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# Significance of substrate temperatures on the deposition of $ZnGa_2Se_4$ thin films by flash evaporation technique

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**Abstract -** *Bulk $ZnGa_2Se_4$ was grown by melt-growth technique, using the stoichiometric mixture of constitute elements. The ternary compound semiconductor $ZnGa_2Se_4$ thin films deposited by flash evaporation technique. The grown material was characterized by x-ray diffraction technique. The influence of the substrate temperature on the structural, morphological and optical properties of the films has been studied. The films deposited at substrate temperature range 573 K ≤ Tsub ≤ 673 K have been identified to be single phase, stoichiometric and polycrystalline with having (112) and (204, 220) preferred orientations. The topography and the surface roughness of films were studied by Atomic Force Microscopy. Optical analysis of the films revealed that band gap energy increases with increase in the substrate temperatures.*

***Key Words***: Flash evaporation, Transmission Electron Microscopy, Stoichiometry, Atomic Force Microscopy, Optical Band gap

## 1. INTRODUCTION

The Zinc tetraselenodigallate ($ZnGa_2Se_4$) is member of the II-III2-IV4 group semiconducting compounds. This ternary group have increasing interest because of their wide applications such as memory devices, narrow band optical filters, nonlinear optical devices, schottky diode, ultra – violet photodetectors, etc. [1][2][3][4]. Most of these compounds form in tetragonal type structure [5][6][7]. Polycrystalline $ZnGa_2Se_4$ was first synthesized by Hahn et al. [8]. Structural and optical properties of the $ZnGa_2Se_4$ thin films by thermal evaporation technique was reported by Fadel et al. [9]. $ZnGa_2Se_4$ can be used for phase change memories [10]. The current-voltage characteristics of $ZnGa_2Se_4$ heterojunction diode was studied by Yahia et al. [11]. Although, to our knowledge the influence of substrate temperatures on the structural and optical properties of $ZnGa_2Se_4$ thin films has not yet been reported.

In the present investigation, we report in details the study of the deposition of $ZnGa_2Se_4$ thin films by flash evaporation technique and the significance of substrate temperatures on the structural, morphological and optical characteristics like orientation of the films, elemental composition and optical band gap.

## 2. Experimental

### 2.1 Growth of Material

A single phase, polycrystalline ingot of $ZnGa_2Se_4$ was grown by direct fusion of stoichiometric amounts of their constituent elements (Zn, Ga, and Se of purity 99.999%) in a sealed evacuated quartz ampoule at high vacuum. Then the ampoule was kept in a programmable rotating furnace. The temperature of the furnace was programmed with increasing rate of 100 K/h until it reach upto the 1423 K melting point of $ZnGa_2Se_4$ [12] and was kept constant for 3 hours. During this constant period of time, the ampoule was rotated at the rate of 10 rpm. The rotation for three hours duration by mechanical shaking of the mixture ensures the high homogeneity and quality of the compound. Then, the furnace was cooled down in steps until it reached the subsequent temperatures 873 K, 773 K and 643 K and kept constant for 1 h at every stage [8]. The ampoule was finally cooled down to the room temperature. The ingot of reddish color obtained by breaking the ampoule which was finely powdered with a mortar for X - ray study.

### 2.2 Growth of Thin film

$ZnGa_2Se_4$ thin films were grown by flash evaporation technique. The source material was single phase $ZnGa_2Se_4$ with average grain size of ~ 100 μm. The evaporant charge was reduced to the average grain size for complete evaporation of the material effectively to produce stoichiometric compound thin film. A flash evaporation system consists of controllable vibratory feeder system attached with a relay. An electrical pulse applied to the relay will drop the material from the feeder into the quartz crucible placed into a tungsten helical wire. The evaporant charge (~ 5 mg) was dropped step by step in to the preheated quartz crucible in order to deposit stoichiometric thin films. The substrates were placed in the middle of the cylindrical heater

to get the homogeneous heating monitored by chromel - alumel thermocouple.

### 2.3 Experimental Methods

The ingot obtained by breaking the ampoule was characterized by X – ray diffractometer (Philips, Model: X'Pert) using CuKα radiation. The elemental analysis was verified by energy dispersive X-ray analysis (Philips, Model: XL 30; ESEM). The films were deposited on to cleaned glass substrate and freshly cleaved NaCl crystals by vacuum coating unit (Hind Hivac-Model 12A4D). The rate of deposition was ~20 nm/s of all the films and residual pressure was ≈ $10^{-4}$ Pa. The distance between source and substrate was 18 cm. Film thickness was monitored and controlled by digital thickness monitor (DTM - 101) and it was found to be around 100 nm. The micrographs and its corresponding diffraction patters of $ZnGa_2Se_4$ thin film deposited on NaCl crystal were examined by transmission electron microscope (TEM, Model: Tecnai 20). The surface topography and roughness of the thin films were examined by Atomic Force Microscopy (AFM, Model: NT-MDT NTEGRA). The absorbance and transmittance spectra of $ZnGa_2Se_4$ thin films deposited at different substrate temperatures were recorded using UV-Vis-NIR spectrophotometer (Perkin Elmer, model: Lambda 19) in the wavelength range of 200 to 1500 nm.

### 3. RESULTS AND DISCUSSION

### 3.1 Structural Properties

The bulk $ZnGa_2Se_4$ material was characterized by X-ray powder diffraction technique using CuKα radiation. The obtained X-ray diffractogram of $ZnGa_2Se_4$ is shown in figure 1. Table 1 shows the d-values obtained from powder X-ray analysis were indexed using Bragg's formula $n\lambda = 2d\sin\theta$. Good agreement has been observed from the calculation of the lattice constants of $ZnGa_2Se_4$ powder diffraction data were found to be a = 5.48 Å and c = 10.97 Å, with reported values of a = 5.50 Å and c = 10.99 Å (ICDD No. 01-089-4208) [13]. No additional peak other than $ZnGa_2Se_4$ was evident in XRD pattern.

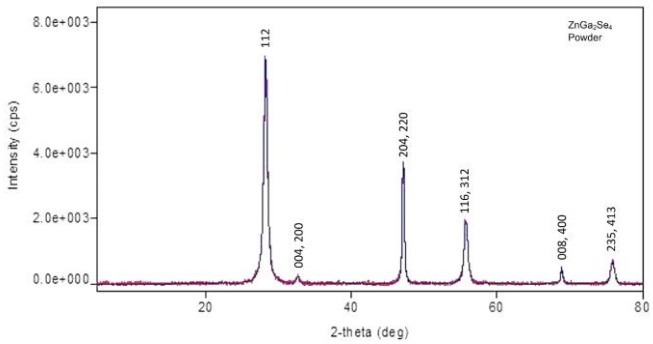



**Figure 1**: X-Ray Diffraction pattern of $ZnGa_2Se_4$ powder

Figure 2 shows that the substrate temperatures have significant influence on the grain size and orientation of thin films deposited at 523 K, 573 K, 623 K, 673 K and 723 K respectively. From the electron micrographs it is evident that the grain size increases with increasing substrate temperatures. The d-values have been calculated for all the electron diffraction patterns and compared with the standard reported data as shown in table 1. Attention may be drawn to the fact that the film grown at substrate temperature 523 K was amorphous in nature. However, the films deposited above 573 K are all polycrystalline in nature. As the further increment in substrate temperatures at 573 K, 623 K and 673 K the electron diffraction patterns revealed the improvement in the sharpness and intensity of (112), (220, 204) planes of the $ZnGa_2Se_4$ thin films. The films deposited at these substrate temperatures show (112) preferred orientation of the crystallites. At higher substrate temperature of 723 K thin film become polyphase. As it is evident from [Figure 2(e)] several additional phases were identified due to the formation of ZnSe and $Ga_2Se_3$.

### 3.2 Morphological Properties

Figure 3 shows the AFM 2D and 3D images of films deposited at 573 K, 623 K and 673 K substrate temperatures which had different surface morphologies as a result of the substrate temperature variation. Topography of film deposited at 573 K, 623 K and 673 K shows uniformly distributed needle like grains with RMS surface roughness 0.37 nm, 0.46 nm and 1.45 nm respectively. This may be attributed to the enhanced atomic mobility which could enable granules to grow more, resulting in an increase in the grain size.

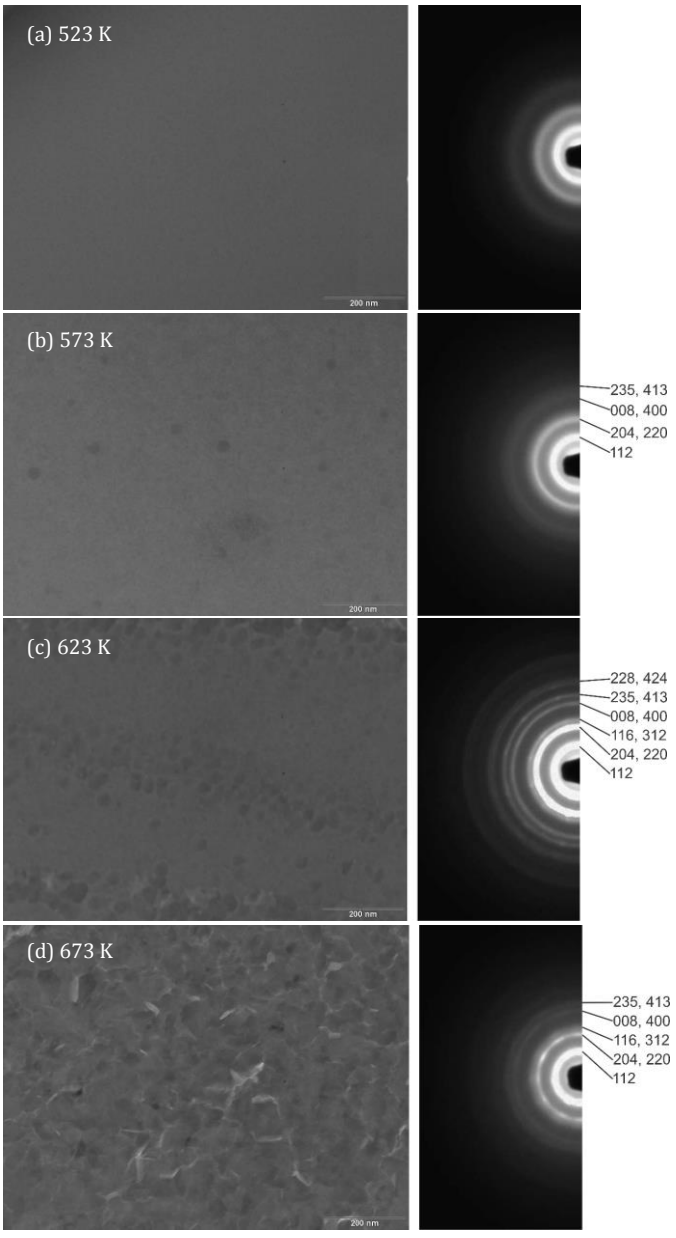
### 3.3 Elemental Properties

Figure 4 shows that the elemental weight percent of Zn, Ga and Se depend critically on the substrate temperatures. The films are nearly stoichiometric up to 673 K. The film deposited at 723 K are Zn and Se deficient. The Zn and Se deficiency may be attributed to re-evaporation of the Zn and Se from substrate surface, since both the elements have higher vapor pressure than Ga [14].

**Table 1:** Comparison between the reported and observed diffraction data for bulk ZnGa2Se4 and thin films.

| Reported d-values (Å) | Observed d-values (Å) | | | | | | hkl |
|---|---|---|---|---|---|---|---|
| | Bulk | | d – spacing values from electron diffraction patterns | | | | |
| | Int. | d-values | Ts=573 K | Ts=623 K | Ts=673 K | Ts=723 K | |
| 3.4300 a) | - | - | | | | 3.4105 b) | 100 e) |
| 3.1729 | 100 | 3.1650 | 3.1609 | 3.1595 | 3.1682 | 3.1765 | 112 |
| 2.7480 | 2.65 | 2.7327 | - | - | - | - | 004, 200 |
| 1.9430 | 56.50 | 1.9266 | 1.9343 | 1.9475 | 1.9440 | 1.9343 | 204,220 |
| 1.9190 c) | - | - | - | - | - | 1.9115 d) | 220 e) |
| 1.6570 | 33.94 | 1.6503 | - | 1.6500 | - | - | 116, 312 |
| 1.3740 | 9.56 | 1.3624 | 1.3642 | 1.3718 | 1.3690 | - | 008, 400 |
| 1.2526 | 10.92 | 1.2537 | 1.2582 | 1.2505 | 1.2461 | - | 235, 413 |
| 1.1218 | - | - | - | 1.1207 | - | - | 228, 424 |

Ts= Substrate Temperature, a) Standard d-values for ZnSe, b) d-values matching with ZnSe, c) Standard d-values for $Ga_2Se_3$, b) d-values matching with $Ga_2Se_3$, e) Indicates additional indices.



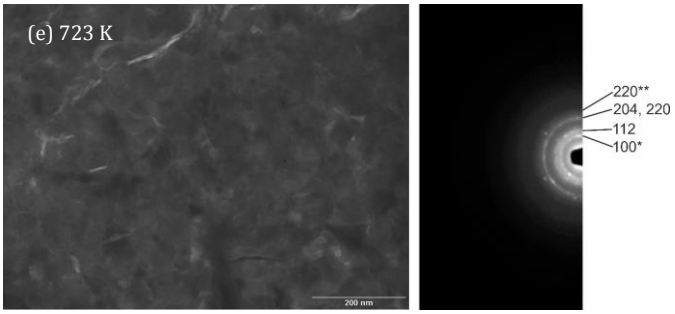




**Figure 2:** Transmission electron micrographs and its corresponding electron diffraction patterns of $ZnGa_2Se_4$ thin films deposited on NaCl crystal at substrate temperatures of (a) 523 K, (b) 573 K, (c) 623 K, (d) 673 K and (e) 723 K (magnification 19000X). * Indicates the d-value matching with ZnSe. ** Indicate the d-values matching with $Ga_2Se_3$.

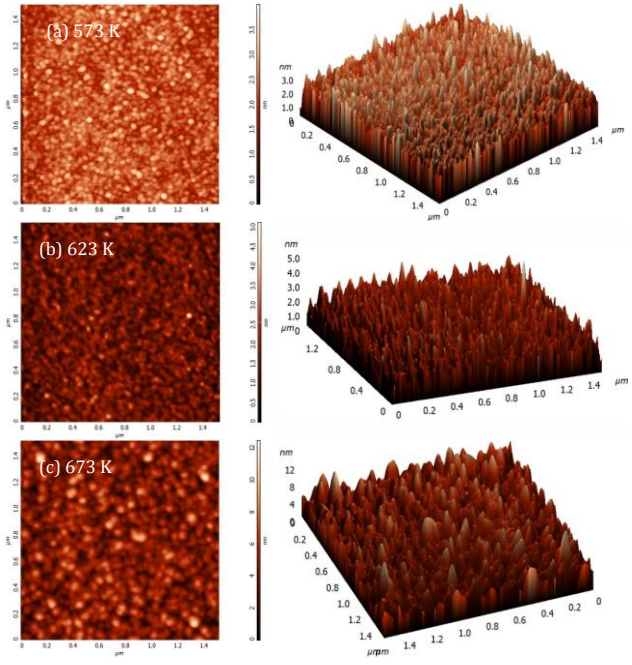



**Figure 3:** 2D and 3D AFM image (1.5 x 1.5 μm2) profiles of $ZnGa_2Se_4$ thin films deposited at (a) 573K, (b) 623K and (c) 673K substrate temperature, respectively.

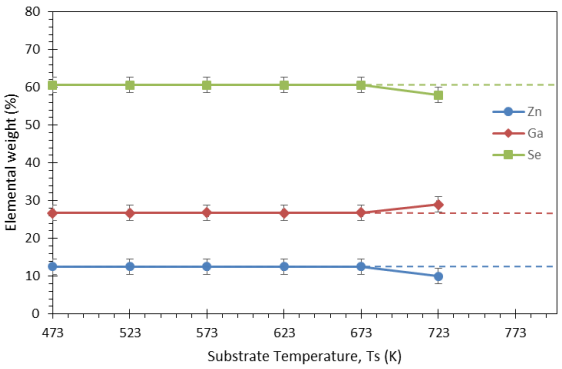



**Figure 4:** Elemental weight percent of Zn, Ga and Se with the different substrate temperature for $ZnGa_2Se_4$ films. The dashed lines represent the stoichiometric $ZnGa_2Se_4$ compound elemental weight percent.

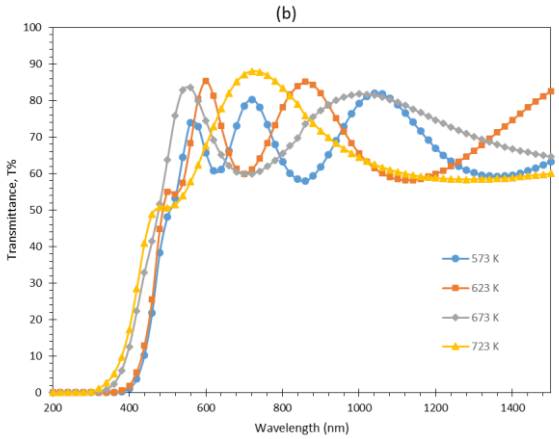
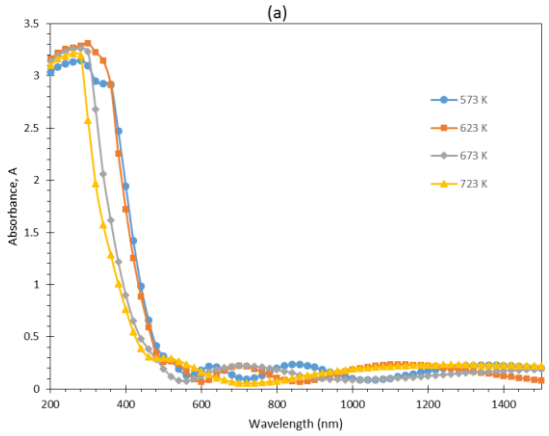



**Figure 5:** (a) Absorbance, A and (b) Transmittance, T% Spectra of ZnGa2Se4 thin films deposited at different substrate temperatures.

### 3.4 Optical Properties

The variation of the absorbance (A) and transmittance (T %) spectra with wavelength range from 200-1500 nm for the $ZnGa_2Se_4$ thin films deposited at different substrate temperatures shown in figure 5. It is clearly observed that as the wavelength increases the absorbance from the films decreases. In the transmittance spectra the change was not considerable up to wavelength value of 300 nm. However, with further increasing the wavelength above 500 nm changes with oscillatory behavior. The average higher transmittance of around 70% - 80% was observed.




The optical absorption coefficient for allowed transition in a semiconductor near to the gap obtained by using

$$\alpha h\upsilon = A(h\upsilon - E_g)^n$$

Where $E_g$ is the optical energy gap, A is a constant, $h\upsilon$ is the photon energy and n is the exponent to characterizes the nature of the transition. Figure 6 shows the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$, photon energy for $ZnGa_2Se_4$ films deposited at different substrate temperatures with the equal thickness of 100 nm. The straight lines extrapolated upto the photon energy axis indicate that $ZnGa_2Se_4$ is direct band gap semiconductor. The direct energy gap, Eg are found to be 2.42 eV, 2.45 eV, 2.47 eV and 2.56 eV for the films deposited at 573 K, 623 K, 673 K and 723 K, respectively. It has been noted that the band gap energy increases as the substrate temperature increases. It is observed from the structural and morphological analysis that the grain size increases with the increase in the substrate temperature. As the film deposited at lower substrate temperature, the grain size are lower and grain boundaries are highly disordered which give high absorption for the films, whereas the films deposited at higher substrate temperatures resulting the growth of larger grain sizes and strong orientation of the crystallites giving a less contribution to the absorption [15]. The energy gap values of the films deposited at 573 K to 673 K are found to be more or less equal to that of the reported value[16]. At higher substrate temperature 723 K, the higher value of energy gap can be explained due to the presence of additional phase in the film.

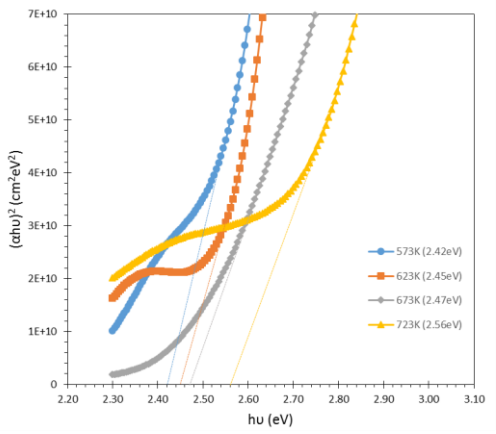



**Figure 6:** Plot of $(\alpha h\upsilon)^2$ versus hυ for $ZnGa_2Se_4$ films deposited at 573 K, 623 K, 673 K and 723 K.

## 4. CONCLUSIONS

The $ZnGa_2Se_4$ thin films deposited by flash evaporation technique in the temperature range 573 K ≤ Tsub ≤ 673 K are single phase, polycrystalline and stoichiometric in nature. Below the substrate temperature of 573 K the films are amorphous and above Tsub = 673 K the films are of polyphase. The AFM images were investigated to know the surface roughness and the effect on the topography of the films deposited at different substrate temperatures. The optical analysis showed that the direct band gap increases with increasing the substrate temperature.

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