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# Synthesis and characteristics of $Zn_{1-x}Cr_xSe$ composite thin film materials

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ABSTRACT

ZnSe and $Zn_{1-x}Cr_xSe$ ($0 \leq x \leq 0.35$) composite thin films were deposited by a chemical growth technique. The energy dispersive spectroscopy, X-ray diffraction analysis, scanning electron and atomic force microscopies, optical and electrical transport techniques were used to study the characteristic properties of thin composite films. An EDS analysis showed that the expected elements (Zn, Se and Cr) exist in the thin solid films. XRD analysis confirmed hexagonal wurtzite structure with dominant preferred orientation along <100>. SEM studies revealed that, both ZnSe and $Zn_{1-x}Cr_xSe$ films grow in a definite fashion. AFM images showed formation of almost spherical crystallites of ZnSe and $Zn_{1-x}Cr_xSe$. The optical bandgaps of $Zn_{1-x}Cr_xSe$ films found to be decreased from 2.71 eV to 2.53 eV for the change of x from 0 to 0.05. The electrical conductivity of $Zn_{1-x}Cr_xSe$ films found to be increased continuously with x up to 0.05 and then decreased for higher x-values.



## 1. Introduction

There has been a growing interest in recent years for the development of functionally important materials particularly, thin composite films with nano sized crystallites of II–VI semiconductor compounds. Zinc selenide with a direct band gap of 2.7 eV is a potential candidate of high performance owing to its suitability in a vast number of optoelectronic devices, viz. red, blue and green light emitters, laser screens, window material in solar cells [1–13], etc and can be synthesized with ease and without the use of sophisticated instrumentation and process control [1,5,11,12,14,15]. As a window material, it has overriding features such as nontoxic, environmentally friendly and higher bandgap buffer material for industrial production and for environmental protection, in addition to higher transparency in blue spectral range [3,5,6,11,15,16], over the traditional cadmium sulphide. It is reported to be appropriately synthesized with an extremely simple and costless chemical bath processes [1,5,11,12,14,15]. Through these investigations we attempt to fabricate excellent quality $Zn_{1-x}Cr_xSe$ composite thin films and characterize them through the composition, structure, and surface morphology, optical and electrical characteristics to check their suitability for window and PV applications. The intentional incorporation of $Cr^{3+}$ in the lattice of ZnSe is hoped to improve the materials characteristics because $Cr^{3+}$ is a trivalent magnetic material and the charge and spin could be coupled together to enhance them significantly [17–20].

Although a host of deposition technologies have been utilized for the fabrication of high quality zinc selenide thin films; we have synthesized both ZnSe and ZnSe:Cr thin films employing our chemical growth process set for its deposition conditions and preparative parameters [1,15].

## 2. Experimental details

### 2.1. Preparation of the samples

The ZnSe and $Zn_{1-x}Cr_xSe$ ($0 \leq x \leq 0.35$) thin films were obtained onto the commercial glass micro-slides using a chemical growth process set by us [1,15]. The precursor chemicals used were of the analytical grade. Zinc sulphate (0.5 M), chromium sulphate (0.5 M)

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and sodium selenosulphate (0.25 M) were taken (x, 1−x proportion) in an alkaline bath to produce ZnSe and $Zn_{1-x}Cr_xSe$ ($0 \leq x \leq 0.35$) thin films. For the deposition of ZnSe films, 10 ml zinc sulphate solution was taken in a 100 ml glass beaker to which 5 ml (25%) ammonia and 10 ml (85%) hydrazine hydrate were added chronologically as the complexing and reducing agents, respectively. 20 ml sodium selenosulphate was added to the bath to provide $Se^{2-}$ ions. The pH of the final reaction mixture was 10 ± 0.2. For deposition of the $Zn_{1-x}Cr_xSe$ composite films, $Cr_2(SO_4)_3$ solution was used to define x and 1−x values. The volume of the reaction bath was then made 100 ml by adding double distilled water and bath was then transferred to a constant temperature oil bath whose temperature was maintained at 70 °C. Thoroughly cleaned glass substrates were mounted on a specially designed substrate holder and suspended vertically into the reaction bath. The deposition was allowed for 210 min. The samples were then taken off the reaction bath and detached from the substrate holder, washed with double distilled water, dried in air and then preserved in a dark desiccator.

### 2.2. Characterization of the samples

The as-deposited ZnSe and $Zn_{1-x}Cr_xSe$ films were then characterized through the composition, structure, surface microscopic, optical and transport properties. The film thicknesses were measured by a KLA-Tencor P-16+ surface profilometer. The film composition and surface morphologies were investigated by the energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) techniques. An OXFORD instruments scanning electron microscope was used for this purpose. The structure and crystalline nature of the materials were then determined by an X-ray diffraction (XRD) technique (Bruker-AXS-D8, 40 kV/40 mA) with CuKα line (λ = 1.5406 Å, 2θ = 20° to 80°). The surface topography was also viewed through a Bruker (Dimension icon 004-1023-000) atomic force microscope (tapping mode). The optical transmittance was measured using a Shimadzu UV-VIS-NIR 3600 spectrophotometer in the wavelength range from 200 nm to 1900 nm. The electrical conductivity was measured by a two probe method in the 300–550 K temperature range. Ag-paste was utilized as a contact material.

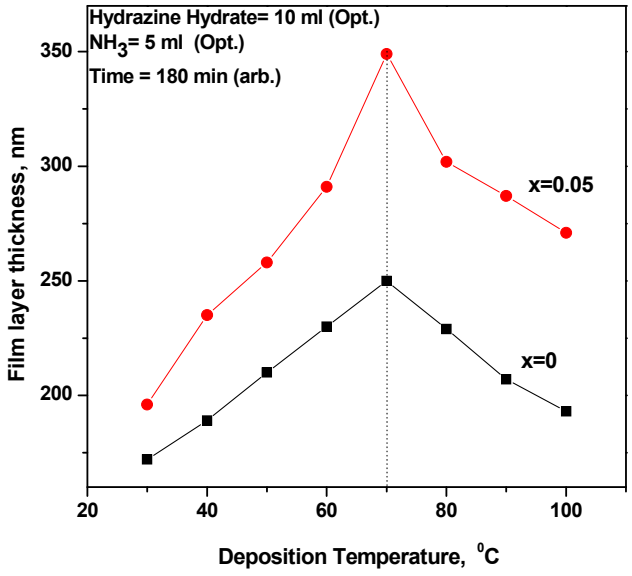
## 3. Results and discussion

### 3.1. Reaction and growth mechanism

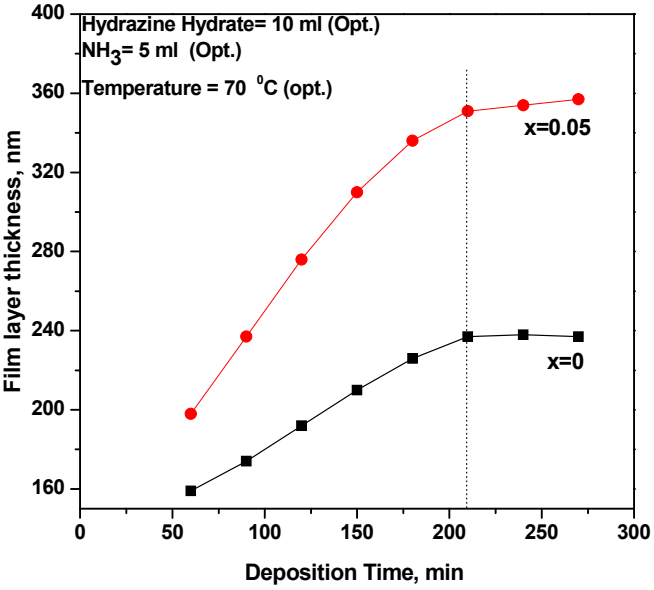
The deposition of ZnSe and $Zn_{1-x}Cr_xSe$ ($0 \leq x \leq 0.35$) thin films was carried out using a chemical growth process. The film growth was examined for the crucial parameters namely deposition temperature and deposition time.

#### 3.1.1. Influence of deposition temperature on the growth of $Zn_{1-x}Cr_xSe$ thin films

The deposition temperature was varied from 30 °C to 100 °C and the terminal layer thickness was measured. It is seen that, at low temperature, the film growth is very slow and the growth rate increased almost linearly with increasing temperature (up to 70 °C). Beyond this temperature, precipitation results at a faster rate causing decrease in layer thickness. It is observed that the terminal layer thickness increased almost linearly with increase in the deposition temperature, attains a maximum at 70 °C and then decreased for higher deposition temperature. This is shown in Fig. 1(a). It has been seen that deposition of film at low temperature (<70 °C) is much delayed, however, the deposition rate is found to be increased with increase in bath temperature. This can be explained as usual [22]. The films deposited at 70 °C are uniform, tightly adhernt and diffusely reflecting.




(a)




(b)

**Fig. 1.** Influence of growth parameters on growth of $Zn_{1-x}Cr_xSe$ thin films. a) Variation in film layer thickness with deposition temperature. b) Variation in film layer thickness with deposition time.

#### 3.1.2. Influence of deposition time on the growth of $Zn_{1-x}Cr_xSe$ thin films

The deposition time of the film growth was also optimized. The time of the film growth was varied from 60 min to 270 min. Terminal layer thickness was measured as a function of the deposition time. A deposition time of 210 min is found to be suitable for getting maximum film thickness. This is shown in Fig. 1(b). It is seen that, the layer thickness is time dependent and increased almost linearly with deposition time up to 210 min and remained more or less same for further increase in deposition