

Available online at www.sciencedirect.com**ScienceDirect**

Procedia Materials Science 6 (2014) 1104 – 1109

Procedia
Materials Sciencewww.elsevier.com/locate/procedia

3rd International Conference on Materials Processing and Characterisation (ICMPC 2014)

Molybdenum Heteropolyoxometalate Thin Films for Solar Cell Applications

S. R. Mane^a, B. J. Walekar^a, R. M. Mane^b, V. V. Kondalkar^b, V. B. Ghanwat^b,
P. N. Bhosale^b^a*Department of Chemistry, Smt. Kusumtai Rajarambapu Patil
Kanya Mahavidyalaya, Islampur. 415 409, India.*^b*Materials Research Laboratory, Shivaji University, Kolhapur. 416 004, India.*

Abstract

Thin films of nanocrystalline Thallium doped Molybdenum heteropolyoxometalate (TIPMA) have been deposited on to glass and fluorine-doped tin oxide (FTO) coated glass substrates from aqueous acidic bath using simple chemical bath deposition technique. The different preparative parameters like concentration of bath, deposition time, bath temperature, pH of the bath have been optimized in order to get good-quality photosensitive thin films of Thallium doped Molybdenum heteropolyoxometalate material. Different techniques have been used to characterize nanocrystalline Thallium doped Molybdenum heteropolyoxometalate thin films annealed at 250 °C for 2 hours at heating rate 10 °C/min. Optical absorption study shows the presence of direct transition with band gap energy 2.15 eV. The X-ray diffraction (XRD) analysis of the annealed films showed the material is nanocrystalline in nature with simple cubic spinal structure. Energy-dispersive analysis by X-ray (EDAX) study for the sample deposited at optimized preparative parameters shows that presence of P, Mo, O and Tl in the films without any major impurity. Scanning electron microscopy (SEM) for samples deposited at optimized preparative parameters reveals that spherical grains are uniformly distributed over the surface of the substrate indicates the well-defined growth of nanocrystalline (TIPMA) on thin film. PEC characterization of the films is carried out by studying photo response, spectral response and photovoltaic output characteristics. The fill factor (ff) and power conversion efficiency (η) of the cell are 15.0 and 0.42 %, respectively.

© 2014 Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Selection and peer review under responsibility of the Gokaraju Rangaraju Institute of Engineering and Technology (GRIET)

Keywords: Chemical bath deposition; XRD, SEM, EDAX.

1. Introduction

In this modern era, rising living standards of a growing world population can no longer be satisfied through conventional means. Depleting oil sources and ecological factors force us to find alternative energy sources. It has

E-mail address: sambhaji_mane@rediffmail.com

been estimated that by 2050 the energy gap will be around 15 tW. The majority of today's energy is produced from fossil fuels. The consequence of the growing dependence on fossil fuels has created an augmentation of the greenhouse effect and resulted in global warming. Solar energy is a clean, reliable and renewable source of energy responding to future demands. As a source of alternative energy supplies solar cells are the best choices due to the abundance of uncaptured solar energy on the earth. More solar power strikes the surface of the earth in one hour than the energy provided by the fossil fuels that are currently consumed globally in one year. Over the past two decades Silicon technology has dominated the domain of PV cells using flat single layer p–n junction diodes; however, now-a-days this photovoltaic technology is facing a strong challenge from third generation PV technologies (Ruan et al. 2006; Xun et al.; Rahmanab et. Al. 2013; 2000; Murli et al. 2005; Lade et al. 2001).

Our aim of the present work is to study and develop the low cost, good efficiency devices using molybdenum heteropolyoxometalate thin films. Photoelectrochemical studies on these materials are found to be very rare. Hence this research article is an account of the photoelectrochemical investigations of molybdenum heteropolyoxometalate thin films.

2. Experimental Details

2.1. Deposition of pure Phosphomolybdic acid thin films [$H_3(PMo_{12}O_{40})$].

For the deposition of thin films of pure phosphomolybdic acid [$H_3(PMo_{12}O_{40})$], 2% solution of phosphomolybdic acid in acetone was taken in 50 cm³ glass beaker. The cleaned and dried glass as well as FTO substrates were fitted to Bakelite substrate holder and dipped in the in this solution. The speed of substrate rotation was kept 50-60 rpm. After half hour, there was yellow colored and uniform deposition of [$H_3(PMo_{12}O_{40})$] on glass and FTO substrates. As deposited thin films were dried in constant temperature oven at 110°C. After cooling at room temperature, these films were dipped in 0.1% aqueous solution of polyacrylamide (PAM) in order to get the adhesive thin films. Thickness of the as deposited films was measured by surface profilometer and it was 517.3 nm.

2.2. Deposition of Tl (I) doped Phosphomolybdic acid [$Tl_3(PMo_{12}O_{40})$] thin films.

90 cm³ 2 % aqueous solution of phosphomolybdic acid was taken in 150 cm³ capacity beaker having side arm and temperature of this solution was kept at 60°C. The clean & dry glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in the phosphomolybdic acid solution. After five minutes 0.2% aqueous solution of thallos acetate was added drop wise through side arm in phosphomolybdic acid solution. The speed of substrate rotation was kept 50-60 rpm. After 1¹/₂ hour, there was yellow colored and uniform deposition of [$Tl_3(PMo_{12}O_{40})$] HPOM on glass substrates. As deposited thin films were dried in constant temperature oven at 110 °C. After cooling at room temperature, these films were dipped in 0.1% aqueous solution of polyacrylamide (PAM) in order to get the adhesive thin films. Thickness of the as deposited films was measured by surface profiler and it was 408.3 nm.

3. Results and discussions

3.1. SEM Analysis

The scanning electron microphotographs of these films were recorded on JEOL - 6360 scanning electron microscope (SEM). Grain sizes were determined using the linear intercept technique (Nogami et al. 2001). Typical scanning electron microphotographs of PMA [$H_3(PMo_{12}O_{40})$] and TIPMA [$Tl_3(PMo_{12}O_{40})$] thin films are shown in Fig. 1.

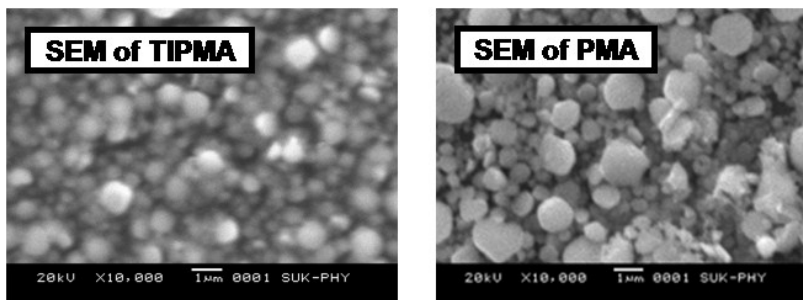


Fig. 1 Typical scanning electron microphotographs of PMA [H₃(PMo₁₂O₄₀)] and TIPMA [Tl₃(PMo₁₂O₄₀)] thin films.

The microphotographs of pure PMA and Tl⁺ doped PMA thin films showed that, material is nanocrystalline in nature with uniform distribution of crystallites. After doping Tl⁺ the average grain size decreases and spherical shaped crystals are formed. The average grain size (Ga) of pure PMA and TIPMA calculated by linear intercept technique was found to be 340 nm and 216 nm respectively.

3.2. Compositional analysis by EDS

Theoretical and practical atomic percentage of phosphorus, oxygen, molybdenum and thallium in the sample was confirmed by analyzing annealed thin films on JEOL - 6360 Energy Dispersive X-ray Analyzer. In Fig.2a and 2b we present EDS spectra of PMA and TIPMA.

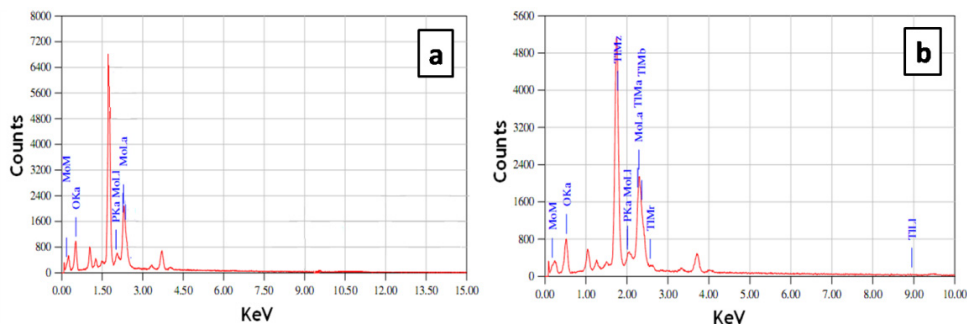


Fig.2. (a) EDS of phosphomolybdic acid (PMA) (b) EDS of Tl⁺ doped phosphomolybdic acid (TIPMA)

The EDS patterns show the presence of P, Mo, O and Tl in the films without any major impurity. Table 1 shows theoretical and practical atomic percentage of P, Mo, O and Tl.

Table 1 Compositional analysis of Tl₃ (PMo₁₂ O₄₀) by EDS

Element	Theoretical Atomic %	Practical Atomic %
O	84.27	71.43
P	1.78	2.32
Mo	21.43	11.35
Tl	5.36	2.39

3.3. Structural analysis of PMA and TIPMA by XRD

The X-ray diffractograms of PMA and TIPMA thin films annealed at 250°C temperature are presented in Fig. 3. The presence of planes (110), (210), (221), (311), (321), (400), (420), (332), (422) (521), (531), (620), (622), (631) etc. in the XRD pattern of the samples shows that the material is nanocrystalline in nature with simple cubic spinel structure. The crystallite sizes (D) of PMA and TIPMA are 31.48 and 22.64 nm respectively. The calculated and observed 'd' values of interplaner distances are in good agreement (Nakamura et al. 1981; Kim et al. 2004; Lin et al. 2005; Aparicio et al. 2005; Patil et al. 2008).

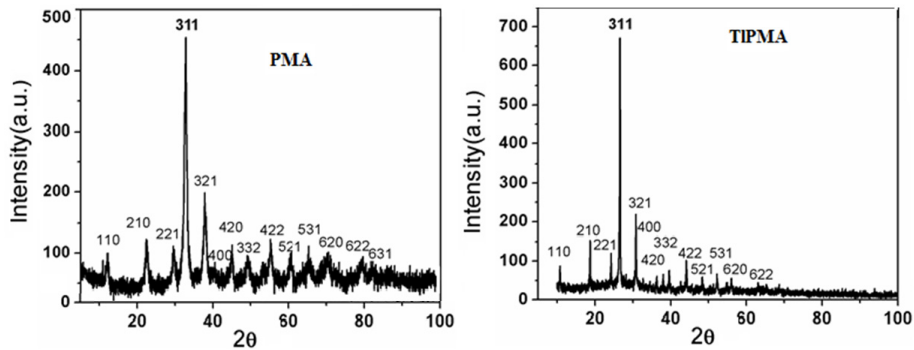


Fig.3. XRD of phosphomolybdic acid (PMA) TI doped phosphomolybdic acid (TIPMA) thin film.

3.4. Optical characterization

In present study, UV-Visible spectrophotometer (Hitachi model 330, Japan) was used to determine absorption spectra of molybdenumheteropolyoxometalate in the wavelength range 350-850 nm. A glass slide of same thickness and size was used as reference throughout all the measurements. One side of the film was removed with the help of cotton swab moistened in dil. HCl. The layer thickness of the as deposited samples was measured by surface profilometer. Absorption spectra was analyzed to determine absorption coefficient, optical band gap 'Eg' and mode of optical transition for molybdenum heteropolyoxometalate thin films.

The optical absorption coefficient of pure PMA and Tl^+ doped PMA was calculated using the absorbance value measured for a particular wavelength (λ) and film thickness (t) using the relation.

$$\text{Absorption Coefficient } (\alpha) = \text{Optical density} / \text{Thickness (t)}$$

The optical band gap (E_g) was found graphically from the calculated values of the absorption coefficient (α). Fig. 4 shows the plot ' $(\alpha h\nu)^2$ ' versus ' $h\nu$ ' for PMA and Tl^+ doped PMA thin films. The presence of single slope in the curves suggests that films are of single phase in nature and the type of transition is direct and allowed. It was found that the optical energy gap (E_g) decreases from 2.45 eV to 2.15 eV after Tl^+ doping (Nogami et al. 2001; Uma et al. 2005; Uma et al. 2006; Iyuke et al. 2003; Castanon et al. 2005).

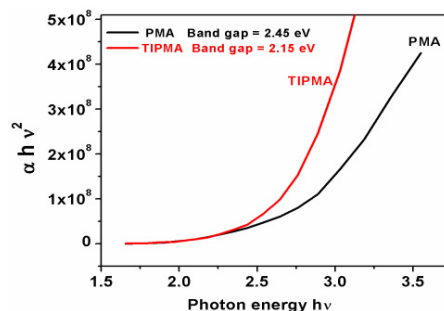


Fig. 4 Plot of $(\alpha h\nu)^2$ versus $h\nu$ for PMA and TI PMA thin films.

3.5. Photoelectrochemical measurements for molybdenum heteropolyoxometalate thin films

Fig. 5 shows the photocurrent-voltage (I-V) curves for phosphomolybdic acid (PMA) and Tl^+ doped phosphomolybdic acid (TIPMA) thin films in dark and under illumination with visible light. For all the films under visible illumination in terms of open circuit voltage (V_{oc}), short circuit current density (I_{sc}), fill factor (FF) and electron conversion efficiency are compared in Table 2. In dark and under illumination current-voltage (I-V) characteristics of “Glass / FTO / PMA, TIPMA / SCE” cells were measured. These (I-V) curves in dark indicate good junction rectification property. From the I-V measurements it is observed that the higher magnitudes of fill factor and conversion efficiency were increased after doping thallium in phosphomolybdic acid. The densely-packed spherical grains of 216 nm of TIPMA films can absorb enough light. Furthermore, the photogenerated electrons can transport through the compact layers to the conducting substrates with minimum loss. This greatly reduces the recombination losses of the photogenerated charge-carriers due to decrement in grain boundary resistance in charge transportation process.

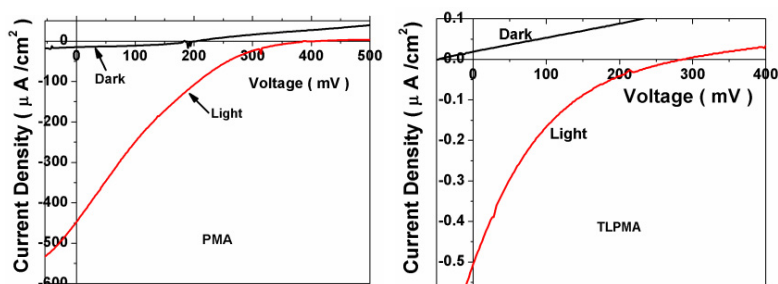


Fig. 5 Photocurrent-voltage (I-V) curves for PMA and TIPMA

In conclusion, the improvement in the PEC properties of the TIPMA thin films is due to (i) Morphological modifications that enhance active surface area and (ii) Quenching of the defect levels responsible for recombination losses. From Table 2, it is observed that as grain size reduces from 340-216 nm, the fill factor and conversion efficiency increases. This appreciable change into fill factor and conversion efficiency is due to increment in surface area to volume ratio of grains (Iyuke et al. 2003; Castanon et al. 2005).

From above discussion we observed that the morphology of films have profound impact on the performance of the solar cells. Because densely-packed compact layered films can provide the faster conduction pathway (less grain boundaries, which associate with traps or/and barriers) for charge transport and the electron transfer time from the point of carrier generation to the collection electrode is significantly reduced. It can be seen that the cell performance is greatly improved by thallium doping in to phosphomolybdic acid.

Table 2. PEC parameters of the cell with “Glass/FTO/ PMA, TIPMA/SCE” configuration

Sample	Grain size (nm)	I_{sc} ($\mu A/cm^2$)	V_{oc} (mV)	I_{max} ($\mu A/cm^2$)	V_{max} (mV)	Fill factor %	Conversion efficiency η %
PMA	340	505	288	140	113	12.0	0.29
TIPMA	216	447	384	147	170	15.0	0.42

4. Conclusion

Fabrication of photoelectrochemical cell using molybdenum HPOM thin film photoelectrode is very simple, cheap, and convenient. The cell structures were formed for PMA and TIPMA thin films. The photoelectrochemical behavior of these cells has been examined. The cell properties under illumination suggest that in molybdenum heteropolyoxometalate, addition of thallium increases cell performance and is found to be maximum as compared to undoped film. After thallium doping in to phosphomolybdic acid, the grain size has been reduced and conversion efficiency has been increased. This appreciable change into fill factor and conversion efficiency is due to increment in surface area to volume ratio.

Acknowledgement

One of the author Dr. R. M. Mane thankful to DST-SERB, New Delhi, under Fast Track Scheme for Young Scientists Major Research Project for Financial Support (No. SR/FT/CS-158/2011).

References

- Aparicio M., Castro Y. and Duran A., 2005, Synthesis and characterisation of proton conducting styrene-co-methacrylate-silica sol-gel membranes containing tungstophosphoric acid, *Solid State Ionics*, 176, 333.
- Castanon T. R., Arriaga L. G. and Castillo U. C., 2003, Impedance spectroscopy as a tool in the evaluation of MEA's, *J. Power Sources*, 118, 179.
- Iyuke S. E., Mohamad A. B., Kadhum A. A. H., Daud W. R. W., and Rachid C., 2003, Improved membrane and electrode assemblies for proton exchange membrane fuel cells, *J. Power Sources*, 114, 195.
- Kim J. D. and Honma I., 2004, Synthesis and proton conducting properties of zirconia bridged hydrocarbon/phosphotungstic acid hybrid materials, *Electrochimica Acta*, 49, 3179.
- Lade S. J., Uplane M. D. and Lokhande C. D., 2001, Photoelectrochemical properties of Cd_x (X=S, Se, Te) films electrodeposited from aqueous and non-aqueous baths *Mater. Chem. Phys.* 68 36.
- Lin C. W., Thangamuthu R. and Chang P. H., 2005, PWA-doped PEG/SiO₂ proton-conducting hybrid membranes for fuel cell applications, *J. Membr. Sci.*, 254, 197.
- Murali K. R., Srinivasan K. and Trivedi D.C., 2005, Vacuum evaporated CdSe thin films and their characteristics *Mater. Lett.* 59, 15
- Nogami M., Usui Y. and Kasuga T., 2001, Proton Conducting Organic-Glass Composites, *Fuel cells*, 1, 181.
- Nakamura O., Ogino I. and Kodama T., 1981, Temperature and humidity ranges of some hydrates of high-proton-conductive dodecamolybdophosphoric acid and dodecatungstophosphoric acid crystals under an atmosphere of hydrogen or either oxygen or air, *Solid State Ionics*, 3 & 4, 347.
- Nogami M., Goto Y. and Kasuga T., 2003, Proton Conductivity in Zr⁴⁺ - Ion-Doped P₂O₅-SiO₂ Porous Glasses, *J. Am Ceram Soc.* 86, 9, 1504.
- Patil N.S., Sargar A.M., Mane S.R., Bhosale P.N., 2008. Growth mechanism and characterization of chemically grown Sb doped Bi₂Se₃ thin films, *Journal of Applied Surface Science*, 254, 5261-5265.
- Ruan, C., Paulose, M., Varghese, O. K., Mor, G. K., Grimes, C. A. 2005 Fabrication of highly ordered TiO₂ nanotube arrays using an organic electrolyte. *J. Phys. Chem. B*, 109, 15754.
- Rahmanab G. and Joo O. S., 2013, Facile preparation of nanostructured α -Fe₂O₃ thin films with enhanced photoelectrochemical water splitting activity *J. Mater. Chem. A*, 1, 5554.
- Uma T. and Nogami M., 2005, Influence of TiO₂ on proton conductivity in fuel cell electrolytes ...sol-gel derived P₂O₅-SiO₂ glasses *J. Non-Cryst Solids*, 351, 3325.
- Uma T. and Nogami M., 2006, Synthesis and characterization of P₂O₅-SiO₂-X (X = phosphotungstic acid) glasses as electrolyte for low temperature H₂/O₂ fuel cell application, 280, 744.
- Xu N., Sun M., Cao Y. W., Yao J. N., Wang E. G., 2000, Influence of pH on structure and photochromic behavior of nanocrystalline WO₃ films *Applied Surface Science*, 157 81.