ISSN (Online) 2321-2004
ISSN (Print) 2321-5526

INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH IN ELECTRICAL, ELECTRONICS, INSTRUMENTATION AND CONTROL ENGINEERING
Vol. 3, Issue 5, May 2015

Significance of substrate temperatures on the electrical properties of flash evaporated polycrystalline $ZnIn_2Se_4$ thin films

D. K. Dhruv[1], B. H. Patel[2]

Department of Electronics, Sardar Patel University, Vallabh Vidyanagar-388120, Gujarat, India[1,2]

Abstract: The electrical properties of $ZnIn_2Se_4$ thin films grown on glass substrates by the flash evaporation technique at different substrate temperatures (T_s) ranging from 473-623 K are studied. The influence of substrate temperature (T_s) on the electrical characteristics such as resistivity (ρ), Hall coefficient (R_H), carrier concentration (ɳ), and Hall mobility (μ_H) of $ZnIn_2Se_4$ thin films were studied. It is observed that the films deposited at 573 K have minimum resistivity. The activation energies (ΔE) were evaluated in the temperature range 303-423 K.

Keywords: $ZnIn_2Se_4$, Polycrystalline, Substrate temperature, Activation energy, Hall Effect.

I. INTRODUCTION

The ternary semiconducting compounds with the composition II-III$_2$-VI$_4$ (where II=zinc, cadmium or mercury; III=aluminium, gallium or indium; VI=sulphur, selenium or tellurium) have been widely investigated because of their potential applications as photoconductors , non-linear harmonic generators , IR detectors, temperature sensors , narrow-band optical filters, etc. , , . Among the II-III$_2$-VI$_4$ chalcopyrites, $ZnIn_2Se_4$ has drawn special interest because it has relatively high photoelectronic sensitivity in the spectrum range from visible to near infrared and also, it is expected as a promising material for optoelectronic applications. Many studies have been made on the crystal structure , , , photoconductivity properties , photosensitive properties , photoelectrical memory effect , intraband transition , solar cell , and thermal properties of $ZnIn_2Se_4$. We recently reported the growth of $ZnIn_2Se_4$ thin films by flash evaporation technique and its application as a memory switching device , .

Substrate temperature (T_s) is one of the key deposition parameters in the vacuum deposition technique. It influences the composition and crystallinity of the deposited films, and offers a wide range of applications in various fields. Hence the investigation of the effect of substrate temperatures (T_s) on the properties of vacuum deposited thin films is of great importance. In the present paper, an attempt has been made to obtain more detailed information on the effect of substrate temperature (T_s) on the electrical properties such as resistivity (ρ), activation energy (ΔE), carrier concentration (ɳ) and Hall mobility (μH) of $ZnIn_2Se_4$ thin films. The results obtained are reported and discussed

II. EXPERIMENTAL DETAILS

$ZnIn_2Se_4$ thin films were deposited by flash evaporation technique on clean glass substrates using a vacuum coating unit (model: 12A4D; make: Hind High Vacuum Co. Pvt. Ltd, Bangalore, India) pumped down to ≈7.5×10^{-4} Pa. The source material was single-phase $ZnIn_2Se_4$ with grain size of 100-150 µm. The evaporation was carried out from tungsten (W) boat maintained at sufficiently high temperature (≈1300 K) in order to evaporate the material instantaneously. Glass substrates were kept at different temperatures ranging from 473 to 623 K to deposit thin films. The film thickness and the rate of deposition were determined and/or controlled by the built in quartz crystal thickness monitor (model: DTM-101) of the Hind High Vacuum coating unit. The rate of evaporation was found to be 10 nm/sec in all the experiments and thickness of the deposits were around 200 nm. The Hall Effect measurement setup (model: 7805, make: Lake Shore Corporation, Inc., USA) was used for the electrical characterizations of the $ZnIn_2Se_4$ thin films by establishing pressure contacts on the films. The I-V measurements were made by an electrometer (model: 6517B, make: Keithley, USA). Calibrated chromel-alumel thermocouple was used for the temperature related measurements.

III. RESULTS AND DISCUSSION

Our previous studies on the growth of $ZnIn_2Se_4$ thin films revealed that single-phase, polycrystalline, stoichiometric thin films of $ZnIn_2Se_4$ have been grown in the substrate temperatures (T_s) range 473 K ≤ T_s ≤ 573 K. The films deposited at lower substrate temperatures, (T_s < 473 K), were amorphous in nature, while at higher substrate temperatures, (T_s > 573 K), the films were polyphase.

A. The effect of Substrate Temperature on Resistivity

The variation of the electrical resistivity (ρ) of $ZnIn_2Se_4$ thin films (having film thickness around 200 nm) with the substrate temperature is shown in Fig. 1. It is observed from Fig. 1 that the electrical resistivity (ρ) decreases with increasing substrate temperature (T_s) and reaches a minimum value at 573 K. The decrease in resistivity of the films with increase in substrate temperature (T_s) upto 573 K can be explained using Petritz barrier model : according to this model, the crystallites do not grow sufficiently large at low temperature and the large inter-crystalline regions offer high resistance for the movement of charge

ISSN (Online) 2321-2004
ISSN (Print) 2321-5526
INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH IN ELECTRICAL, ELECTRONICS, INSTRUMENTATION AND CONTROL ENGINEERING
Vol. 3, Issue 5, May 2015

carriers. At higher substrate temperatures (T_s), the formation of fewer nucleation centres results in larger crystallite sizes, which ultimately decreases the number of inter-crystalline barriers. The charge carriers, therefore, have to cross comparatively narrow inter-crystalline barriers. The films deposited at higher substrate temperatures (T_s) are nearly stoichiometric and have larger grains and this may be responsible for the decrease in the resistivity. This is in good agreement with our morphological observations made from the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) studies which provided evidences for the improvement of the crystallinity and the increase of the crystallites size in the films with the increase of the substrate temperature (T_s) .

Nevertheless, the electrical resistivity (ρ) of the $ZnIn_2Se_4$ thin films deposited at higher substrate temperatures (T_s) above 573 K has increased and it can be attributed due to the deviation from stoichiometric composition of the films, since the films grown at temperatures above 573 K are Zn & Se deficient. Moreover, the formation of additional phase may be responsible for this deviation in resistivity; at higher substrate temperatures (T_s > 573 K), the additional phase was identified due to the formation of In_2Se_3 in the $ZnIn_2Se_4$ films. When the substrate temperature (T_s) was raised to values higher than 573 K, the films were found to be dissociating as can be seen from the diffraction pattern of the film deposited at T_s=623 K . Therefore, the films grown at substrate temperatures (T_s) higher than 573 K are not of single phase but they are of polyphase. Similar dependence of the resistivity has also been reported in other zinc ternary compound films .

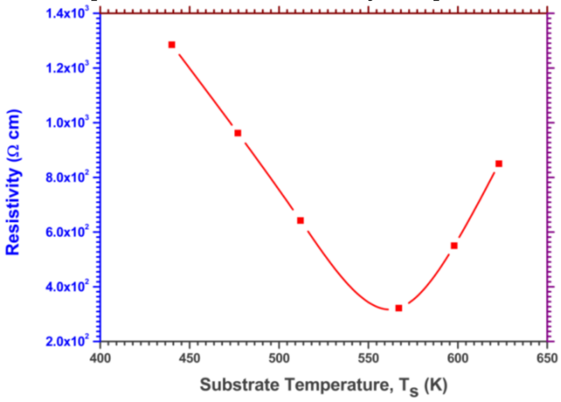

Fig. 1 Variation of the electrical resistivity (ρ) of the $ZnIn_2Se_4$ thin films deposited at different substrate temperatures (T_s)

B. The effect of Substrate Temperature on Activation Energy

A plot of log R versus 1/T of $ZnIn_2Se_4$ films grown at different substrate temperatures (473-623 K) is shown in Fig. 2. The studies were carried out in the temperature range of 303-423 K in a vacuum of 1.333 Pa to avoid contamination of the film. The temperature dependence on resistance is expressed as,

$$\Delta E = \frac{\Delta(\log R)}{\Delta\left(\frac{1}{T}\right)} \times 2k \times 2.303 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where ΔE is the thermal activation energy, k is the Boltzmann constant and T is the temperature.

The thermal activation energies were calculated from Fig. 2 is presented in Table 1. The activation energies are found to increase with the increase of the substrate temperature (T_s). The substrate temperature (T_s) has a significant influence on structure, orientation, and stoichiometry of $ZnIn_2Se_4$ thin films. The crystallinity of the films increased with increasing the substrate temperatures and the films grown at lower substrate temperatures have a random orientation and consist of dispersed microcrystallites. The activation energy of the films grown below 573 K is found to be slightly less than the value reported for $ZnIn_2Se_4$ bulk (2.0 eV) . However, the activation energy of the film grown at a substrate temperature of 573 K is in good agreement with the bulk value. At higher substrate temperature (T_s = 623 K), the higher value of activation energy may be due to the presence of additional phase in the film , , .

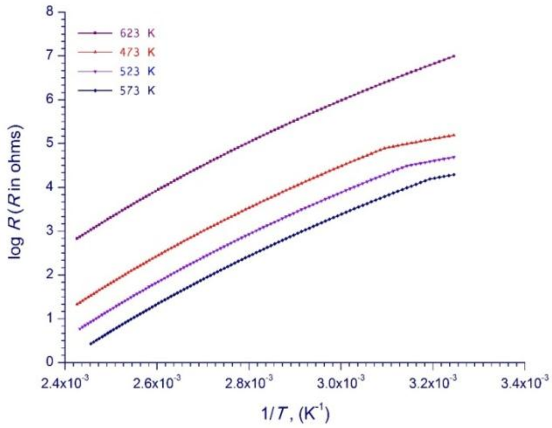

Fig.2 Log(R) versus 1/T plots of films deposited at different substrate temperatures (T_s)

TABLE I: THE THERMAL ACTIVATION ENERGIES FOR $ZNIN_2SE_4$ THIN FILMS DEPOSITED AT DIFFERENT SUBSTRATE TEMPERATURES

Substrate Temperature (T_s), K	Activation Energy (ΔE), eV
473	1.90
523	1.95
573	2.03
623	2.15

C. The effect of Substrate Temperature on Carrier Concentration and Hall Mobility

Thin films of $ZnIn_2Se_4$ were found invariably to be p-type from hot probe tests. This result was in agreement with the results obtained from Hall Effect measurements. Non-rectifying (ohmic) contacts could be easily produced by depositing gold (Au) on $ZnIn_2Se_4$ thin films and using platinum wires for establishing electrical connection.

ISSN (Online) 2321-2004
ISSN (Print) 2321-5526

IJIREEICE

INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH IN ELECTRICAL, ELECTRONICS, INSTRUMENTATION AND CONTROL ENGINEERING
Vol. 3, Issue 5, May 2015

The Hall effect measurement was carried out on $ZnIn_2Se_4$ films by using van der Pauw geometry. Hall mobility and carrier concentration of $ZnIn_2Se_4$ thin films deposited at different substrate temperatures (T_s) having constant thickness of 200 nm are shown in Fig. 3. It evident from the Fig. 3 that decrease in carrier concentration with increasing substrate temperature ultimately results in an increase in Hall mobility in the $ZnIn_2Se_4$ films , , , . This may be explained as being due to the increase in substrate temperature of the films increases the grain size. The grain growth affects the nature of the barrier and lowers the barrier potential at higher substrate temperature, which ultimately increases the Hall mobility. Thus the effect of substrate temperature on the resistivity, activation energy, carrier concentration, and Hall mobility are dominated by grain-boundary scattering phenomena.

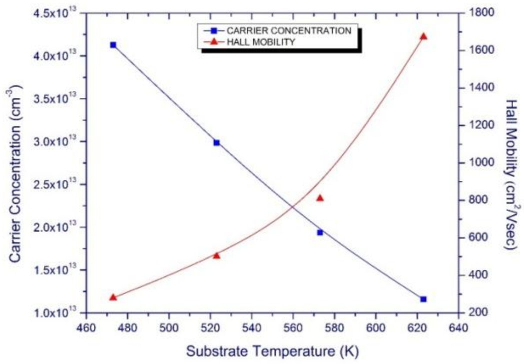

Fig.3 Variation of carrier concentration and hall mobility of $ZnIn_2Se_4$ thin films with substrate temperatures (T_s)

IV. CONCLUSIONS

Flash evaporation technique was employed to deposit $ZnIn_2Se_4$ thin films on glass substrates and the substrate temperature was used as a tool for tailoring the electrical properties of the films. The decrease of the electrical resistivity with increasing of the substrate temperature upto 573 K was explained based on Petritz's barrier model, while the increase of the resistivity for films grown at substrate temperatures higher than 573 K was explained due to the formation of non-stoichiometric polyphase films. The activation energies increase with increase in substrate temperatures. The carrier concentration and Hall mobility have been shown to depend primarily on the grain boundary scattering mechanisms for the $ZnIn_2Se_4$ films deposited at different substrate temperatures.

REFERENCES

[1]. G. B. Abdullaev, V. G. Agaev, A. B. Antonov, R. Kh. Nani, E. Yu. Salaev, Soviet Physics-Semiconductors, vol. 6, p. 1492, 1972.
[2]. B. F. Levinne, C. G. Bethea and H. M. Kasper, "Nonlinear Optical Susceptibility of Thiogallate $CdGa_2S_4$," IEEE Journal of Quantum Electronics, vol. 10, pp. 904-906, 1974.
[3]. S. A. Lopez-Rivera, L. Martinez, J. M. Briceno-Valero, R. Echeverria and G. G. de Armengol, Progress in Crystal Growth and Characterization, vol. 10, p. 279, 1985.
[4]. S. I. Radautsan and I. M. Tiginyanu, "Defect Engineering in II-III_2-VI_4 and Related Compounds," Japanese Journal of Applied Physics, vol. 32, pp. 5-9, 1993.
[5]. N. V. Joshi, Jorge Luengo and Fatima Vera, "Optical activity in $ZnGa_2S_4$," Materials Letters, vol. 61, pp. 1926-1928, 2007.
[6]. Y. Ayeb, T. Ouahrani, R. Khenata, Ali H. Reshak, D. Rached, A. Bouhemadou and R. Arrar, "FP-LAPW investigation of structural, electronic, linear and nonlinear optical properties of $ZnIn_2Te_4$ defect-chalcopyrite," Computational Materials Science, vol. 50, pp. 651-655, 2010.
[7]. L. Gastaldi, M. G. Simeone and S. Viticoli, "Structure refinement of $ZnIn_2Se_4$," Journal of Solid State Chemistry, vol. 66, pp. 251-255, 1987.
[8]. R. E. Marsh and W. R. Robinson, "On the Structure of $Znln_2Se_4$," Journal of Solid State Chemistry, vol. 73, pp. 591-592, 1988.
[9]. S. Locmelis, E. Milke, M. Binnewies, S. Gruhl and C. Vogt, "Chemical Vapor Transport of Solid Solutions. 18.[1] Chemical Vapor Transport of $ZnIn_2S_4$, $ZnIn_2Se_4$ and $ZnIn_2S_{4-x}Se_x$-mixed crystals," Zeitschrift Fur Anorganische Und Allgemeine Chemie, vol. 631, pp. 1667-1674, 2005.
[10]. Serpi and S. Gariazzo, "Photoconductivity relaxation in $ZnIn_2Se_4$," Physical Review B, vol. 41, pp. 7718-7723, 1990.
[11]. A. Vaipolin, Yu. A. Nikolaev, V. Yu. Rud, Yu. V. Rud and E. I. Terukov, "Photosensitive structures based on $ZnIn_2Se_4$ single crystals," Semiconductors, vol. 37, pp. 414-416, 2003.
[12]. J. Filipowicz, N. Romeo and L. Tarricone, "Photoelectrical memory effect in $ZnIn_2Se_4$," Solid State Communications, vol. 38, pp. 619-623, 1980.
[13]. N. M. Mekhtiev, Z. Z. Gusenov and E. Yu Salaev, "Interband transitions in $ZnIn_2Se_4$," Soviet-Physics Semiconductors, vol. 18, pp. 677-678, 1984.
[14]. F. J. Garcia and M. S. Tomar, "n-CdS/p-$ZnIn_2Se_4$ thin film solar cell," Thin Solid Films, vol. 69, pp. 137-139, 1980.
[15]. L. I. Soliman, M. H. Wasfi and T. A. Hendia, "Thermal properties of polycrystalline $ZnIn_2Se_4$," Journal of Thermal Analysis and Calorimetry, vol. 59, pp. 971-976, 2000.
[16]. K. Dhruv and B. H. Patel, "Growth of flash evaporated $ZnIn_2Se_4$ thin films," International Journal of Applied Sciences and Engineering Research, vol. 3, pp. 121-128, 2014.
[17]. K. Dhruv, A. Nowicki, B. H. Patel and V. D. Dhamecha, "Memory switching characteristics in amorphous $ZnIn_2Se_4$ thin films," Surface Engineering, p. In Press, 2015.
[18]. Richard L. Petritz, "Theory of photoconductivity in semiconductor films," Physical Review, vol. 104, pp. 1508-1516, 1956.
[19]. S. M. Patel and M. H. Ali, "Growth of $ZnIn_2Te_4$ thin films," Materials Letters, vol. 5, pp. 350-356, 1987.
[20]. P. Manca, F. Raga, and A. Spiga, "Photoconductivity of $ZnIn_2Se_4$ and $ZnIn_2Te_4$," Physica Status Solidi A, vol. 16, pp. K105-K108, 1973.
[21]. S. M. Patel and M. H. Ali, "The electrical properties of polycrystalline $ZnIn_2Te_4$ thin films," Jounal of Materials Science, vol. 24, pp. 3176-3179, 1989.
[22]. L. L. Kazmerski and Y. J. Juang, "Vacuum - deposited $CuInTe_2$ thin films: Growth, Structural, and Electrical Properties," Journal of Vacuum Science and Technology, vol. 14, pp. 769-776, 1977.
[23]. F. Fray and P. Lloyd, "Electrical and Optical properties of thin p - type films prepared by vacuum evaporation from the chalcopyrite $CulnSe_2$," Thin Solid Films, vol. 58, pp. 29-34, 1979.
[24]. L. L. Kazmerski, M. S. Ayyagari and G. A. Sanborn, "$CuInS_2$ thin films: preparation and properties," Journal of Applied Physics, vol. 46, pp. 4865-4869, 1975.
[25]. L. L. Kazmerski, M. S. Ayyagari, F. R. White and G. A. Sanborn, "Growth and properties of vacuum deposited $CuInSe_2$ thin films," Journal of Vacuum Science and Technology, vol. 13, pp. 139-144, 1976.
[26]. J. H. McFee, B. I. Miller and K. J. Bachmann, "Molecular Beam Epitaxial Growth of InP," Journal of the Electrochemical Society, vol. 124, pp. 259-272, 1977.
[27]. H. Patel and S. S. Patel, "Growth and electrical properties of flash evaporated $AgGaTe_2$ thin films," Crystal Research and Technology, vol. 41, pp. 117-122, 2006.