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Growth of heteroepitaxial $AgInSe_2$ layers on Si (100) substrates by hot wall method

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$AgInSe_2$ films have been prepared onto the Si (100) substrate at 135^{o}C by hot wall method at pressure of 10^{-5} m bar. Hot wall technique was used to prepare $AgInSe_2$ films which work close to thermodynamic equilibrium and considered as most suitable for growth at low temperatures. The structural and optical properties of hot wall grown $AgInSe_2$ films has been studied. X ray diffraction pattern indicate that the prepared films appear to be highly oriented in (400) direction suggesting epitaxial growth. The band gap calculated from reflectance data is found to be 1.36 and 2.11 eV which is assigned to the fundamental absorption edge and transition originating from crystal field splitting, respectively. The crystallite size of 99 nm has been obtained. Our result may be of interest for better understanding of epitaxial growth of chalcopyrite films at low temperature.

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Keywords: Semiconductors, Optical properties of thin films, X-ray diffraction, Atomic force microscopy

1. Introduction

In recent years, the ternary chalcopyrite semiconductors have received considerable attention because of their adaptability as an absorber component in thin film solar cells. The I-III-VI_2 compounds are ternary analogues of II-VI compounds having high absorption coefficient and good thermal stability [1]. They crystallizes in chalcopyrite structure and is closely related to Zinc blende. Ternary chalcopyrite compounds have potential for photovoltaic applications since their optical band gap lies in the range 0.8-2.0 eV and can be grown either n or p type [2]. An efficiency of 19.5 % has been reported by M.A. Contreras et.al in case of $CuInGaSe_2$ [3]. $AgInSe_2$ with band gap energy of 1.20 eV and melting point of 780^{0}C, find applications in photovoltaic and optoelectronic devices. H Matsuo et. al. have studied $AgInSe_2$ films grown by thermal evaporation technique by taking Ag_2Se and In_2Se_3 as starting materials [4]. P.P. Ramesh et. al observed an efficiency of 7.5 % p-$AgInSe_2$ /n-CdS solar cell in which $AgInSe_2$ is used as absorber material [5]. The number of techniques such as flash evaporation [6], r.f. sputtering [7], thermal evaporation [8,9,10] , solution growth [11, 12] ,hot press [13],hot wall method [14] and pulse laser ablation [15-16] have been used for the preparation of $AgInSe_2$ films under different experimental conditions .These techniques have advantages and disadvantages depending on the type of application intended for the films. In this communication a hot wall technique is exploited for the preparation of $AgInSe_2$ films on Si (100) kept at 135^{0}C. The hot wall has an advantage to deposit the films at very low temperature which opens the possibility of growth even on polymers as well as on already processed substrates. This technique has also been successfully exploited for the preparation of $CuAlSe_2$ [17] ,$Cu(InGa)S_2$ [18], $CuInSe_2$ [19], $AgInTe_2$ [20] and organic semiconductors [21-25]. Such materials bear the possibility for the monolithic integration of semiconductors with direct band-gaps into Si technology. However, it is well known that the performance of such heterojunction devices depends critically on the interface between epilayer and substrate as well as the morphology and structure of the grown films. Heteroepitaxy is a kind of epitaxy performed with materials that are different from each other. Here, the ternary system AIS is explored which offers the possibility to grow lattice matched layers, in order to reduce the density of mismatch driven defects like dislocations to a minimum.

In this communication an attempt has been made to grow $AgInSe_2$ films on Si substrates with (100) orientation by hot wall technique in order to gain insight into the influence of the lattice matching on the morphology and properties of samples. The structural and optical properties of heteroepitaxial silver indium selenide films on Si (100) grown has been investigated.

2. Experimental

Hot wall has been proved as very successful growth method for thin film deposition. A quartz tube [fig 1] with the source material at the bottom, the substrate on the top closing it tightly and the in between region called hot wall, is heated with three different heaters. The hot wall guaranties uniform flux, less wastage of material and deposition to take place near to thermodynamic equilibrium, hence growth at low substrate temperature.

The silver indium selenide was synthesized from high purity (99.999%), silver , indium and selenium obtained from Thomas Baker (India) ,CDH(India) and Nuclear Fuel Complex (India), respectively. 3.078 g of silver, 3.282 g

of indium and 4.716 g of selenium were taken in evacuated quartz ampoule at pressure of 1.3 x 10^{-3} m bar and heated at 850^0C in horizontal furnace for 48 hours and then broken in ice cooled water. The product so obtained was powdered and again sealed in quartz ampoule for retreatment for 24 hours to ensure the homogeneity of the product. The ampoule was then quenched in ice cooled water and the material was powdered to 150-mesh size. The homogeneity of the alloy was confirmed by the X ray diffraction. The films were prepared by hot wall set as shown in Fig 1.

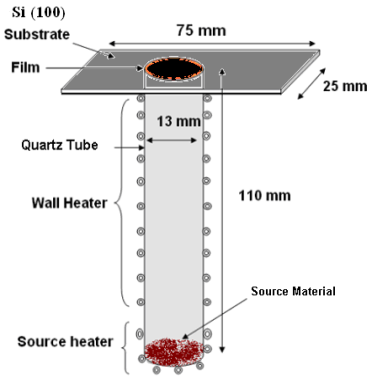


Fig. 1. Systematic diagram of hot wall deposition system.

It consists of heated linear quartz tube which serve to enclose and direct vapors from source to substrate. The kanthal wire wounded along the length of the quartz tube was used to heat the wall. Separate three heaters were used to heat the source, wall of the tube and the substrate. The substrate was held on the open end of quartz tube. The bottom of the quartz tube was filled with prepared AIS powder and the whole arrangement placed inside the vacuum chamber. A pressure of 10^{-5} Torr was achieved prior to the growth of films. $AgInSe_2$ films were grown by hot wall technique onto the Si (100) substrate. The silicon substrate was etched in dilute HF (2-3%) solution and rinsed in deionized water. The substrate was then cleaned ultrasonically with trichloroethylene and placed in vacuum chamber of coating unit. The Si substrates were mounted on the substrate holder with heating arrangement and the temperature was measured with the help of K-type thermocouple obtained from Omega Engineering Inc. (USA). AIS films have been deposited in quartz tube of length 110 mm and diameter 13mm with different source and wall temperature. Due to heat radiations from hot wall, the substrate temperature was found to increase suggesting that the film deposition at room temperature could not be possible. The films were grown onto the Si (100) substrate kept at 135^0 C. The temperature of different regions was measured with the help of K-type thermocouple obtained from Omega Engineering Inc. (USA). The thickness of the films was measured using a depth profiler (Dektek 3030, XT)

The optical studies were carried out on AIS films grown on Si substrate using reflection data. The structural properties of AIS films were investigated by means of XRD scans taken using Cu Kα (wavelength =1.5405 A^0) radiations in 2θ range 20^0-80^0 by Bruker diffractrometer. The reflection spectra of $AgInSe_2$ films deposited on Si(100) substrate were measured in the wavelength range 200-1100 nm using UV-VIS spectrophotometer (Perkin-Elmer). The surface morphology of $AgInSe_2$ films was studied by Atomic force microscope (NT-MDT: Ntegra). Field Emission Scanning Electron Microscopy (FEI QUANTA - 200F) has been used to study the distribution of grains

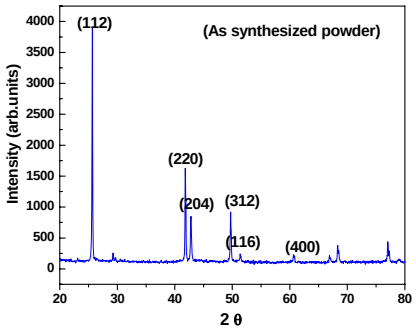


Fig. 2. XRD pattern of as prepared powder.

3. Results and discussion

The XRD profile spectra of the chalcopyrite Silver Indium Selenide (AIS) powder sample is shown in Fig 2. It shows that the AIS powder is polycrystalline in nature and exhibit (112) as dominant peak along with the peaks of low intensity corresponding to reflections from (204), (220), (312), (400) and (116) planes [6, 13]. XRD pattern of $AgInSe_2$ films prepared by hot wall set up on Si (100) substrate kept at 135^0C is shown in figures 3. The films grown indicate intense peak corresponding to reflection (400) [ASTM card no.35-1099]. It is interesting to note the disappearance of (112) peak completely. A few reflex of negligibly small intensity of impure phases corresponding to In_2Se_3 and Ag_2Se are also observed. This suggest that the film is highly oriented in (400) direction showing the growth of epitaxial AIS layers on Si (100). A sharp peak close to 69.1^0 has been observed which is assigned to Si (100) reflection. Similar peak has also been noticed for preparation of $CuInSe_2$ films on Si (100) wafers.[26] Considering the lattice constant of Si (5.45 A^0) and AIS (a=6.10 A^o and c= 11.645A^o), AIS may grow on Si (100) along the a - axis with small strain contributing the growth of AIS along (400) direction. According to ASTM cards, the 2 θ value for Chalcopyrite AIS (400) is 60.6^0, Sphalerite (ZnS-type: High Pressure Form) AIS (400) is 61.3^0. These are smaller than the observed peak at 2θ, 61.55^0 as shown in Fig. 3. This can be explained due to decrease in stress/strain because of lattice matching between AIS and Si (100) which results in shifting the peak to higher 2θ value.

The epitaxial growth of films may be attributed to the significant lowering of the energy of film substrate system [9] due to lattice matching between AIS and Si (approx. 91%). In the earlier reported [9] work we have observed the mixed region of polycrystallinity as well as epitaxy for AIS films deposited by thermal evaporation on Si (100) substrate. Hot wall method appears to improve the epitaxial growth due to the fact that it allow high ad atoms

mobility which results the formation of a well ordered structure[27].Similar observations have also been observed for CdTe deposited on Si(100) by hot wall method [28,29]. The crystallite size of films was calculated using Scherer's equation [30]

$$D = k\ \lambda / \beta \cos\theta \qquad (1)$$

where k is shape factor of crystallites which provides information about roundness of particles, λ is the wavelength of X-rays , β is full width half maximum (FWHM) in radian, θ is Bragg angle. Shape factor is given by

$$\text{Shape Factor, } k = 4\pi.(\text{area}) / (\text{perimeter})^2 \qquad (2)$$

which is 1 for spherical crystallites and less for others. Depending upon the shape of crystallites in AIS films deposited on Si (100) substrate shape factor is calculated around k = 0.9 and is used to determine the crystallite size. The size of crystallites calculated along (400) reflex has been found around 99 nm. The FWHM can be interpreted in terms of lattice strain and average crystallite size, which can be expressed by the following Hall equation [31]

$$\beta \cos\theta / \lambda = 1/D + \varepsilon \sin\theta / \lambda \qquad (3)$$

where D is the effective crystallite size and ε is the effective strain. The Hall equation for the different phases of the films which corresponds to different peak positions, is plotted in Fig. (4).The average crystallite size using this equation that include average size and magnitude of strain is found to be 20 nm. Also the strain determined from the slope of the curve is estimated around 0.0107.

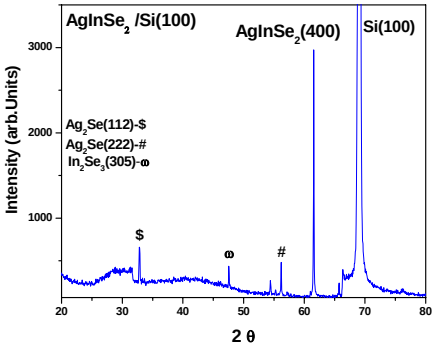


Fig. 3. XRD pattern of film prepared at Ts 135^{0}C by Hot wall technique.

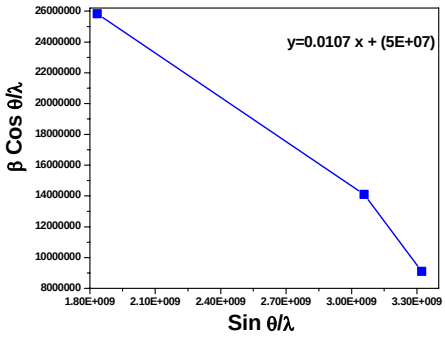


Fig. 4. Plot of Hall equation for deposited films.

Fig. 5 shows Field Emission Scanning Electron Micrograph (FESEM) of the grown $AgInSe_2$ films on Si (100) substrate kept at 135^0 C.

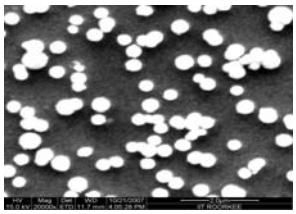


Fig. 5. FESEM photograph of prepared at Ts 135^{0}C by Hot wall on Si(100).

It reveals the growth of films with grains of nearly spherical symmetry. The grain size distribution appears to be uniform and continuous. The additional thermal energy supplied by the hot wall to the particles colliding on it helps its migration towards substrate resulting the growth of highly uniform films comparatively at low substrate temperature [32]. Also the growth of AIS films deposited by hot wall set up takes place very near to thermo dynamical equilibrium. It has been suggested by Otero [27] that hot wall technique permits film deposition near thermo dynamical equilibrium.

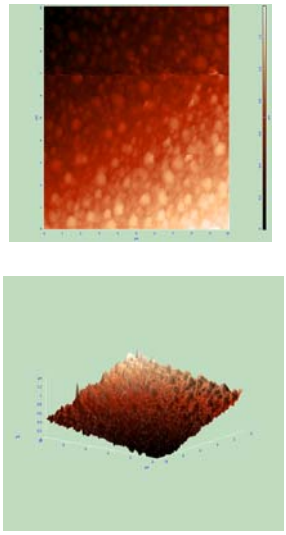


Fig. 6. (a) and (b) 2D and 3D AFM image of $AgInSe_2$ films prepared by hot wall technique.

The surface morphology of hot wall grown films onto the Silicon wafers kept at 135^{0}C was studied using digital multimode operated AFM in tapping mode. Fig. (6 a, b) shows 2D and 3D, 5 µm x 5µm images of 1 µm thick sample .Investigations point out the uniformity of the AIS coatings on the Si substrates. It has been observed that the surface topography of the AIS deposits is continuous, smooth with densely packed grains having dumbbell like growth. The surface morphology shows a roughness of about 240 nm which is comparatively less than that of the films deposited by thermal evaporation technique [9]. However the roughness is found to be larger than those prepared by Pulse laser deposition technique [15]. It is interesting to note that the surface of the films contain good morphology well suited for solar cell applications. It is believed [33] that the rough surfaces encourage

reduction in reflectance and trapping of photons within the film due to scattering at the surface.

The Reflectance spectra of films recorded in the energy range 1.1- 2.1eV show two absorption humps in the photon energy range 1.25 > hν > 1.48 eV and 1.7> hν.> 2.1eV as shown in Fig. 7.

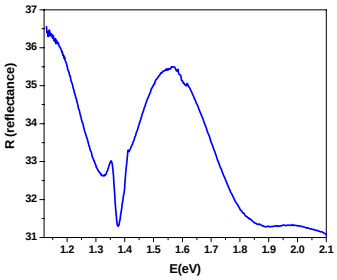
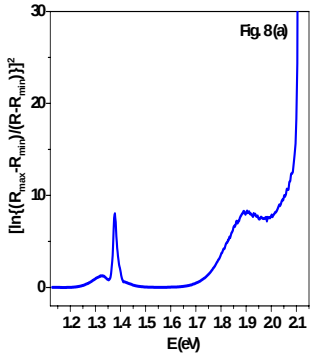


Fig. 7. Reflectance spectra of AIS films deposited on Si (100) wafers.



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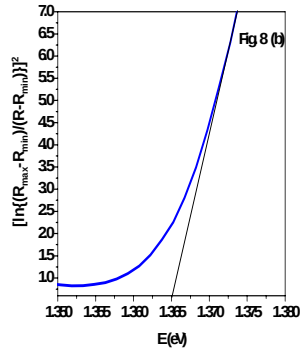

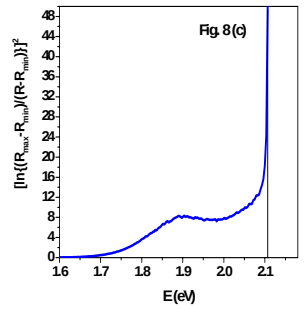

Fig. 8. Energy band gap of Hot wall deposited AIS films (a) complete spectrum (b) Eg_1 (c) Eg_2.

Silicon wafers show very high absorption coefficient in the energy range 1.1-3 eV[34,35] So optical studies for AIS films has been performed by using reflectance data. The absorption coefficient for direct band gap materials can be represented with reflection parameters using the relation [36]

$$2\alpha t = \ln\left[\frac{(R_{\max} - R_{\min})}{R - R_{\min}}\right] \quad (4)$$

where R is the reflectance and is given by R =I/I_0. For a direct band gap material, the absorption

Coefficient is determined as [37]

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^{1/2} \quad (5)$$

where A is a constant which is different for different transitions. From Eqs. (4) and (5) it is clear that there is a proportionality relation between ln $((R_{max}-R_{min})/(R-R_{min}))$ and α ,where R_{max} and R_{min} are the maximum and minimum reflectance in reflection spectra and R is the reflectance for any intermediate energy photons. As in case of absorption spectra, we plot a graph between $(\alpha h\nu)^2$ (as ordinate) and hν (as abscissa), a straight line is obtained. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the direct band gap. Similarly here we plot a graph between hν (abscissa) and the square of ln $((R_{max}-R_{min})/(R-R_{min}))$ and as ordinate we can got the band gap of semiconductor. Figure 8(a) show complete absorption spectrum of AIS films deposited on Si (100). It indicate the existence of two absorption humps for this chalcopyrite material .The extrapolation of linear portion gives the value of optical band gap Eg_1 under direct allowed transition for $AgInSe_2$ films (Fig. 8 (b)). The second hump has been observed in the energy range 1.7 > hν > 2.1 with energy gap Eg_2 (Fig. 8 (c)) which is due to the transition from crystal field split valance band that result from interaction between the valance electron and the non-cubic crystal field of chalcopyrite to the conduction band minimum. The increase in optical band gap for these nearly epitaxial $AgInSe_2$ films deposited on Si(100) as compared with those deposited on glass substrate [14] by hot wall technique may be attributed due to the reduction of defects like dislocations to a minimum which give comparatively less contribution to the absorption. It can be deduced that two characteristic band gaps for AIS were found. These results are in good agreement with those reported for other chalcopyrites like $AgGaSe_2$ [38] and $AgGaTe_2$ [39]

4. Conclusions

In summary, AIS has been grown epitaxially on Si (100) substrates by hot wall vacuum deposition method. It is found that AIS crystallizes exclusively in the chalcopyrite structure with lattice parameters very close to the literature values for bulk samples. Such a low temperature processing of films has not been reported earlier for $AgInSe_2$ and opens the possibility for the growth on pre-processed substrates containing electronic circuits and on polymers. The AIS films appear to be highly textured along (400) direction and show comparatively high degree of crystallinity as compared to those obtained by thermal evaporation technique. Two

characteristics band gaps 1.36 eV and 2.11eV of these epilayers have been observed, which may be assigned to fundamental edge and transition originating from crystal field splitting, respectively. Interestingly, the surface roughness of AIS films deposited by hot wall set up is found to be less than that of thermally evaporated ones. These results may be of interest for better understanding of epitaxial growth of chalcopyrite films at low temperature.

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