International Science Journal (Peer-Reviewed)
ISSN: 2348 – 604X (p); 2348 – 6058 (e)

SURFACE MORPHOLOGY AND PROPERTIES OF MOLYBDENUM OXIDE THIN FILMS

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ABSTRACT
There is a growing necessity of transition metal oxide thin film for many important technological applications such as smart windows gas sensors, solar cells, super capacitors etc. Among the other transition metal oxides, Molybdenum oxide is a potential material as it exhibits interesting structural, optical, chemical, electrical properties. In this investigation Molybdenum oxide thin films have been synthesized using spin coating technique. The films were deposited on glass substrate by using 0.1 M Ammonium Molybdate tetrahydrate and annealed at a temperature of 600°C for 10 minutes. The thin films were characterized for their structural and morphological, optical and electrical analysis by using XRD, SEM, FTIR, UV and DC conductivity measurements. Structural Study showed the monoclinic structure and morphology in the form of nanorods grouped in clusters. The infrared spectrum of as deposited MoO3 thin film depicted strong absorption bands at 899 and 764 cm-1 indicating the stretching mode of Mo=O. The experimental band gap value observed was 3.0 eV.

KEY WORDS: Metal Oxide, Molybdenum Oxide, Spin-Coat, XRD, SEM, FTIR, Conductivity.

INTRODUCTION

Among the transition- metal oxides, Molybdenum oxide (MoO_3) is a material that finds potential applications due to its abundance (Subbarayudu, 2013). MoO_3 has been extensively investigated as a key material for fundamental research and technological applications in optical devices, smart windows, catalysts, sensors, lubricants, and electrochemical storage (Mai, 2007). MoO3 is a wide bandgap *n*-type semiconductor (Navgire, 2011). Molybdenum oxide thin films have their absorption peak close to the human eye sensitivity peak. This property makes MoO_3 very attractive applications in optoelectronic devices (Ganguly, 2007) MoO_3 thin films exist in three phases namely: orthorhombic α- phase, monoclinic β- phase and hexagonal phase. The thermodynamically stable orthorhombic α-MoO3 and the metastable monoclinic β-MoO3 with ReO_3 –type structure are the mostly studied ones (Klinbumrung, 2012). In order to prepare MoO_3 in the form of thin films, number of methods have been used, such as electro-deposition (Patil. R. S, 2006), thermal evaporation (Sian. T. S, 2005), pulsed laser deposition, hot wire chemical vapor deposition (Hsu, 2008), magnetron sputtering method (Dhanasankar, 2011), Sol-gel, Spray Pyrolysis etc. In this work, thin films of MoO_3 were deposited at atmospheric pressure on glass substrates, by Spin Coating process, In the present investigation, efforts are taken to report synthesis of MoO_3 thin films by a low cost spin coating technique and structural, optical, electrical characterization of the same by XRD, FTIR, UV and DC conductivity techniques.

MATERIALS AND METHODS

Deposition of MoO3 Thin Films

MoO_3 thin films have been synthesized by a spin coating technique using ammonium molybdate as a source of Molybdenum oxide. In a typical experiment, 0.1 M solution of ammonium molybdate tetrahydrate was prepared. To obtain homogeneous solution a magnetic stirrer was used. To avoid the effect of contaminations, it is necessary to clean the substrate. First the substrates were washed with double distilled water then washed with concentrated chromic acid. After that they were ultrasonically cleaned, finally dried and greased with acetone. An excess amount of the solution was prepared and deposited on glass substrate by Spin coating unit manufactured by Millman Thin Films Systems Pvt. Ltd. After setting the substrate on the holder, by using nozzle 0.2ml of solution was placed on the glass substrate. Thickness and uniformity of the films with respect to the substrate can be tuned by adequately adjusting the concentration of the precursor solution, the solvent, and the spin-rate during spin-coating. The sample was then rotated at a controlled rotational speed of about 3000 rpm for a period of 3 minutes in order to spread the fluid by centrifugal force and evaporate the solvent. After that, it was transferred to a high temperature furnace for

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heat treatments. The thin films were annealed at a temperature of 600 °C for 10 minutes. The chemicals reacted on the substrate and formed the desired solid thin film. The deposition was repeated for number of time to increase the thickness of the film. During processing, ammonium molybdate decomposes as follows:

$$(NH_4)_6Mo_7O_{24}.4H_2O \xrightarrow[600°C]{\Delta} 7MoO_3+6NH_3+7H_2O$$

NH_3 and H_2O were diffused out and MoO_3 was left as final product.

Characterization

The structural evolution was observed by XRD using Cu Kα radiation (λ [K α(Cu)]=1.54A°) in a Brucker D8 Advanced instrument employing a voltage of 30kV and current of 15 mA. This analysis was carried out at the 10°≤ 2θ≤ 80°range, with a goniometer speed of 5° per min and a step size of 0.02. The spectral analysis was based on the fact that the structure of MoO_3 for which their bending IR active model occur in the range 500 to 4000 cm^{-1} at room temperature infrared spectrophotometer (Nicolet IR-10 Thermofischer Scientific, USA). The optical absorption in the range 200 nm-1000 nm had been investigated by Double Beam Photo spectrometer 'Hitachi - 330', Japan. The two-probe technique was employed for measurement of variation of electrical conductivity of MoO_3 film with increasing temperature.

RESULTS AND DISCUSSIONS

Physical Analysis

The as deposited thin films were well adherent to substrate and uniform. The color of sample was white with blue tinge. The thickness of the film was calculated by weight difference method and it lies in the range of 6.80 micrometer.

Structural Analysis

The structural changes and identification of phases were studied. Fig-1 shows X-ray diffraction pattern for MoO_3 thin films deposited on glass substrate annealed at a temperature 600^0C by spin-coating technique. Table 1.gives the details of calculated and standard'd' values and planes of MoO_3 deposited thin films.

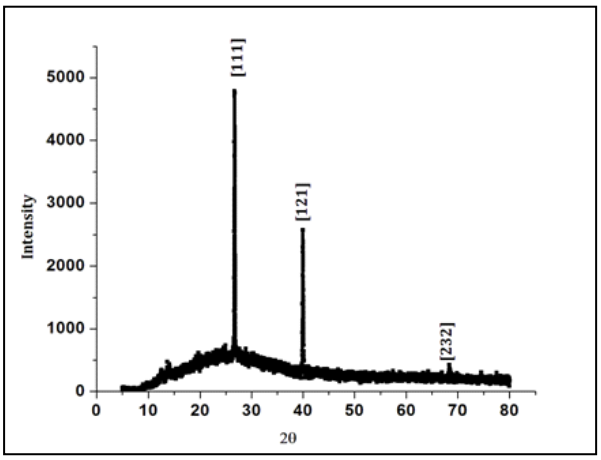

Figure-1. XRD Pattern for Molybdenum Oxide Spin Coated Thin Films.

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Table-1: Comparison of observed'd' values, obtained from XRD data with the standard'd' values, from JCPDS card No-89-1514.

	MoO_3 (films from this work)		MoO_3 (Card No. 89-1514)	
Peak No.	**2θ**	**d**	**d**	**[hkl]**
1	26.68	3.33856	3.3605	[111]
2	39.94	2.25540	2.2778	[121]
3	68.40	1.37040	1.39	[232]

The reported pattern exhibits [111] phase (d=3.338), [121] phase (d=2.255), [232] phase (d=1.370) XRD peaks corresponding to MoO_3 monoclinic phase. These peaks were indexed by comparing the experimental data with JCPDS card (JCPDS. No- 89-1514). The obtained values of lattice parameters were a= 6.881A°, b= 5.297 A°, c= 5.56 A° which are in good agreement with the values as compared with JCPDS card No.89-1514, which verifies the structure of as deposited thin films as monoclinic.

Surface morphological studies

The two-dimensional surface morphology study of MoO_3 thin film has been carried out from SEM. Figure-2 shows the SEM images of MoO_3 thin film on the glass substrate for various magnifications. The morphology showed that the substrate is well covered with MoO_3 material having smooth and fine features. From the figure one can see the porous nature of as- deposited MoO_3 thin film. The developed grains are grouped in clusters which are observed in SEM image. At higher magnification these clusters are formed with composition of Nanorods or Nanotubes.

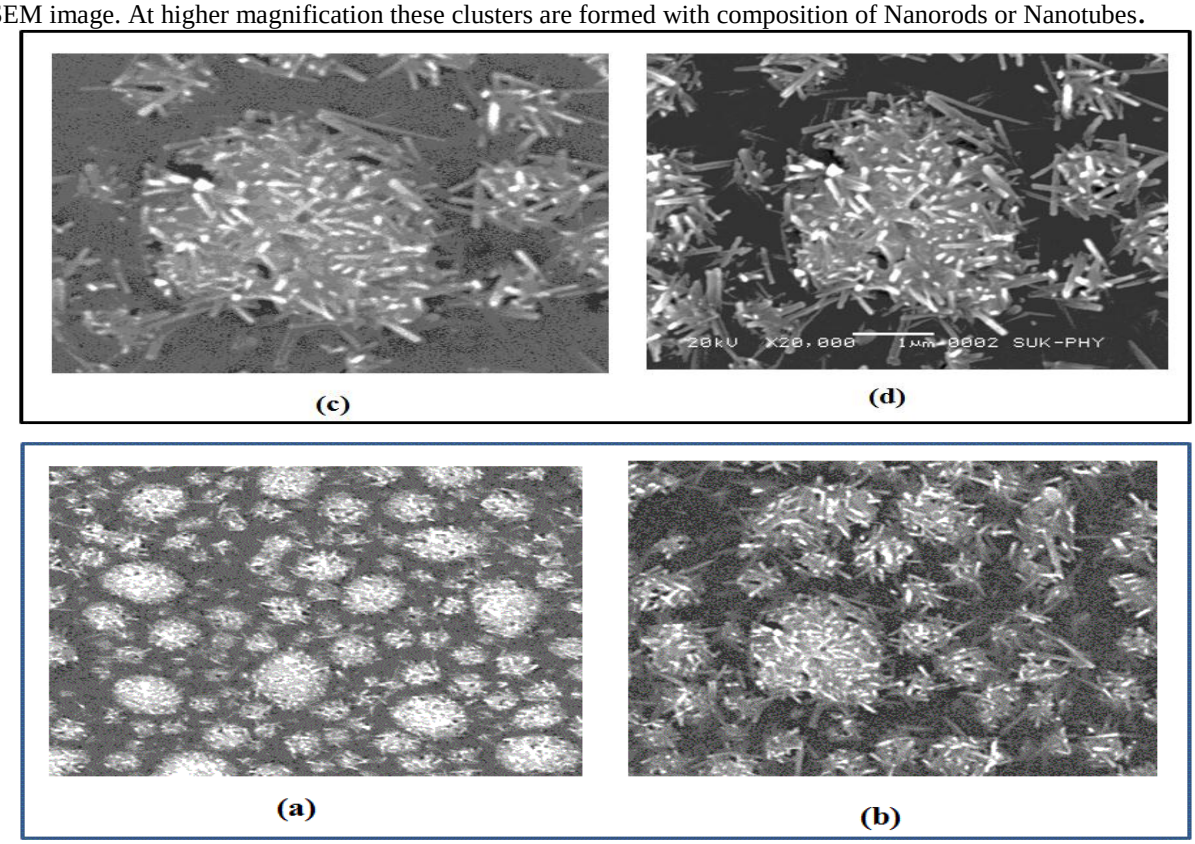

Figure-2. Morphological images of MoO3 Thin Films (a) X2000, (b) X5000, (c) X10000 (d) X20000 magnification.

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FTIR Spectroscopy

I.R. spectroscopy was used to obtain additional information on the phases as well as structure transformations of MoO_3 phases.Fig-3 describes the dependence of optical spectra in the range 500 to 4000 $cm^{-1}$for Molybdenum Oxide thin films.

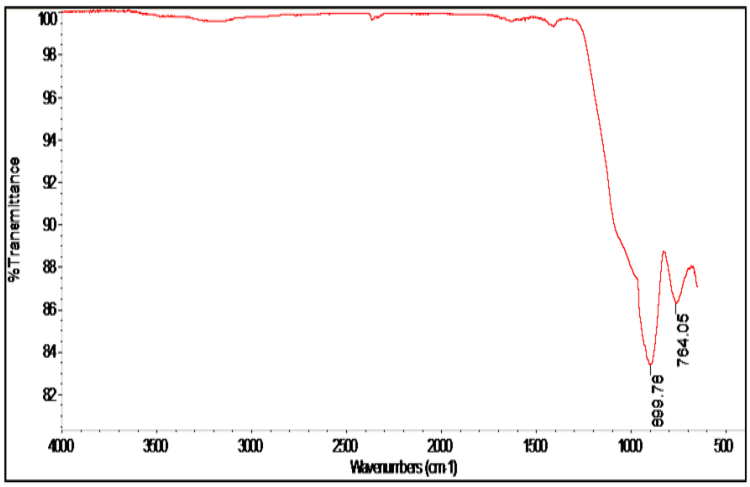

Figure- 3. FTIR Spectrum of MoO_3 Thin Films.

The infrared spectrum of as deposited MoO_3 thin film depicts strong absorption bands at 899 and 764 cm^{-1} indicating the stretching mode of Mo=O. The dominant band at 899 $cm^{-1}$is associated with the vibration of Mo=O stretching (Taher**,** 2010; Irmawati, 2009) and band at 764 cm^{-1} indicates the weak O-Mo-O stretching. Bouzidi et al., observed the similar results (Bouzidi, 2003).

Optical Properties

The optical absorption is a useful method for the investigation of optically induced transition and the provision of information about the band structure. The principle of this technique is that photons with energy greater than the band gap energy will be absorbed. The MoO_3 thin films on glass substrate were used to study the optical absorption.

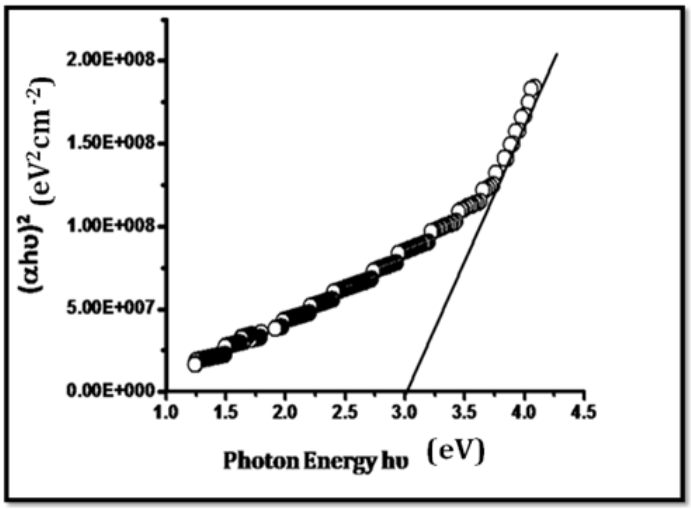

Figure 4. Plot of $(\alpha h\nu)^2$ versus $(h\nu)$ of MoO_3 thin Films

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Fig-4 shows plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for MoO_3 thin films. The value of E_g was estimated from the intersection of the extrapolated linear part of $(\alpha h\upsilon)^2$ curves with the energy axis. The experimental E_g value observed was 3.0 eV. According to quantum confinement theory, the band gap energy of a semiconductor increases with decrease in particle size. Bouzidi et al., (2003) and Patil et al., (2012), reported nearly same band gaps for MoO_3 thin films.

Electrical Properties: DC Conductivity Measurement

The variation of Log conductivity (σ) with reciprocal temperature (1000/T) is depicted in figure**.** From figure-5, it was observed that the conductivity of film increased with increase in temperature from 500 K to 645 K from 10^{-4} to $10^{-2}(\Omega\ cm)^{-1}$. Further it was observed that conductivity obeys Arrhenius behavior which indicates semiconducting transport behavior. Though MoO_3 is having wide band gap of nearly 3.0 eV, when the oxide is reduced, due to oxygen deficiency, electronic double levels are created near the bottom of the conduction band and therefore the reduced oxides behave as semiconductors (**Patil,** 2012). The conductivity in the solid state is mainly dependent on: the concentration of charge carriers, temperature of the crystal, the availability of vacant-accessible sites and the ease with which an ion can jump to another site etc (**Rao,** 2013).

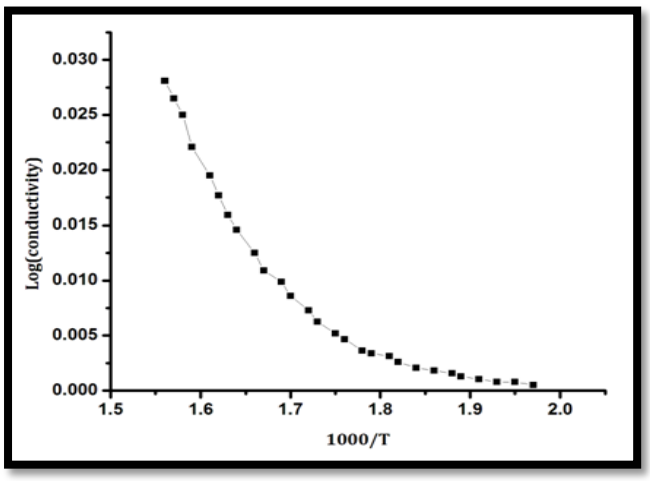

Figure-5. Arrhenius Plot of dc conductivity vs. 1000/T of MoO_3 Thin Films.

The last factor, namely, the ease with which an ion can jump to a neighboring site is controlled by the activation energy. The activation energy is the free energy barrier an ion has to overcome for a successful jump between the sites. Among the various factors that influence the ionic conductivity of a crystal the activation energy is of utmost importance since the dependence is exponential. The activation energies are most commonly deduced using the Arrhenius expression, given by,

$$\sigma = \sigma_0 \exp(-E_a / kT)$$

Where,
σ = conductivity at temperature T,
σ_o = constant,
k = Boltzmann constant,
T = absolute temperature
E_a = activation energy.

The calculated activation energy is nearly 3.5 eV which represents the location of trap levels below the conduction band.

CONCLUSION

Thin films of Molybdenum Oxide were prepared by spin coating technique. The MoO_3 thin films were annealed at a temperature of 600 °C. The as deposited films were uniform, white in colour with blue tinge and well adherent to the substrate. The XRD results revealed the monoclinic structure of MoO_3 thin film. The SEM shows the porous nature of MoO_3.The Fourier transform infrared transmittance spectra of the films indicated that the presence of characteristic vibrational modes of Mo = O and Mo – O – Mo related to the growth of MoO_3.The dc electrical conductivity was increased from 10^{-4} to 10^{-2} ($\Omega.cm^{-1}$) with increase in temperature from 500 K to 645 K. Optical Absorption spectrum showed the band gap of 3.0 eV.

ACKNOWLEDGEMENTS

Authors wish to acknowledge the U.G.C, New Delhi for financial support through the Major Research Project F No. 42-123/2013(SR).

REFERENCES

Bouzidi A., Benramdane N. and Tabet-Derraz. H. (2003). Effect of substrate temperature on the structural and optical properties of MoO_3 thin films prepared by spray pyrolysis technique. Materials Sci. Engineering, B97. 5.

Dhanasankar M., Purushothaman K. and Muralidharan K. (2011). Effect of temperature of annealing on optical, structural and electrochromic properties of sol-gel dip coated molybdenum oxide films. *Appl. Surf. Sci.* 257: 2074

Ganguly A. and George. R. (2007). Synthesis, characterization and gas sensitivity of MoO3 nanoparticles. *Bull. Mater. Sci.* 30:183,

Hsu. C. S. Chan C.C. Huang C., Peng H. and Hsu W. C. (2008). Electrochromic properties of nanocrystalline MoO3 thin films", Thin Solid Films, vol. 516, no. 15, pp. 4839–4844

Irmawati R. and Shafizah M. (2009). The Production of High Purity Hexagonal MoO3 through the Acid Washing of As-prepared Solids. *Int. J. Basic Applied Sci.* 09: 34-36.

Klinbumrung A., Thongtem T. and Thongtem S. (2012). Characterization of Orthorhombic α-MoO3 Microplates Produced by aMicrowave Plasma Process. *Hindawi Publishing Corporation J. Nanomaterials.* Article ID 930763,1-5

Mai L., Hu B., Chen Y., Lao C., Yang R., Dai Y. and Wang Z. (2007). Lithiated MoO3 Nanobelts with Greatly Improved Performance for Lithium Batteries", *DOI: 10.1002/adma*.

Navgire M. E. Lande M. K., Gambhire A. B., Rathod S. B., Aware D. V. and Bhitre S. R. (2011). Effect of poly (ethylene glycol) surfactant on carbon-doped MoO3nanocomposite materials and its photocatalytic activity. *Bull. Mater. Sci.* 34: 535

Patil G.E., Ahire G.E. and Shinde S.D. (2012). Preparation of MoO_3 Thin Films by Spray Pyrolysis and ITS Gas Sensing Performance. *Int. J. Smart Sensing Intelligent Systems.* 5 (3): 592-605.

Patil R. S., Uplane M. D. and Patil P. S. (2006). Structural and optical propertiesof electrodeposited molybdenum oxide thin films. *Appl. Surf. Sci.* 252: 354-358.

Rao M. C., Ravindranath K., Kasturi A. and Shekhawat M. S. (2013). Structural Stoichiometry and Phase Transitions of MoO3Thin Films for Solid State Microbatteries. *Res. J. Recent Sci.* 2(4):6.

Sian T. S and Reddy G. B. (2005). Stoichiometric amorphous MoO3 films: a route to high performance electrochromic devices. *J. Applied Phy.* 98: 2, Article ID 026104.

Subbarayudu S., Madhavi V. and Uthanna S. (2013). Post-deposition annealing controlled structural and optical properties of RF magnetron sputtered MoO3 films. Adv. Mat. Lett. 4(6): 637.

Taher M A., Jarelnabbi S. E. and Bayouy B. E. (2010). Synthesis and Spectroscopic Studies of Some New Molybdenum, Tungsten, and Ruthenium Carbonyl Derivatives of 2-Hydroxymethylpyridine. *Int. J. Inorganic Chem.* Article ID 29621.

