Optical properties of $Pb_{1-x}Sn_xSe$ epitaxial layers on (100)KCl, NaCl and (111)CaF_2 substrates.

Mohammad M. Ali and Seif M. Meshari
Department of Physics, Cellege of Science, University of Basrah,Iraq
ISSN –1817 –2695
(Received 19 December 2010; Accepted 27 February 2011)

Abstract

Epitaxial $Pb_{1-x}Sn_xSe$ layers were grown onto cleaved and polished (100) KCl,(100) NaCl and (111)CaF_2 substrates in a high vacuum system by means of the hot-wall-epitaxy (HWE) method. The source temperature of $Pb_{1-x}Sn_xSe$ ~ 570 ^oC and substrates temperature are ranging from 200 to 275 ^oC by increasing step 25 ^oC, growth rate (1.51-2.4 μm/h). The optical absorption constant is determined using FTIR in the (0.496-0.062) eV photon-energy range at room temperature. The data have been analyzed to estimate the forbidden bandwidth.

Key words: $Pb_{1-x}Sn_xSe$ optical properties, HWE, varies substrates of epitaxial growth.

1. Introduction

$Pb_{1-x}Sn_xSe$ belongs to the family of Pb-Sn chalcogenide alloy semiconductors [1-2] whose energy gaps follow the band inversion model. As the Sn content is increased, the energy gap first decreases, goes to zero at a band inversion composition which depends on the type of alloy and its temperature, then increases. The band inversion in $Pb_{1-x}Sn_xSe$ was first observed by optical absorption measurements on thin films, and later confirmed by photovoltaic studies [3], laser emission studies [3-5] and electrical studies[6].

It has been observed that PbSe occurs in rock salt structure, whereas SnSe in orthorhombic structure, which transforms into a rock salt structure under various temperature and pressure conditions. For the mixed crystal $Pb_{1-x}Sn_xSe$, the rock salt structure occurs for various values of x ranging from 0 to 0.43[7].

$Pb_{1-x}Sn_xSe$ has a smaller band gap and larger refractive index than PbSe, so it can be used as the active layer in heterostructure lasers [8]. These semiconductors are characterized by a narrow band gap, a low effective mass of electrons and light holes and a high effective mass of heavy holes. For effective use of these materials in instrumentation, it is essential to obtain as much information as possible about the energy-band separation between the light-and heavy-hole valence bands and their effective mass as a function of dopant concentration[9].

$Pb_{1-x}Sn_xSe$ bulk crystals have been grown by both the closed tube vapor growth and Bridgeman methods [2]. $Pb_{1-x}Sn_xSe$ thin films oriented in the (100) direction have been deposited on cleaved (100) KCl and NaCl substrates by an evaporation method similar to the one-boat method developed for Pb chalcogenide compounds[10,11]. This communication reports briefly the growth of $Pb_{1-x}Sn_xSe$ films deposited on cleaved (111) CaF_2 and BaF_2 substrates by flash evaporation and one-boat evaporation methods. We found that both (100) and (111) films can be obtained depending on the evaporation method and deposition condition. The lattice mismatch of, e.g.,$Pb_{1-x}Sn_xSe$ (x=0.082) with respect to KCl, NaCl and CaF_2 are about 2.6%, 7.8% and 10.8% respectively, while the thermal expansion coefficient mismatches are about 0.022%, 1.2% and ~0.005% respectively.

The HWE which is the same as vapor phase epitaxy (VPE) technique yield inter diffusion between the substrate and the film due to the relatively high growth temperature. Some renewed interest resulted when it was shown that IV-VI layers can be grown by HWE on KCl (100), NaCl (100) and CaF_2 (111) substrates,

and that epitaxy is quite easy due to the ability nature of these materials.

We work on HWE method to epitaxial growth of $Pb_{1-x}Sn_xSe$ on three substrates ($CaF_{2(111)}$, $KCl_{(100)}$ and $NaCl_{(100)}$), and study the effect of different lattice parameters between them and the growth condition to obtain good features the same as optical, electrical and structural for the films or layers which is useful in different applications.

2. Experimental Procedure

2.1. Crystal Growth

For the growth of single crystal of $Pb_{1-x}Sn_xSe$, a quartz ampoule of length 25cm with inner and outer diameter of 20 and 22mm respectively was thoroughly cleaned. A highly pure powder (99.99%) of Pb, Sn and Se were taken in a stoichiometric proportion in the ampoule. It was evacuated to a pressure of 10^{-6} Torr and then sealed. The sufficient care was taken for vigorous shaking so as to distribute the mixture along the length uniformly. The ampoule was set in a horizontal furnace. Its temperature was slowly raised at the rate of (2°C/h) till it reaches to 1100°C. It was maintained at this temperature for a period of 2 days. The ampoule was then slowly cooled and brought to room temperature. The resulting crystal was crashed to fine powder and then was transferred to another cleaned quartz ampoule, which was evacuated at a pressure of 10^{-6} Torr. This charged ampoule was placed in a dual zone horizontal furnace. The temperatures of hot-zone and cold-zone of the ampoule were kept (1150°C) and (500°C), respectively. Initially the temperature was increased at a rate of (2°C/h). The ampoule with these desired zone temperatures were maintained growth period (144h). The furnace was then cooled down slowly at the rate of (2°C/h). The entire material got converted in the form of single crystals at the cooler end of the ampoule. The grown crystals were collected after breaking the ampoule.

2.2. Structural Characterization

The powder of $Pb_{1-x}Sn_xSe$ (x=0.082) obtained during the growth process was prepared for the x-ray diffraction study experiment. The x-ray diffractograms were obtained with Philips x-ray diffractometer PW 1350 employing CuKα radiation (wavelength =1.541Å). The x-ray diffraction patterns obtained for $Pb_{0.918}Sn_{0.082}Se$ powder and single crystal bulk are shown in fig.(1) we can show that $Pb_{0.918}Sn_{0.082}Se$ has a (cubic or NaCl) structure and single phase. The lattice parameter (lattice constant) is equal to (6.112Å).

2.3. Sample Preparation

Epitaxial $Pb_{1-x}Sn_xSe$ layers were grown onto cleaved and polished (111) CaF_2, (100) KCl and (100) NaCl substrates in a high-vacuum system by means of the hot-wall-epitaxy (HWE) method. The $Pb_{1-x}Sn_xSe$ were sublimated from the source whose temperature was controlled (source heated to 570°C) and the substrates were temperature ranging from 200 to 275°C by increasing step 25°C, leading to a growth rate of (1.51-2.4μm/h). In epitaxy, there are so many experimental variables that are important in achieving single-crystal growth (e.g. condition and history of substrate, purity of materials, degree of lattice register between overgrowth and substrate, equilibrium factors, method of deposition, rate factors).Some of the properties of these substrates and compound are shown in table 1.

Tale-1: Some physical properties for substrates and material are used.

Material	Crystal structure	Lattice parameters (Å)	Linear thermal expansion coeff. (K^{-1})
NaCl	Cubic	a_o = 5.64	~ $40x10^{-6}$
KCl	Cubic	a_o = 6.28	~ $37x10^{-6}$
CaF_2	Cubic (fluorite)	a_o = 5.46	~ $19x10^{-6}$
PbSe	NaCl	a_o = 6.124	~ $19.4x10^{-6}$
SnSe	Orthorhombic	a=4.2, b=11.6, c=4.48	--------
$Pb_{1-x}Sn_xSe$ (x=0-0.2)	NaCl	a_o =(6.124-6.06)	~ $19.8x10^{-6}$

Substrates heated to 200-275°C subsequently in the high vacuum about 10^{-5} torr for about 1hour prior to epitaxial growth to degas the absorbed molecules for obtaining a clean surface, and to prepare with thermal expansion that gives good interdiffusion and adherence between layers and substrates.

2.4. Optical Band Measurements

The optical absorption and transmition spectra for grown films were obtained using (FTIR) spectrophotometer in the wavelength region 2.5-20μm with incident radiation perpendicular to the cleavage plane. The absorption spectrum for each crystal layers was analyzed for the determination of absorption coefficient α. For near the fundamental absorption edge, the absorption [12] behaves as:

$$\alpha h\nu = A\,(h\nu - E_g + E_p)^n \qquad (1)$$

Here A is a constant, hν is photon energy, E_p is the phonon energy and E_g is the electron energy at band gap. For direct transition (E_p =0), n is equal to 1/2 for allowed transition and 3/2 for forbidden transition. For indirect transition, n=2 for allowed transition and 3 for forbidden transition. In order to determine the optical band gap square of αhν was plotted against hν for each sample.

3. Results and Discussion

Although we have not fully investigated the growth of epitaxial $Pb_{1-x}Sn_xSe$ films on fluoride substrates and correlated the deposition conditions with the structural and optical properties of the films, following trends that have been observed from our preliminary results.

The substrate temperature plays an important role in affecting the structural properties of the film. It is in agreement with the common observation that in order to obtain crystalline rather than amorphous films by vapor deposition, the substrate temperature must exceed some value so that the atoms will have sufficient surface mobility on the substrate to make their way to regular lattice sites.

The study of $Pb_{1-x}Sn_xSe$ films deposited on BaF_2 and CaF_2 substrates is interesting because the thermal expansion coefficients of BaF_2 and CaF_2 seem to match more closely to those of $Pb_{1-x}Sn_xSe$ than KCl does.

The orientation and the lattice constant, a_o, were determined from the x-ray diffraction lines measured with a diffractometer using Cu radiation. The composition of the film was then calculated from "a_o" by using the relation [13]:

$$a_o\,(\text{Å}) = 6.124 - 0.12x \qquad (2)$$

It is known that the forbidden-band width E_g of the $Pb_{1-x}Sn_xSe$ system depends on the composition x and the temperature T. Strauss [14] has given such data and has established an empirical dependence of E_g on the x and T:

$$E_g = 0.13 + 4.5*10^{-4}T - 0.89x \quad \text{eV} \qquad (3)$$

The absorbance (α) was calculated from the calculated values of R and t using the relation [9]:

$$\alpha = (1-R-T)/t \qquad (4)$$

Also, we can calculate (α) from another relation [15]:

$$\alpha = 2.303(A - A')/t \qquad (5)$$

Where "t" is the thickness of the films, A is the absorption of the films and A' the correct absorption limited. In order to determine the difference between the direct and indirect transition the data were plotted in accordance with the relation [16].

$$\alpha\,(h\nu - E_g)^{1/2} \qquad (6)$$

$$\text{and } \alpha\,(h\nu - E_g')^2 \qquad (7)$$

Where E_g and E_g' are forbidden band widths for direct and indirect transitions, respectively.

For the optical band gap study the square of αhν was plotted against hν for each sample as shown in fig.(2).The extrapolation of the each curve to zero$(\alpha h\nu)^2$ yields a direct character of

band gap. The values of band gap (E_g) obtained are represented in table(2).

It can be seen that some physical parameters obtained from the experimental procedure for all films are grown on the substrates in table (2).

Table-2: Some physical parameters of the grown films of $Pb_{1-x}Sn_xSe$.

Substrate	Temperature of substrate (T_s) °C	Thickness (μm)	E_g (eV)
CaF_2	200 225 250 275	1.432 2.266 0.378 3.548	~0.17 ~0.172 ~0.18 ~0.2
KCl	200 225 250 275	1.632 2.014 0.252 3.399	~0.21 ~0.178 ~0.16 ~0.156
NCl	200 225 250 275	1.245 1.636 0.126 3.37	~0.24 ~0.22 ~0.13 ~0.12

Surface Quality

Several of the films grown have had optical quality surfaces (mirror like in appearance). A photograph of films grown on CaF_2 or KCl is presented in fig.(3). The nail was placed in front of the film to indicate the reflective nature of the surface. Our understanding of the experimental parameters controlling the surface quality of films is incomplete. However, we have observed several general relationships which appear to be significant. First, surface quality is critically dependent upon both substrate temperature and evaporation rate.

4. Conclusion

The epitaxial of $Pb_{1-x}Sn_xSe$ layers have been successfully grown on KCl(100), NaCl(100), and CaF_2(111) and exhibit a high quality. A HWE evaporation system has been designed which yields epitaxial films of $Pb_{1-x}Sn_xSe$ on substrates of KCL, NaCl, and CaF_2. This system is used to produce films or layers with mirror like surfaces, and improve film adherence to the substrate. The x-ray, and optical properties indicate that these films are homogeneous and of high crystalline quality, the deduction from the (FTIR) spectrophotometers showed that the band gap ranged between 0.12 and 0.24 eV; the thickness ranged between 0.126 and 3.548 μm. The grown layers properties depend on substrates, temperature, and growth conditions, therefore, if we have the same structure parameters of the layers and substrates like lattice constant and thermal expansion, we can obtain single crystal layers and high adherence.

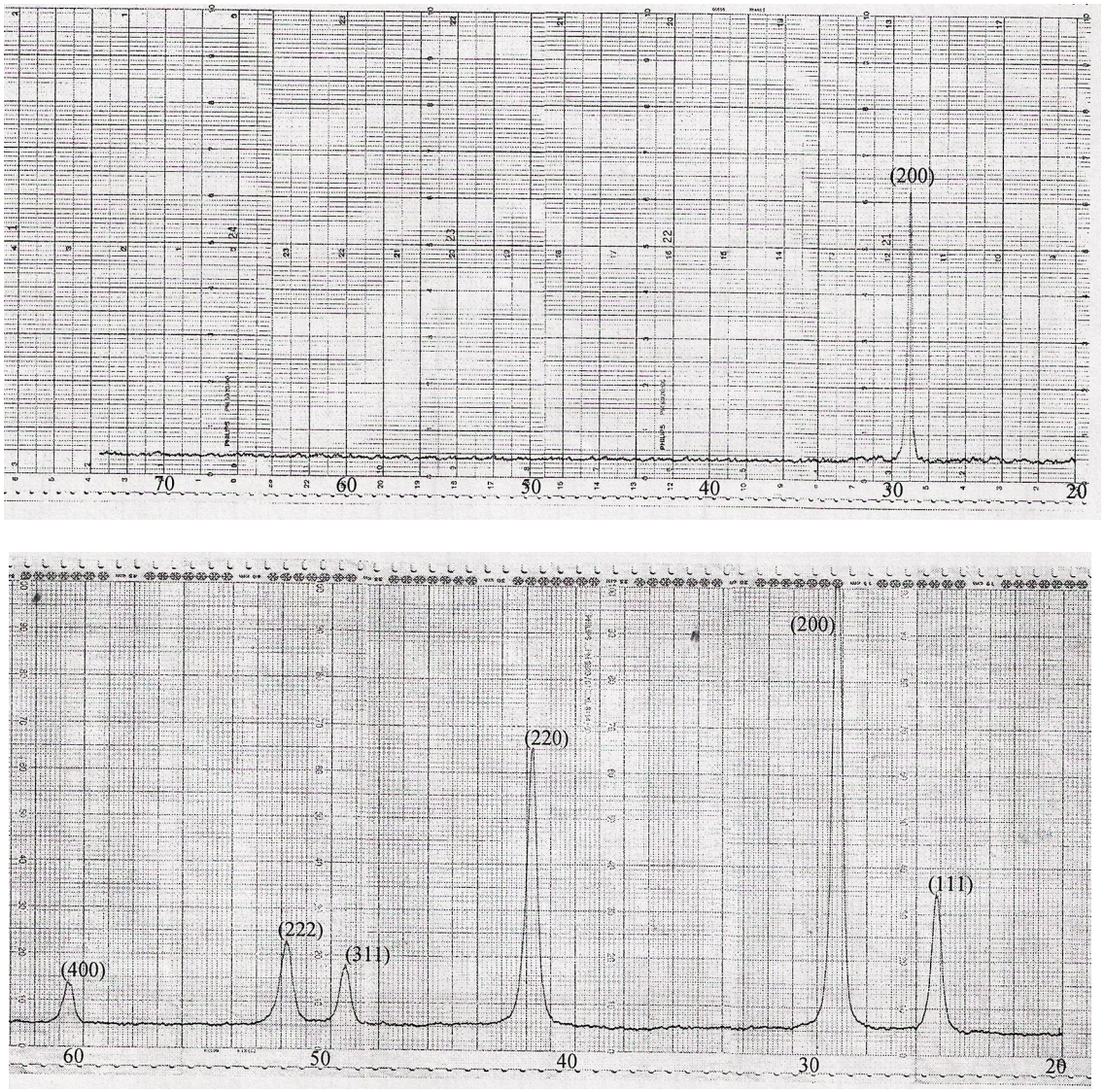

Fig (1):The X-Ray diffraction pattern of the powder and single crystal bulk as circle disk of PbSnSe.

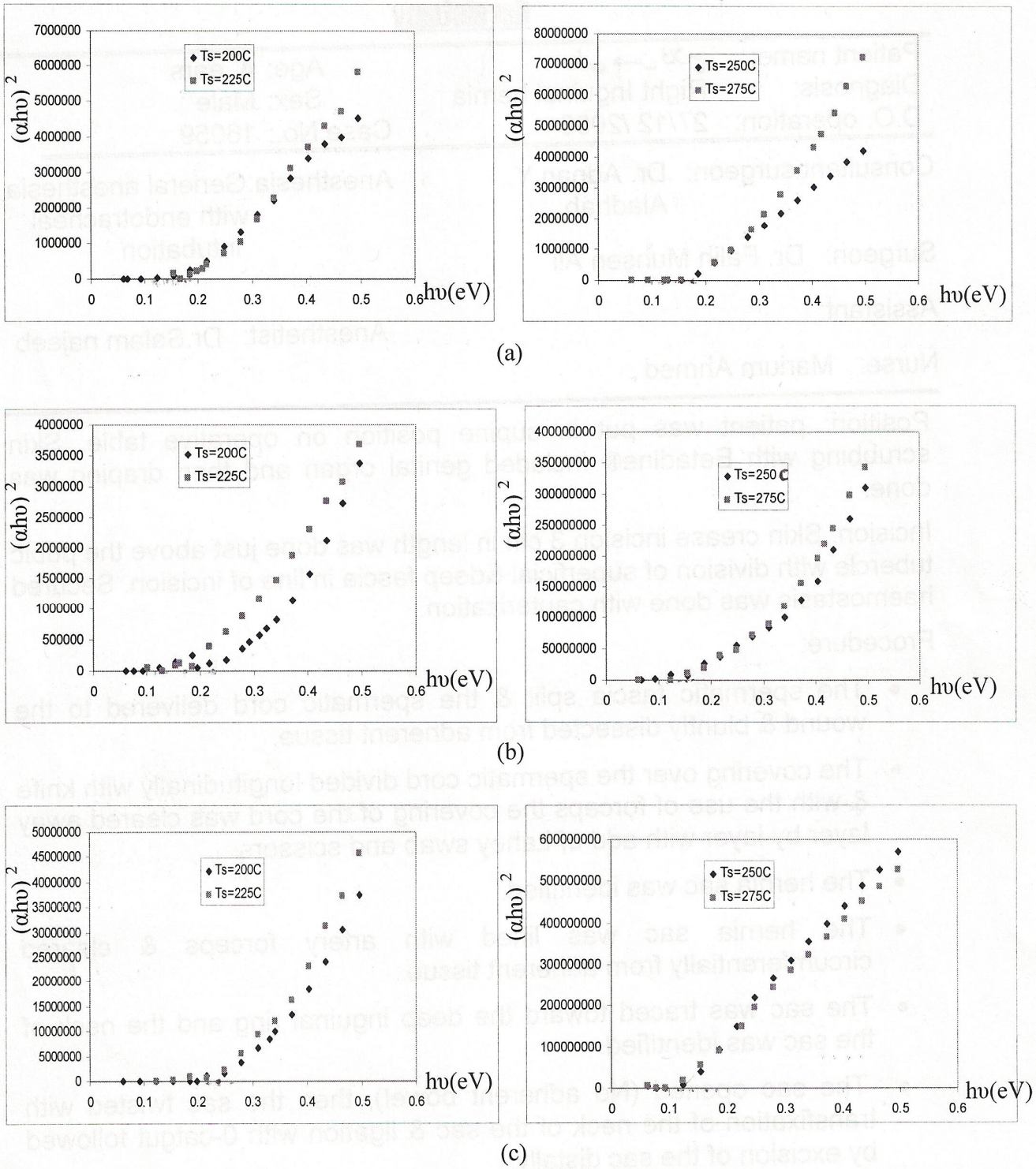

Fig (2): Square of αhυ was plotted against hυ to obtain the values of band gap (Eg) in range of Ts (200,225,250,275 ^{o}C) on substrates: (a) CaF2 (111). (b) KCl (100). (c) NaCl (100).

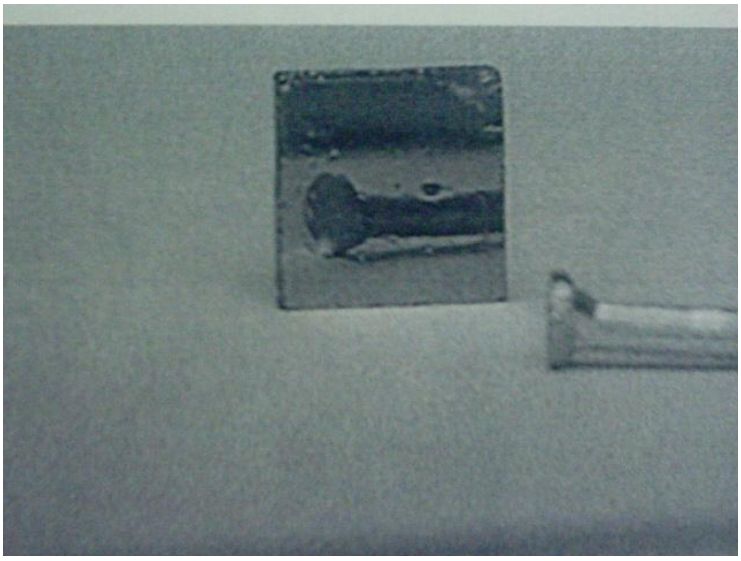

Fig (3): A nail was placed in front of the film to show the optical quality of the surface mirror like.

References

[1] S.Dal corso, B.Liautard, and J.C.Tedenac, J.Phase Equilibria, Vol.16, No.4 (1995).

[2] Melingailis and T.C. Harman, Semiconductors and Semimetals, edited by R.K. Willardson and A. Beer , Vol. 5, (1970).

[3] T.F. Tao, C.C. Wang, J.Appl.Phys., Vol.43, 3, pp.1313-1316(1972).

[4] Joachim Hesse and Horst Preier, Lead Salt Laser Diodes, pp.229(1975).

[5]] A.R. Calawa, J.O. Dimmock, T.C. Harman, and I. Melingailis, Phys. Rev. Letters 23, 7 (1969).

[6] J.R. Dixon and G.F. Hoff, Science Direct Solid State commun., 7, 1777 (1969).

[7] S. Prakash, H.C. Gupta, and B.B. Tripathi, J. Chem. Phys.78 (10) (1983).

[8] H.K. Sachar, I. Chao, P.J. McCann, and X.M. Fang, J. Appl. Phys. Vol. 85, N0.10 (1999).

[9] K.V. Narasimham, J.C. Joshi, K.N. Chopra, C. Jagadish, and A.L. Dawar, Infrared Phys. Vol. 23, No. 6, pp.349-353 (1983).

[10] M.H.Brodsky and J.N.Zemel, Phys.Rev. 155, 780-785(1967).

[11] H.R.Riedl,J.R.Dixon,and R.B.Schoolar, Phys. Rev. 162, 692-700(1967).

[12] T.H. Patel, Rajiv Vaidya, and S.G. Patel, J. Crystal Growth 253, 52-58 (2003).

[13] A.J. Strauss, Phys. Rev. Vol. 157, No. 3, 608 (1967).

[14] V.G. Gutsulyak and M.M. Kondratenko, Inorg. Mater. (USA), Vol.19, No.9, pp.1263-5 (1983).

[15] J. Jeorg, S. Pyung Choi, K.J. Hong, H.J. Song, and J.S. Park, J. Korean phys. Sco. Vol. 48, 960 (2006).

[16] Bube R.H., Photoconductivity of solids, pp.213, wiley, New York (1980).

الخلاصة:

الشرائح الفوقية للمركب الثلاثي $Pb_{1-x}Sn_xSe$ نُميت على القواعد الأحادية KCl(100) و NaCl(100) و CaF_2(111) تحت ظروف تفريغ عالي باستخدام طريقة HWE، حيث كانت درجة حرارة المصدر للمركب الثلاثي ما يقارب 570 ^oC بينما تدرجت درجة حرارة القاعدة من 200 الى 275 ^oC بمقدار زيادة 25 ^oC لكل مرحلة تبخير، معدل النمو للشرائح أثناء التبخير بحدود (1.51-2.4μm/h). حُددت بعض الخواص الضوئية لهذا المركب باستخدام مطياف FTIR في مدى طاقة الفوتون (0.496-0.062) eV في درجة حرارة الغرفة، تم تحليل هذه الخواص للحصول على حزمة الطاقة الممنوعة أو فجوة الطاقة الضوئية (E_g^{op}).