Chapter-IV

Summary and Conclusions

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4.1 Introduction:-

Thin film technology is a relatively young and ever growing field in the physical &chemical sciences which is confluence of materials science, surface science, applied physics, applied chemistry. Thin film technology has its objectives in the provision for scientific bases for the methods & materials used in thin film electronics. Heteropolyoxometalates have been receiving a lot of attention and have been extensively studied by many researchers across the world due to its small, compact, oxide cluster with keggin type structure. The HPOM of V,Mo,and W are widely studied due to their redox properties of 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. An enormous patent and journal literature is devoted to the applications of small no. of heteropolyanions.

The heteropolyanions of V,Mo,W finds applications in biochemical industrial catalysis,proton conductor,ion exchange materials,thin layer chromatography,materials for separation of amino acids.Heteropolyoxometalates (HPOM) in addition to their considerable applications in catalysis and medicine are attracting attention as compounds for advanced materials.HPOM also exhibits antiviral,anti –HIV and antitumoral properties.

Due to the more applications of heteropolyoxometalates, especially metal ion doped/ substituted heteropolyoxometalates, the thin film of Cu (II) substituted Vanadium heteropolyoxometalate have been tried. In the field of materials research, a relatively simple and quick method is preferred in order to reduce the cost and quick access to the physico-chemical properties of the materials. The preparation of materials in thin film form is relatively simple and less expensive as compared to that of growing single crystals. Among the chemical deposition techniques,simple Chemical bath deposition technique used for the deposition of the Cu (II) substituted Vanadium heteropolyoxometalate thin films. This technique is relatively simple, economic, quick and easy one for thin film deposition with large area processing capability.

It is therefore of considerable interest to work systematically on the synthesis of doped/ substituted heteropolyoxometalates thin films especially, C (II) substituted Vanadium heteropolyoxometalate thin films by simple chemica bath deposition method. There is no single report available on the dopec substituted thin films of heteropolyoxometalates.

In the present work, Cu (II) substituted Vanadium heteropolyoxometalat thin films have been prepared from aqueous bath onto glass substrates usin simple chemical bath deposition method. The preparative parameters such a concentration of the precursor solution, pH of the bath solution, bat temperature, deposition time etc. of the films have been optimized. The characterization of these films are carried out using, X-ray diffraction (XRD) Scanning electron microscopy (SEM), TGA-DTA, Electrical resistivity and therme electric power measurement techniques.

The quanta of the work that was carried out into several parts is briefl summarized in four chapters

Chapter I is devided into two parts IA &IB and begins with the introduction to thir film technology and introduction of the heteropolyoxometalate chemistry.

section-A deals with introduction to thin film technology, Basics of thin filr deposition, various thin film deposition techniques, theoretical background o chemical bath deposition, basic of chemical bath deposition, factors governing chemical bath deposition.

section-B describes the history of heteropolyoxometalates, fundamenta polyoxometalate structures, build up of polyoxometalate structures, Properties o heteropolyoxometalates and applications of heteropolyoxometalates

Chapter II has been devoted to experimental details, devided into two sections section A & B. Section A describes the synthesis of Cu (II) substituted Vanadium heteropolyoxometalate thin films. The substrate cleaning, preparation of the solution and experimental setup of chemical bath deposition is described in detail. The various preparative parameters such as solution concentration, bath temperature, pH of the bath, and deposition time of the films were included.

section B describes theory of experimental characterization techniques which are used for analytical studies on Cu(II) substituted Vanadium HPOM thin films, like X-ray diffraction (XRD), Scanning electron microscopy (SEM), TGA-DTA, Optical absorption, Electrical resistivity measurement.

Chapter III:-

It is fully devoted to experimental characterization of Cu (II) substituted Vanadium HPOM thin films. It is pertaining the studies on structural, UV-visible absorption spectra and morphological characterization of thin films. It also includes study of electrical transport properties of as deposited samples namely electrical resistivity, thermoelectrical power measurements.

Chapter IV:-

This chapter is Pertaining the summary and conclusions drawn on the present investigation.

4.2 Synthesis and growth mechanism of $Cu_4HPV_{14}O_{42}$ thin films.

Cu (II) substituted Vanadium heteropolyoxometalate thin films were deposited onto glass substrates by chemical bath deposition.For the deposition of Cu (II) substituted vanadium HPOM thin films, 1:4 ratio of aqueous solutions of diammonium hydrogen phosphate and ammonium metavanadate were taken, in acidic medium at pH 5.5. The ions formed condense on an ion by ion basis onto the well processed substrates that are vertically mounted in a reaction solution.

The various preparative parameters and deposition conditions are as follows.

A]	Deposition temperature	Room temperature.
B]	pH of the reaction mixture	5.5 ± 0.2
C]	Deposition time	24 hours

The probable chemical reactions involved in the formation of Cu (II) substituted vanadium HPOM thin films are,

$$[PV_{14}O_{42}]^{9-} + 4\,Cu^{++} \xrightarrow{RT} [Cu_4HPV_{14}O_{42}]$$

(aq.) (aq.) pH 5.5 Thin film

As grown samples are thin relatively uniform, smooth and tightly adherent to the substrate support. The colour of the deposit is slightly yellowish.

4.3 The Thin film properties:-

Cu (II) substituted vanadium heteropolyoxometalate thin films were characterized for their microstructure,uv-visible absorption, thermal stability and electric properties.

4.3.1 The structural properties:-

As deposited HPOM sample were characterized by X-ray diffraction technique using Cu-Kα radiation (λ= 1.54056 A°) from the diffractograms, it was found that the sample deposited shows nanocrystalline in nature. The X-ray analysis showed that the material is sample cubic spinel in nature with grain size 33.30 nm.The calculated and deposited values of interplaner distances are listed in table.No.2 are in good agreement. Thin films of same composition were annealed at 50°C ,150°C and 250°C. It was found that ,peak intensity of prominent peak i.e. (311) plane was increased from 50°C to 250°C hence crystallite size and lattice constant were increased as shown in Table No.1

4.3.2 The microscopic study (SEM):-

The surface morphology of the thin film material were examined through a scanning electron microscopy. From SEM study it is observed that, less uniformly distribution of particles with a large intergrannular spacing in them. Grain size which is calculated by formula is 310 nm.

4.3.3 The optical properties:-

The optical studies were performed in the wavelength range 250-650 nm and the absorption spectra were evaluated to determine the absorption coefficient (α), optical energy gap (Eg). The optical gap of the as deposited thin film is mode of optical transition is direct and allowed.The optical gap is 2.6 ev.

4.3.4 TGA-DTA study:-

Thermal stability of the Cu (II) substituted vanadium heteropolyoxometalate thin film was investigated by taking TGA-DTA. The material is thermally stable up to 250°C. TGA-DTA shows weight loss upto 29.43 % occurred in the temperature range 126 °C to 420 °C. The results from studies of stability are dependent not only on the method employed for such evaluations ,but also on the conditions under which the experiment was performed. Low temperature endotherm is attributed to the removal of water whereas the high temperature exotherm signals the decomposition of the anion.

4.3.5. The electrical transport properties:-

The electrical conductivity and thermoelectric power measurement were carried out in the temperature range 300-500 K. The temperature dependence of an electrical resistivity shows linear decrease in –ve temperature coefficient; this confirms semiconducting nature of the films. The negative temperature coefficient of electrical resistivity in the temperature range 393 K to 453 K.