Influence of Oblique Angle Deposition on Nanostructured CuSe Thin Films and Their Structural, Morphological and Optical Properties

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Abstract

The nanocrystalline thin films of CuSe of thickness about ~300 nm were deposited on precleaned glass substrate by thermal vacuum evaporation technique under high vacuum conditions at different oblique angles (0^0, 15^0, 30^0, and 45^0). Phase formation and crystal structure of as deposited films have been analyzed by using X-ray diffractometer. Surface morphology and microstructure of these films are investigated by scanning electron microscope, UV-VIS-NIR spectroscopy was used to find out band gap of the films. The influence of oblique angle depositions on microstructural features and hence change in optical parameters has been presented and explained in this paper.

Keywords: CuSe, Oblique Angle Deposition, XRD.

Introduction

In past three decades oblique angle deposition has been bountiful awareness due to applications in optical interference devices, photonic crystals, micro sensors, microelectronics and interference filters. Now a day's oblique angle deposition of thin films is being well familiar for fabricating interference filters using single optical materials by changing refractive index along the film thickness [1-3]. This refractive index variation is achieved by changing the angle of deposition and is the result of changeable porosity due to atomic shadowing and limited ad-atom diffusion [4-7] during growth. Oblique angle deposition usually works at an angle greater than 30 degree with normal to substrate. Oblique angle deposition ending in special morphological nanostructures & microstructure and by employing substrate rotation and varying deposition angle, helix, pillar, zigzag, erect columns etc. have been achieved effectively [8-11]. Researchers have made up multi stop band interference rugate filter exploiting GLAD technique [12]. Stephan Fahr *et. al*., have shaped optical filters for light trapping in solar cells [13]. Many researchers have also developed selective polarization transmission filter [15], antireflection coating [14], narrow band pass filter [16] and relative humidity sensors [17] by taking advantage of oblique angle deposition of optical materials.

The I-VI group (CuSe) semiconductors are used in microelectronic techniques [18]. CuSe is a P-type semiconductor material which has suitable electrical and optical properties for photovoltaic applications and also as a super ionic conductor [19], optical filters [20], and radiation filters [21].

This paper includes the detailed investigation of CuSe thin films obtained through the oblique angle deposition via thermal vacuum evaporation techniques under the pressure of 10^{-5}torr. Here we studied the structural, surface morphological and optical properties of CuSe thin films as a function of deposition angle.

The grown CuSe thin films were characterized by using XRD, SEM and UV-VIS spectroscopy. This study will helps in fabrication of opto-electronic devices.

Material Preparation

The CuSe compound ingots was obtained by taking appropriate amount of 99.999 % pure copper powder and selenide metal in the atomic proportion 1:1 in an evacuated quartz ampoule. The mixture was then sealed under a pressure of 10^{-5} torr and was placed in double zone rotating furnace. The temperature of the furnace was raised gradually to 1100 K and left at this temperature for about 10 h. Well mixed charges were then quenched in an ice bath. The CuSe ingot was taken out from the ampoule and made into fine powder and used for film preparation.

Synthesis of Thin Films

Polycrystalline CuSe films have been deposited by thermal vacuum evaporation with OAD technique is used under vacuum of about 10^{-5} torr. The substrate to source distance was kept 8 cm. The vapor flux incident angle was kept at 0^0, 15^0, 30^0 and 45^0 and substrate rotation speed, about 0.1 rpm, were employed to control the columnar nanostructures of the films. The thickness of the films was controlled by quartz crystal thickness monitor model No. DTM-101 provided by Hind-Hi Vac. The deposition rate was maintained 5-10 Ǻ/sec throughout sample preparation. Before evaporation, the glass substrates were cleaned thoroughly using concentrated chromic acid, detergent, isopropyl alcohol and distilled water. X – Ray diffractogram (Bruker, Germany) were obtained of these samples to find out structural information and to identify the film structure qualitatively. The scanning angle (2θ) range was from 20^0 - 80^0 (CuK_α line). Surface morphological studies of the thermally deposited CuSe thin films were done using the Scanning Electron Microscope (Zeiss) operating with an accelerating voltage 15 kV. Optical absorption was measured by UV-VIS spectrophotometer model No. Shimadzu -2450.

Structural Characterizations of CuSe Thin Films

XRD Analysis

X ray diffraction study of CuSe thin films was carried out using BRUKER AXSD8 (Germany) advance model X ray diffraction with $Cu_{k\alpha}$ (λ=1.54056 Å) radiation in the 2θ range 20^0- 80^0. The scanning speed of the sample was maintained 0.5^0 /min. Fig. 1 (a-d) shows the XRD pattern of CuSe thin films deposited at 0^0,15^0, 30^0 and 45^0. The 2θ peak observed at 26.38^0, 32.15^0 44.06^0, 52.49^0, and 63.6^0 which correspond to the (111), (200), (220), (311) and (400) planes of reflections. The XRD spectrum reveals that the films are polycrystalline in nature and hexagonal (wurtzite) in structure (JCPDS card No. 08 - 0456).

It can be seen that the incident angle strongly affects the XRD pattern. For lower incident angle, the films have random particle orientation, identified by the presence of various peaks at (111), (200), (220) and (311) planes etc. As the incident angle increases, the (111) diffraction peak becomes more and more dominant. This means that, at the initial stage of film formation i.e., during the atomistic condensation of the film formation, the deposited atoms are at arbitrary orientation. As the flux incident angle of the film increases the polycrystalline grains begin to orient mainly along (111) direction which is evident from the Fig. 1 (a-d). The value of the lattice parameters obtained from the analysis of x-ray diffraction pattern were a

= 14.291 and c = 17.001. Unit cell volume is found to be 103.2. The average grain size is found to be 220 nm calculated by using the Scherrer's formula:

$$D = \frac{0.94\,\lambda}{\beta \cos\theta} \qquad \ldots (1)$$

The average dislocation density was found to be 0.1947 X10^{14}lines/m^{2} calculated by:

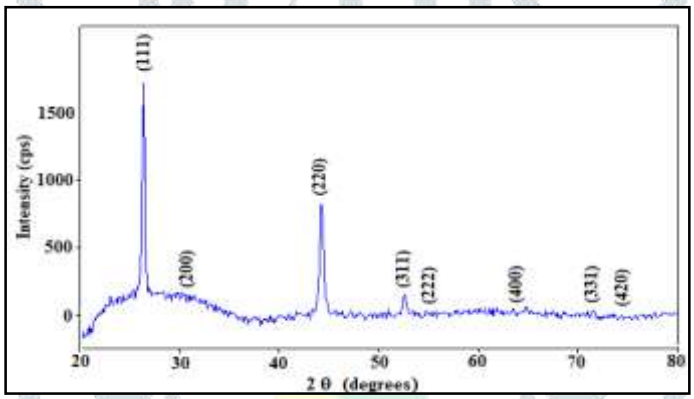
$$\delta = \frac{1}{D^2} \qquad \ldots (2)$$

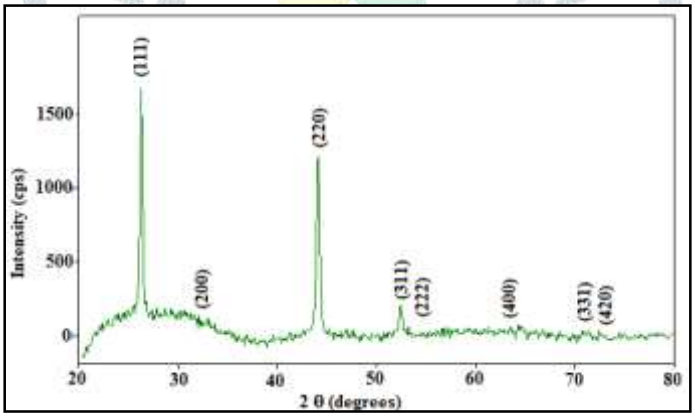
The number of crystallites per unit area (N) and the strain (ε) of the films were determined by following relations:

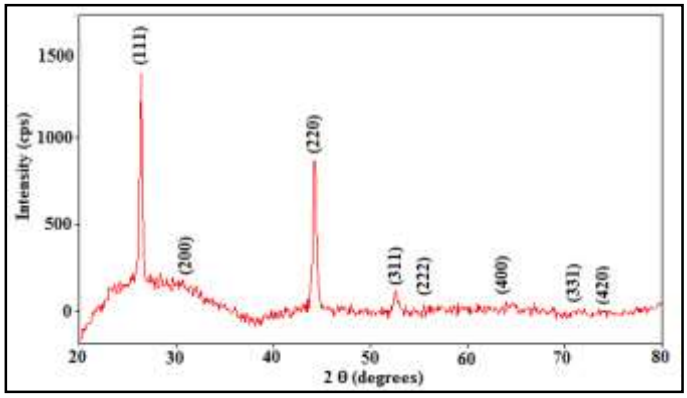
$$N = \frac{t}{D^3} \qquad \ldots (3)$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad \ldots (4)$$

Where, t is the thickness of the film. The calculated structural parameters are N = 0.843 X 10^{15}, ε = 0.00901 lines^{-2}m^{-4}. The small values of δ obtained in the present study confirm the good crystalline of thin films fabricated by the OAD technique.







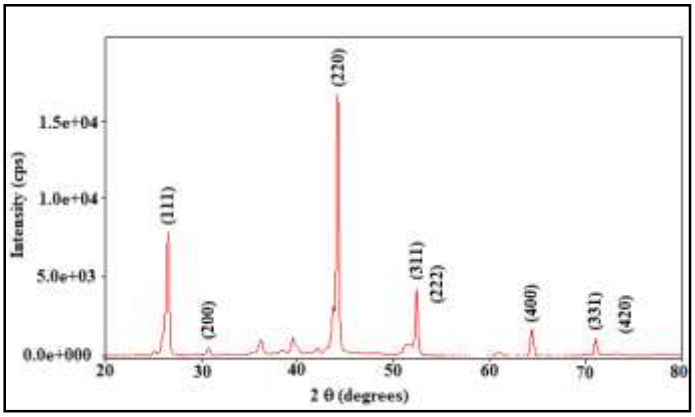


Fig. 1 (a-d) XRD of CuSe Thin Films for oblique angle 0^0 to 45^0

SEM Analysis

SEM images of CuSe thin film of different angle 0^0-45^0 shows that the film is uniformly deposited but there are some defects like holes are found. Nano size grains were dispersed almost homogeneously over smooth substrate. The grains are well defined, granular & almost of similar size. It is found that the nano grains forms clusters with some amount porous. The presence of fine grain surroundings is an indication of one step growth by multiple nucleation. As angle increases SEM image is look like texture, the small grains are found and the nano rods are clearly seen. The small gains are the tips of nano rod, it is clear that these nano rods are uniformly distributed over smooth substrate.

It is probable that thermal evaporation, have been the most extensively used methods for the OAD of thin films. This has surely been true regarding the efficient control of the geometry of the nano features through shadowing effects; thermal diffusion of ad-particles make use of the OAD geometrical configuration to construct new microstructures, textures and general properties in films can manipulate the deposition process of shadowing mechanisms.

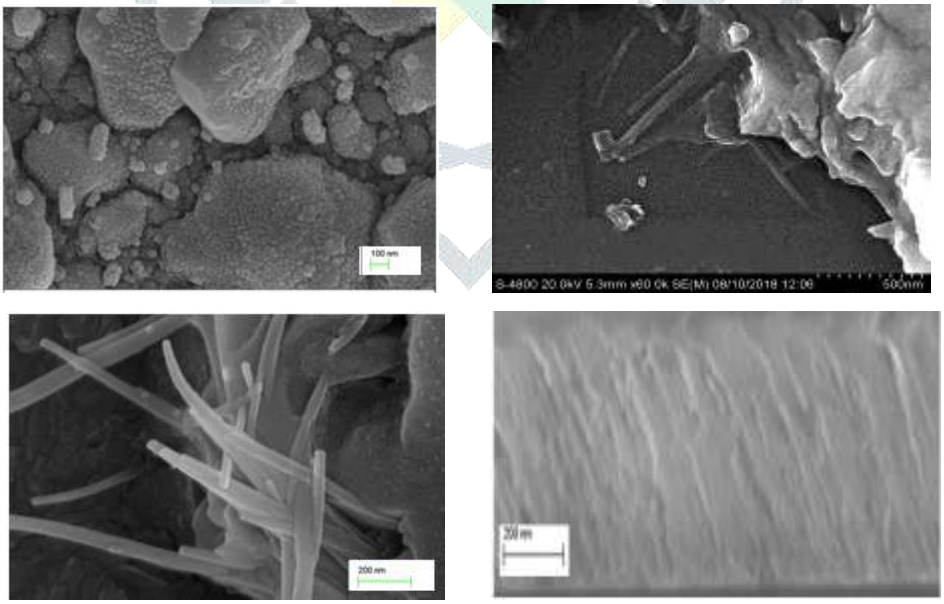


Fig. 2 (a-d): SEM images of OAD deposited CuSe Thin Films (0^0 to 45^0)

UV-VIS Spectroscopy

The optical band gap of semiconducting materials plays an significant role in a variety of applications such as deciding the energy conversions, efficiency of a solar cell [22] as well as for

construction of semiconducting devices. The main aim of the work accessible is to study the optical band gap of CuSe thin films.

The optical constants of the films are requisite for correct design of optoelectronic devices and to establish the losses in detectors and optical coatings. The Fig. 3 shows the transmittance spectra of the CuSe thin films recorded between the 200 - 900 nm wavelengths ranges by employing a Shimadzu 2450 UV Visible model of the spectrophotometer

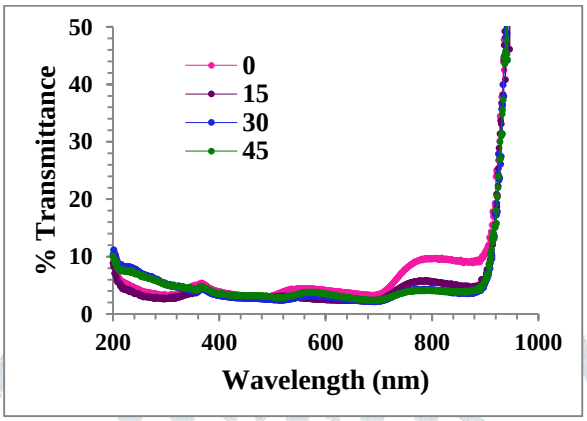


Fig. 3: Transmittance Spectra of CdSe Thin Film

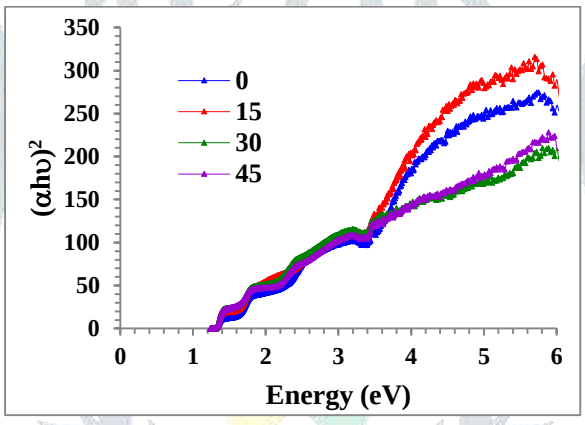


Fig. 4: Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of CdSe thin film

The optical band gap of these films has been calculated by the Tauc relation:

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \qquad \ldots. (5)$$

Where, hν is the photon energy, α is the absorption coefficient, E_g the band gap, A is constant and, n = 0 · 5 for direct bandgap material, n = 2 for indirect band gap material. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for these CuSe films is presented in Fig. 4.

The plot of $(\alpha h\nu)^2$ vs. $h\nu$ has direct transition with direct band gap energies. The observed drift at absorption edge towards lower photon energies for the increasing film angle could be accredited to the change in the grain size and the stoichiometry. The straight line portion is extrapolated to cut the x axis, which gives the energy gap. All graphs show straight line portions supporting the interpretation of direct band gap for all the films. The evaluated band gap values were obtained near about 2.12 eV constant for all oblique angle. Hence the CuSe can be used in development of efficient photovoltaic application and in photo sensor.

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