Asian Journal of Chemistry Vol. 21, No. 6 (2009), 4721-4727

Morphological and Structural Studies on Cu(II) Substituted Vanadium Heteropolyoxometalate Thin Films

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Copper(II) substituted vanadium heteropolyoxometalate thin films were deposited on glass substrates by simple chemical bath deposition technique. The thin films were characterized for their structural, morphological, compositional and optoelectronic, properties using XRD, SEM-EDAX data, UV-visible spectra, TGA-DTA, electrical resistivity. X-ray diffraction study confirmed that the films are nanocrystalline in nature having cubic spinel structure. UV-visible spectroscopy revealed that, direct band to band transition with 2.6 ev band gap. The d.c electrical resistivity was measured in the temperature range of 27-270 °C, shows negative resistance region in the temperature range of 120 to 250 °C indicating semiconducting nature of heteropolyoxometalate material. Compositional analysis (EDAX) of samples shows the Cu(II) is intercalated in phosphovanadate anion. The TGA-DTA data revealed that the vanadium heteropolyoxometalate sample is thermally stable upto 250 °C.

Key Words: Thin films, Chemical synthesis, Optical properties.

INTRODUCTION

The chemistry of the early transition elements, particularly vanadium, molybdenum and tungsten in aqueous solution is dominated by the formation of polyoxoanions which constitute a class of metal-oxygen cluster containing compounds called polyoxometalates. Heteropolyoxometalates (HPOM) have been extensively studied by many researchers across the world due to its small, compact oxide cluster with keggin type structure. The HPOM of vanadium, molybdenum and tungsten are widely studied due to their redox properties and high electron density are ideal for their use as a catalysts, photochromic and electrochromic materials. Metal ion doped HPOM materials are technologically important due to its high electrical and thermal conductivities[1]. An enormous patent and journal literature is devoted to the applications of small no. of heteropolyanions.

The heteropolyanions of vanadium, molybdenum and tungsten finds applications in biological industrial catalysis,proton conductor, ion exchange materials, thin layer chromatography,materials for separation of amino acids[2-4]. Heteropolyoxometalates (HPOM) in addition to their considerable applications in catalysis and medicine are attracting attention as compounds for advanced materials. Heteropolyoxometalate also exhibits antiviral, anti-HIV properties.

EXPERIMENTAL

Preparation of solutions: Thin films of Cu(II) substituted vanadium HPOM were prepared by dissolving following AR grade chemicals in double distilled water. (a) 0.1 M solution of ammonium meta vanadate [NH_4VO_3], (b) 0.1 M aqueous solution of diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] (c) 0.6 % aqueous solution of polyacrylamide [PAA].

Preparation of HPOM thin films: Aqueous solutions of vanadium and phosphate were taken in 4:1 ratio at pH 5.5. In 100 mL capacity beaker x mL of 0.1 M diammonium hydrogen phosphate and 4x mL solution of 0.1 M ammonium meta vanadate were taken and pH was adjusted at 5.5 by slowly adding 1:1 HCl solution. One third portion of clean glass substrate were dipped ino this solution at room temperature. After a day yellow coloured thin films were obtained on substrate supports. As deposited thin films were dried in constant temperature oven at 110 °C. After cooling at room temperature these films dipped in 0.6 % aqueous solution of polyacryl amide (PAA) in order to get the adhesive thin films.Thickness of the deposited films was measured by weight difference density method and it was found 0.115 µm.

Experimental techniques used for characterization of thin films

Structural analysis by XRD: Thin films sintered at 240 °C were analyzed by X-ray diffraction technique using Cu-K radiations (λ = 1.5425 Å) on a PW3710/ 1710 Philips make X-ray diffractometer. The interplaner distances d (Å) were calculated using Bragg's law. The lattice constants (a) of the sample was determined using the relation:

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

The crystallite size of the HPOM material was determined by considering fwhm of most intense peak [peak having (311) planes] and other X-ray data using Debye-Scherrer formula:

$$D = 0.94\ \lambda/\beta \cos\theta$$

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

SEM Analysis: To observe the external morphology and grain size of the material as deposited thin films were sintered at 240 °C for 2 h at heating rate 10 °C /min in muffle furnace.The scanning electron micrographs of these annealed films were recorded on Jeol-6390 scanning electron microscope (SEM). Grain size (Ga) was calculated using the relation,

$$Ga = 1.5\ L/MN$$

where 1.5 is the geometry dependent proportionality constant, L the total test line length, M is the magnification and N is the total no. of intercepts.

Compositional analysis by EDAX: The compositional analysis of Cu(II) substituted vanadium HPOM was carried out by taking thin films which are annealed at 240 °C using Jeol-6360 energy dispersive X-ray analyzer.

Optical characterization: Optical transmittance measurements were carried out by using Cu(II) substituted vanadium HPOM thin films on to glass substrates. For optical transmittance measurements Hitachi model 330 Japan make UV-Vis spectrophotometer was used.The measurements was carried out in the wavelength range 350 to 600 nm. The value of band gap is then determined by plotting the graph of $(\alpha h\nu)^2$ *vs.* hν.

TGA-DTA measurements: TGA-DTA measurements were carried out in nitrogen atmosphere on TG-DTA-DSC-SDT-2960 TA Incl.USA make thermogravimetric analysis with heating rate of 10 °C/min.

Electrical resistivity measurements: The direct current (DC) electrical resistivity measurements of thin film were done by using dc 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 Chromel-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 4 digit picoammeter (Model Roorkee DPM 111).

RESULTS AND DISCUSSION

XRD measurements: X-ray diffractograms of Cu(II) substituted vanadium HPOM sample is presented in Fig. 1. The presence of planes (211), (311), (420), (441), (321), (322), (333), (620), (622) and (632) in the XRD pattern of the sample shows that the material is polycrystalline in nature with simple cubic spinel structure. The crystallite size (D) of the material calculated by using Debye scherrer formula is 33.30 nm[12]. The calculated and observed values of interplaner distances (d-obs) & d (cal) are listed in Table-1.

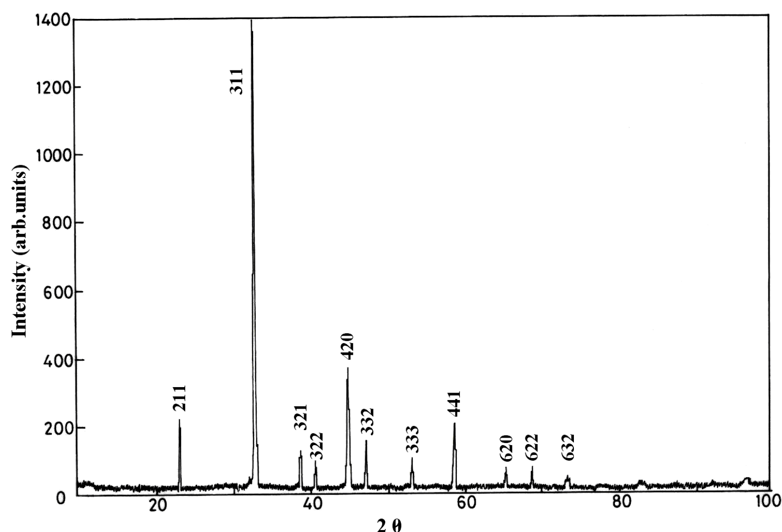

Fig. 1. XRD of Cu(II) substituted vanadium heteropolyoxometalate

TABLE-1
CALCULATED AND OBSERVED VALUES OF INTERPLANER DISTANCES (d-obs) AND (d-cal)

Planes	d cal (Å)	d obs (Å)
211	3.7013	3.8527
311	2.7350	2.7336
321	2.3456	2.3454
322	2.2338	2.2338
332	1.9365	1.9361
333	1.7320	1.7319
420	2.0329	2.0325
441	1.5837	1.5837
620	1.4339	1.4339
622	1.3668	1.3695
632	1.2950	1.2920

The calculated and observed values of interplaner distances are in good agreement. The value of lattice constant (a) calculated for this sample was 9.06633.

SEM studies on external morphology: A typical scanning electron microphotograph of Cu(II) substituted vanadium HPOM thin film (Fig. 2) shows less uniformly distribution of particles with a large intergrannular spacing in them. Grain size which is calculated by formula is found to be 310 nm.

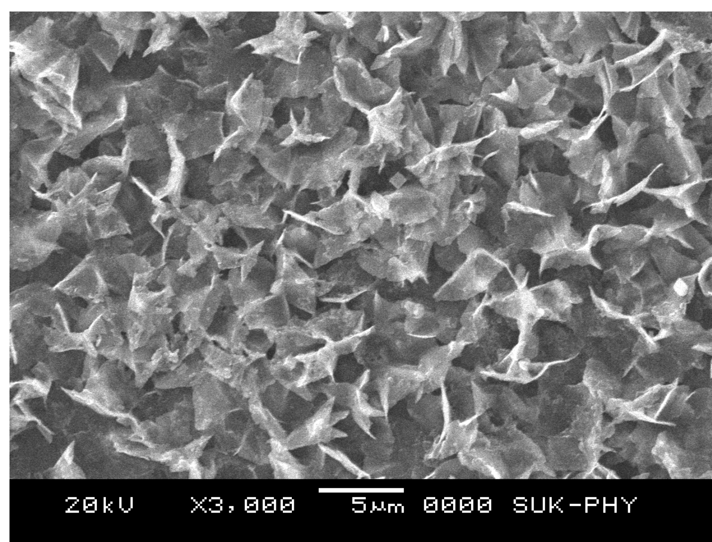

Fig. 2. SEM of Cu(II) substituted vanadium heteropolyoxometalate thin film

EDAX results on compositional analysis: The average grain size (Ga) calculated by linear intercept technique was found to be 310 nm. EDAX results on compositional analysis[13-16].

EDAX spectrum of Cu(II) substituted vanadium HPOM thin film (Fig. 3) showed that, Cu(II) is intercalated in phosphovanadate anion. Compositional analysis of the sample annealed at 240 °C is listed in Table-2 which shows somewhat higher and lower atomic % of elements than the expected values.

Fig. 3. EDAX of Cu(II) substituted vanadium heteropolyoxometalate thin film

TABLE-2
COMPOSITIONAL ANALYSIS OF Cu(II) SUBSTITUTED VANADIUM HPOM by EDAX

Element	Expected atomic (%)	Actual atomic (%)
P	5.25	11.03
V	72.00	68.21
Cu	22.75	20.45

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

$$\underset{\text{Ammonium } meta \text{ vanadate}}{14\,NH_4VO_3} + \underset{\text{Diammonium hydrogen phosphate}}{(NH_4)_2HPO_4} + 8H^+ \rightarrow [PV_{14}O_{42}]^{9-} + 16NH_4OH$$

$$\underset{\text{Phosphovanadic acid}}{[PV_{14}O_{42}]^{9-}} \xrightarrow{Cu(II)} \underset{\text{Cu(II) substituted vanadium heteropolyoxometalate}}{[Cu_4HPV_{14}O_{42}]}$$

Optical property: Fig. 4 represents plot of of $(\alpha h\nu)^2$ *vs.* $h\nu$ of $Cu_4(HPV_{14}O_{42})$ thin films. The optical absorption spectra of as deposited and annealed thin films shows direct band gap of 2.6 eV.

TGA-DTA analysis: Thermal stability of the film was determined by TGA-DTA measurements. TGA-DTA curves of Cu(II) substituted vanadium heteropoly-oxometalate is presented in Fig. 5. The DTA curve shows endothermic peak at 126.68 °C due to removal of water from material, peak at 639.50 °C indicates total decomposition of vanadium HPOM. TGA-DTA curve show that sample is thermally stable upto temperature 250 °C.

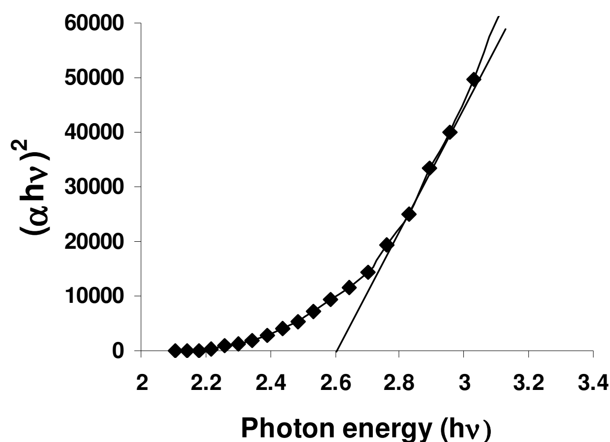

Fig. 4. Plot of $(\alpha h\nu)^2$ *vs.* hν of Cu(II) substituted vanadium heteropolyoxometalate

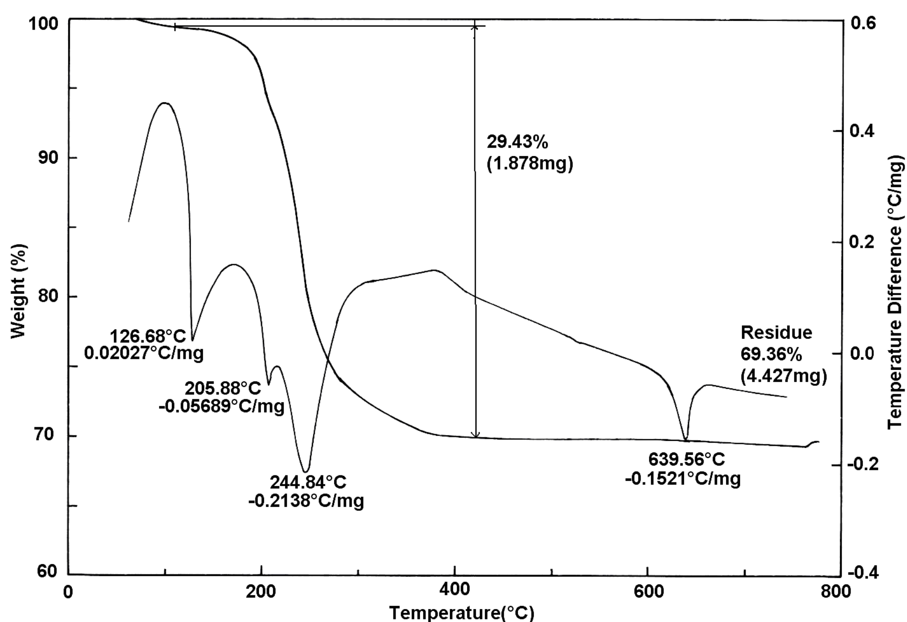

Fig. 5. TGA-DTA of Cu(II) substituted vanadium heteropolyoxometalate

Electrical resistivity of vanadium HPOM: The plot of log resistivity against 10^3/T of vanadium HPOM (Fig. 6) shows that, initially resistivity of material slowly increases with increase in temperature indicating conducting behaviour of the material and then decreases gradually in the temperature range of 120-250 °C shows semi-conducting nature of $[Cu_4HPV_{14}O_{42}]$. Beyond this, the resistivity remains constant. By the TGA-DTA measurements it was found that decomposition of vanadium HPOM take place upto 250 °C, hence resistivity remains constant beyond it.

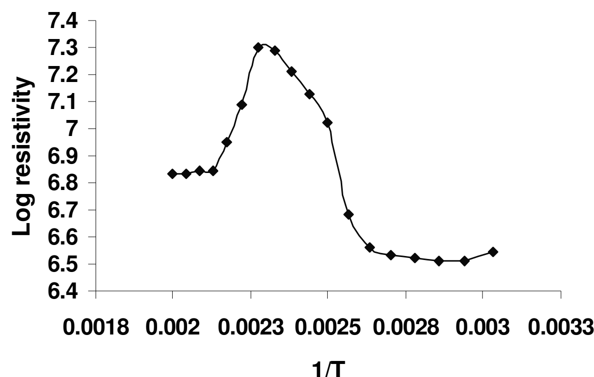

Fig. 6. Plot of log resistivity *vs.* 1/T of Cu(II) substituted vanadium heteropolyoxometalate

Conclusion

The simple chemical bath deposition is suitable technique for the deposition of Cu(II) substituted vanadium HPOM thin films. As deposited material is polycrystalline, having simple cubic spinel structure and thermally stable upto 250 °C. Thus the thin films can be used as a suitable material for device applications.

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(*Received*: 28 August 2008; *Accepted*: 30 March 2009) AJC-7385