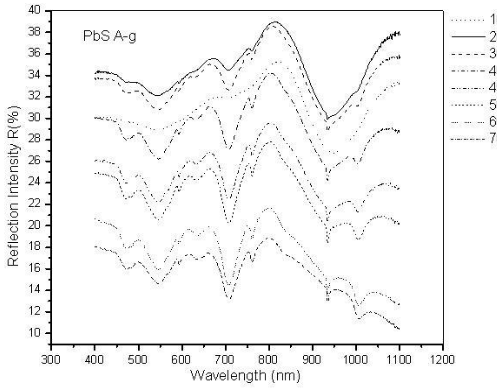

Figure 2. Reflectivity of the sample undoped PbSA-g

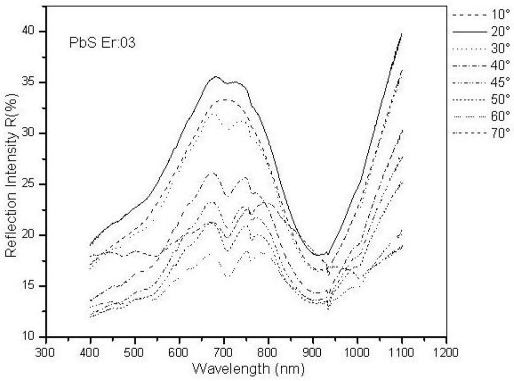

Figure 3. Reflectivity of the sample PbSEr03.

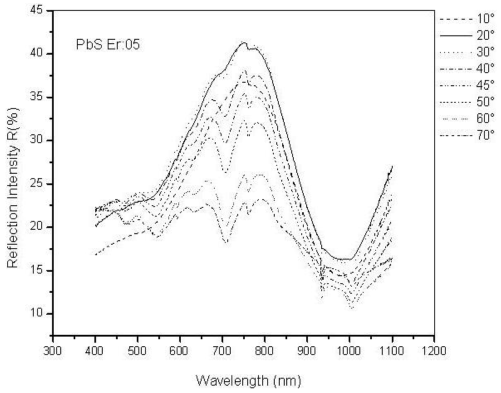

Figure 4. Reflectivity of the sample PbSEr05.

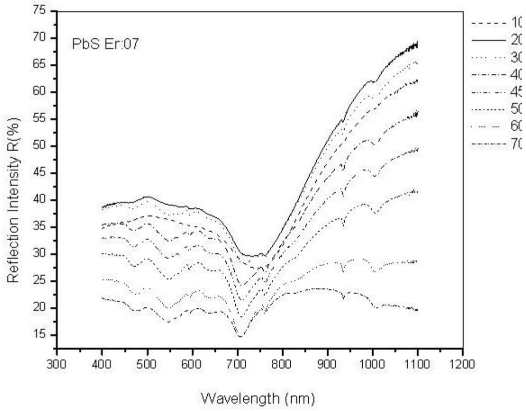

Figure 5. Reflectivity of the sample PbSEr07.

The effect of increasing the reflectivity the film doped, this reflectivity is about 40% for 900nm wavelength.

The optical absorption spectra obtained for doped films and PbSA-g are shown in Figures 6-9. The data were obtained and plotted with the team of optical reflectivity using the expression T(%)= (1-R)d, here α is the absorbance coefficient defined by the expression [17]

$$\alpha = \frac{1}{d} ln\left(\frac{1-R}{R-100}\right)$$

Where d is the thickness of the sample, T is the percent transmittance and the reflection coefficient R, against units of energy α absorbance units squared (From these spectra is located directly relevant electronic transitions to the range of energies in the respective angles of incidence).

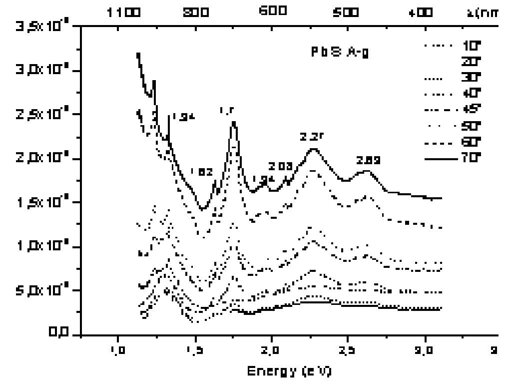

Figure 6. O.A. of the sample PbSA-g

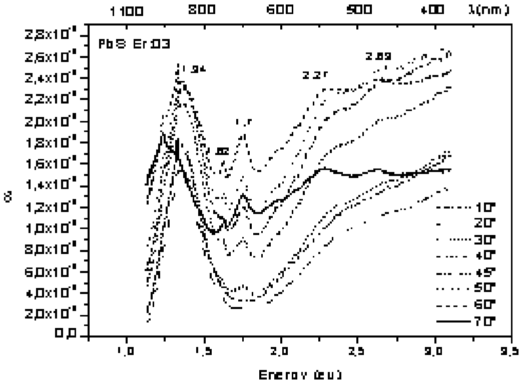

Figure 7. O. A. of the sample PbSEr03

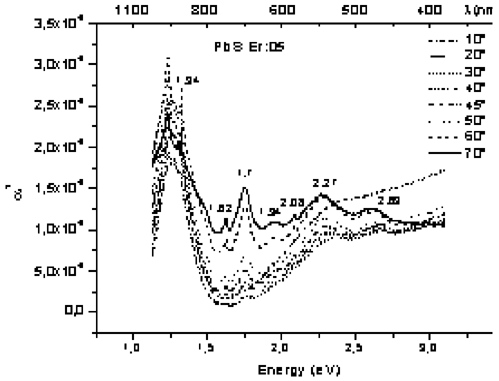

Figure 8. O.A. of the sample PbSEr05.

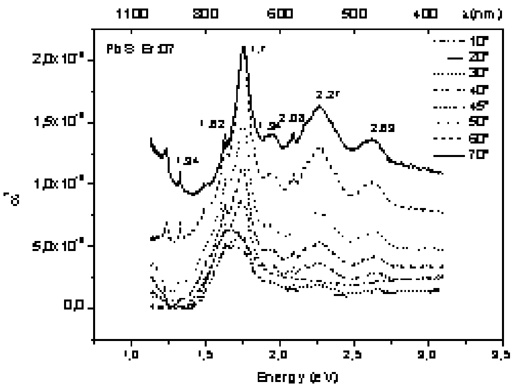

Figure 9. O.A. of the sample PbSEr07.

The peaks in the figures are associated with electronic transitions. It is observed that the intensities of peaks decreased with the decrease of the angle of incidence. The film PbSEr07 has the higher maximum intensity. The critical point energies are related to transitions e. g. Σ (4→7), wich means transition occurring along Σ –symmetry line between in 4th and 7th band. The bands are counted in such a away that the uppermost valence band has number 5 and the lowest conduction band number 6. The transitions for all films are located at 1.34eV, 1.62eV, 1.7eV, 2.08eV, 2.27eV. A. Popa *et. al.* and observed transitions in 1.4 eV, 2.0eV and these researchers were attributed this effect of exciton radii PbS in nanocrystals [18] the electronic transition ($\sum$ 4→7) have been reported and associated with band-band transitions [19].

E_1 = 1.85 eV, T = 300K E_1 = 2.0 eV, T = 5 °K

The electronic transition: Σ (5→6) have been reported [18]

E_1 = 2.1eV, T = 5 K, E_1 = 2.3eV, T = 5 K, E_1 = 2.5eV, T = 5 °K

These transitions are very similar to those observed by us, 2.08eV, 2.27eV, 2.63eV, but the temperature used in this work is T = 300 K, these transitions correspond to the interband type. The samples doped with absorption coefficient less than the sample PbSA-g this is attributed to the optical response of the ions in Er^{3+} for all films is observed, however decrease in the intensities of the transitions with the addition of ion Er^{3+}. Atomic force microscopy shows the texture and surface topology of the thin films. Figure 10 shows a micrograph of the film PbSA-g, this surface can be seen fairly regularly. All films presented similar morphology, which was not significantly modified by the effect of dopant and therefore only shows a single image, however J. Puiξo, *et. al. Seen a* significant change using different precursor solutions of Pb^{2+} deposited on Si substrates [19].

The Figure 11 shows the spectra of the dark conductivity measured (DC) in the temperature range 100-500 K in these are plotted against the log σ, shows for PbSA-g, is lower than those obtained in log σ that the values of doped samples. Doped films increase in 4 orders of magnitude conductivity however, it can be not establish an order between conductivity and relative concentration of dopant, the sample more conductive due to the incorporation of the cation Er^{3+} in the crystalline structure of PbS more efficiently as an impurity and not as a contaminant in the form of $Er(OH)_3$. This effect of increased conductivity has been reported for CdS doped with: Cu^{2+}, In^{3+} and Er^{3+} and displays a certain similarity in the concentration dependence of dopant and conductivity effects [11, 22, 23].

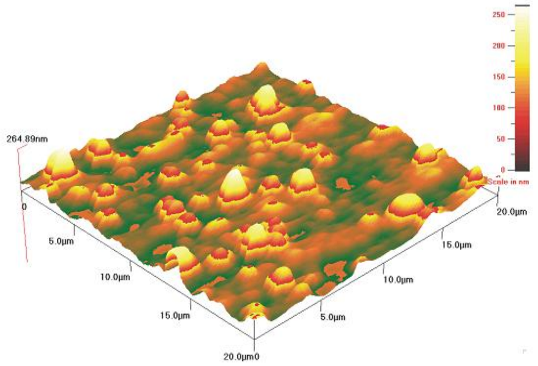

Figure 10. Atomic force micrograph of the sample PbSEr0_3

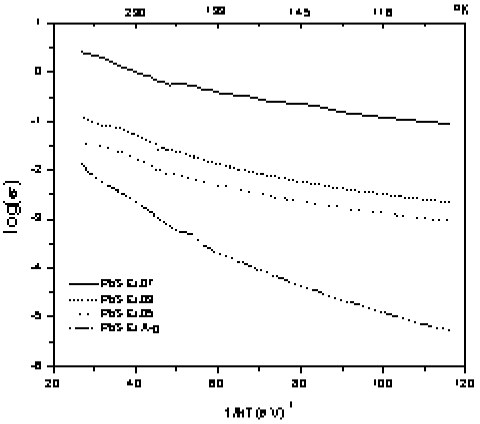

Figure 11. Dark conductivity for the film without doping and doped

Figure 12 shows a graph of conductivity taken at 290 K in terms of volume dopant, this is observed for the sample PbSEr07 has the highest conductivity compared to all the films. This behaviour in DC observed in PbS films by thermally stimulated current experiments was associated with the existence of regions with polycrystalline disorder [24].

The thermoelectric power measurements are performed at 23° C and the sign *observed* in these measurements indicates that the samples are n-type obtained the value of T for α each sample, applies a theoretical model, this is to locate the graphic Fermi functions the value of the carrier density. Figure 13 shows the spectrum of α T against the concentration of carrier charge.

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Figure 14 shows a graph of the concentration of carrier charge (n) against the volume of doped, this is appreciated carrier density is maximum for the film PbSEr07.

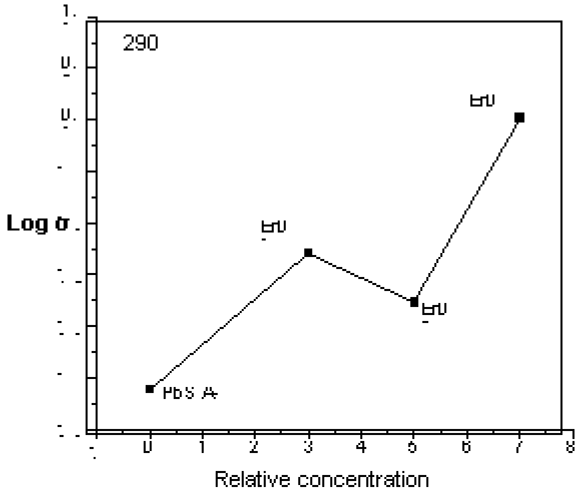

Figure.12. Conductivity against volume of doped taken at room temperature.

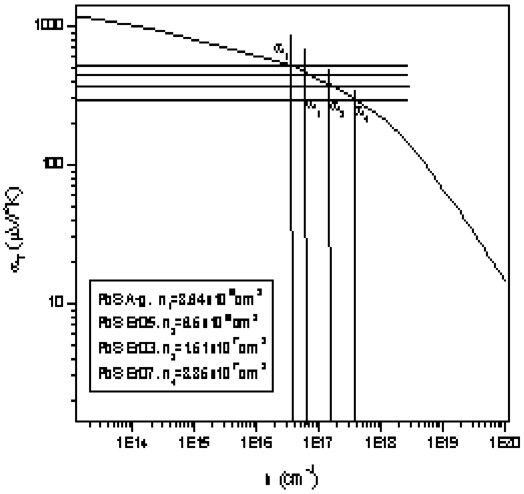

Figure.13. Fermi functions for the PbS doped films and without doping

The carrier concentration is $3.85x10^{17}cm^{-3}$ for the film PbSEr07, a value very close to that reported in monocristal PbS, $2x10^{17}cm^{-3}$ [3], however, the results of the D C and the carrier concentration load, no simple relationship is established, this behaviour our results are close to linearly with the relative volume of dopant and density of carriers, there is increased density of carrier charge compared with non contaminate the sample.

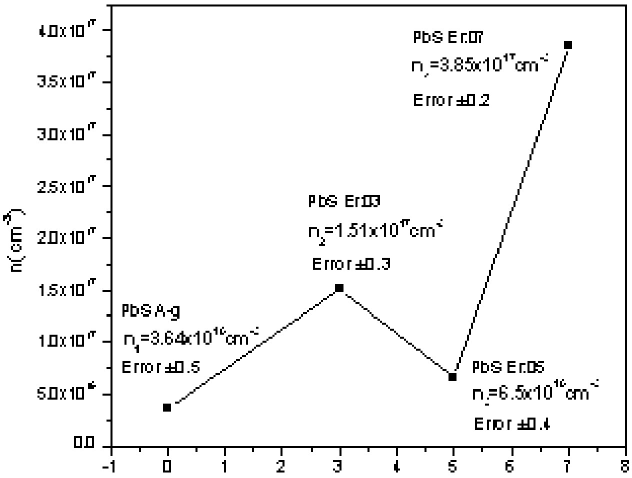

Figure 14. Graphic doped volume against number of charge Carriers

In a previous study using the technique CB the CdS doped with Er^{3+} is observed similar behaviour and this is associated with the annihilation of vacancies and interstices when Cd^{2+} ions back to their original position in the stage of deposition [22].

4. Conclusions

The CBD technique is used to obtain films doped with Er^{3+}. They grow in cubic phase with preferred orientation to the plane [111] by the incorporation of Er^{3+} ion. The reflectivity is increased by approximately 70% in the visible region and band-band transitions are observed close to those reported in other papers. Conductivity and carrier charge concentration increase by the addition of dopant. Furthermore, the high atomic weight of Er may be important for the elimination of doping-material diffusion toward the interface region of the heterostructured solar cell. Briefly, Er doped level is better for electrical properties of PbS films.

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References

[1] Harman, T. C. Melngailis, I: Appl. Solid. State Sci. 4 (1974) 1

[2] Nimtz, G., Schlicht, B: Springer Tracts in Modern Phisics, Vol. 98, Berlin Heidelberg, New York, Tokyo: Springer Verlang 1983.

[3] G. A. Kitaev, A. A. Uritskaya, and S.G. Mokrushin, Russ. J. Phys. Chem. 39 1101 (1965).

[4] G. B. Reedy, V. Dutta, D. K. Pandya, K. L. Chopra. Solar Energy Mater. 15 (1987) 153.

[5] A. Martucci, J. Fick, J Shell, G. Battaglin, M. Guglieelmi, J. Appl. Phys. Vol. 86, 1, (1999).

[6] L. Pintilie, E. Pentia, I. Pintilie, J. Appl. Phys. 91, 9, 5782-5786 (2002)

[7] P. H. Roussingnol, D. Richard, C. H. R. Flytzanis, Appl. Phys. B 51, 437 (1990)

[8] R. K. Watts and W.C. Holton, Phys. Rev. 173, 417 (1968).

[9] R. Boyn, Phys. Status, Solidi B 148, 11 (1988).

[10] P. K. Nair, M.T. S. Nair, J. Phys. D : Appl. Phys. 23 (1990) 150-155

[11] O. Portillo Moreno, H. Lima Lima, V. Ramírez Falcón, J. Martinez Juárez, G. Juárez Diaz, R. Lozada Morales, B. Rebollo Plata, R. Palomino Merino, A. B. Soto Guzmán, and O. Zelaya Ángel. J. of Electrochem. Soc. 153 (2006) 926.

[12]. A. J. Bethune and N. A. S. Loud, in Standard Aqueous potential Coefficients at 25ºC, C. C. C. Hampel, Stokie. 1 c (1969).

[13] O. Portillo Moreno, H. Lima Lima, R. Lozada Morales, R, Palomino Merino, O. Zelaya Ángel, J. Mater. Sci. 40 4489 (2005)

[14] International Center for Diffraction Data, JCPD 05- 0592.

[15] Dehidre Ledwit, C. Pillalli, Graeme W. W. Kelly, Chem Comm, www rsc.org/chemcomm. (2004).

[16] Yajuan Sun, Yue Chen Tian, Yi Yu, Xianggui Kong, Quinghui Zeng, Yaolin Zhang Hong Zhang, Journal of Luminescence, 128 (2008) 15- 21.

[17] Sharma, T. P., Sharma, S. D. and Singh, V., C.S.I.O Communication, 1992 19 (3-4), 63-66.

[18] A. Popa, M. Lisca, V. Stancu, M. Buda, E. Pentia, T. Botila, J. of Optoelectronics and Advanced Materials, 8 (2006) 43-45.

[19] Cardona, M. Greenway, D. L.: Phys. Rev. A 133 (1964) 1685.

[20] Mitchel, D. L. Palik, E. D. Zemel, J. N. Proc. 7th Int. Conf. Phys. Semicond. 1964, 325.

[21] J. Puiξo, S. Lindroos, S. Tamulecius, Leskela and V. Snitka Thin Solid Films, 428 (2003) 233-226.

[22] J. A. Dávila Pintle, R. Lozada Morales, M. R. Palomino Merino, B. Rebollo Plata, C. Martínez Hipatl, O. Portillo Moreno, S. Jiménez Sandoval, and O. Zelaya Ángel, Mat., Adv. In Tech. of Mat. Proc. J. 8 1- 4 (2005).

[23] J. A. Dávila Pintle, R. Lozada Morales, M. R. Palomino Merino, J. A. Rivera Márquez, O. Portillo Moreno, O. Zelaya Ángel, J. Appl. Phys. 101, 013712 (2007).

[24] E. Pintia, L. Pintile, I. Matei, T. Botila, E. Osbay, J. Optoelectronics and Advanced Materials, 3 (2001) 525-530.