

Photoconductive properties of pulse plated $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ films

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Abstract: $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ thin films of different composition were deposited at 50 % duty cycle by the pulse electrodeposition technique. The films were polycrystalline possessing single phase chalcopyrite structure. The lattice parameters were observed to change from AgInSe_2 to AgGaSe_2 side as the gallium concentration increased. The microstructural parameters were determined. The composition of the films was nearly same as the composition of precursors used. The grain size increases as the gallium content increases and surface roughness increases from 0.25 nm to 3.5 nm with increase of gallium content. Photoconductive studies on the films indicated the films to exhibit photoactivity.

Keywords - I-III-VI₂, electronic material, semiconductor, thin films.

I. INTRODUCTION

AgInSe_2 and AgGaSe_2 have proved to be stable and efficient absorber materials for fabricating polycrystalline thin film heterojunction solar cells [1]. These ternary chalcopyrite compounds are direct band gap semiconductors showing a three-fold optical structure [2] near the fundamental edge due to crystal-field and spin-orbit splitting of the upper most valence band. Studies on $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ thin films as absorber material are still more attractive, since they allow tailoring of the optical band gap and other properties. By gradually substituting indium by gallium, the optical band gap can be increased from 1.25 to 1.75 eV. The number of reports on $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ thin films is very scanty. The flash evaporation technique has been mainly employed for the deposition of these films. This is the first report on pulse electrodeposited $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ thin films. In this work, structural, morphological and photoconductive properties of $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ are reported and discussed.

II. MATERIALS AND METHODS

$\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ films were deposited by the pulse electrodeposition technique at room temperature from a bath containing Analar grade 10 mM silver nitrate, gallium nitrate, indium nitrate and 10 mM SeO_2 . The concentration of gallium nitrate and indium nitrate was varied as indicated in TABLE -1. The deposition potential was maintained as -0.68 V (SCE). Tin oxide coated glass substrates (5.0 ohms/sq) were used as the substrate. The duty cycle was kept constant as 50 %. Thickness of the films measured by surface profilometer increased from 500 to 1000 nm as the gallium concentration increased. Structural, electrical and photoconductive properties were studied. Structural characteristic was studied by using Philips x-ray diffraction unit. using $\text{CuK}\alpha$ radiation. Surface morphology was studied by using molecular imaging systems Nanoscope E-3138J AFM/STM atomic force microscope. Photoconductive measurements were made

In pulse electrodeposition [3] the potential or current is alternated swiftly between two different values. This results in a series of pulses of equal amplitude, duration and polarity, separated by zero current. Each pulse consists of an ON-time (T_{ON}) during which potential and current is applied, and an OFF-time (T_{OFF}) during which zero current is applied. It is possible to control the deposited film composition and thickness in an atomic order by regulating the pulse amplitude and width [4]. They favour the initiation of grain nuclei and greatly increase the number of grains per unit area resulting in finer grained deposit with better properties than conventionally plated coatings. The sum of the ON and OFF times constitute one pulse cycle. The duty cycle is defined as follows:

$$\text{Duty Cycle (\%)} = (\text{ON time}) / (\text{ON time} + \text{OFF time}) \times 100 \text{ ----- (1)}$$

A duty cycle of 100% corresponds to conventional plating because OFF time is zero. In practice, pulse plating usually involves a duty cycle of 5% or greater. During the ON time the concentration of the metal ions to be deposited is reduced within a certain distance from the cathode surface. This so-called diffusion layer pulsates with the same frequency as the applied pulse current (i_p). Its thickness is also related to i_p but reaches a limiting value governed primarily by the diffusion coefficient of the metal ions. During the OFF time the concentration of the metal ions build up again by diffusion from the bulk electrolyte and will reach the equilibrium concentration of the bulk electrolyte if enough time is allowed. These variables result in two important

characteristic features of pulse plating which make it useful for alloy plating as well as property changes as mentioned earlier.

(i) Very high instantaneous current densities and hence very high negative potentials can be reached. The high over potential causes a shift in the ratio of the rates of reactions with different kinetics. This high over potential associated with the high pulse current density greatly influences the nucleation rate because a high energy is available for the formation of new nuclei.

(ii) The second characteristic feature is the influence of the OFF time during which important adsorption and desorption phenomena as well as recrystallization of the deposit occurs.

Pulse plating technique has distinct advantages compared to conventional electrodeposition namely, crack free, hard deposits and fine grained films with more uniformity, lower porosity and better adhesion. It is well known that by using pulse current for electrodeposition of metals and alloys it is possible to exercise greater control over the properties of electrodeposits and to improve them by modifying their microstructures [5]. It has been reported that a significant reduction in internal stress could be obtained when pulse current was used, compared to the use of conventional direct current [6]. pulsed electrodeposition improved the hardness compared to direct current deposits [7].

Table. 1
Concentration of Gallium nitrate and Indium nitrate in the deposition bath to obtain AgGa_xIn_{1-x}Se₂ films of different composition

Composition(x)	concentration of gallium nitrate(mM)	concentration of indium nitrate (mM)
0.1	2.0	18.0
0.2	4.0	16.0
0.3	6.0	14.0
0.4	8.0	12.0
0.5	10.0	10.0
0.6	12.0	8.0
0.7	14.0	6.0
0.8	16.0	4.0
0.9	18.0	2.0

III. RESULTS AND DISCUSSION

Fig.1 shows the x-ray diffraction (XRD) pattern of AgGa_xIn_{1-x}Se₂ films of different composition deposited at 50 % duty cycle. All the XRD peaks observed in the films were corresponding to the diffraction lines from AgGa_xIn_{1-x}Se₂ and no peaks were found from GaSe – Ga₂Se₃ or InSe–In₂Se₃ phases. All of the thin films were strongly oriented to the (112) plane. Peaks corresponding to the (112),(204),(312) planes of the chalcopyrite phase was observed in all cases. The lattice parameters 'a' and 'c' were calculated from the diffraction spectra using the built in software. The lattice parameters 'a' and 'c' increase with increase in gallium content. Fig.2 shows the variation of 'a' and 'c' with increase of gallium content.

The crystallite size was calculated using the Scherrer's equation

$$\text{Crystallite size (D)} = 0.9 \lambda / \beta \cos\theta \dots\dots\dots(1)$$

where, λ is the wavelength of x-ray (CuK α radiation), β is the full width at half maximum (FWHM) of the x-ray diffraction peak. The values of crystallite size and thickness are shown in Table.2. The crystallite size decreases with increase of Indium content.

The composition of films was confirmed by energy dispersive analysis of X-ray technique (EDAX). The composition of the films is shown in Table.3. Based on the defect chemistry model of ternary compounds [8], compositional deviations of the AgGa_xIn_{1-x}Se₂ can be expressed by non-stoichiometry parameter ($\Delta y = [2\text{Se}/\{\text{Ag} + 3(\text{In} + \text{Ga})\}] - 1$). The parameter Δy is related to the electronic defects. For $\Delta y > 0$, the film has a p-type conductivity and it has an n-type conductivity for $\Delta y < 0$. In this study the value of Δy is greater than zero and the films exhibit p-type conductivity. Table.3 shows the composition of the films of different composition.

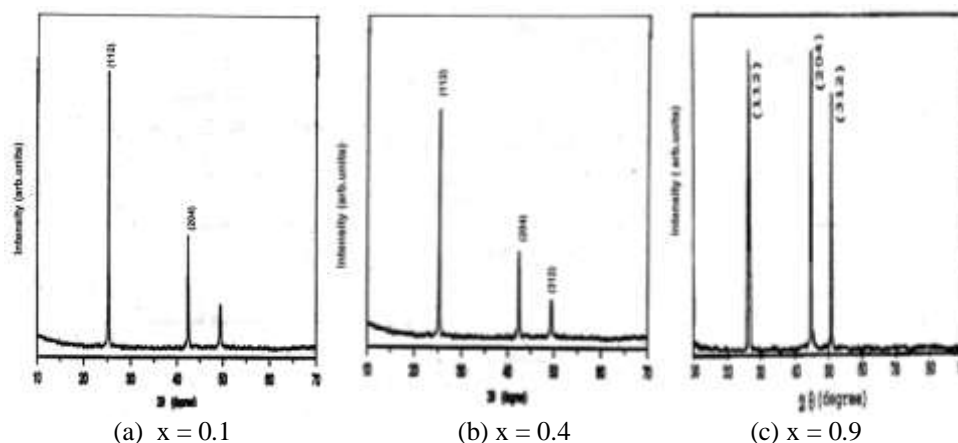


Figure.1 – X-ray diffraction pattern of $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ films of different composition deposited at 50 % duty cycle

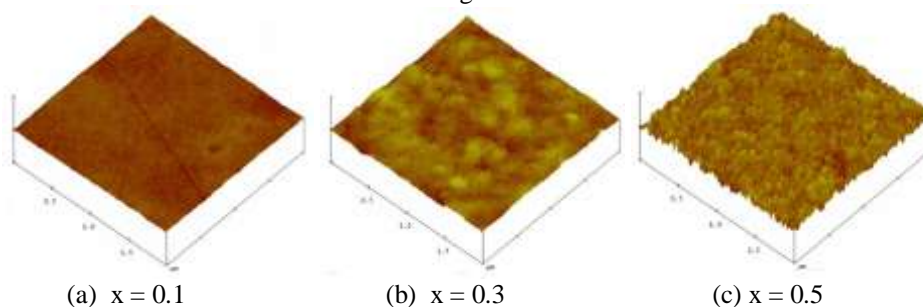
Table.2
Variation of crystallite size with composition

Comp(x)	Crystallite size(nm)
0.1	50
0.2	70
0.3	85
0.4	97
0.5	104
0.6	109
0.7	114
0.8	120
0.9	128

Table – 3
Composition of $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ films deposited at 50 % duty cycle

Comp (x)	Ag (at%)	Ga (at%)	In (at%)	Se (at%)	Ag/(Ga + In)	2Se/[Ag + 3(Ga + In)]
0.1	27.05	3.25	20.15	49.55	1.16	1.01
0.2	26.80	3.55	19.80	49.85	1.14	1.02
0.3	26.55	4.50	19.47	49.48	1.14	1.005
0.4	26.00	6.54	17.45	50.01	1.08	1.02
0.5	25.90	8.10	15.95	50.05	1.07	1.02
0.6	25.74	10.25	14.07	49.94	1.06	1.01
0.7	25.70	12.65	11.37	50.28	1.07	1.03
0.8	25.60	14.78	9.65	49.97	1.05	1.005
0.9	25.40	18.34	6.17	50.09	1.04	1.01

Fig.2 shows the Atomic force micrographs of the $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ films of different composition, deposited at 50 % duty cycle. It is observed that the morphology of the films are very smooth without any pin holes. Grain size increase is observed as the Ga concentration increases. This is supported by the XRD results where the grain size increases from 50 – 150 nm as the gallium concentration increases. The rms value of surface roughness increases from 0.25 nm – 3.5 nm as the gallium concentration increases.



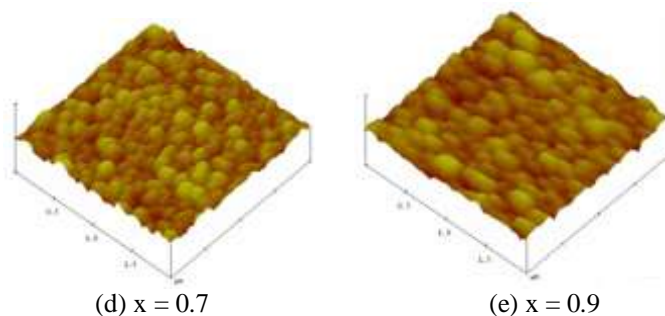


Figure.2 - Atomic force micrographs of $\text{AgGa}_x\text{In}_{1-x}\text{Se}$ films deposited at 50 % duty cycle (2.0 μm x 2.0 μm) (Z - 1 div - 150 nm)

Various crystalline imperfections in the film, such as vacancies, dislocations and grain boundaries act as trapping or recombination centers of the carriers and play an important role in photoconduction. These traps act as localized positive potential centers for electrons and negative potential centers for holes. Therefore some localized discrete energy levels are formed in the band gap, in the vicinity of the conduction and valence bands respectively. Fig.3 shows the variation of photocurrent with light intensity of $\text{AgIn}_{1-x}\text{Ga}_x\text{Se}_2$ films deposited at different duty cycles. The photocurrent is found to increase with an increase of duty cycle due to increase in film thickness and light intensity. As the thickness of the film increases the crystalline nature increases and this helps in the improvement of photocurrent. The increase in photocurrent is attributed to an increase in the majority carrier concentration and/or an increase in impurity centers acting as traps for minority carriers. The variation of photocurrent with applied voltage in $\text{AgIn}_{1-x}\text{Ga}_x\text{Se}_2$ films is shown in Fig. 4. The photocurrent increases with an increase in voltage.

Photosensitivity is the ratio of the increase in conductivity of the material in the presence of light to the conductivity in darkness and is given by the relation:

$$\text{Photosensitivity} = \Delta\sigma / \sigma = (I_L - I_d) / I_d \dots\dots\dots(2)$$

where I_L and I_d represent the current under illumination and in the dark respectively. It seems that some transitions that create additional free carriers effectively increase the free life time increasing the photosensitivity of the material. Fig.5 shows a plot of photosensitivity versus light intensity of $\text{AgIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin films. Thinner films exhibit moderate photosensitivity, whereas thicker films are found to exhibit higher photosensitivity. Crystallographical imperfections acting as trapping centers will enhance the photosensitivity, whereas the recombination centers decrease the photosensitivity.

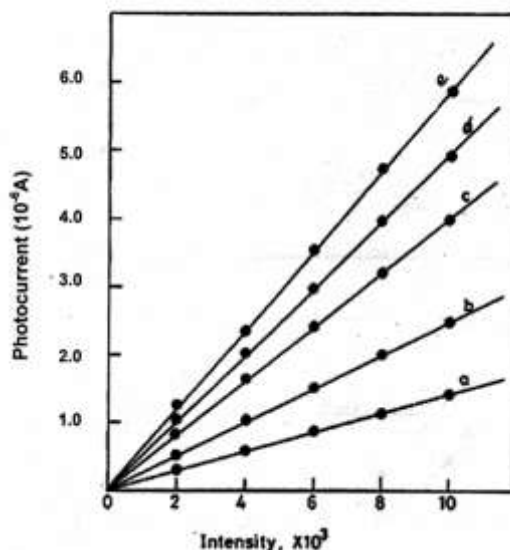


Fig.3 – Variation of photocurrent with intensity of $\text{AgIn}_{1-x}\text{Ga}_x\text{Se}_2$ films of different composition (a) $x = 0.1$ (b) $x = 0.3$ (c) $x = 0.5$ (d) $x = 0.7$ (e) $x = 0.9$

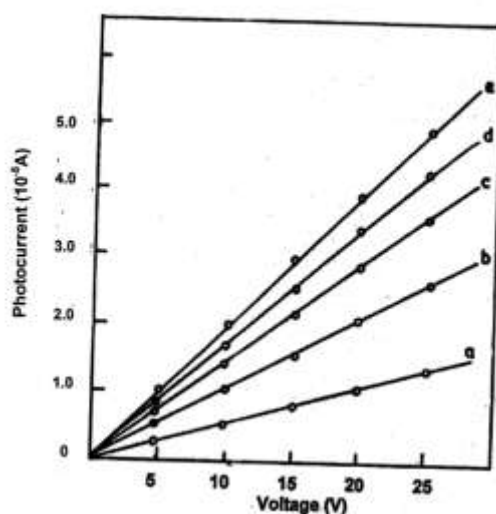


Fig.4 – Variation of photocurrent with voltage of $\text{AgIn}_{1-x}\text{Ga}_x\text{Se}_2$ films of different composition (a) $x = 0.1$ (b) $x = 0.3$ (c) $x = 0.5$ (d) $x = 0.7$ (e) $x = 0.9$

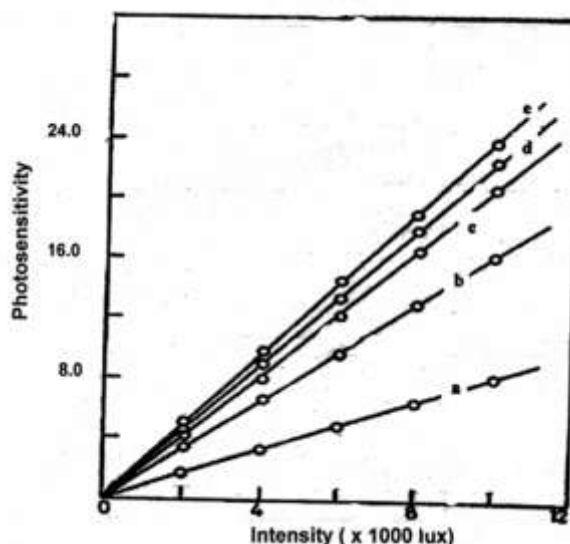


Fig.5 – Variation of photosensitivity with intensity of $\text{AgIn}_{1-x}\text{Ga}_x\text{Se}_2$ films of different composition (a) $x = 0.1$ (b) $x = 0.3$ (c) $x = 0.5$ (d) $x = 0.7$ (e) $x = 0.9$

IV. CONCLUSIONS

The results of this investigation clearly points to the possibility of depositing nanocrystalline films with grain size in the range of 50 – 128 nm. Films with resistivity in the range of 21 ohm cm – 710 ohm cm. Films exhibiting photoconductive response can be obtained.

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