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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.13, pp 5382-5386, November 2014

MESCon 2014 [4th -5th September 2014]
National Conference on Material for Energy Storage and Conversion- 2014

Synthesis and Characterization of Tungsten Trioxide (WO_3) Thin Films by Advanced Microprocessor Controlled Spray Pyrolysis Method

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Abstract : One of the simplest method in thin film preparation is the spray pyrolysis technique, which involves many technical aspects for the preparation of uniform coating. Homogeneous, high quality and nano crystallite sized WO_3 thin films are prepared by microprocessor controlled spray pyrolysis technique which is compared with WO_3 thin films prepared by classical manual hot plate spray technique. The WO_3 films prepared by both techniques have been characterized by X-ray diffraction analysis and found to be polycrystalline with monoclinic structure. The characteristic precessional peaks of (200), (020) and (002) planes are observed in both the techniques with enhanced formation in the advanced method. Surface of the films are found to be smooth from the scanning electron micrographs and the annealed films consist of nano crystals with spherical shape. The optical band gap is found to be 3.5 and 3.3eV for the as deposited and annealed films respectively with indirect transition. The microprocessor controlled and annealed films show enhancement in the film quality.
Keywords: Spray pyrolysis technique; Tungsten trioxide; Structural and Optical properties; Surface Morphology

1 Introduction

Spray Pyrolysis Technique has been one of the simple, cost effective and important technique to deposit a wide variety of materials in thin film form. For obtaining good quality thin films, the necessary optimum conditions required are substrate temperature, pressure, spray rate, concentration of the solution, the distance between spray nozzle and substrate etc.,[1]. The improvement in the quality of the thin films can be achieved with automization techniques such as microprocessor based controller spray pyrolysis.

Tungsten trioxide, a wide band gap semiconductor with excellent optical properties has been investigated for gas sensors[2-4] and electrochromic devices[5]. The characteristics of WO_3 films depend on the film preparation conditions. Various deposition methods have been utilized to prepare WO_3 thin films including pulsed laser deposition, sputtering, sol-gel process, spray pyrolysis, electron beam evaporation etc., Among these techniques, the spray pyrolysis technique is preferred due to its simplicity, low cost and more versatile than any other technique[1]. In the present work, the preparation of WO_3 thin films by spray pyrolysis method was investigated.

2 Experimental Details

In this paper, Tungsten trioxide films were deposited on glass substrates by two methods. One the manual controlled old hot plate spray pyrolysis technique and the other the advanced microprocessor based controller spray pyrolysis method.

2.1 Preparation of precursor solution and WO_3 thin film coating

The precursor solution of concentration 0.05M was prepared by dissolving an appropriate quantity of pure analor grade WO_3 powder in hot (80°C) ammonia solution with continuous stirring and diluted with de-ionised water to desired volume and then filtered.

The WO_3 films were deposited by spraying the precursor solution through glass nozzle on to the preheated glass substrates kept at 350°C in simple hot plate technique. The temperature was monitored by a chromel-alumel thermocouple fixed to the metallic hot plate. In microprocessor based controller spray pyrolysis method, the precursor solution was sprayed through specially designed steel nozzle on to the substrates kept at 350°C. The other parameters like pressure, spray rate and the distance between spray nozzle and substrate were idealized for obtaining good quality WO_3 thin films after many trials in manual controlled hot plate technique whereas in advanced microprocessor controlled spray unit, the above parameters were controlled by microprocessor. After the deposition, some of the prepared samples were annealed at 400°C for 1 hour and then cooled naturally.

2.2 Characterisation

The crystal structure was investigated by XRD analysis. Surface morphology was examined by a Scanning Electron Microscope with Energy Dispersive X-ray analysis spectrometer in STIC, Cochin. The optical studies were carried out by the UV –VIS double beam spectrophotometer.

3 Results and Discussion

The WO_3 films were found to be uniform, pin hole free and well adherent to the glass substrates. The colour of the as deposited film was pale white and changes to greenish yellow when annealing at 400°C in air[1].

3.1 Structural Properties

The XRD patterns of the WO_3 films as-deposited at 350°C and annealed at 400°C by manual controlled spray pyrolysis method is shown in Fig 1. The corresponding patterns for microprocessor based controller spray pyrolysis unit is shown in Fig 2. All the as-deposited films are amorphous and the crystallinty increases after annealing with well defined peaks along with triplet peak which shows the monoclinic structure. The three predominant peaks are (200), (020) and (002) at 23.1°, 23.7°and 24.4° corresponding to d=0.385, 0.375 and 0.365nm. The obtained 2θ values and the interplanar spacing d-values are compared with standard values in JCPDS card no. 83 – 0951 for monoclinic WO_3. The lattice constants calculated from the peak positions are a= 7.33209A°, b= 7.54300A° and c=7.67968A° with β=90.884° for microprocessor controlled spray pyrolysis setup and are found to be in good agreement with the literature[1,6].

The crystallite size of WO_3 thin film D was estimated by the Debye – Scherrer formula $D = 0.9 \lambda / \beta \cos\theta$. The average crystallite size of the film is found to be 40 nm.

3.2 Surface morphology

Irregular aggregates of particles are present in the as deposited WO_3 film at 350°C (figure 3a) and micron sized spheres are present in the film when annealed at 400°C with some cracks and cavities (figure 3b) for manual controlled spray unit. Their diameter ranging from 1.00µm to 1.76µm. The cracks and cavities are due to the heat treatment[6,9]. For microprocessor controlled spray unit, the as deposited film at 350°C reveals a moderately smooth surface with irregular features (figure 4a) and the nanosphere diameters of WO_3 thin film are distributed in the range 380-506nm when annealed at 400°C (figure 4b). Thus by using the advanced microprocessor based system, nano crystallite sized WO_3 thin films can be obtained.

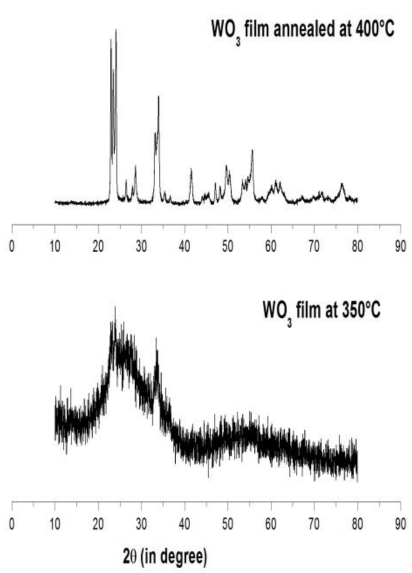

Fig 1)XRD pattern for WO_3 film deposited at 350°C and annealed at 400°C for 1 hr by manual controlled spray unit

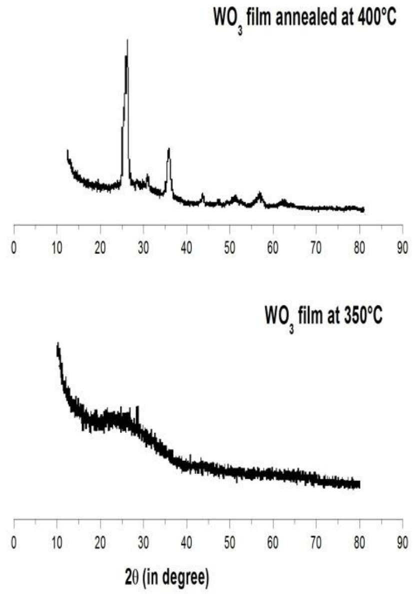

Fig 2) XRD pattern for WO_3 film deposited at 350°C and annealed at 400°C for 1 hr by microprocessor controlled spray unit

As-deposited film at 350°C

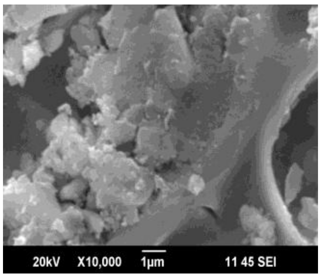

Fig 3a

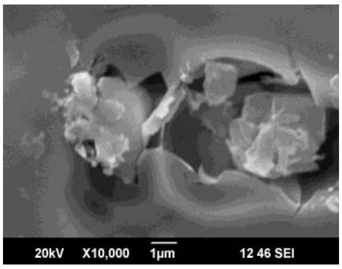

Fig 4a

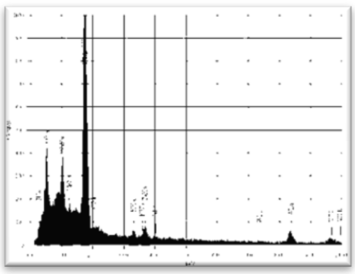

Fig 5a

Annealed film at 400°C

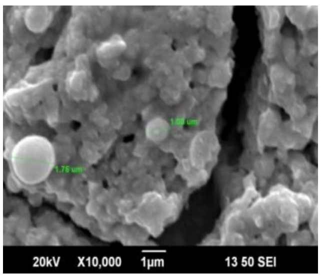

Fig 3b

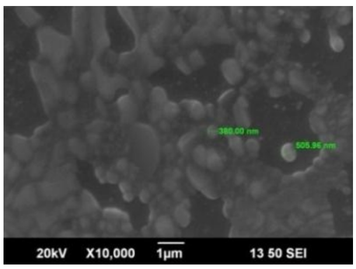

Fig 4b

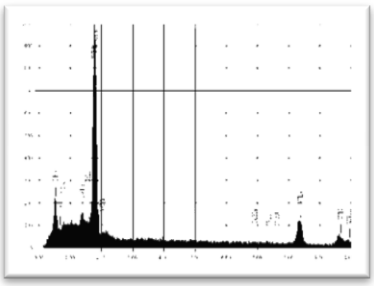

Fig 5b

SEM image by manual controlled spray unit

SEM image by microprocessor controlled spray unit

EDAX spectrum by microprocessor based spray unit

3.3 Optical properties

The optical transmittance spectra of the WO_3 films were recorded (Fig 6) by the UV-VIS double beam spectrophotometer. The as-deposited films show 75% transmittance in the visible region[6,9] and the heat effects reduce the transmittance to 45% for the annealed films[9] in both methods.

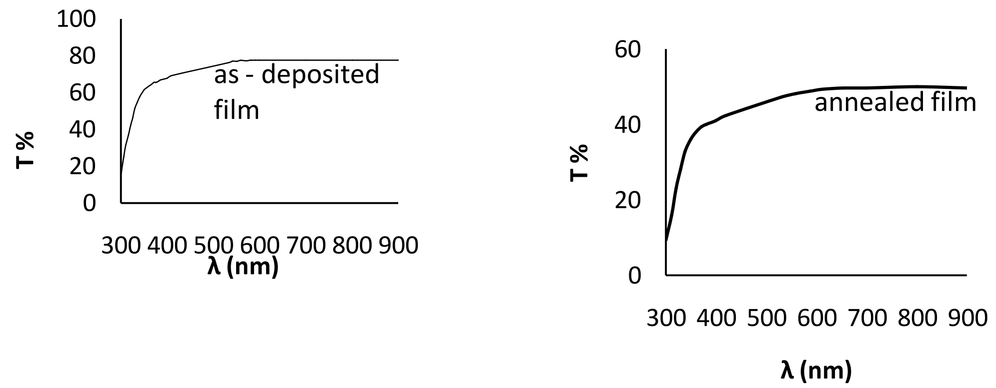

Fig 6) Transmittance curve for the microprocessor controlled spray unit

The indirect optical band gap has been estimated from the plot of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for the WO_3 films (Fig 7). The optical band gap is found by extrapolating the linear portion of the curve to $\alpha h\upsilon = 0$ and equal to 3.5 and 3.3 eV for the amorphous and crystalline WO_3 films respectively[8,9].

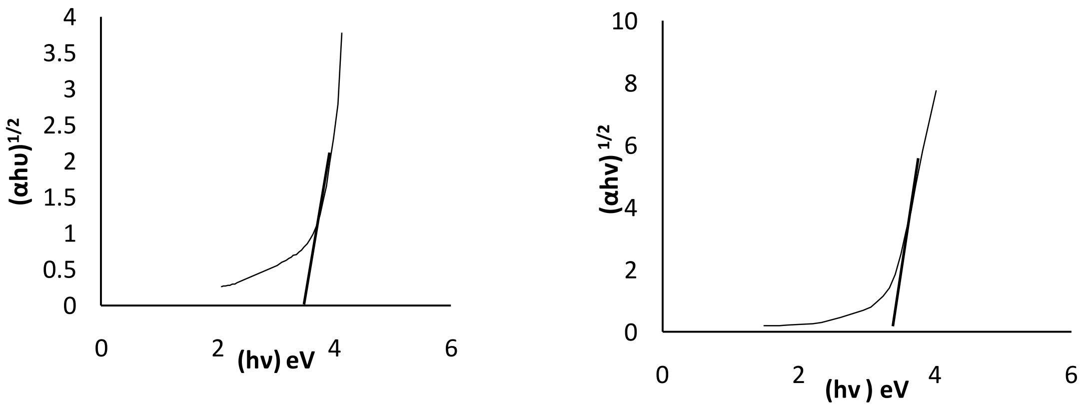

Fig 7: Plot of $(\alpha h\upsilon)^{1/2}$ vs $h\upsilon$ for the microprocessor controlled spray unit

4 Conclusion

With advanced microprocessor based controller for spray pyrolysis technology, good quality Tungsten trioxide (WO_3) thin films were prepared. Compared to the manual controlled simple hot plate spray technology, the microprocessor controlled spray unit improves the coating deposition. Uniform and defect free WO_3 films were prepared in a simple manner at a lower cost. Structural properties confirmed the formation of WO_3 film. The as-deposited films were amorphous and the annealed films exhibited well defined peaks along with the triplet peak which confirms the polycrystalline monoclinic structure in the microprocessor controlled spray method. The average crystallite size of the film was 40 nm. The surface morphological studies revealed the spherical type of features with diameter 380 - 506nm in the surface with some cavities due to annealing. The composition of the film was confirmed by EDAX spectrum. The optical studies showed an indirect transition with optical band gap energy of 3.5 and 3.3 eV and the average transmittance was around 75% and 45% for the amorphous and crystalline WO_3 films respectively.

Acknowledgements

P. Shanthini Grace wishes to thank the UGC - XI plan for sanctioning the Minor Research Project to carryout some part of the experimental work by designing the microprocessor controlled spray pyrolysis unit.

References

1. P.S. Patil, P.R. Patil, E.A. Ennapio. Thin Solid Films, 2000, 370; 38 – 44.
2. M. Penza, M.A. Tagliente, L. Mirenghi, G. Gerardi, C. Martucci, G. Cassano, Sens. Actuators B chem.,1998, 50; 9.
3. M. Gillet, K. Aguir, C.Lemire, E. Gillet, K. Schierhanum, Thin solid films, 2004, 467; 239.
4. Georg. W. Graf, V. Wittwr, Vacum, 2008, 82; 730.
5. G.E. Buono – Core, a.H.Klahn, C. Castillo, M.J. Bustanmante, E. Munez, G.Cabello, B. Chornik, Poly hedron, 2011, 201 – 206.
6. M. Regragui, M. Addou, A. Outzourhit, J.C. Bernede, Elb, EI. Idrissi, E. Benseddik, A. Kachouane, Thin solid films, 2000, 358; 40 -45.
7. Camelia Matei Ghimbeu, Robert C. Van Labdshoot, JoopSchoonman, Martine Lumbreras, Thin solid films, 2007, 515; 5498 – 5504.
8. M.G. Hutchins, D. Abu-Alkhair, M.M. EI –Nahass, K. Abb El–Hady, Proc.2nd Saudi Scr. Conf. Fac.Sci.KAU, 15 – 17 March 2004, Part II, PP – 267 – 276 (2005 AD / 1425 A. II).
9. Abdoljavad Novinrooz, Masoomeh Sharbatdaran, Hassan Noorkojouri, Central European Journal of Physis, 2005, 3(3); 456 – 466.

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