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Optical Study of Electrodeposited Vanadium Oxide Thin Films: Effect of Deposition Time

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ABSTRACT
Vanadium oxide thin films were prepared by potentiostatic mode of electrodeposition method. X-ray diffraction study confirms formation of vanadium oxide thin film. Surface morphological study was carried out with the help of Scanning Electron Microscopy. Structural and morphological analyses revealed that the deposited vanadium oxide is polycrystalline in nature with porous nanostructure. The effect of deposition time on optical properties was studied by means of UV-Visible absorption spectroscopy. The UV-Visible absorption spectroscopy reveals that the films deposited at lower deposition times show a relatively low degree of optical absorption, while the spectral absorbance of the films increases with the increase in deposition time. From Tauc's plot, the calculated values of forbidden energy gap E_g vary from 2.33 eV to 2.54 eV.
Keywords: Electrodeposition, Vanadium oxide, thin films, UV-Visible absorption spectroscopy, forbidden energy gap

Introduction:
Vanadium oxides tuning their phase from semiconductor to metal and hence they have flexibility to tune electrical resistivity and optical absorbance. Due to this researchers have taken efforts to use vanadium oxides in variety of applications like optical switching, high capacity lithium batteries, and smart windows for solar cell and optoelectronic devices [1-4]. Vanadium pentoxide (V_2O_5) is the most stable vanadium oxides and because of orthorhombic structure it exhibits anisotropic electric and optical properties [5-6]. The optical properties of vanadium oxide thin films are generally depending upon films crystalline nature, surface morphology and thickness etc. So, basically all these things are connecting to numerous synthesis parameters.
Researcher across globe made efforts to optimize the deposition parameters to receive best quality film with superior phase transition performance, through some physical methods, like magnetron sputtering, molecular beam epitaxy (MBE), sol gel, pulsed laser deposition (PLD) and post annealing [7-10]. But, preparation of vanadium oxide thin film by physical method requires highly sophisticated instruments. Also, maintaining the experimental conditions during the preparation is a hard task. So, the alternative way is to use chemical methods for synthesis of vanadium oxide thin films. Most preferred chemical methods includes electrochemical deposition [11], chemical vapour deposition [12], hydrothermal growth [13] and sol–gel [14] etc. Amongst chemical methods, electrodeposition has some special advantages over others like easy synthesis, not required sophisticated instruments etc.
Bahgat and et al. [15] have reported electrical and optical properties of highly oriented nanocrystalline vanadium pentoxide. They have reported direct and indirect band gap of vanadium oxide thin films as 2.22 eV and 0.27 eV, respectively. Dultsev and et al. [16] have reported structural and optical properties of vanadium pentoxide films prepared by sol-gel method. They have reported that thickness of film affects the optical band

gap energy of vanadium oxide films. The shift of the optical band gap is assigned to change in the stoichiometric composition of the film.

In this paper we present an inexpensive and easy-to-process electrodeposition method to produce vanadium oxide thin film. An effort has been taken to study effect of deposition time on optical properties of electrodeposited Vanadium Oxide thin films.

2. Experimental details:

2.1 Film deposition:

We have deposited vanadium oxide thin films using two electrode systems. In two electrode system of electrodeposition, working electrodes were stainless steel (SS304) and ITO coated glass substrate and counter electrode was graphite. The deposition bath was maintained at constant temperature of 333 K. We have prepared a deposition bath consisting of vanadyl sulphate for the electrodeposition of vanadium oxide thin film electrodes on stainless steel and ITO coated glass substrates. The pH of the bath was adjusted by adding few drops of concentrated HNO_3. To obtain good quality of vanadium oxide thin film, we have optimized preparative parameters like precursor concentration, deposition potential and temperature. All other rest of the deposition parameters are kept constant during the experiment, mentioned in Table1. After deposition films were rinsed with distilled water to remove excessive growth of the film and kept for drying in air. The dried film is used for characterizations.

Table 1: Optimized parameters

Details	Optimized values
Mode	Electrodeposition
Deposition Potential	1.5 V
Bath composition	0.05 M $VOSO_4.H_2O$ + few drops of concentrated HNO_3
pH	~ 3
Deposition bath (medium)	Aqueous
Deposition time	(a) 2 min; (b) 4 min; (c) 6 min.
Temperature	333 K
Substrate	Stainless steel and ITO coated glass

2.2 Characterization techniques:

Crystal structure of the electrodeposited vanadium oxide thin films was studied by using XRD in the range of diffraction angle 2θ from 20–80^0 by using Rigaku D/max 2550Vb+ 18 kw with Cuk$_\alpha$ diffractometer. The SEM images were used to study the surface morphology of the vanadium oxide thin film. UV-Visible absorption study of vanadium oxide thin films was studied by UV-Visible absorption spectrometer.

3. Result and discussion

3.1 X-Ray diffraction study:

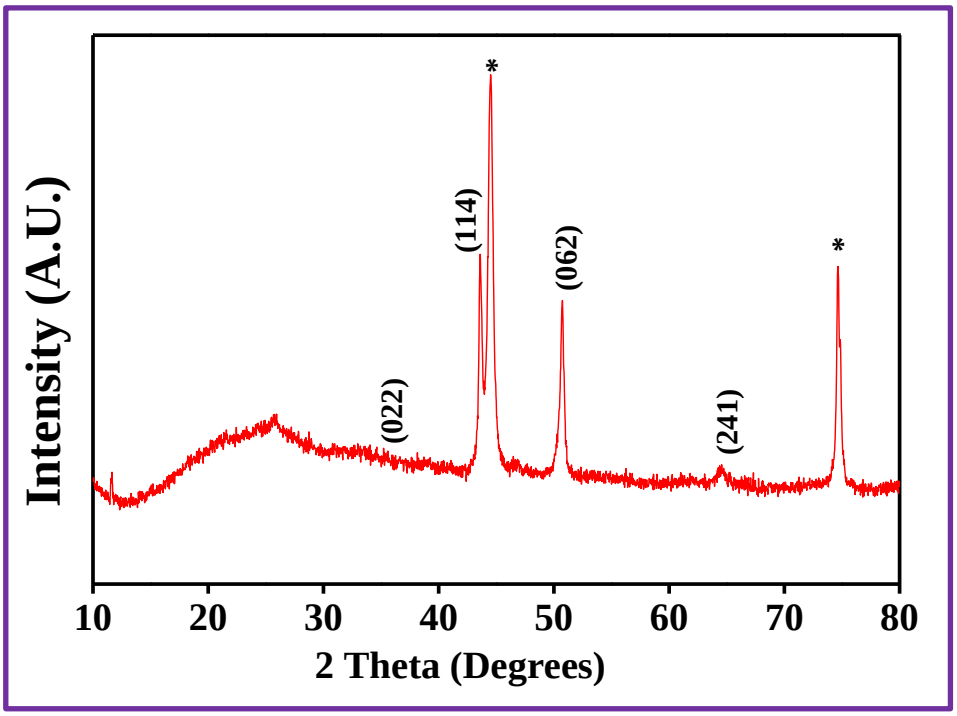


Figure 1: XRD pattern of electrodeposited vanadium oxide thin film deposited at 6 min.

Figure 1 illustrates XRD pattern of vanadium oxide thin film deposited at 6 min. The XRD pattern exhibited four broad peaks, which appear at 2θ values of 34°, 44°, 50° and 65°. The diffraction peaks matches with the standard data (JCPDS: 41-1426). According to the standard diffraction data (JCPDS: 41-1426), these diffraction peaks correspond respectively to the (022), (114), (062) and (241) planes of an orthorhombic structure of vanadium oxide. From Figure 1, it is observed that the deposited vanadium oxide is in polycrystalline in nature. The electrodeposited vanadium oxide thin film does not show any additional peaks, which indicates no secondary phase was formed. The average crystallite size of the vanadium oxide thin film was estimated from the full width at half maximum (FWHM) according to the (062) plane using Debye- Scherrer equation (1) [17]:

$$D = \frac{0.9\lambda}{\beta.\cos\theta} \quad \text{------ (1)}$$

Where, λ is the X-ray wavelength, β is the full width at half maximum of the XRD peak and θ is the Bragg diffraction angle. The calculated value of crystallite size was found to be 10 nm.

3.2 Surface morphological study:

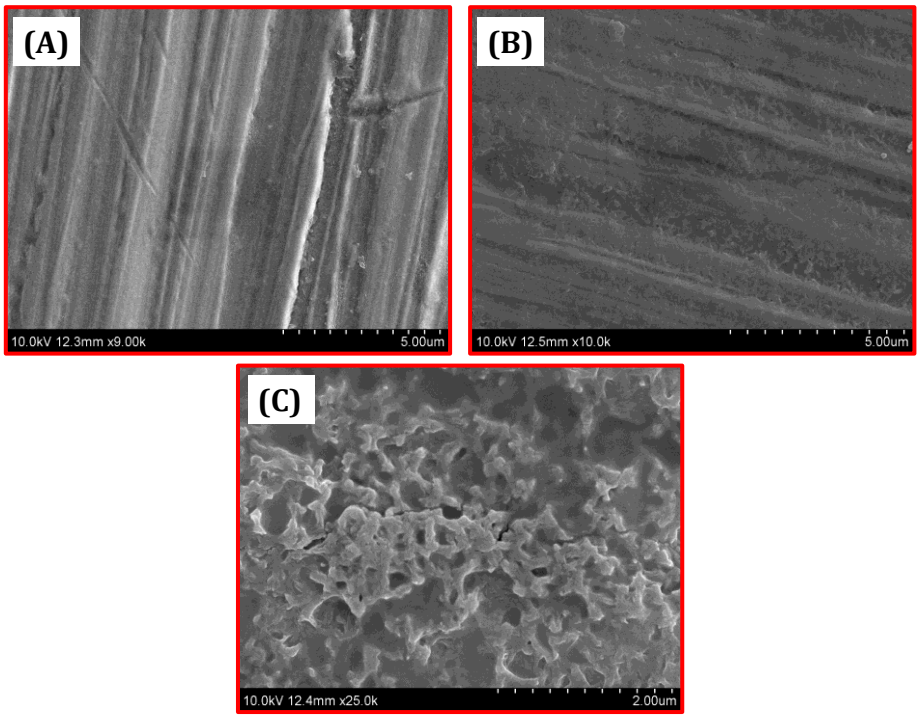


Figure 2: SEM images of electrodeposited vanadium oxide thin films for film deposited at a) 2 min; b) 4 min and c) 6 min.

The surface morphologies of the vanadium oxide thin films obtained with different deposition times at 333 K were determined by using scanning electron microscopy (SEM) and are shown in Fig. 2. When the SEM images of the films were examined, it was observed that as electrodeposition time increased from 2 min to 6 min, the number of coalescence in the film increased and further surface area of substrate covered. At the same time as, it was observed that because of the clusters collections (ion-by-ion mechanism) and clusters growth (cluster-by-cluster mechanism) on the surface of substrate a porous structure formed. These results are in good agreement with the literature. Guneri and et al [18] have reported that effect of deposition time on structural, electrical, and optical properties of SnS thin films deposited by chemical bath deposition. They reported that as deposition time increases the number of aggregations in the film increased and a more homogeneous structure formed.

3.3 UV-Visible absorption spectroscopy:

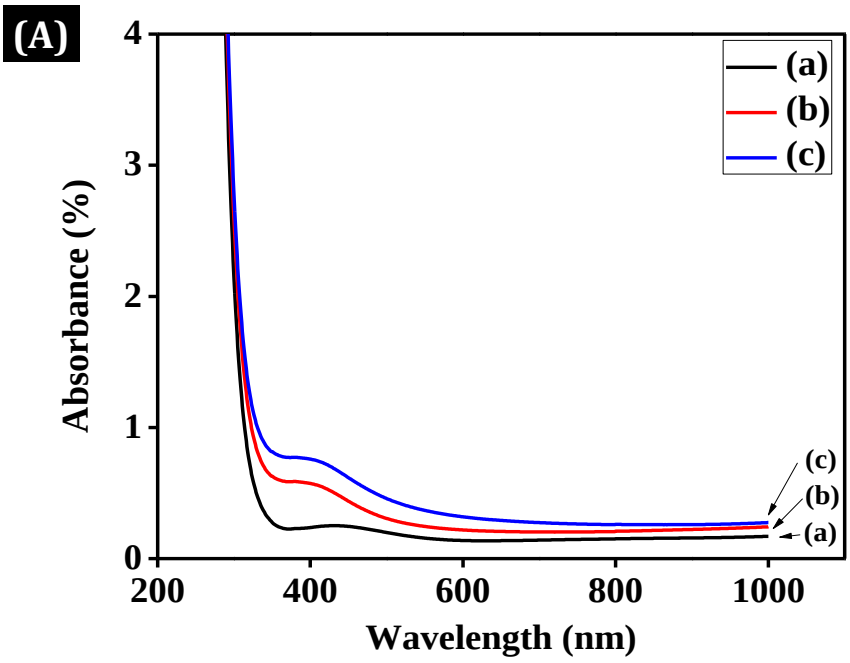
The spectral absorbance characteristics of electrodeposited vanadium oxide thin films at different deposition times are shown in Figure 3 (A). The curves indicate that the films deposited at lower deposition times show a relatively low degree of optical absorption, while the spectral absorbance of the films increases with the increase in deposition time. The spectral characteristic curves show that the optical absorption decreases with increase in wavelength. The effect of the deposition time on the forbidden energy gap values was calculated by the optical absorbance measurements. The optical absorbance A and the optical absorption coefficient were determined by measuring log (1/T) and using the formula;

$$\alpha = \left(\frac{1}{d}\right)\left[\log\left(1/T\right)\right] = A/d \quad \text{----- (2)}$$

Where T is the transmittance and d is the film thickness. Fig. 3 (A) shows the optical absorbance of the films deposited at a) 2 min, b) 4 min and c) 6 min. Fig. 3(B) shows the Tauc's plot of the films deposited at a) 2 min, b) 4 min and c) 6 min. The optical absorption coefficient α as a function of photon energy hν is given as

$$\alpha h\nu = B\left(h\nu - E_g\right)^n \quad \text{-------- (3)}$$

where n is an exponent, ν is the frequency of the incident photon, h is the Plank's constant, B is a constant, and Eg is the forbidden energy gap of the material. The exponent n can take the values 2, 3, ½ and 3/2 for indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively [19-22]. Plotting of $(\alpha h\nu)^2$ versus (hν) and extrapolating to $(\alpha h\nu)^2=0$ gives the value of E_g. The calculated E_g values vary from 2.33 eV to 2.54 eV.



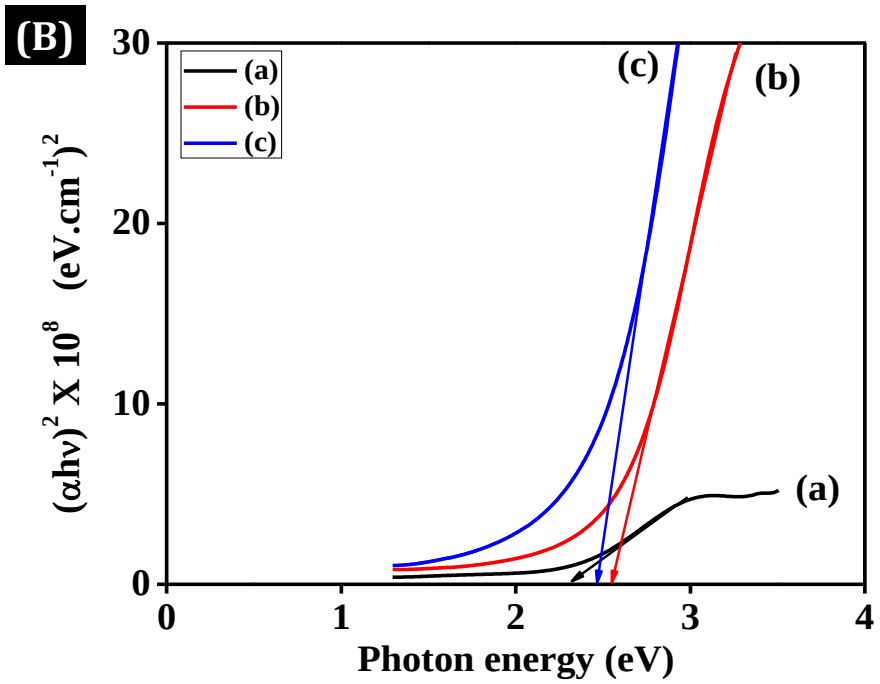


Figure 3: (A) UV-Visible absorption spectra of films deposited at a) 2 min, b) 4 min and c) 6 min; (B) Tauc's plot for films deposited at a) 2 min, b) 6 min and c) 8 min;

Conclusions

In summary, we have successfully deposited vanadium oxide thin film by low cost and simple method i.e. potenetiostatic mode of electrodeposition. By varying deposition time between 2 min to 6 min, may alter the structural, morphological and optical properties of vanadium oxide thin films. XRD study confirmed the polycrystalline nature of vanadium oxide thin film. SEM images showed that a porous structure formed due to two types of mechanism as ion-by-ion mechanism and cluster-by-cluster mechanism on the surface of substrate. From UV-Visible absorption study it is observed that the spectral absorbance of the films increases with the increase in deposition time.

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