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Physical, structural and topographical aspects of $Zn_{1-x}Co_xSe$ thin films

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ABSTRACT

In the present study, $Zn_{1-x}Co_xSe$ ($0 \le x \le 0.275$) thin films were synthesized via a chemical route and characterized through the physical, compositional, structural and morphological properties. The change in colour appearance from ash-grey to charcoal-black suggested integration of Co^{2+} into ZnSe host lattice. Similar conclusions on the colour appearance were drawn from colorimetric studies. The hydrophobic nature of the as-obtained sample surface was revealed in wettability measurements. Zn^{2+}, Co^{2+} and Se^{2-} states of constituents in the thin films were found in the elemental analysis. Formation of ternary alloy was confirmed by shift in (111) X-ray diffraction peak. The surface topography was analysed by an atomic force microscopy (AFM). A variety of AFM parameters were determined to study the effect of Co^{2+} addition onto the surface topography. Magnetic mapping of the surface topography concluded the existence of magnetic domains of irregular sizes and shapes.

1. Introduction

An idea of impurity addition revitalized the semiconductor physics by blending number of material properties into a single material. Impurity addition influences the electronic structure and thus offers unparalleled opportunities in the fields of micro- and nano-applications [1]. To cope up with the needs of advancing tech-applications, inexpensive techniques for the synthesis of doped semiconductor thin films on a large scale are highly desirable [2]. Selenium based doped semiconductor thin films have gained much popularity owing to their applications in a variety of fields ranging from thermoelectrics to lasers, optical filters, sensors, optical recording materials, solar cells, etc. [3].

A ternary $Zn_{1-x}Co_xSe$ system, composed of ZnSe and CoSe, can be engineered for better application perspectives. This ternary system can be engineered to suit the needs of cutting-edge applications by fine tuning of the optical and electrical properties. Albeit, the synthesis of Co(ZnSe) based thin films were reported through a variety of methods [4,5], none of them proposes modular approach to the physical, structural and topographical aspects with prominance given to the impurity concentration. Through this article, we report on the solution growth of $Zn_{1-x}Co_xSe$ ($0 \le x \le 0.275$) thin films and their primordial characterizations. Modular studies on the physical, structural and topographical aspects with reference to the cobalt concentration has been reported. The article climaxes characterization of Co(ZnSe) thin films through the techniques like colorimetry and magnetic force microscopy which are seldom used in the thin film science.

2. Tools and techniques

2.1. The synthesis of ZnSe and $Zn_{1-x}Co_xSe$ thin films

The ZnSe and $Zn_{1-x}Co_xSe$ ($0 \le x \le 0.275$) thin films were deposited onto the glass substrates using previously reported procedure [4]. In actual, thin film deposition was carried out from an aqueous bath containing Zn^{2+}, Co^{2+} and Se^{2-} ion precursors. ZnSe and $Zn_{1-x}Co_xSe$ thin films thus obtained by a solution deposition were characterized for elemental composition, structural and surface topographic features.

The terminal layer thicknesses of the samples were measured by the AMBIOS Make XP-1 stylus profilometer. The contact angle measurements, based on the sessile-drop method consisting of the observations on the water drop through a microscope coupled to goniometer, were performed. In addition to the physical observations on colour appearance of the thin films, we tested colour tuning possibilities of the as-deposited ZnSe and ternary $Zn_{1-x}Co_xSe$ thin films by employing a

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colorimetric technique. The valence states of constituent elements were investigated by an X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, Thermo Scientific, UK). The structural changes as a function of the film composition were studied using a Rigaku X-Ray diffractometer with Cu k_α radiation (λ=1.5406 Å, V=40 kV, 2θ=20–80°). The FTIR spectra were recorded using a Perkin Elmer spectrophotometer in the 400 cm^{-1}–4000 cm^{-1} range. Surface topography was viewed through the atomic force (AFM) and magnetic force (MFM) microscopes. An Innova: Bruker AFM was used for this purpose. The 10 μm×10 μm MFM scan images were obtained using a low coercive sensing probe.

3. Results and discussion

3.1. Reaction kinetics and physical observations

Chemical deposition of both ZnSe and $Zn_{1-x}Co_xSe$ (0≤x≤0.275) thin films in an alkaline solution state was made feasible using the salt solutions of Zn^{2+}, Co^{2+} and sodium selenosulphate as the Se^{2-} ion source.

In an alkaline medium, a complex is required to prevent rapid bulk precipitation of the desired product. In the present case, TEA and ammonia act as the complexing agents and facilitates the ZnSe and $Zn_{1-x}Co_xSe$ deposition on the surface of the glass substrates as [6];

$$Zn^{2+} + 4TEA + NH_3 + 2\overline{O}H \rightarrow Zn(TEA)_4^{2+} + NH_4OH \quad (1)$$

and

$$Co^{2+} + 4TEA + NH_3 + 2\overline{O}H \rightarrow Co(TEA)_4^{2+} + NH_4OH \quad (2)$$

The addition of hydrazine hydrate presumably reduces the selenosulphate to give a high enough concentration of Se^{2-} ions for reaction to take place as;

$$Na_2SO_3 + Se \rightarrow Na_2SeSO_3 \quad (3)$$

$$Na_2SeSO_3 + \overline{O}H \leftrightarrow Na_2SO_4 + HSe^- \quad (4)$$

$$HSe^- + \overline{O}H \leftrightarrow H_2O + Se^{2-}. \quad (5)$$

Finally, ternary $Zn_{1-x}Co_xSe$ thin films were formed as follows,

$$1 - x(Zn^{2+}) + x(Co^{2+}) + Se^{2-} \rightarrow Zn_{1-x}Co_xSe \quad (6)$$

The effect of diverse concentration of Co^{2+}(x) on the growth of ZnSe so as to form $Zn_{1-x}Co_xSe$ (0≤x≤0.275) thin films was physically observed. Fig. 1 shows variation in the film colour with respect to the Co^{2+} content in $Zn_{1-x}Co_xSe$ films. It appeared that as-deposited Zn-Co-Se films show change in colour from ash-grey to charcoal-black. This is an indication of the substitution of Zn^{2+} by Co^{2+} in the ZnSe lattice [1]. The incorporation of Co^{2+} in ZnSe host causes change in bandgap which causes change in colour appearance. Credit from quantum confinement has also to be considered as the reason of bandgap tuning and thus the colour change. The contact angle measurement is the angle made by the tangent to the liquid-vapour interface drawn at the contact line that makes an angle (measured inside the liquid) with the solid surface. The contact angles were measured for all the samples and it has been seen that, the increase in Co^{2+} content in ZnSe host increased the contact angle from 93° to 160°. Contact angle or wettability depends on surface energy and geometrical features of the solid surface. In our case Co^{2+} increased the surface roughness of thin films which thus caused increase in contact angle. The contact angle measurement results are shown in Fig. 2. This shows that the growth of $Zn_{1-x}Co_xSe$ on the glass surface is hydrophobic in nature and can be attributed to the high surface energy and microstructural amendments in the deposited films [1].

3.2. Colorimetric studies

Homogeneity of the thin films deposited onto the transparent substrates can simply be described by viewing through them. For instance, if viewing through thin films shows a highly reflecting surface or a darker surface, the darker surface may be a different nucleation or a reaction than the shiny surface. For quality thin film yield, the film deposition appearance should be uniform over the whole substrate area indicating homogeneous deposition process, whereas a varied deposition appearance indicates the nonhomogeneous deposition process [7]. In our case deposited thin films are highly uniform in nature.

A colorimetry is a light sensitive tool used for the measurement of transmittance and absorbance of the light passing through a sample; the device measures the intensity or concentration of the colour. According to Commission Internationale d′E´clairage (CIE), each colour in colorimetry is represented by three coordinates in a three-dimensional phase [8]. Fig. 3 shows the L*a*b* coordinates for varying cobalt concentration. L* is the lightness variable of the sample, while a* and b* correspond to the two antagonistic chromatic processes (red-green and yellow-blue). In the L*a*b* chromaticity diagram, + a* is the red direction, − a* is the green direction, + b* is the yellow direction and − b* is the blue direction. The centre (0, 0) of the chromaticity diagram is achromatic and as a* and b* values increase, the saturation of the colour increases [9]. In our case, as the Co^{2+} incorporation in ZnSe is increased, the lightness (L) changes from brightest white (L^*=51.89) to the darkest black (L^*=12.19). The red opponent colours are in negative values while green opponent colours are in positive values. The colorimetric data is in agreement with the physical observations in Fig. 1.

3.3. The compositional studies

The X-ray photoelectron survey spectra for all the samples were recorded in the B.E. range from 0 eV to 1400 eV. The appearance of oxygen and carbon in the XPS spectra is attributed to the surface-adsorbed CO_2 and O_2 impurities. To determine the chemical states of the elements of interest, narrow region scans were analysed by original XPS spectra being de-convoluted for separate elements. Fig. 4(A, B, C) shows narrow scan regions of Zn(2p), Co(2p) and Se(3d) core levels. The Zn 2p core level spectra are mainly characterized by two components appearing due to spin-orbital splitting- Zn $2p_{3/2}$=1021.65 ± 0.01 eV and Zn $2p_{1/2}$=1044.66 ± 0.01 eV with the B.E.

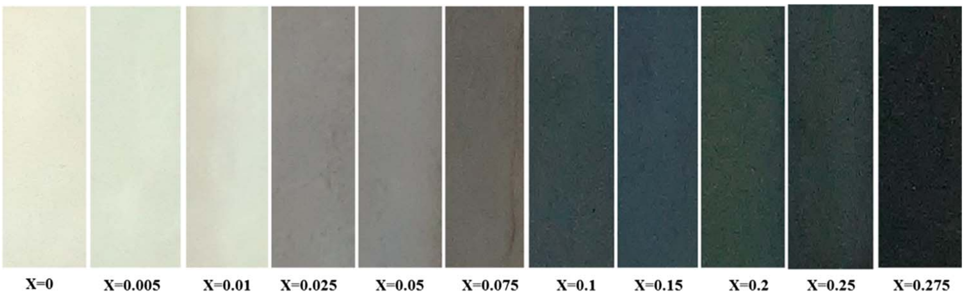

Fig. 1. Variation in film colour as a function of the Co^{2+} integration into ZnSe host lattice (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)