

PULSE ELECTRODEPOSITED ZINC SELENIDE FILMS AND THEIR CHARACTERISTICS

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Zinc selenide (ZnSe) thin films were pulse deposited for the first time using polycyclic acid. The films exhibited hexagonal structure. The band gap of the films varied in the range of 2.7 – 3.1 eV as the concentration of silico-tungstic acid increased. Atomic force microscopy indicated grain size decreased from 60 – 15 nm after addition of silico-tungstic acid. Laser Raman spectrum exhibited LO phonons corresponding to ZnSe. The photoluminescence spectrum peaks at 675 nm. As the concentration of silico-tungstic acid increases, the PL emission peak shifts to shorter wavelengths.

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1. Introduction

ZnSe is a technologically important opto-electronic semiconducting material with a wide band gap of 2.7 eV. It can be substituted for CdS in photovoltaic solar cells [1]. There are several techniques for the growth of ZnSe thin films, but the deposition from aqueous solution is attractive due to the low cost, suitable for the commercial solar cell devices [2]. There are several reports available on the aqueous solution deposition technique such as chemical bath deposition [3] and electro-deposition [4 - 6] of ZnSe. In this work, the pulse electrodeposition technique has been employed for the first time to deposit ZnSe film in the presence of silicotungstic acid.

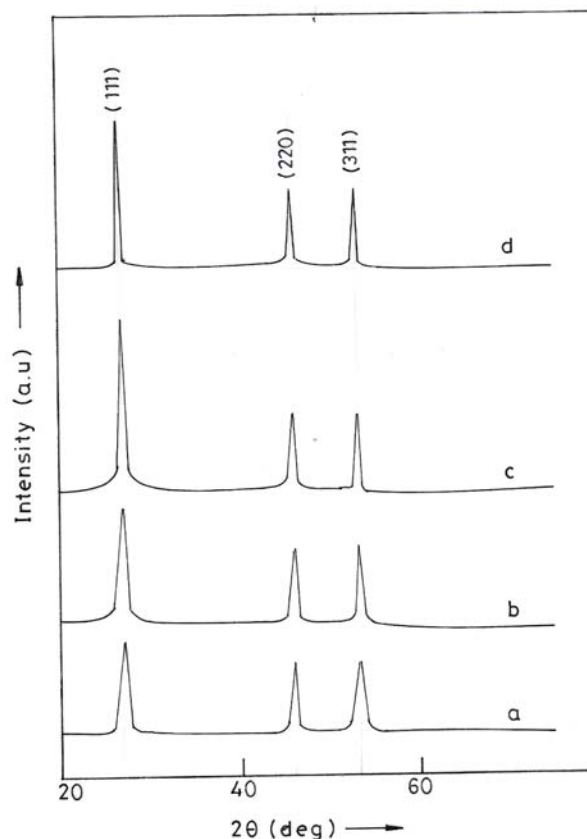
2. Experimental

Thin films of ZnSe were deposited by the pulse plating technique at a current density of 100 mA cm⁻² on titanium and conducting glass substrates at room temperature. The precursors used were 20 ml of 0.25M ZnSO₄ and 2 ml of 0.01M selenium di oxide, the concentration of silicotungstic acid was varied in the range of 0.01 mM – 0.1 mM. The duty cycle was varied in the range 6- 50%. The duration of deposition was 30 min. Thickness of the films estimated by the weighing method was in the range of 1.0 to 2.5 μm.

3. Results and discussion

XRD pattern of the films deposited at different duty cycles is shown in Fig.1. It is observed that the films exhibit cubic structure with peaks corresponding to the (111), (220) and (311) reflections. As the duty cycle increases the intensity of the peak corresponding to the (111) reflection increased, indicating the preferential orientation in this direction, the peaks

corresponding to the Ti substrate is absent. The thickness of the films increases from 1.5 to 2.5 μm as the duty cycle increases, due to the availability of a large flux of ions for deposition at every new pulse at higher duty cycles. At lower duty cycles, since the pulse is ON only for a short period, only a small flux of ions are available for deposition, moreover due to the application of a pulse for a short duration, the crystallite size is also small for lower duty cycles. This is evident from the broad peaks for the films deposited at lower duty cycles. As the duty cycle increases, the peaks become sharper due to improved crystallinity.



*Fig.1 - X-ray diffraction pattern of ZnSe films plated at different duty Cycles
(a) 6 % (b) 15 % (c) 33 % (d) 50 %.*

The XRD pattern of the films deposited with silico-tungstic acid (Fig.2) did not show any additional features. They also exhibited only the peaks corresponding to the hexagonal phase similar to the films deposited without silico-tungstic acid but the peaks were broad indicating small crystallite size.

The XPS spectrum (Fig.3) exhibit the binding energies of the Zn(2p_{3/2}) and Se(3d_{5/2} and 3d_{3/2}) level. The peak energy levels associated with Zn(2p_{3/2}) appeared at about 1022 eV, which is in good agreement with the literature value[7]. It is also observed that the area under the curve increases as the duty cycle increases. Peak energy associated with the Se(3d_{5/2} and 3d_{3/2}) level, appeared at 53.9 and 59.2 eV respectively.

Atomic force microscopic images were obtained for the films deposited at different duty cycles. The best ordering is observed for the films deposited at a duty cycle of 6%. Larger grains are observed for the films deposited at higher duty cycles, these results are consistent with the XRD results. For the films deposited with silico-tungstic acid, the grain size decreased with the increase of the acid concentration. The AFM micrographs of the films deposited with

silicotungstic acid (Fig.4) indicated that the grain size of the films deposited at 50 % duty cycle decreases from 60 nm to 15 nm when the acid was present in the precursor.

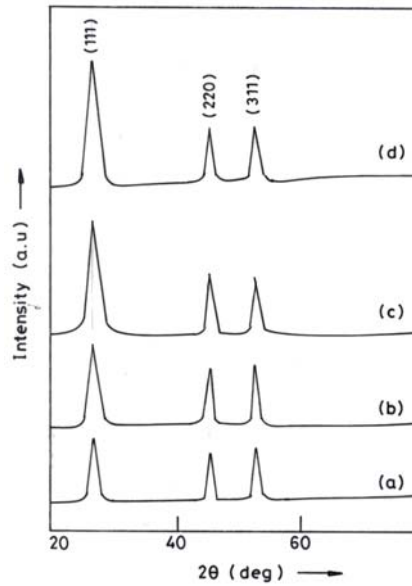


Fig.2 - X-ray diffraction pattern of ZnSe films deposited with different concentrations of silicotungstic acid (a) 0.01 mM (b) 0.05 mM (c) 0.075 mM (d) 0.1 mM.

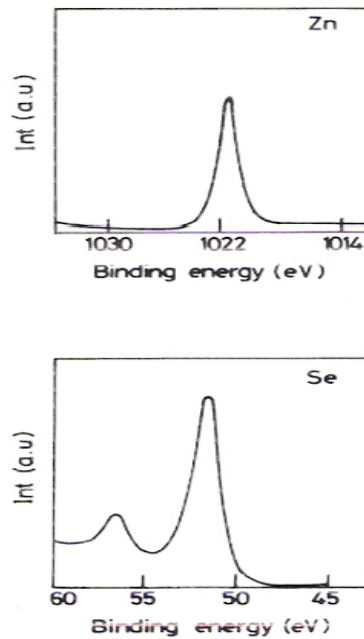


Fig.3 - XPS spectra of ZnSe film deposited at a duty cycle of 50 %

The band gap of the films were determined by plotting a graph between $(\alpha h\nu)^2$ vs $h\nu$. Extrapolation of the linear region to the $h\nu$ axis gives the band gap of the material. An absorption coefficient of 10^4 cm^{-1} was observed. The plots were linear, extrapolation of the plot to the $h\nu$ axis yields the band gap in the range of 2.64 – 2.68 eV for the films deposited at different duty cycles.

The plot for the films deposited at a duty cycle of 50% and with different concentrations of silicotungstic acid (Fig.5) indicated the band gap to vary in the range of 2.70 – 3.10 eV. The increase in band gap is due to quantum size effects.

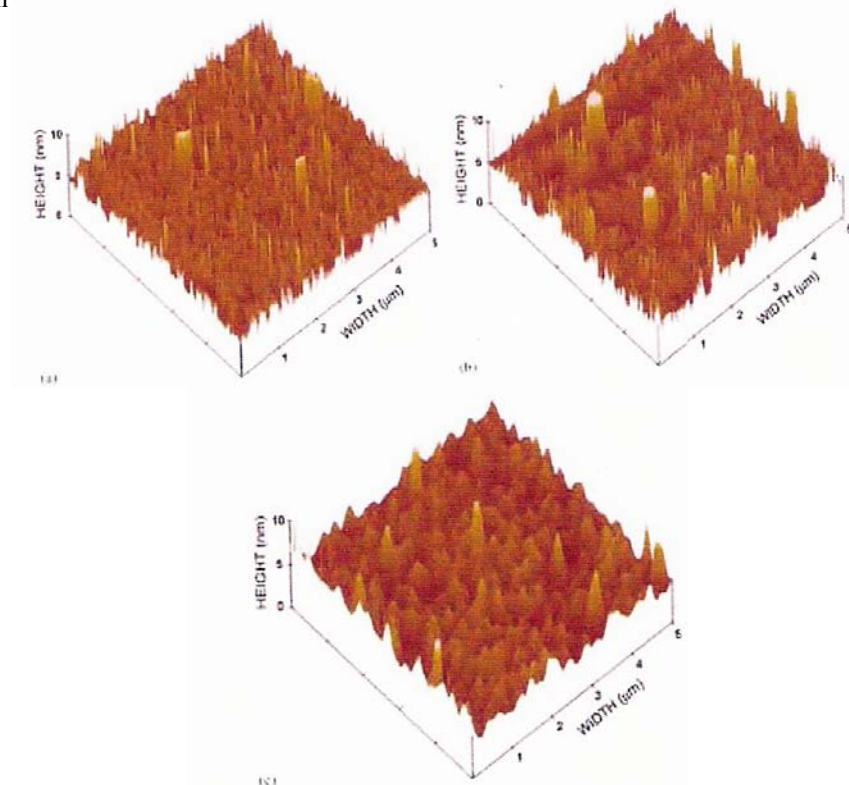


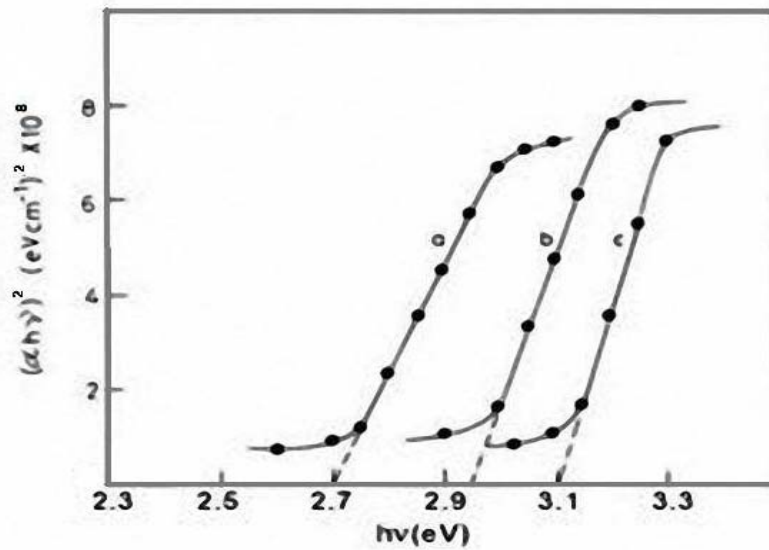
Fig.4 - AFM micrographs of ZnSe deposited with different concentrations of silicotungstic acid (a) 0.1mM (b) 0.05mM (c) 0.01 mM ($5\mu\text{m} \times 5\mu\text{m}$ area), Z – 10nm/div.

Laser Raman studies were made using 633nm laser radiation. The films deposited at lower duty cycles, indicated a broad and small peak at 252 cm^{-1} (Fig.6). This peak corresponds to the longitudinal optical (LO) phonon in ZnSe [8]. As the duty cycle increases, the peak becomes sharper and increase in intensity, this is due to the improved crystallinity of the films deposited at higher duty cycles supported by the XRD and AFM results. This is similar to the results obtained with photochemically deposited ZnSe films.

The photoluminescence spectra (Fig.7) were recorded at room temperature using an excitation wavelength of 450 nm. The spectrum exhibits peaks at 675 nm. As the concentration of silico-tungstic acid increases, the PL emission peak shifts to shorter wavelengths. This may be due to the increase in band gap with decrease in grain size. The PL emission from undoped ZnSe has been attributed to the presence of native defects like zinc and selenium vacancies or interstitial, which are likely to be introduced during the growth process [8]. Self activated centers arising from the complexes of zinc vacancies and shallow donors (selenium interstitials) would occur around 2.0 eV [9]. The emission band was observed at different wavelengths in the range 635 nm – 670 nm depending on the concentration of silicotungstic acid used during deposition. The shift may be attributed to the decrease in grain size which results in an increase of band gap of the films. Selenium vacancies or interstitial, which are likely to be introduced during the growth process. Self activated centers arising from the complexes of zinc vacancies and shallow donors (selenium interstitials) would occur around 2.0 eV.

4. Conclusion

The results of this work indicate that nanocrystalline films with crystallite size of the order of 15 nm can easily be obtained. This points out to the possibility of using them in luminescent devices.



With different concentrations of silico-tungstic acid (a) 0.01mM
(b) 0.05 mM (c) 0.1 mM

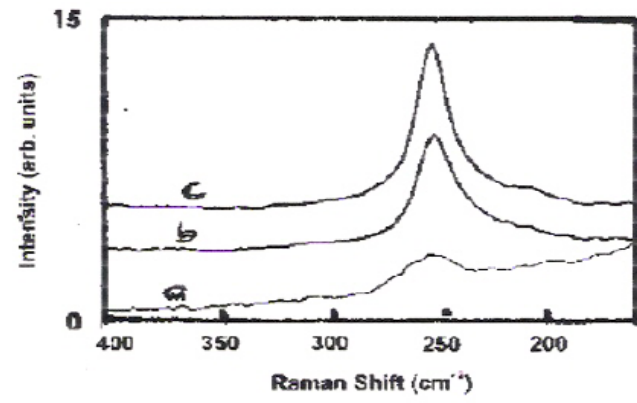


Fig.6 - Raman spectrum of ZnSe films deposited at different duty cycles
(a) 6 % (b) 25 % (c) 50 %

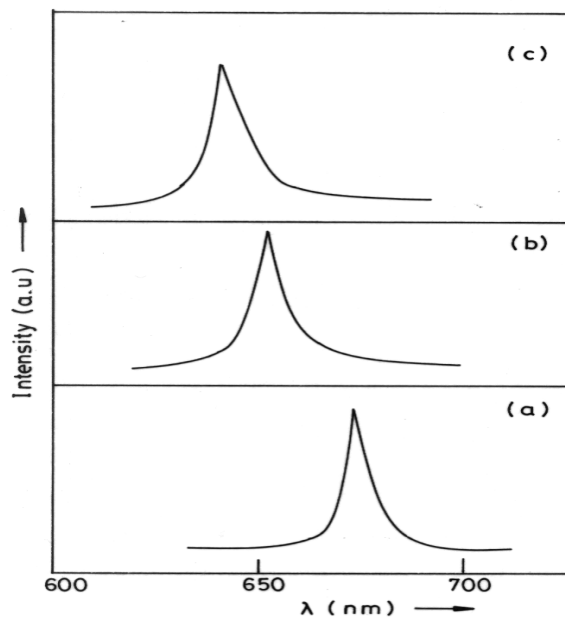


Fig.7. PL emission spectra of the ZnSe films deposited with different concentrations of silico-tungstic acid (a) 0.01 mM (b) 0.05 mM (c) 0.1 mM

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