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Archives of Applied Science Research, 2010, 2 (2):294-303 (http://scholarsresearchlibrary.com/archive.html)



Synthesis and characterization of chemically deposited $Tl_3(PW_{12}O_{40})$ semiconducting thin films

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Abstract

 $Tl_3(PW_{12}O_{40})$ semiconducting thin films have been synthesized by using simple chemical bath deposition technique. Morphological, optostructural and thermal properties of the title compound have been characterized by SEM, EDS, XRD, UV-VIS, electrical resistivity, thermoelectric power, TGA-DTA techniques. SEM and XRD data of material shows that, it is polycrystalline and having simple cubic spinel structure. UV-vis spectroscopy revealed that, Tl_3 $(PW_{12}O_{40})$ heteropolyoxometalate material is a direct gap semiconducting material with band gap 2.7 eV. The dc electrical resistivity and thermoelectric power was measured in the temperature range 300-573°K. The variation of resistivity with respect to temperature showed there is negative resistance region indicating semiconducting nature of material. The thermoelectric power for sample was positive over the whole range of the temperature showing that it is p-type semiconductor. EDS of sample shows that, the Tl (I) is intercalated in phosphotungustate anion. The TGA-DTA study revealed that, material is thermally stable up to 265.12°C.

Keywords: Semiconductors, Chemical synthesis, Thermoelectric power, Optical properties, scanning electron microscopy.

INTRODUCTION

Heteropolyoxometalate (HPOM) have been a matter of interest in basic and applied science for more than a century. From their first synthesis, many advances have been made to promote the use of HPOM in different ways in science and technology. The applications of HPOM are associated with their interesting properties such as anionic size, high ionic weight, high redox characteristics, polarity, surface charge distribution, electron and proton transfer/storage ability and the formation of high Brønsted acid centers and the labiality of lattice oxygen. Metal ion doped HPOM materials are technologically important due to its high electrical and thermal conductivities [1-7]. The heteropolyanions of V, Mo, and W find applications in biochemical industrial catalysis, proton conductor [8], ion exchange materials, thin layer chromatography, materials for separation of amino acids [9]. Heteropolyoxometalates (HPOM), in addition to their considerable applications in catalysis and medicine, are attracting attention as compounds for advanced materials due to their antiviral and anti-HIV activity and potential applications in optro-electronic devices [10]. The most advantageous feature of HPOM is that nearly every molecular property can be altered under defined conditions during the synthesis.

The literature survey and internet search of heteropolyoxometalates of tungsten have shown that there is no report available on thin films prepared by chemical bath deposition technique. In the present investigation, we report synthesis and characterization of chemically deposited Tl_3 (PW₁₂ O₄₀) heteropolyoxometalate semiconducting thin films.

MATERIALS AND METHODS

2.1 Preparation of Solutions

Thin films of Tl (I) doped tungsten HPOM were prepared by using following AR grade chemicals by dissolving in double distilled water.

- a) 2% aqueous solution of Phosphotungustic acid. [H₃ (PW₁₂ O₄₀)]
- b) 0.1%, aqueous solution of thallous acetate (CH₃COO- Tl)
- c) 0.2% aqueous solution of polyacrylamide (PAM)

2.2 Preparation of HPOM Thin films

90 cm³ 2 % aqueous solution of phosphotungustic acid acid was taken in 150 cm³ capacity beaker having side arm and temperature of this solution was kept at 55°C. The clean & dry glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in the phosphotungustic acid solution. After five minutes 0.1% aqueous solution of thallous acetate was added drop wise through side arm in phosphotungustic acid solution. The speed of substrate rotation was kept 50-60 rpm. After 11/2 hour, there was white colored and uniform deposition of [Tl₃(PW₁₂O₄₀)] HPOM on glass and FTO substrates. As deposited thin films were dried in constant temperature oven at 80°C. After cooling at room temperature, these films were dipped in 0.6% 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 221.0 nm.

The reactions involved during the growth of tungusten HPOM thin films are---

$$H_{3} (PW_{12} O_{40}) \longrightarrow (PW_{12}O_{40})^{3^{-}} + 3H^{+}$$
(i)
phosphotungustic acid phosphotungustate anion
$$3 CH_{3} - COO - TI \longrightarrow 3CH_{3} - COO^{-} + 3TI^{+}$$
(ii)
hallous Acetate Acetate ion



The overall reaction is,

$$P^{H} = 1.0$$

$$H_{3} (PW_{12} O_{40}) + 3 CH_{3} - COO - Tl \xrightarrow{P^{H}} Tl_{3} (PW_{12} O_{40}) \qquad (v)$$

$$Temp. = 55 \text{ oC}$$

2.3 Experimental techniques

2.3.1 SEM Analysis

To observe the external morphology and grain size of the HPOM material, as deposited thin films were annealed at 300° C for 2 hours at heating rate 10° C/min in muffle furnace. 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 [12]. The average grain size (Ga) was calculated using the relation,

$$G_a = \frac{1.5L}{MN}$$

Where,

1.5 is geometry dependent proportionality constant,

L = the total test line length,

M = magnification,

N = the total number of intercepts.

2.3.2 Compositional analysis by EDS

Theoretical and practical atomic percentage of phosphorus, tungsten and thallium in the sample was confirmed by analyzing as deposited thin films on JEOL - 6360 Energy Dispersive X-ray Analyzer.

2.3.3 Structural analysis by XRD

Thin films annealed at 300°C for 2 hours at heating rate 10°C/min in muffle furnace were analyzed by x-ray diffraction technique using Cu-K α radiations (λ =1.5425 A°) on a PW3710/1710 PHILIPS make X-ray diffractometer. The interplaner distances d (A⁰) were

calculated using Bragg's law. The lattice constant (a) of the sample was determined using the relation.

$$a = d_{hkl} \quad \sqrt{h^2 + k^2 + l^2}$$

The crystallite size of the HPOM material was determined from most intense peak (peak having 311 planes) using Debye-scherrer formula [11]

$$D = \frac{0.94\lambda}{\beta\cos\theta}$$

Where,

 λ - wavelength of X-ray β - full width at half maximum θ - Bragg's diffraction angle

2.3.4 TGA- DTA measurements

TGA- DTA measurements of as deposited thin films were carried out in nitrogen atmosphere on TG-DTA-DSC-SDT- 2960 TA. Inc.-USA make thermogravimetric analyzer with heating rate of 10° C/min.

2.3.5 Optical characterization

Optical absorbance measurements were carried out by taking as deposited thin films of thallium (I) doped tungsten HPOM using UV-vis spectrophotometer [HITACHI model 330] in the wavelength range 350 nm to 850 nm. The absorption coefficient (α) and band gap (Eg) was determined from optical studies.

2.3.6 Electrical resistivity measurements

The direct current (dc) electrical resistivity measurements of as deposited thin films were done by using d.c. two probe method. The area of the film was defined and silver paste was applied to ensure good electrical contact to the film. The working temperature was recorded using Chromal- Alumel thermocouple. The potential drop across the film was measured with the help of Meco-801 digital multimeter and current passed through the sample was recorded with a sensitive four digit Picoammeter (Model Roorkee DPM 111)

2.3.7 Thermo electric power(TEP) measurements

Thermoelectric power measurements of annealed thin film were carried out under the condition of maximum temperature difference and minimum contact resistance. The temperature difference of the ends of the samples was measured with Chromel–Alumel thermocouple placed in such a way so as to touch the sample ends. The thermoelectric voltage or seebeck voltage developed across the sample and the temperature of the ends was read on Testronix microvoltmeter and Meco-801 digital multimeter respectively. A set of the values of thermoelectric voltage at various temperatures thus obtained were plotted against the respective absolute temperatures. Thermoemf measurements have also been carried out to determine the type of conduction.

RESULTS AND DISCUSSION

3.1 SEM results on external morphology

In Fig. 1 we present a typical scanning electron microphotograph of $Tl_3(PW_{12}O_{40})$ thin film. The microphotograph of film showed that, material is polycrystalline in nature with uniform distribution of crystallites. The average grain size (Ga) calculated by linear intercept technique was found to be 1.27 μ m.



Fig 1. SEM of Tl₃(PW₁₂O₄₀) thin film



Fig. 2. EDS of Tl₃(PW₁₂O₄₀) thin film



Fig. 3. XRD of Tl₃ (PW₁₂O₄₀) thin film



Fig. 4. TGA-DTA curves for Tl₃(PW₁₂O₄₀) thin film

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3.2 EDS results on compositional analysis

A typical EDS spectrum of $Tl_3(PW_{12}O_{40})$ shown in Fig.2 revealed that, Tl (I) is intercalated in phosphotungustate anion [17]. Theorotical and practical atomic percentage of the tungusten HPOM is listed in Table 2 which shows that, atomic percentage of phosphorous, oxygen and thallium is slightly less than theoretical atomic percentage while practical atomic percentage of tungsten is more than theoretical atomic percentage.

3.3 XRD Measurements

A typical X-ray diffractogram of thallium (I) doped tungsten HPOM sample is presented in Fig.3. The presence of planes (110), (210), (221), (311), (321), (400), (420), (422), (511) (520), (531) (620), (631), (642), (731), in the XRD pattern of the sample shows that, the material is polycrystalline in nature with simple cubic spinel structure [13-16]. The crystallite size (D) of the HPOM material calculated by using Debye-scherrer formula is 14.16 nm. The calculated and observed values of interplaner distances ($d_{obs.}$ and $d_{cal.}$) are listed in Table 1. The calculated and observed values of interplaner distances are in good agreement. The value of lattice constant (a) calculated for this sample was 11.15 A°

3.4 TGA – DTA

Thermal stability of the film was determined by TGA-DTA measurements [18]. Fig. 4 shows the TGA and DTA curves for Tl (I) doped tungusten HPOM. Endothermic peaks were observed at 62.12, 157.87, 433.64, 713.45°C and exothermic peaks were observed at 110.86, 240.12, 556.10, 952.45°C on the DTA curve. From the TGA curve, only one weight loss region could be observed at 265.12°C. TGA-DTA curves show that, $Tl_3PW_{12}O_{40}$ material is thermally stable up to temperature 265.12°C

3.5 Optical property

Fig. 5 represents plot of $(\alpha h v)^2$ Vs hv of Tl₃ (PW₁₂O₄₀) thin films. The optical absorption spectra of as deposited and annealed thin films shows direct band gap of 2.6 eV.



Fig. 5. Plot of $(\alpha h \nu)^2$ vs. $h\nu$ for Tl₃ (PW₁₂ O₄₀) thin films

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3.6 Electrical resistivity of Tungusten HPOM

The plot of Log ρ against 10^3 / T [Fig.6] of tungsten HPOM shows that initially resistivity of material slowly increases with increase in temperature indicating conducting behavior of the material and then decreases gradually in the temperature range 150 °C- 270 °C, showing the semiconducting behavior. Thus the negative temperature coefficient of electrical resistivity in the temperature range 150°C-270°C shows semiconducting nature of Tl₃(PW₁₂O₄₀). Beyond the temperature 270°C, the resistivity remains constant due to the decomposition of HPOM material.



Fig. 6. Plot of Log ρ against $10^3/T$ for Tl₃ (PW₁₂O₄₀) thin film



Fig. 7. Plot of Thermoelectric power μ (mV/ K) against T (K) for Tl₃ (PW₁₂ O₄₀) thin film

| Sr. No. | hkl planes | d _{observed} (A ^o) | d _{calculated} (A ^o) |
|---------|------------|---|---|
| 1 | (110) | 8.2485 | 8.2448 |
| 2 | (210) | 4.7572 | 4.7550 |
| 3 | (221) | 3.6875 | 3.6858 |
| 4 | (311) | 3.3618 | 3.3602 |
| 5 | (321) | 2.9056 | 2.9043 |
| 6 | (400) | 2.7415 | 2.7409 |
| 7 | (420) | 2.4838 | 2.4826 |
| 8 | (422) | 2.2873 | 2.2863 |
| 9 | (511) | 2.1243 | 2.1233 |
| 10 | (520) | 2.0621 | 2.0611 |
| 11 | (531) | 1.8889 | 1.8881 |
| 12 | (620) | 1.7566 | 1.7558 |
| 13 | (631) | 1.6520 | 1.6512 |
| 14 | (642) | 1.4814 | 1.4807 |
| 15 | (731) | 1.4359 | 1.4352 |

Table 1 $d_{obs.}$ and $d_{cal.}$ for $Tl_3(PW_{12}O_{40})$ thin film

Table 2 Compositional analysis of Tl₃ (PW₁₂ O₄₀) by EDS

| Element | Theoretical | Practical |
|---------|-------------|-----------|
| | Atomic % | Atomic % |
| 0 | 71.43 | 69.23 |
| Р | 1.78 | 1.14 |
| W | 21.43 | 25.49 |
| Tl | 5.36 | 4.14 |

3.7 Thermoelectric

3.8 power measurements

The thermoelectric power (TEP) measurement for the Tl_3 (PW₁₂O₄₀) sample is illustrated in Fig. 7. From TEP measurements it was found that, the TEP possessing plus sign over the whole range of temperature providing that, p-type semiconducting behavior [19-21] and the dominant contributing carriers are holes. The contribution of holes is thermally activated and hence the TEP increases continuously with increasing temperature.

CONCLUSION

 $Tl_3(PW_{12}O_{40})$ heteropolyoxometalate material prepared by chemical growth process is polycrystalline in nature having simple cubic spinel structure and shows p-type semiconducting nature with thermal stability up to 300°C. Chemical growth process is suitable for deposition of $Tl_3(PW_{12}O_{40})$ HPOM thin films on any substrate support. Thus the thin films can be used as a suitable material for device applications.

REFERENCES

[1] Ying-Hua Sun, Ji-Qing Xu, Ling Ye, Xiao-Bing Cui, Yong Li, Hai-Hui Yu, Guang- Hua Li, Guang-Di Yang and Yan Chen, *J. Mol. Str.* **2005**,740, 193.

[2] Laurent Lisnard, Anne Dolbecq Pierre Mialane, Jerome Marrot and Francis Secheresse J. *Inorganica Chimica Acta* **2004**, 357, 845.

[3] L.Marosi, J. Cifre and C.Otero Arean, J. Powder Diffraction 2003, 18, 236.

[4] T. Yamse. Chem. Rev. 1998, 98, 307.

[5] Wei Feng, Tierui Zhang, Yan Liu, Ran Lu, Cheng Guan, Yingying Zhao and Jiannian Yao *Mater. Chem. Phy.* **2003**, 77, 294.

[6] B. Keita, L. Nadjo. J. Mat. Chem. Phy. 1989, 22, 77.

[7] Wei Feng, Tie Rui Zang, Yan Liu, Ran Lu, Ying Ying Zhao, Tie Jin Li, and Jian Nian, Yao, J. *Solid State Chem.* **2002**, 169, 1.

[8] U. B. Mioc, M.R.Todorovic, M.Davidovic, Ph.Colomban and I. Holclajtner- Antunovic. J. *Solid State Ionics* **2005**, 176, 3005.

[9] Shin-Ya Fujibayashi, Kouichi Nakayama, Masatoshi Hamamoto, Satoshi Sakaguchi, Yutaka Nishiyama and Yasutaka Ishii. *J. Mol. Cat.-A: - Chemical* **1996**, 110, 105.

[10] M. T. Pope, A. Muller (Eds.) Polyoxometalates: - Kluwer Academic, Dordrecht. 1994.

[11] Klug H P, Alexander L E , X-ray diffraction procedure For Polycrystalline and Amorphous Materials, 2nd Edition. Wiley-Interscience New York **1974**, 656.

[12] J. C. Wurst, J. A. Nelson, J. American. Ceramic. Soc. 1972, 55, 109.

[13] B.D.Cullity, Elements of X-ray Diffraction, Addison-Wesley Publishing Company 1956, 471.

[14] H. Hayashi and J. B. Moffat, J. Catl. 1982, 77,473.

[15] H. Hayashi and J.B. Moffat, J Catl. 1983, 83, 192.

[16] B.K. Hodnett and J.B. Moffat, J Catl. 1984, 88, 253.

[17] M.T.Pope, Heteropoly and Isopolyoxometalates, Springer, Berlin 1983

[18] D. H.Brown, J.Chem. Soc. 1962, 3189.

- [19] M.Morsli, A.Bonnet and A Conan, J. Phys. Rev. B 1989, 39, 3735.
- [20] A.H.Abou El Ela, A.Abdelghani and H.H.A. Labib. J. App. Phys. 1982, 27, 161

[21] M.M.Abd El-Raheem, J. World Applied Science, 2007, 2, 204.