Preparation and Characterization of Aluminum Doped Zirconium Sulphide Thin Films.

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ABSTRACT

Spray deposition and characterization of Aluminum doped zirconium sulphide (Al:ZrS_2) thin films deposited onto a glass plates from an aqueous solution containing zirconium oxy chloride ($ZrO_2Cl_2.8H_2O$), thiourea (CH_4N_2S), and aluminum acetate $Al(CH_3COO)_3$ is discussed in this manuscript. Three different films were prepared by varying the concentration of the aluminum acetate in zirconium sulphide. The prepared films were characterized by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and optical absorption techniques. The structure was found to be hexagonal with preferential orientation along (110) plane. SEM study shows that the total substrate surface is well covered with densely packed nanotubes. Optical absorption study shows the presence of direct transition having band gap energy in the range of 2.4-2.46 eV.

(Keywords: thin films, structural properties, optical band gap)

INTRODUCTION

The fourth column transition metals have interesting properties resulting from their exhibition of both metallic and covalent bonding characteristics. The covalent crystalline properties are high melting point; extreme hardness and brittleness; and chemical inertness.

The metallic characteristics are electrical conductivity and metallic reflectance [1]. The great demand for less expensive metal sulphide and passive films which can be used in various electronics and optical devices makes the study of zirconium based thin films important. ZrS_2 belong to the group 4B transition metal di-chalcogenides which are semiconductors with layered structures. In the past many experiments on the optical properties of the group 4B transition metal dichalcogenides including ZrS_2 and HfS_2 have been reported. Greenaway and Nitsche [2] found the indirect transition in the absorption edge of ZrS_2 and HfS_2.

The DICHALCOGENIDES of transition metals steadily attract a great attention of researchers due to the variety of their properties that are of both fundamental and practical interest [3]. Thin films of zirconium based material can be prepared by number of technique which includes Plasma enhanced CVD method [4] Chemical vapor deposition [5, 6], and Plasma spray method [7]. Among the various thin film deposition technique available home built spray pyrolysis [8] technique is particularly attractive because of its low cost commercially scalable route for uniform deposition of zirconium sulphide thin films over large area substrate [9-11]. To the best of our knowledge, no report is available for Al doped ZrS_2 thin film. On account of the numerous applications of zirconium sulphide thin film, an attempt has been made to prepare zirconium sulphide alloy film using the spray method. In the present manuscript, we report, for the first time, the synthesis of Aluminum doped ZrS_2 thin films by spray technique.

EXPERIMENT

Preparation of Thin Films

Zirconium sulphide thin films doped with aluminum were deposited on an optically flat well cleaned glass substrate by using a home made double nozzle sprayer. The 50ml of the spray solution was prepared from aqueous 0.01M of zirconium oxy chloride ($ZrOCl_2.8H_2O$); 0.01M of thiourea ($CS(NH_2)_2$) and 0.001M of aluminum acetate Al $(CH_3COO)_3$. The chemicals used in

this deposition were of analytical grade. The atomized chemical solution is sprayed on to the preheated substrate maintained at 250^0C with the help of compressed air as carrier gas. The carrier gas flow rate was maintained at 3ml/min at a pressure of 12kg/cm^2.

The distance between the spray nozzle and the substrate is 35cm. To avoid excessive cooling of the substrate, spraying was done with time gap of 30 seconds between successive spray. Details of this setup have been published elsewhere [12]. Films with different doping levels of Al were also deposited by varying the aluminum acetate concentration 0.001M, 0.002M, and 0.003M precursor solution without changing the other process parameter.

For each concentration the reproducibility of the films were verified by repeating the experiments several times. Thickness measurement of the films has been carried out using JEOL, JSM 6701F, Japan, Scanning Electron Microscope (SEM). The film is mounted vertically to measure the thickness directly [13]. The measured thickness of the films is found to be in the range of 2.6 Micrometer-2.9 Micrometer.

RESULT AND DISCUSSION

XRD Studies

XRD pattern of the aluminum doped zirconium sulphide films were studied at room temperature by using RIGAKU diffractometer (model RAD II A) with CuKα radiation (1.15418Å) where other radiations are suppressed using Ni filter. The data were recorded at a scan rate of 0.2^0 /min and in the range of $20^0<2\theta<80^0$. The crystallinity pattern of as deposited films for different molarities of aluminum acetate (0.001 M , 0.002 M and 0.003 M) on clean glass substrate prepared at 250^0 C is shown in Figure (1).

There are no standard JCPDS data available for aluminum doped zirconium sulphide. Hence the plane indices are obtained from comparison between observed 'd' values and standard '*d*' values for ZrS_2 given by JCPDS file no. 03-1099. The film surface found to be smooth, homogeneous and adherent to the substrate with no signature for impurity phases. The observed peaks in all the diffractograms confirm the nanocrystalline nature of the ZrS_2:Al film. The XRD pattern of the films also reveals that the ZrS_2:Al film is polycrystalline with hexagonal crystal structure and preferential orientation along (110) plane.

The absence of the additional peaks in the XRD results of aluminum doped zirconium sulphide thin film samples indicates the formation of single phase ZrS_2. No phase corresponding to aluminum / aluminum sulphide or other aluminum compounds was detected in the XRD. The films exhibited an intense peak oriented along the (110) lattice plane parallel to the substrate. The other strong peaks observed from the XRD spectra correspond to the (101) and (201) orientations. The diffraction peaks appear in the spectrum has been identified as 32.235^0, 49.794^0 and 60.755^0 are verified with the known patterns of standard X-Ray Diffraction data file (JCPDS file No: ZrS_2 03-1099). While comparing the X-ray diffraction (XRD) pattern it is found that with the increase of aluminum composition (0.001 M, 0.002 M and 0.003 M), the position of the Bragg peaks in XRD pattern, shift towards higher angle. It may be attributed to the change in grain size and strain in the film.

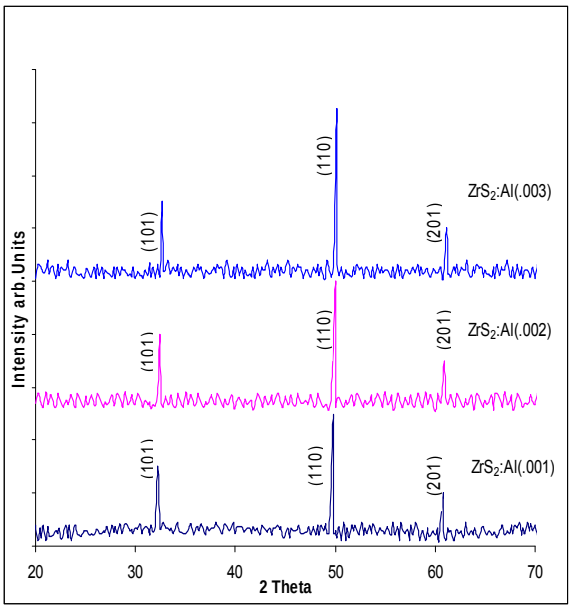

Figure 1: XRD Pattern of Aluminum Doped Zirconium Sulphide Thin Films.

However, the peak position not only depends on the substitution of aluminum in zirconium sulphide ZrS_2: Al films, but also strongly relates with other process parameters such as spray conditions and temperature. The observed slight deviation in the respective values with standard data is probably

due to change in the crystallinity of the films. X-ray diffraction line broadening (XDLB) was used to estimate the grain size of the film by utilizing Scherrer's formula [14-15].

$$D = \left[\frac{K \lambda}{\beta \cos \theta} \right] \rightarrow 1$$

Where k is the shape factor constant (0.89), λ is the wavelength of CuKα line, θ the Bragg's angle of reflection, β is the full width half maximum (FWHM) of intense peak. The average grain size of Al: ZrS_2 calculated using Scherrer's equation is 30nm, 33nm and 35nm for 0.001 M, 0.002 M and 0.003 M molarities of aluminum respectively. It was found that the grain size increases with the increase of aluminum composition in the films. Correspondingly, the value of lattice spacing (d) decreased. Also grain size is less than 50 nm. This small grain size is due to the evaporation of individual fine droplets during the sprayed process [16].

Optical Studies

A computer controlled ELICO make (SL159 UV-VIS) single beam spectrophotometer was used to obtain absorbance (A) of zirconium sulphide thin films over wide wavelength range of 400nm - 900nm at room temperature with unpolarized radiation.

The experimental accuracy of the absorbance is (± 0.005) and the wavelength is (± 0.05 nm). The observed absorbance data were corrected relatively to optically identical uncoated glass substrate. Spectral absorbance of zirconium sulphide doped with different molarities of aluminum (0.001M, 0.002M, and 0.003M) prepared at 250^0C is displayed in Figure 2.

It reveals that the absorbance of the film decreases gradually with increase in wavelength. It also shows that as the concentration of aluminum in the film increases form 0.001M - 0.003M there is a drastic increase in absorbance with maximum peak value of 0.27, 0.31 and 0.325 respectively. This is due to the higher film absorption associated with larger film thickness.

For all doping concentrations of aluminum optical absorbance is found to be least in the visible region. Therefore, the films are measured to be a non absorbing film on non absorbing substrate. The absorption co-efficient (α) is calculated using Lambert's law [17]:

$$\alpha = \left[\frac{2.303 \quad A}{t} \right] \rightarrow 2$$

Where 'A' is the absorbance't' is the thickness of the film, neglecting the reflection co-efficient which is negligible and insignificant near the absorption edge. Then absorption co-efficient (α) is found to be in the order of $10^4 cm^{-1}$.

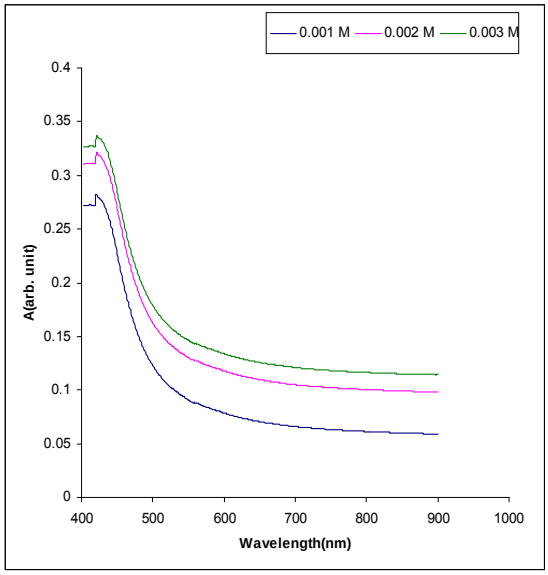

Figure 2: Absorbance Spectra of Al Doped Zirconium Sulphide Thin Films.

The optical band gap Eg was calculated by plotting $(\alpha h\nu)^2$ Vs hv. The photon energy at the point where $(\alpha h\nu)^2$ is zero represents Eg, which is determined by extrapolation of the linear portion of the curve. The typical plots of $(\alpha h\nu)^2$ versus hv for Aluminum doped zirconium sulphide thin films is shown in Fig.(3). The optical band gap of the as deposited film is found to be in the range of 2.4-2.46 eV.

SEM Studies

The SEM micrograph of the Aluminium doped zirconium sulphide thin film is taken using cold field emission of SEM (JEOL, JSM 6701F, Japan) to support the XRD observations. Prior to the observation, using an auto sputter fine coater

(JFC 1600, JEOL Japan) about $50A^0$ gold was sputtered on the thin film surface for better contrast and to avoid charge accumulation.

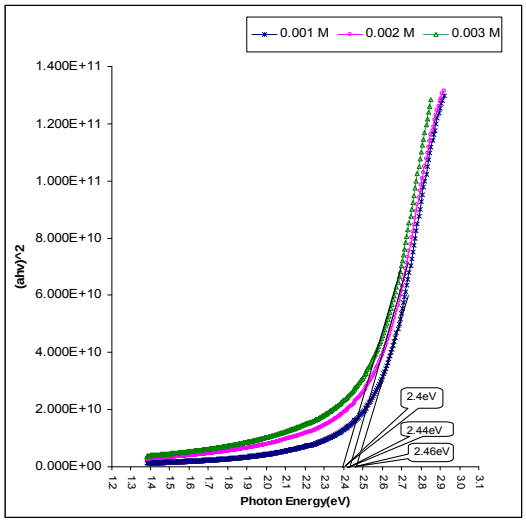

Figure 3: $(\alpha hv)^2$ Vs hv for Al Doped Zirconium Sulphide Thin Films.

Figure (4) is the SEM micrograph showing the Aluminium doped zirconium sulphide thin films with morphology very similar to the others reported earlier [18-20]. The SEM image in Figure 4 reveals that a good yield of the nanostructures is obtained. Interestingly, a large proportion of these nanostructures are nanotubes. The aluminum doped zirconium sulphide nanotubes structures could be created reproducibly and they were well dispersed and randomly oriented as a porous membrane and found to cover the entire substrate.

Although the aluminum doped zirconium sulphide nanotubes are not as well defined as the other non carbon nanotubes reported [18,19]. The nanotubes as can be seen from the SEM image in Figure 4 are closely placed, quite lengthy, some being more than a micron long with a smooth surface. Some nest-shell nano clusters are also presented in Figure 4.

The aluminum doped zirconium sulphide thin films showed compact distribution over the surface and good connectivity between the tubes. Their outer diameters are found using image identifier which is found to be 42 nanometer.

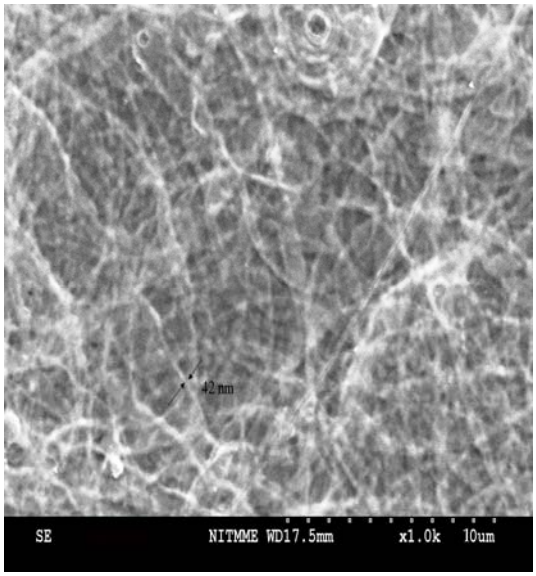

Figure 4: SEM Micrograph of Aluminum Doped Zirconium Sulphide Thin Films.

However, the inner diameters of the aluminum doped zirconium sulphide nanotubes are smaller. Breaks in nanotubes were rarely observed which implies that nanotubes have very high strength [21]. On close inspection; layer fringes are visible along the tube walls. Interrupted layer growth is observed in the inner edge of the tube wall, causing terminated layers and thus non uniformity in the wall thickness. Also visible in Figure 4 is the nanoscale substructure within the aluminum doped zirconium sulphide nanotubes, demonstrating their polycrystalline nature.

Several terminated layers are observed at the outer edge of the tube wall, possibly owing to the absence of growing materials at these edges. A considerable amount of defects are also present along the length of the tube wall.

CONCLUSION

Aluminum doped Zirconium sulphide thin films were prepared by employing home made spray pyrolysis technique using low cost precursors for the first time. By XRD studies it was established that the Al doped ZrS_2 thin films are polycrystalline in nature having a hexagonal crystal structure.

The absorption coefficient and optical band gap were determined from the absorbance spectra recorded in the wavelength range of 400-1000nm. It was found that the absorbance of the Al doped ZrS_2 thin films increases drastically due to increase in molarity of the dopant. The as-deposited thin film exhibited an direct optical transition in the range of 2.4 eV. SEM micrograph shows densely packed nanotubes having average tube diameter of 42nm .

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