Effect of annealing temperature on structural properties of nanocrystalline Tl$_3$(PW$_{12}$O$_{40}$) thin films

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ABSTRACT

Thallium (I) doped tungsten heteropolyoxometalate (HPOM) combinatorial thin films have been deposited on glass substrate using simple chemical bath deposition technique. The deposited films were annealed at 100 °C, 150 °C, 200 °C and 250 °C. These annealed thin films were characterized by using SEM, EDAX, AFM, FT-IR, XRD and TGA-DTA techniques for their structural properties. SEM and EDAX results showed that, tungsten HPOM material is polycrystalline in nature and Tl (I) is intercalated in phosphotungstate anion. AFM studies on the films annealed at different temperatures reveal that the surface roughness increases with the increase in annealing temperature, suggesting an increase of crystallization with temperature. FT-IR study confirms the well formation of heteropolyoxometalate material under investigation. Various structural parameters such as lattice constants, crystallite size and grain size have been calculated and they are found temperature dependent. The lattice constant, crystallite size and grain size of tungsten HPOM material increases with increase in temperature. XRD pattern of annealed thin films shows better crystallinity of tungsten HPOM material having simple cubic spinel structure. The TGA-DTA study revealed that, Tl$_3$ (PW$_{12}$O$_{40}$) material is thermally stable up to 265.12 °C. Copyright © 2013 VBRI press.

Keywords: Nanocrystalline; thin films; annealing; HPOM; tungsten; intercalation.
HIV activity and potential applications in opto-electronic devices [10].

There is no single report available on thin films of thallium (I) doped tungsten heteropolyoxometalate prepared by using simple chemical bath deposition technique. So, in the present investigation, we are reporting preparation, characterization and effect of annealing temperature on structural properties of thallium (I) doped tungsten heteropolyoxometalate thin films.

Experimental

Preparation of solutions

Thin films of Tl₃ (PW₁₂ O₄₀) were prepared by dissolving following AR grade chemicals in double distilled water.

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

![Fig. 1. Photograph of Tl₃(PW₁₂O₄₀) thin film.](image)

Preparation of tungsten HPOM thin films

Thin films of Tl₃ (PW₁₂ O₄₀) were prepared by using simple chemical bath deposition technique using following procedure. 90 cm³ 2 % aqueous solution of phosphotungustic 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 substrates were fitted to bakelite substrate holder and dipped in the phosphotungustic acid solution. After five minutes 0.2% 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 1.5 h, there was white colored and uniform deposition of Tl₃ (PW₁₂ O₄₀) on glass substrates (Fig. 1). As deposited thin films were dried at room temperature and dipped in 0.2% aqueous solution of polyacrylamide (PAM) in order to get the adhesive thin films. As deposited thin films after drying at room temperature were annealed at 100 °C, 150 °C, 200 °C and 250 °C temperatures and studied for their morphological and structural characterization using SEM, EDAX, AFM, FT-IR, XRD and TGA-DTA techniques. Thickness of the annealed films was measured by surface profiler and it was 371.80 nm.

The reactions involved during the growth of tungsten HPOM thin films are:

\[
H₃(PW₁₂ O₄₀) → (PW₁₂O₄₀)⁺ + 3H⁺ \quad (1)
\]

Phosphotungstic acid Phosphotungstate anion

\[
3 CH₃ – COO – Tl → 3CH₃ – COO⁻ + 3 Tl⁺ \quad (2)
\]

Thallous Acetate Acetate ion

\[
3 CH₃ – COO⁻ + 3H⁺ → 3CH₃ – COOH \quad (3)
\]

Acetate ion Acetic acid

\[
H₃(PW₁₂O₄₀)³⁻ + 3 Tl⁺ \quad \text{phosphotungstate anion Thallous ion}
\]

Ion by ion condensation ↓

\[
\text{Tl₃ (PW₁₂ O₄₀)} \quad (4)
\]

Thallium (I) doped Tungsten HPOM.

The overall reaction is,

\[
H₃ (PW₁₂ O₄₀) + 3 CH₃ – COO – Tl \quad \text{pH} = 1.0 \quad \text{Temp. = 55 °C}
\]

\[
\text{Tl₃ (PW₁₂ O₄₀)} + 3CH₃ – COOH \quad (5)
\]

![Fig. 2. Microphotographs of annealed Tl₃(PW₁₂O₄₀) thin films](image)

Results and discussion

SEM results on external morphology

The microphotographs of annealed thin films are shown in Fig. 2. It indicates that Tl₃(PW₁₂O₄₀) material is polycrystalline in nature with uniform distribution of crystallites. It is found that, as the annealing temperature of the film increases crystallite size increases and we got spherical shaped crystals. The average crystallite size calculated by linear intercept technique was in the range 485.0 nm to 942.0 nm.
EDAX results on compositional analysis

In Fig. 3, typical EDAX spectrum of Tl₃(PW₁₂O₄₀) thin film annealed at 250 °C is shown which indicate that, Tl (I) is intercalated in Phosphtungustate anion[11]. The EDAX patterns show the presence of P, W, O and Tl in the films without any major impurity. Table 1 shows theoretical and practical atomic percentage of P, W, O and Tl. From Table 1 it is found that theoretical and practical atomic percentages are in good agreement.

**AFM study**

The AFM images were recorded in order to study the effect of annealing temperature on surface morphologies of Tl₃(PW₁₂O₄₀) thin films deposited by optimizing various parameters. Fig.4 shows 2D and 3D AFM images of Tl₃(PW₁₂O₄₀) thin films annealed at 100 °C and 250 °C. The AFM images are in well agreement with the SEM images recorded. All the results obtained from AFM data are consistent with SEM results. AFM studies on the films annealed at different temperatures reveals that the surface roughness increases with the increase in annealing temperature, suggesting an increase in crystallite size with temperature.

**FTIR Study**

Fourier transform infrared (FTIR) spectra of typical Tl₃(PW₁₂O₄₀) sample was recorded from pressed KBr pellets using a Perkin-Elmer Spectrum-2000 FT-IR Spectrometer which is shown in Fig. 5. In our study, the IR spectrum of the present compound exhibits the characteristic frequencies of structure in the range 2330-524 cm⁻¹. After annealing the bands arising from the HPAs change obviously either in intensity, or in position. The frequency values (cm⁻¹) and assignment of FTIR bands observed for typical Tl₃PW₁₂O₄₀ sample is summarized in Table 2. The strong band at 3303 cm⁻¹ was observed in IR spectra due to the water molecules involved in hydrogen bond interactions with HPA [12-14].

**Table 1. Compositional analysis of Tl₃(PW₁₂O₄₀) by EDS.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Theoretical Atomic %</th>
<th>Practical Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>71.43</td>
<td>69.23</td>
</tr>
<tr>
<td>P</td>
<td>1.78</td>
<td>1.14</td>
</tr>
<tr>
<td>W</td>
<td>21.43</td>
<td>25.49</td>
</tr>
<tr>
<td>Tl</td>
<td>5.36</td>
<td>4.14</td>
</tr>
</tbody>
</table>

**Table 2. Frequency values (cm⁻¹) and assignment of FTIR bands observed for Tl₃(PW₁₂O₄₀).**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency values (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-O-W v₁</td>
<td>799</td>
</tr>
<tr>
<td>W-O-W v₂</td>
<td>891</td>
</tr>
<tr>
<td>W=O</td>
<td>983</td>
</tr>
<tr>
<td>P-O</td>
<td>1080</td>
</tr>
<tr>
<td>H-O-H</td>
<td>3303</td>
</tr>
</tbody>
</table>
XRD measurements

X-ray diffractograms of Tl3(PW12O40) samples annealed at 100 °C, 200 °C and 250 °C are presented in Fig. 6. Increase in temperature shows better crystallinity of tungsten HPOM material. The presence of planes (110), (210), (221), (311), (321), (400), (420), (422), (511) (520), (531) (620), (631), (642), (731) in the XRD pattern of Tl3(PW12O40) sample annealed at 250 °C shows that the material is polycrystalline in nature with simple cubic spinel structure. The crystallite size of Tl3(PW12O40) material was determined by considering most intense peak (311) using Debye-Scherer formula [15-19] which lies in the range 15.80 to 20.14 nm. The calculated and observed values of interplaner distances are in good agreement [8]. The values of lattice constant (a) vary from 11.17 to 11.29 Å. From X-ray diffractograms and Table 3 it is clear that, the lattice constant, crystallite size of tungsten HPOM material increases with increase in temperature.

Table 3. Effect of annealing temperature on crystallite size, lattice constant and average crystallite size of Tl3(PW12O40) material.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Crystallite size ‘D’ from XRD (nm)</th>
<th>Lattice constant ‘a’ (Å)</th>
<th>Average crystallite size from SEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>15.80</td>
<td>11.17</td>
<td>485</td>
</tr>
<tr>
<td>150</td>
<td>15.92</td>
<td>11.20</td>
<td>687</td>
</tr>
<tr>
<td>200</td>
<td>19.13</td>
<td>11.24</td>
<td>856</td>
</tr>
<tr>
<td>250</td>
<td>20.14</td>
<td>11.29</td>
<td>942</td>
</tr>
</tbody>
</table>

TGA-DTA measurements

Thermal stability of the film was determined by TGA-DTA measurements. TGA-DTA measurements were carried out in nitrogen atmosphere on TG-DTA-DSC-SDT-2960 TA. Inc.-USA makes thermogravimetric analyzer with heating rate of 10 °C / min.

Fig. 7 shows the TGA and DTA curves for as deposited Tl3(PW12O40) thin films. The 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, only one weight loss region could be observed at 265.12 °C for Tl3(PW12O40) material. The acid forms of HPAs are usually obtained with large amounts of water of crystallization, and most of these water molecules are released below 100 °C. Decomposition, which takes place at 350-600 °C is believed to occur according to

\[
\text{H}_3\text{PW}_{12}\text{O}_{40} \rightarrow (1/2) \text{P}_2\text{O}_5 + 12\text{WO}_3 + (3/2) \text{H}_2\text{O} \quad (6)
\]

Hodnett and Moffat assumed that this decomposition proceeded via PW12O40 in the case of H3PW12O40. The thermal stability also depends on the environment. In a reducing atmosphere heteropolycompounds decompose more rapidly. The coexistence of oxygen and water vapor enhances the stability at high temperatures and sometimes
causes the reformation of the heteropolystructure from a decomposed mixture. TGA-DTA curves show that, Tl₃PW₁₂O₄₀ material is thermally stable up to temperature 265.12 °C [17-20].

Conclusion

Thin films of Tl₃PW₁₂O₄₀ were prepared by using simple chemical bath deposition technique. X-ray diffraction study confirms well formation of HPOM material with simple cubic spinal structure and nanocrystalline nature. Increase in temperature shows better crystallinity of tungsten HPOM material. Average crystallite size by SEM, crystallite size and lattice constant of the material increases with increase in temperature. It is found that these structural parameters are found to be temperature dependent. Hence after annealing Tl₃PW₁₂O₄₀ material we get good stoichiometric and pure tungsten heteropolyoxometalate material which can be used for device applications.

Reference