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Effect of thickness on the properties of Cobalt doped vanadium oxide thin films

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Abstract

Uniform surfaced Co doped V_2O_5 thin films were prepared by simple sol gel method. The effects of thickness on the basic properties of the prepared films have been investigated with the help of X-ray diffraction, Scanning Electron Microscopy and UV-Vis spectroscopy. The high crystalline nature of the prepared films was evident from the well resolved high intensity peaks. The structure of the crystallites was determined as orthorhombic. The SEM analysis revealed in increase in surface roughness with the emerging of flake like structures as the number of dipping to deposit the films was increased. The optical band gap as calculated from tauc plot was in the range of 2 – 2.5eV and thus the prepared thin films can be used in semiconductor applications.

Keywords: Sol gel, Dip Coating, Thin film, Co doped V_2O_5, band gap.

1 Introduction

In recent decades, one of the main threats faced by humans was the pollution of air due to release of SO_2 and CO_2 from vehicle exhaust. The escalating human population has led to a rise in vehicle production and usage. This has in turn polluted the atmosphere around us. Acid rain was obtained from the sulphur dioxide, which was emitted from the combustion of fossil fuels. Among the other modern technologies, as the capturing of sulphur species was in considerable range in Ca- contained compounds and it was has very low cost it has been widely used for the removal of sulphur dioxide from the post combustion gas. The recycling the calcium compound was a difficult task since, it requires a temperature in the range of 1000°C. Researchers all over the world are looking onto technologies and new materials, which have the properties of both eliminating NO_x, Hg, SO_x, VOCs and transform the removed SO_2 to usable products under simple conditions. Among the other catalysis sorbents, as the ability to uptake large amount of sulphur dioxide e at stack temperature (120–200°C), V_2O_5 was found to be a promising material for industrial applications and due to its moving bed operation. It was already known that the removal of SO_2 process by V_2O_5 was done by number of steps, including adsorption of SO_2 onto the surface, in flue gases the oxidation of SO_2 to SO_3 by O_2 over the sites of. V_2O_5 and the formation of H_2SO_4 from the reaction of SO_3 with H_2O in flue gases

Comparing to other materials vanadium pentoxide thin films have a considerable interest due to its biocompatibility, low cost, easy synthesis, availability, good electrical, optical properties. In addition to that it was well noted that it has several applications in the fields of solar cells, gas sensors, electrochromic devices, catalysis, electro optic switches and as cathode material in rechargeable lithium batteries [1-3]. In between the multiple oxidation states of the vanadium oxides the resultant of easy reduction and oxidation were seems in the catalytic activity. To prepare nanostructured V_2O_5 can be prepared by various methods such as, chemical vapour deposition method, sol gel process, ultrasonic method, thermal decomposition, sol-electrophoretic method. However, on comparing with all the above mentioned method, sol gel dip coating technique was simple, less complex, low cost and easily affordable.

Doping of Sn into V_2O_5 lattice has improved the cyclic stability and enhanced lithium ion storage capacity when compared to pure V_2O_5 thin films. [4]. Y.Wei et al., have prepared Cu doped V_2O_5 as cathode material for rechargeable lithium batteries. They have reported that low level doping of Cu had a significant effect in improving the electrochemical properties of V_2O_5 [5]. N.G Prakash et. al., reported the enhanced specific capacity of V_2O_5 thin film on doping 4% Mo from the results obtained through Galvanostatic charge – discharge experiments. [6]. Chromium doped vanadium pentoxide synthesized by S.Y.Zhan exhibited increased electrochemical performance due to lithium diffusion [7]. Yanwei Li et al. synthesized the homogenous Sn doped vanadium pentoxide thin films, by the drop casting method. They analyzed that the reduction of reaction resistance was caused by the Sn doping and it will increase the electrochemical reaction reversibility and improves the lithium ion diffusivity of the ma

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terial [8]. Pure and Ni doped V_2O_5 nanoparticles have been prepared by thermal evaporation by R. Suresh et. al. who have reported that doping Ni into V_2O_5 lattice has improved the sensing abitily of the nanoparticles [9].

Thus doping V_2O_5 was expected to produce better results when applied and hence in this context proper doping of V_2O_5 can yield a better effect on the control of air pollution by subsiding the SO_2 release from vehicle exhausts. Earlier reports suggest that, a single unit containing both SO_2 removal process and the elemental sulfur production process was ideal. However, this requires the catalyst-sorbent should have both oxidizing ability to convert SO_2 into SO_3 as well as the reduction ability inorder to convert the released SO_2 to elemental sulfur in H_2. To make the process possible, active species such as Mo and Co that are commonly used for reduction of SO2 to elemental sulfur, are added into a V_2O_5. In this study, we reported the deposition of Co doped V_2O_5 thin films via simple sol gel dip coating method. The prepared samples were characterized by various techniques such as XRD, SEM and UV-Vis analysis. The obtained results have been discussed in detail.

2 Experimental

2.1 Synthesis method

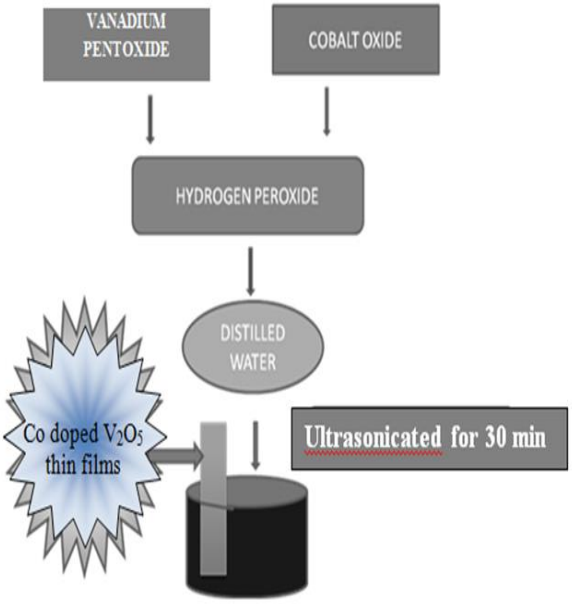

Fig.1 Schematic representation of the experimental procedure

The vanadium pentoxide thin film was synthesized by sol-gel method. The required amount of vanadium pentoxide and cobalt nitrate are dissolved with 30 ml of hydrogen peroxide and 30 ml of DI water. The solution was agitated for 30 min until the yellow color solution changes to orange colour and becomes a sol. The glass substrate was taken and cleaned well with chromic acid, DI water and acetone. The cleaned glass plate was dried and finally dipped in the solution. The number of dipping has been varied in order to increase the thin film thickness. A similar procedure was adopted while preparing cobalt doped vanadium pentoxide thin films. Except that required amount of cobalt oxide was added along with vanadium pentoxide while dissolving in the solution containing 30 ml of hydrogen peroxide and 30 ml of DI water. Finally, thin films were obtained by dipping cleaned glass substrates in this sol.

3 Results and Discussion

3.1 Structural analysis

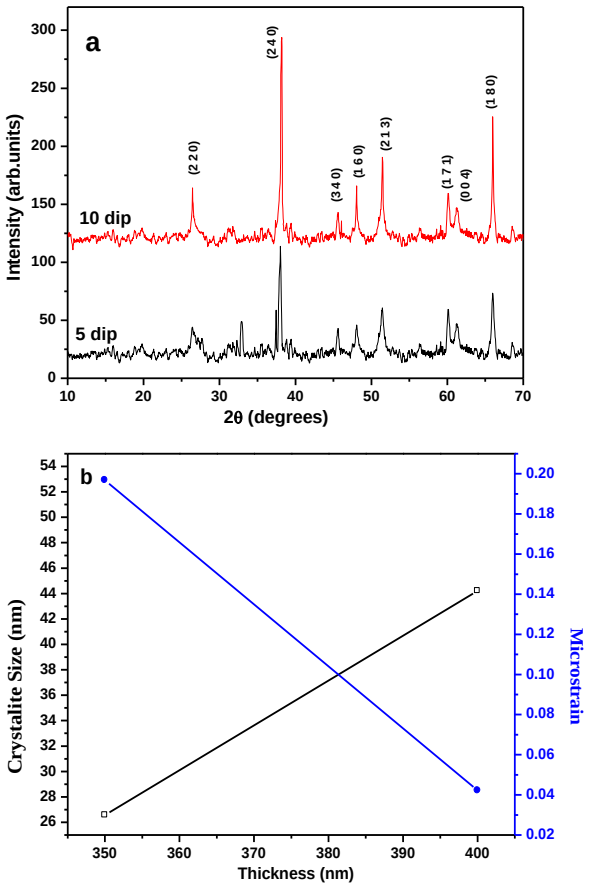

Fig.2 a) XRD pattern of Co doped V_2O_5 thin films b) Film thickness Vs Crystallite size and microstrain

Fig.2a shows the XRD Patterns of the cobalt oxide doped vanadium pentoxide thin films for varying thickness achieved by increasing the number of dippings from 5 to 10 dippings. XRD patterns reveal that both the films show good crystallinity. The degree of crystallinity seems to increase with the increasing film thickness. The XRD pattern of thin films prepared with 5 dippings (fig.2a) show peaks with lower intensity when compared with the samples prepared with 10 dippings. The peaks are indexed using JCPDS 74-1486 and were found to be in exact match. This confirms the formation of cobalt vanadium oxide with an orthorhombic structure. The lattice parameters were found to be a =8.3, b = 11.0, c = 6.03 Å. This in turn reveals the increase in crystallite size with increas-

ing film thickness. Similar results have been reported by Ziaul et. al [10] for thin films prepared by thermal evaporation. The crystallite sizes (D) of the prepared samples are calculated using Debye's Scherrer's formula represented as

$$D = \frac{K\lambda}{\beta \cos\theta} \text{ ------ (1)}$$

Where, K was the Scherer constant, λ was the wavelength of the X-ray, β was the half high width of the diffraction peak of the sample and θ was diffraction angle(radians) The crystallite size of the material was found to be around 26nm and 44nm for films prepared with 5 and 10 dipping respectively. Thus an increase in crystallite size and degree of crystallinity with increase in film thickness but a decrease in microstrain was witnessed as presented in fig.2b. The microstrain value was calculated to be 0.1968 and 0.0422, while the dislocation density values are 5.1 x 10^{+14} lines/m and 14.15 x 10^{+14} lines/m for films prepared with 5 dip and 10 dip respectively.

3.2 Morphological analysis

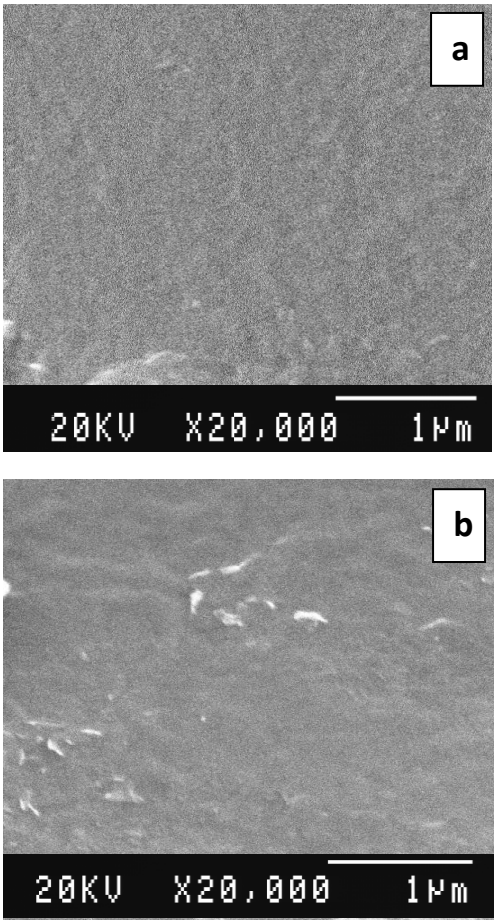

Fig.3 SEM image of V_2O_5 thin films prepared with a) 5 dips and b) 10 dips.

The surface morphology of the prepared thin films was analysed using a Scanning electron microscope. Fig.3 shows the SEM images of samples prepared by varying the number of dipping. The samples prepared with 5 dipping (fig.3a) show a very uniform surface when compared to the samples prepared with 10 dipping (fig. 3b). The thickness measurements reaveal a thickness of 350nm for 5 dip samples and 420nm for samples prepared with 10 dipping. The higher thickness sample shows some flake like structures on their surface that increases the roughness of the surface. This shows that the surface roughness of the films increases with increase in number of dipping which may be due to the variation in the withdrawal speed or ramp. This can be eliminated by the use of equipment fitted with microcontrollers, which was under future consideration

3.3 Optical analysis

The UV- Vis transmission spectra presented in fig..4 (a and b) correspond to the samples prepared with 5 dippings and 10 dippings respectively. The increase in thickness has reduced the transparency of the prepared thin films. The ups and down in the transmission spectra was due to the higher thickness of the prepared thin films.

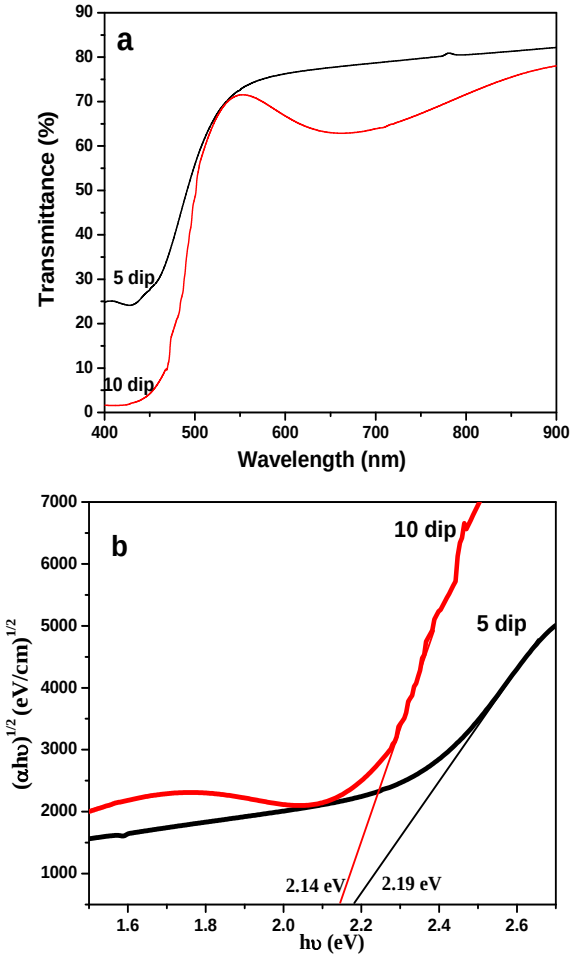

Fig. 4 (a) Optical transmittance spectrum of V_2O_5 thin films (b) Tauc plot.

The samples deposited with 5 dipping show a transmittance percentage of 76% while the higher thickness samples show a maximum transmittance of 68% only. A

Similar percentage of transmittance was obtained by Li-Jian et.al [11], for vanadium pentoxide films prepared by d.c. reactive magnetron sputtering. The idea whether the prepared material was a semiconductor or insulator was obtained through the value of optical band gap obtained. The information about the valence band and conduction band helps us to interpret the amount of absorption and cut off wavelength of the prepared material. Tauc plot was drawn in order to calculate the band gap value. The extinction co-efficient of the prepared sample (k) was calculated using the equation [12].

$$K = [\ln (1/T)\lambda] / [4\pi t] \quad \text{---------- (2)}$$

Where, t was the thickness of the prepared thin film sample, T was the optical transmittance and λ was the absorption wavelength.

The absorption coefficient (α)of the prepared sample was calculated using the formula

$$\alpha = \frac{4\pi k}{\lambda} \quad \text{---------- (3)}$$

The Tauc relation given below was used to calculate the αhν value and to draw the tauc plot

$$(\alpha h\nu)^{1/n} = A\,(h\nu - E_g) \quad \text{---------- (4)}$$

where, α was the absorption coefficient, E_g was the optical band gap energy, A was the absorption constant and n was a value that depends on the type of transition. Direct allowed, direct forbidden, indirect allowed and indirect forbidden were the four transitions obtained in a semiconductor. The momentum was conserved and hence the energy is changes in direct transitions of direct band gap. Hence in a direct band gap material the transitions were vertical. Whereas, the transition in an indirect band gap were oblique i.e., both the energy and momentum vary. In both indirect and direct allowed transitions, the momentum matrix element is not equal to zero. Whereas, in a direct and indirect forbidden transitions the momentum matrix element is equal to zero. The value of n was ½ for direct allowed band gap transition, 2 for indirect allowed band gap transition, 3/2 for direct forbidden transitions and 3 for indirect forbidden transitions. The optical band gap energies thus calculated using the tauc plot in fig 2b were 2.14 eV and 2.19 eV for films deposited with 5 dip and 10 dip respectively. Thus the semiconducting nature of the prepared Co doped thin film was evident. The obtained Eg value (2.14 & 2.19 eV) was in good agreement with Scanlon et al. [13] who reported that the Eg in the range of 2.0–2.4 eV was due to the transition between the O 2p and V 3d transition of V_2O_5 [14]. The band gap value was found to decrease with increase in film thickness. This result was similar to those reported earlier [15-16].

4 Conclusions

Thin films of Co doped V_2O_5 were deposited successfully on glass substrates using sol gel dip coating method. The prepared thin films show a good crystalline nature as obtained from XRD. The crystallites show an orthorhombic structure. The surface of the thin films as investigated using SEM show an increase in surface roughness with increasing film thickness. The optical band gap values increased from 2.14 eV to 2.19 eV when the film thickness increased. The band gap value was well within the semiconductor range and this suggests that the prepared films can be used in optoelectronic applications.

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Conflict of Interest:

All authors have no conflict of interest to report.

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