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Synthesis and characterization of ZnS_xSe_{1-x} films using Brush plating technique

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Abstract

ZnS_xSe_{1-x} films possess several interesting properties making them suitable for use in optoelectronic and optical applications. In this investigation, thin ZnS_xSe_{1-x} films were deposited for the first time by the brush plating technique. Thin films of $ZnSxSe_{1-x}$ were deposited at a constant current density of 80 mA cm^{-2} on titanium and conducting glass substrates at different temperatures in the range of 30 - 80°C. The precursors used were AR grade $ZnSO_4$, sodium thiosulphate and sodium selenosulphate. XRD patterns of the films of different composition deposited at different temperatures exhibited hexagonal structure. An absorption coefficient of 10^4 cm^{-1} was observed. Extrapolation of the linear region to the hν axis yields the band gap in the range of 2.64 – 3.58 eV for the films deposited at different temperatures. EDAX study indicated that the composition of the films obtained were nearly equal to the composition of the precursors taken for deposition. X-ray photoelectron spectroscopy studies on the films of different composition deposited at 80°C. showed the spectra of Zn (2p), Se ($3p_{1/2}$ and $3p_{3/2}$) and S (2p) levels. Atomic force microscope studies indicated that the surface roughness of the films increase from 1.04 – 5.45 nm as the ZnSe concentration increased. The grain size increases from 15 nm – 40 nm as the concentration of ZnSe increased.

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Keywords: Films,Brush Plating, current density, size, concentration

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1. Introduction

ZnS_xSe_{1-x} films possess several interesting properties making them suitable for use in optoelectronic and optical applications. They are used in semiconductor lasers as waveguide layers [1] and has host materials for luminescent centers in electroluminescent devices [2]. Methods used to grow ZnS_xSe_{1-x} films include molecular beam epitaxy [3], metal organic chemical vapor deposition [4] and atomic layer epitaxy [5]. In this investigation, thin ZnS_xSe_{1-x} films were deposited for the first time by the brush plating technique.

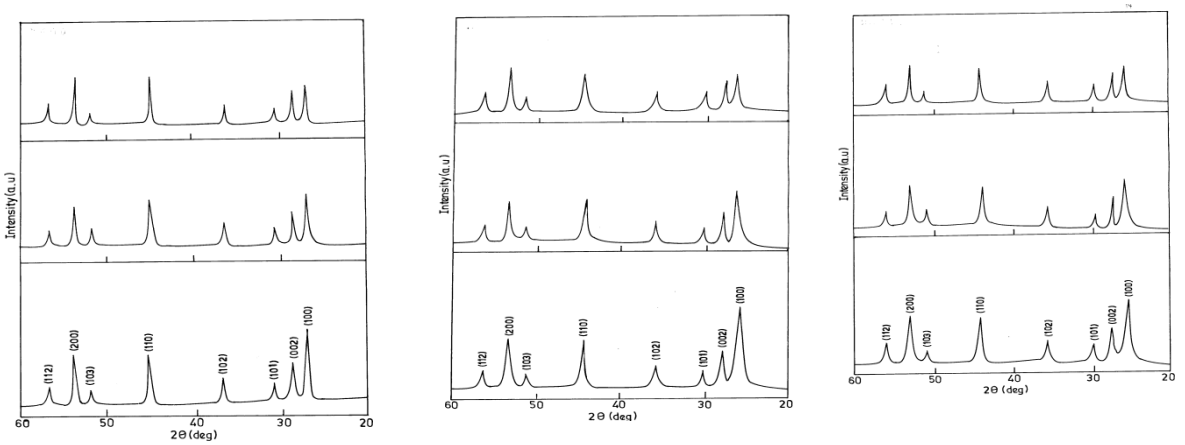
An electroplating process performed with hand held portable tool rather than a tank of solution is known as brush plating. The brush plating processes are also called as contact plating, selective plating or swab platting. This is essentially a plating method, deposition of a metal on the surface by electrochemical means, where the work is connected catholically to the current source. The plating is then applied by means of a brush or swab, soaked with solution and connected to a flexible anode cable. A direct current power pack drives the electrochemical reaction, depositing the desired metal on the surface of the substrate. In practice, movement between the anode and cathode is required for optimum results when plating, stripping, activating and so on. Currently a broad range of metals can be plated by brush plating. The key advantage of selective plating is portability.

2. Experimental Methods

Thin films of $ZnSxSe_{1-x}$ were deposited at a constant current density of 80 mA cm^{-2} on titanium and conducting glass substrates at different temperatures in the range of 30 - 80°C. The precursors used were AR grade $ZnSO_4$, sodium thiosulphate and sodium selenosulphate. Sodium selenosulphate was prepared by heating a solution of selenium powder in sodium sulphite for 8 hours. The concentration of $ZnSO_4$ solution was kept constant at 0.2M, to obtain different compositions of the film, the concentration of selenosulphate and thiosulphate were varied in the range of 0 mM – 50 mM and 50 mM – 0 mM. The thicknesses of the films measured by Mitutoyo surface profilometer are in the range of 1.0 to 1.5 micrometers with increase of deposition temperature.

3. Results And Discussion

The XRD patterns of the films of different composition deposited at different temperatures are shown in the Fig.1. The peaks corresponding to (100), (002), (101), (102), (110), (103),(200) and (112) reflections were observed in all cases.



(a) (b) (c)

Fig. 1. - X-ray diffraction pattern of ZnS_xSe_{1-x} films deposited at different temperatures (a)30°C; (b)60°C;(c)80°C

The diffraction peak shifts towards higher angles with increasing *x*, indicating that the lattice constant decreases with S concentration. This is demonstrated in Fig.2 as a shift in the (002) orientation of the films. All the samples exhibited hexagonal structure and the lattice parameters 'a' and 'c' were calculated using the standard relation. The calculated values of 'a' and 'c' for ZnSe and ZnS are in good agreement with the ASTM data.

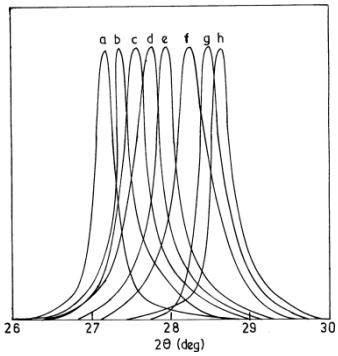


Fig.2.- Shift of the (002) peak composition of ZnS_xSe_{1-x} films (a) x = 0.1 (b) x = 0.2 (c) x = 0.3 (d) 0.4 (e) 0.5 (f) 0.7 (g) 0.8 (h) 0.9

A linear variation of the lattice constants with composition indicates that Vegard's law is obeyed. The films after heat treatment in argon atmosphere at different temperatures in the range 450 - 550°C, exhibited the same peaks as in the case of the as deposited films for all the compositions, but the crystallinity of the XRD patterns improved resulting in decrease of the FWHM of the peaks. The crystallite size, dislocation density, stress etc were calculated from the XRD data and are indicated in Table -1. It is observed that the dislocation density increases with increase in concentration of ZnSe.

Table1. Crystallite size, strain and dislocation density of the as deposited ZnS_xSe_{1-x} films of different composition deposited at 80°C

Composition(x)	Crystallite size(nm)	Strain(ε) x 10^{-4}	Dislocation density(δ) (x 10^{14} lines/m)
0.1	38	1.51	1.5
0.3	32	2.36	2.8
0.5	26	2.51	3.7
0.7	18	2.28	4.9
0.9	12	1.80	5.9

Optical absorbance measurements were made on the films deposited on conducting glass substrates in the wavelength range 300 – 900 nm at room temperature to ascertain the nature of the band gap. Substrate absorption, if any was corrected by placing an identical uncoated tin oxide substrate in the reference beam. The absorption co-efficient(α) at various wavelengths has been calculated using standard relation. Fig.3 shows the transmission spectra of the films of different composition. The films exhibited 80% transmission.

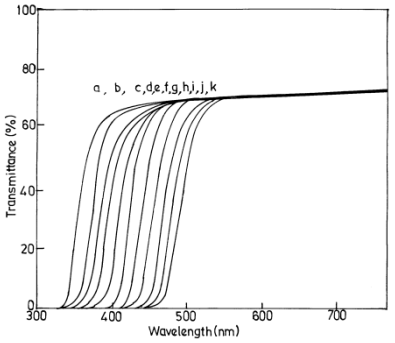


Fig.3 - Transmission spectra of ZnS_xSe_{1-x} films deposited at 80°C (a) x = 1.0 (b) x = 0.9 (c) x = 0.8 (d) x = 0.7 (e) x = 0.6 (f) x = 0.5(g) x = 0.4 (h) x = 0.3 (i) x = 0.2 (j) x = 0.1 (k) x = 0

The band gap of the films was determined by plotting a graph between $(\alpha h\nu)^2$ vs hν. Extrapolation of the linear region to the hν axis gives the band gap of the material. Fig.4 shows the $(\alpha h\nu)^2$ vs hν graph for the films of different composition deposited at 80°C. An absorption coefficient of 10^4 cm^{-1} was observed. Extrapolation of the linear region to the hν axis yields the band gap in the range of 2.64 – 3.58 eV for the films of different composition deposited at 80°C. The value of the bandgap for the films are in good agreement with the literature values [6,18]. The variation of band gap with composition is shown in Fig.5, it is non-linear, similar type of behaviour has been reported for ZnS_xSe_{1-x} films deposited by Atomic layer epitaxy and by sintering techniques [7,12,6,18].

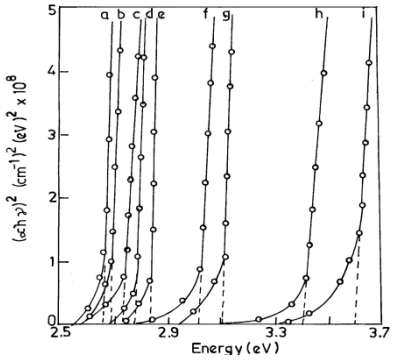


Fig.4 - $(\alpha h\nu)^2$ vs hν plot of the ZnS_xSe_{1-x} films deposited at 80°C a) x = 0.1 (b) x = 0.2(c) x = 0.3 (d) x = 0.4 (e) x = 0.5(f) x = 0.6 (g) x = 0.7 (h) x = 0.8 (i) x = 0.9

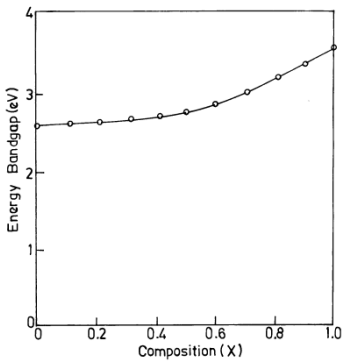


Fig.5-Variation of band gap with composition(x) in ZnS_xSe_{1-x} films

Composition of the films was found by EDAX measurements. Table.1 shows the composition obtained from the EDAX study. It is observed that the composition of the films obtained were nearly equal to the composition of the precursors taken for deposition.

X-ray photoelectron spectroscopy studies were made on the films of different composition deposited at 80°C. Fig.6 shows the XPS spectra of Zn (2p), Se ($3p_{1/2}$ and $3p_{3/2}$) and S (2p) levels for the films of different composition. As observed from the figures, the Zn(2p) peaks appeared in the range 1022.2 -1023.4 eV, the $Se2p_{1/2}$ and $Se2p_{3/2}$ appeared in the range 168.2 – 175.1 eV and 162.5 – 169.1 eV respectively and the S2p appeared in the range 162.1 – 168.2 eV as the x value changes from 0 to 1. These data agree with an earlier report[8] .Further, as the 'x' value increased, the area under the peak for S (2p) also increased and the area under the Se ($3p_{3/2}$) decreased. The values of the binding energy are observed to shift from ZnSe side to ZnS side as the concentration of ZnS in the films increases.

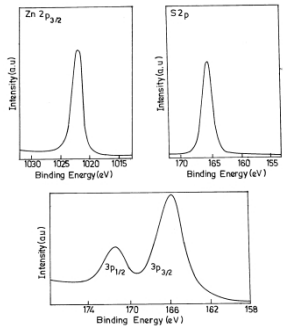


Fig.6 - XPS spectrum of $ZnS_{0.5}$ $Se_{0.5}$ films deposited at 80°C

Fig.7 shows the three-dimensional surface images of the ZnS_xSe_{1-x} films of different composition deposited at 80°C, these images were obtained on an area of 2.5 μm^2. As the ZnSe concentration increases, the amplitude of the surface modulations increase. The surface roughness of the films increase from 1.04 – 5.45 nm as the ZnSe concentration increased. The grain size increases from 15 nm – 40 nm as the concentration of ZnSe increased.

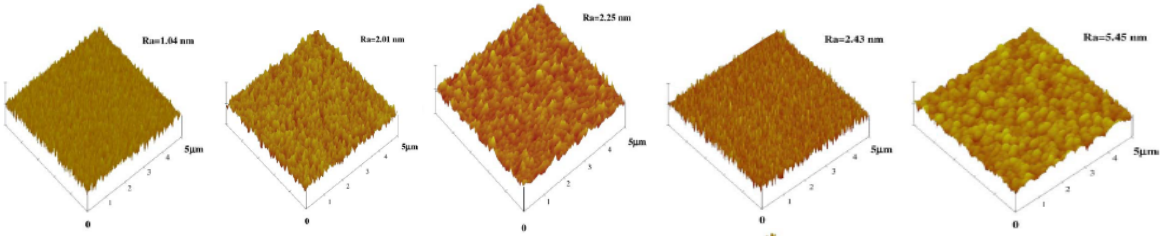


Fig.7 - Atomic force micrograph of ZnS_xSe_{1-x} films(a) x = 0,9 (b) x = 0.7(c)x = 0.5 (d) x = 0.3 (e) x = 0.1 (Z – 1000 nm) Area - 5µm x 5µm

Conclusions

Zinc sulpho selenide films have been deposited by brush plating technique. X-ray diffractogram of the films of different composition exhibit hexagonal structure. EDAX studies indicated the composition to be almost equal to the composition of the precursors taken for the growth of films. XPS study indicated the presence of S and Se in the ratio of the starting composition. The results of this study clearly suggest that thin films of $ZnSxSe1_{-x}$ of different composition can be easily deposited by the brush plating technique. Films with nano crystallites in the range of 15 – 40 nm and with surface roughness in the range of 1.04 – 5.45 nm can be deposited. Films with band gap in the range of 2.64 – 3.58 eV can be obtained.

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