STRUCTURAL AND OPTICAL PROPERTIES OF WS₂ THIN FILMS IN SPRAY PYROLYSIS

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ABSTRACT

Tungsten Disulphide (WS₂) thin films were prepared by thin film Spray Pyrolysis technique.

Cleaned glass substrates were used. The Substrate was maintained 400° c the films were Characterized by X-ray diffraction (XRD). The structure of these films studied by X-ray diffraction were polycrystalline monoclinic phase. Direct band gap values of 2.24 eV -2.79 eV were obtained from optical absorption measurements. The thickness of these films were determined by Weighing method and in the range of t = 235 nm, t = 425 nm and t = 436 nm.

Keywords: Structural and Optical Properties, Spray Pyrolysis

1. INTRODUCTION

Tungsten Disulphide (WS₂) thin films are regarded as one of the most promising materials for thin films solar cells. Wide band gap copper oxide (Eg=2.2eV) has been used as the window material together with several semiconductors such as CdTe [1], Cu₂S [2], InP [3] and CuInSe₂ [4] with 12-16% efficiency [5]. However due to high cost of such a material, studies were developed towards polycrystalline compound semiconductors and particularly thin polycrystalline films. The spray pyrolysed WS₂ films has been explored by different techniques. Thermal evaporation [6,7], Chemical bath deposition (CBD) [8], molecular beam epitaxy [9], and spray pyrolysis [10]

Several methods are reported for the preparation of WS_2 thin film such as electrodeposition, [11], Pulsed laser deposition [12], Physical vapor deposition [13], vacuum evaporation [14], close space sublimation [15], But all these methods have sophisticated requirement in other to precise temperature control, high pressure etc. Besides all above methods Spray pyrolysis techniques simple, convenient and cheaper.

2. MATERIALS AND METHODS

The spray pyrolysis technique is a simple technology in which an ionic solution-containing the constituent elements of a compound in the form of soluble salts-is sprayed onto over heated substrates using a stream of clean, dry air. The tungsten disulphide thin films were prepared by spraying an aqueous Solution of copper acetate 400°C. The atomization of the chemical solution into a spray of fine droplets is effected by the spray nozzle, with the help of compressed air as carrier gas. The spray rate was about 17cm3/min, through the nozzle ensures a uniform films thickness. The substrates are glass substrate temperature of substrate was controlled by an iron constant a thermocouple. After deposition, the films were allowed to cool at room temperature. Spray pyrolysis through is expensive, requires the use of sophisticated materials and overall, it is not impressive, now good quality semiconductors which allows fabrication of diode applications with satisfactory efficiency. Copper oxide thin films have received considerable attention due to their applications in thin film solar cells [16], electrochemical cells [17] and semiconductor metal schottky barrier cells [18].

Tungsten disulphide thin films is a technologically useful material, as many devices based on WS₂, including

sensors have come up in the recent years. The thin film tungsten disulphide applications have for several years been considered to be a promising alternative to the more widely used silicon devices.

One of the most promising techniques for producing large areas of inexpensive WS_2 film for terrestrial photovoltaic application is spray pyrolysis and here we followed this method to synthesize the WS_2 film. The structural properties of this films are carried out by X-ray diffraction and optical study in the UV-VIS region by spectrophotometer.

The aim of this work is to produce WS_2 thin films by means of the spray pyrolysis technique and to investigate their structural optical properties. Optical properties were obtained by transmission spectra. (TS).

3. **RESULT AND DISCUSSION**

3.1 STRUCTURAL PROPERTIES

In order to study the crystalline phase, the spray pyrolysed tungsten disulphide thin films XRD pattern are recorded in the 2θ range 400°C. Fig. 1 shows the XRD pattern of tungsten disulphide thin film coated for 12 min. The pattern shows polycrystalline nature of film. The peaks observed at 38.87° corresponding to (200) plane respectively.



By matching this peak values with the JCPDS data 84-1938 hexagonal phase have been confirmed. The maximum peak intensity is observed at 36.43° showing preferential orientation of tungsten disulphide film in (200) direction [19].

3.2 SURFACE MORPHOLOGY

This Fig. 2 shows that the Scanning Electron Microscopy (SEM) images of tungsten disulphide thin films. The surface morphology of the sample of tungsten thin film at temperature 400°C films sample show smooth coating of tungsten on the substrate with dense uniform grains. From the SEM images, the thicknesses of all the samples are measured and the values are 435 nm. It is observed that as the temperature varies, the thickness of the sample is also found to increase which is a consistent with the reported results. This may be result of high stress on the films that can lead to a peeling off from this substrate [20].



Fig 2 Scanning Electron Microscopy (SEM)

In this section we present the result of the realized diode applications based on WS_2 thin film. The diode applications fabrication and measurement procedures are described in previous sections. In order to characterize sensor performance towards ethanol vapor gas a set of characteristics parameters are investigated namely: operation temperature, sensitivity, detection limit, response times.

3.3 OPTICAL PROPERTIES

The values of absorbance wavelength spectra were recorded graphically for the WS_2 film at 400°C temperatures to obtain information of optical properties wavelength of the tungsten disulphide thin films. These absorbance spectra of the tungsten disulphide films obtained in the range between the 200 and 900 nm is shown in Fig 3.





These absorbance values slightly increase in the range of 250 to 800nm and then rabidly increases revealing the modification of the glass substrate and temperature [7]. Besides, as can be seen in Fig 3. shows the optical absorbance varies with respect to the temperature value. The effect of solution temperature on the absorbance of the tungsten disulphide films may be due to the variations associated with film thickness, structural properties, surface smoothness and defect density, etc. From (XRD) x-ray diffraction analyses, we have determined that the films consist of WS₂ hexagonal phase. On the other hand, WS₂ crystalline is a hexagonal structural and it has a biaxial and optically anisotropic. The double refraction is a polycrystalline films brings that the light scatterings. Hence the reduced absorbance in higher solution temperatures prepared film is a due to that light scatterings from the WS₂ thin films. Also, the decrease of absorbance values can also be interpreted with inferences from the (XRD) x-ray diffraction spectra. The absorbance spectrum shows the surface Plasmon's resonance indicating that crystallite sizes are in the nanometer ranges. It is observed that absorbance decreases with the wavelength from 60 to 50%. The values and maximum range of absorbance for WS₂ thin film deposited at concentration 0.2. Since tungsten disulphide thin films are some n-type materials, and their absorption property is important. Also, all films have

direct band gaps, and this is a property is suitable for the photovoltaic applications. These optical parameters such as absorption coefficient and band gap measurement are determined from the optical absorption measurements.

The value of absorption coefficient for strong absorption co-efficient region of thin films are calculated using that following Eq. (1),

$$\alpha = \frac{1}{t} In\left(\frac{A}{t}\right) \qquad (1)$$

where α is the absorption coefficient in cm⁻¹, t is that thickness off the films, A is that absorbance and T is that transmittance. The nature of transition is determined using the following Eq. (2) [21],

$$\alpha h\vartheta = A \left(h\vartheta - Eg\right) \quad (2)$$

where α is the absorption coefficient in cm⁻¹, hv is the photon energy in eV, Eg is an energy gap in that eV and K is constant which is then related to effective masses of associated with the valence and conduction band.



Fig.6.5 Optical Band Gap Energy

The values of 'n' determine that types of transition and present in the materials. In this case $n = \frac{1}{2}$ indicate that the transition involved in the material is direct allowed. A plot of hv versus $(\alpha hv)^{1/2}$ for WS₂ thin films obtained at solution 0.2 concentration of values shown in Fig 6.5. shows the extrapolation of linear portion of the graph to X-axis [energy (hv) axis] gives the bandgap values of present in the material. Mainly bandgap values of the material obtained in the present work is found be 2.38 eV for solution concentration of 0.2 respectively. This is close agreement with the value reported earlier for WS₂ thin films [21]. It is found that there are significant variations in the optical band edge, it will be due to a thickness of the thin films.

4. CONCLUSION

Tungsten Disulphide thin films were deposited by a spray pyrolysis technique using a solution of Tungsten thiousulphate. The films were deposited onto the glass substrate at the selected temperature 400^{0} C. Substrate temperature during deposition was found to have influenced the hexagonal phase. The films have good optical quality properties and are well-suited for diode applications. The films exhibited a direct transition 2.25 eV. These results suggest that the method of spray pyrolysis for the deposition of WS₂ thin films should be further investigated for application towards the fabrication of diode applications. The optical properties of WS₂ thin films were studied using transmittance spectra.

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REFERENCES:

[1]. Dobson K.D., Visoly Fisher I, Hodes G. and Cahen D., Solar Energy Materials and Solar Cells, 62, (2000), 295.

[2]. Das S.R., Nath P., Banerjee A and Chopra K.I., Solid State Commun, 21 (1977)1 49.

[3]. Frass L.M. and Ma Y., J. Cryst. Growth, 39 (1977), 92.

[4]. Tuttle J.R., Ward J.S. and Dudn J., Proc. **1996** Spring MRS Meet, San Francisco, CA 486, **1996**, p. 143.

[5]. Su B. and Choy K.L., Thin Solid Films, 359 (2000), 160

[6]. Ashour A., El-Kadry N. and Mahmoud S.A., Thin Solid Films, 269, (1995), 117.

[7]. Mahmoud S.A., Ibrahim A.A. and Riad A.S., Thin Solid Films, 372, (2000), 144.

[8]. Oliva A.I., O. Solis-Canto, R. Castro-Rodriguez and Quintana P., Thin Solid Films, 391, (2001), 28

[9]. Hofimann Ph, Horn K., Bradshaw A.M., Johnson R.L., Fuchs D. and Cardona M., Phys. Rev., B47, (1993),1639.

[10]. Battisha I.K., Afify H.H., Abd El-Fattah G. and Badr Y., Fizika, A11, (2002), 31

[11]. Gopal V., April GC and Schrodt VN, Sep Purif. Technol., 1998, 14, 85.

[12]. Pouzet JC, Bernede, Kelil A., Essaidis H., Benhida, Thin Solid Films, 1994, 15, 252.

[13]. Birkmire RW, MccandlessBE. Hegedes SS, Solar Energy, 1992, 13, 303.

[14]. Ugwn EI, Ugwn and Onan DU, Pacific Journal Sci. Tech., 2007, 8,160

[15]. Chu TL, Chu SS, Int. J. Sol Energy, 1992, 12, 121.

[16]. George F.Fine, Leon M.Cavanagh, Ayo Afonja and Russell Binions, Metal Oxide Semi-Conductor Gas Sensors in Environmental Monitoring, International Journal of Sensors, Vol. 10, 5469-5502, 2010.

[17]. Ramesh H.Bari, Sharad.B.Patil, Anil.R.Bari, Synthesis, Characterization and Gas Sensing Performance of Sol-gel Prepared Nanocrystalline SnO_2 thin films, International Journal on Smart Sensing and Intelligent Systems, Vol.07, 610-629, 2014.

[18]. Shivanand G.Sonkamble and Anil B.Gambhire, Gas Sensing Properties of Nanocrystalline Silver/Tin Dioxide Sensor Prepared by Co-precipitation Method, Advances in Applied Science Research, Vol. 05, 12-18, 2014.

[19]. Roy.S.S, Bhuiyan.A, Podder.J, Optical and Electrical Properties of Copper Oxide Thin Films Synthesized by Spray Pyrolysis Technique, Journal of Sensors and Transducers, Vol.191, 21-27, 2015.

[20]. Mariob Alberto Sanchez-Garcia, Arturo Maldonado, Luis Castaneda, Rutilo Silva-Gonzalez, Maria de la Luz Olvera, Characteristics of SnO₂: F Thin Films Deposited by Ultrasonic Spray Pyrolysis: Effect of Water Content in Solution and Substrate Temperature, Journal of Materials Sciences and Applications, Vol.3, 690-696, 2012.

[21]. Helen.S.J, Suganthi Devadason and Mahalingam.T, Improved Physical Properties of Spray Pyrolysed Al:CdO Nanocrystalline Thin Films, Sci, Journal of Materials Science: Materials in Electronics, Vol.27, 4426 – 4432, 2016.