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Annealing Effect on Structural, Optical and Electrical Properties of V_2O_5 Thin Films by Dip Coating

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ABSTRACT
Vanadium pentoxide (V_2O_5) solution was synthesized by melt quenching method. Ultrasonically and chemically cleaned quartz substrates were dip coated with V_2O_5 solution by withdrawal speed of 2 cm min^{-1} and the films dry at Room Temperature (RT). The prepared films were subjected for annealing at different temperatures 473, 573 and 673 K for 1 h. The crystallinity of the V_2O_5 films was examined by X-ray Diffraction (XRD). XRD pattern of the V_2O_5 thin films confirmed the polycrystallinity of the film with orthorhombic structure with preferred orientation along (0 0 1) direction. Optical and electrical characteristics of the V_2O_5 thin films were studied by optical double beam UV-Visible spectrophotometry and two probe techniques. The optical results show that the optical optical bandgap (E_g) was found to decrease with increasing annealing temperature. The dependence of the crystallite size, optical bandgap (E_g) and activation energy (E_a) has been reported for V_2O_5 thin films.

Key words: V_2O_5 thin film, melt quenching, optical bandgap, activation energy

INTRODUCTION
Vanadium exhibits many phases with oxygen; these different phases of vanadium oxide show optical, electrical, structural and chemical properties. The different phases of vanadium oxides like VO, VO_2, V_2O_3 and V_2O_5 depend on their structure. This influences the properties of the materials to the greater extent. Different forms of vanadium oxides can be obtained by changing the deposition conditions. Out of the above mentioned phases of vanadium oxide, vanadium pentoxide (V_2O_5) thin films were shown wide spread attention owing to their excellent applications in smart windows and information displays (Alamria and Joraid, 2011), gas sensors (Liu *et al*., 2005), electro chromic devices (Shimizu *et al*., 1992) and infrared detector (Kumar *et al*., 2003). V_2O_5 thin films were synthesized by various chemical and physical methods, namely physical evaporation (Al-Kuhaili *et al*., 2004), pulsed laser deposition (Ramana *et al*., 2001), spin coating (Kumar *et al*., 2011) and dip coating (Raj *et al*., 2012). In the present investigation, the more advantageous and low cost dip coating method was used to prepare V_2O_5 thin films. The thin films obtained were annealed at different temperatures to study their structural, optical and electrical properties.

MATERIALS AND METHODS
V_2O_5 films were synthesized by dip coating method with melt quenched solution (El Mandouh and Selim, 2000). Three g of V_2O_5 (99.9% purity, Merck India) powder was taken in

a ceramic crucible and melted at 1173 K for 30 min and the molten liquid was quickly poured into 100 mL of de-ionized water maintained at room temperature. A brown colour V_2O_5 solution was formed after stirring for sufficient time. Then, it was kept stationary for 24 h. Chemically and ultrasonically cleaned quartz slides were used for dip coating. The quartz slides were dipped into solution and withdrawn with a speed of 2 cm min^{-1}. These films were dried at Room Temperature (RT) for 10 min. The above procedure was repeated twice to get the desired thickness for the films. These films were finally dried at room temperature for 48 h. The as prepared films were subjected for annealing at different temperatures i.e. 473, 573 and 673 K for 1 h. The structural properties of the films were studied with X-ray diffractometer (Philips Xpert diffractometer of Cu K_α radiation = 1.54 Å) in the angle (2θ) range between 10 and 70°. The optical bandgap (E_g) was calculated from the transmission spectra recorded against wavelength using a Lab India UV-Visible 3000 spectrophotometer. Resistance was measured by two-point probe method using Keithley electrometer in the temperature range of 300-373 K. The metallic contacts over the films were made by silver paint.

RESULTS AND DISCISSION

Structural properties: X-ray Diffraction (XRD) pattern of V_2O_5 thin films at various temperatures were shown in Fig. 1. All the XRD patterns of the films indicates the polycrystalline nature with orthorhombic V_2O_5 phase. Due to annealing of these films at temperatures 473, 573 and 673 K in air exhibits the predominant (0 0 1) peak of the orthorhombic V_2O_5 phase. Further the dominance of the (0 0 l) peak in the XRD patterns suggests that the texture of the V_2O_5 thin film was oriented along the c-axis. Moreover, the colour of V_2O_5 films change from light green colour to brown colour with increase in annealing temperature. This change in colour of the films with increase of temperature could possibly due to change in valence state of vanadium, which is in confirmation with the earlier reports (Kumar *et al.*, 2008). Using XRD data the crystallite size of the films was estimated with the help of Debye sherrer's equation (Vasanth Raj *et al.*, 2012):

$$d = \frac{0.94\lambda}{\beta\cos\theta} \quad (1)$$

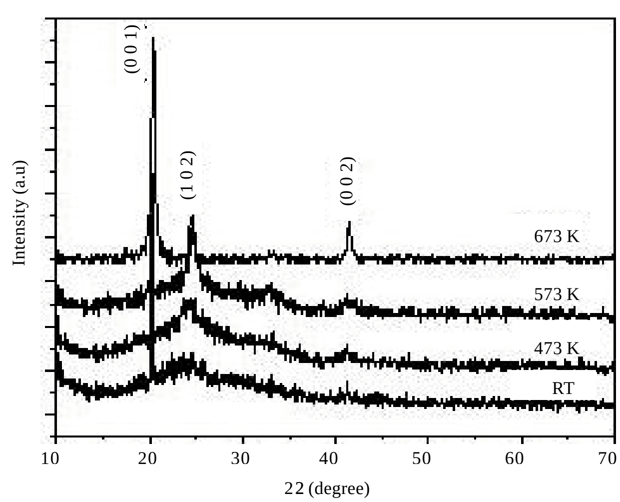

Fig. 1: XRD patterns of the V_2O_5 films at RT, 473, 573 and 673 K temperatures

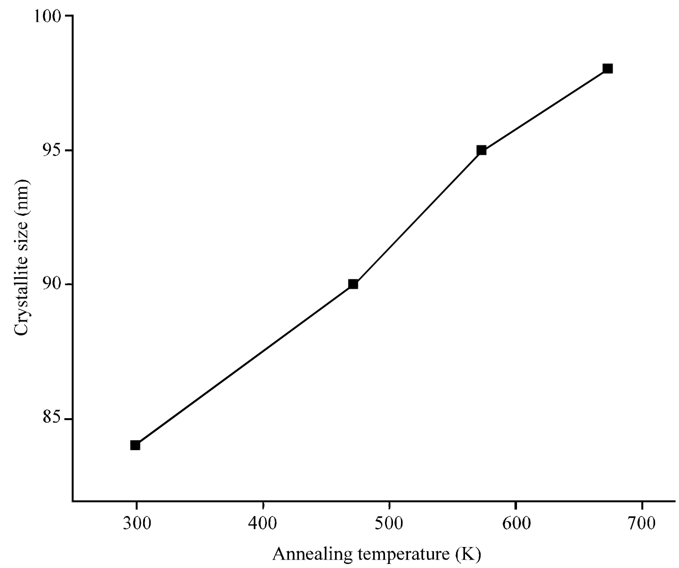

Fig. 2: Crystallite size vs. annealing temperature

where, d is the crystallite size λ is the X-ray wavelength (1.54 Å), β is full width half maximum and θ is Bragg's diffraction angle. From the XRD data the crystallite size of the V_2O_5 films prepared at RT and annealed at 473, 573 and 673 K was found to be 84, 90, 95 and 98 nm, respectively. The variation in crystallite size with annealing temperature was shown in Fig. 2. As the films are annealed at low temperatures, the surface atoms having less energy and less mobility, this results in formation of imperfections in V_2O_5 films. As the films are annealed at high temperatures, these atoms gain sufficient kinetic energy and mobility to occupy stable equilibrium positions inside the V_2O_5 crystals. XRD patterns observed in Fig. 1 confirms the improvement in intensity for all the indexed planes with increase in annealing temperature. This can be attributed to improvement in crystallinity of V_2O_5 films with increase in annealing temperature.

Optical properties: The transmittance spectra of the as prepared and annealed V_2O_5 films were presented in Fig. 3. The spectra was recorded over the wavelength range 300-800 nm. The as grown and annealed films at 473, 573 and 673 K temperatures have an average transmittance value up to 72, 68, 61 and 55%, respectively. As described above, with increase in annealing temperature the films were shown polycrystalline phase. Due to annealing the surface of the films becomes rough and it may be possible that the surface of the films allows more scattering of light, this may further causes in lowering the transmittance of the films.

The optical absorption coefficient (α) was calculated by the following relation (Kumar *et al*., 2011):

$$\alpha = \frac{1}{t}\log\left(\frac{1}{T}\right) \tag{2}$$

where, t is the film thickness and T is the transmittance.

According to inter-band absorption theory, optical bandgap of the films was calculated from Fig. 4 using the following relation:

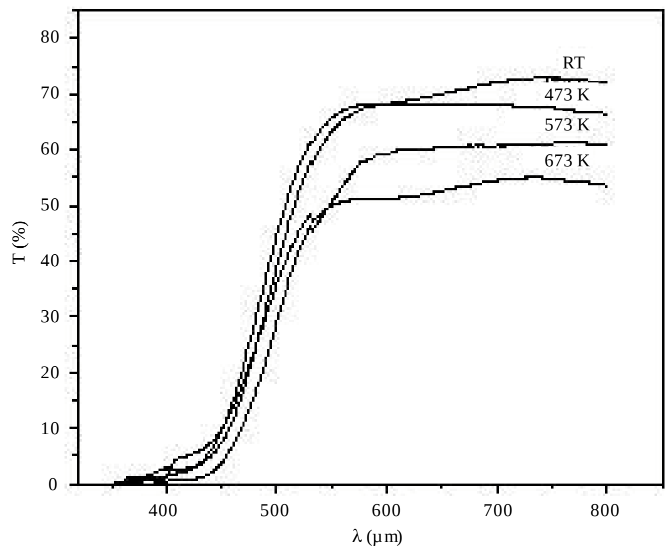

Fig. 3: Transmittance spectra of V_2O_5 thin films at RT, 473, 573 and 673 K

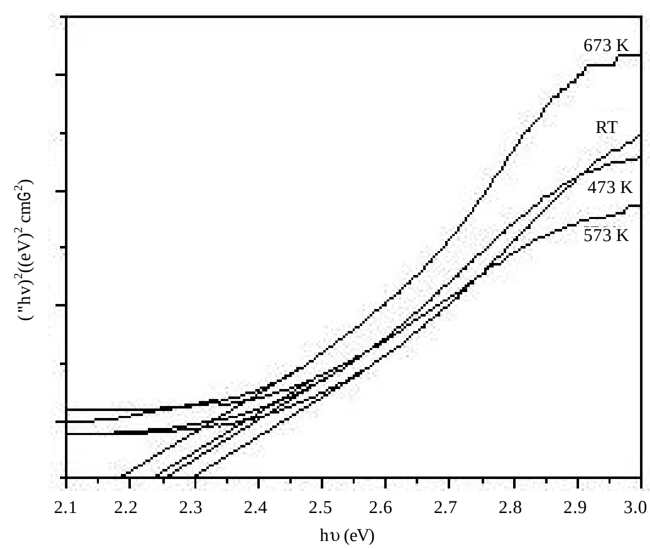

Fig. 4: αhυ vs. hυ of the V_2O_5 thin films at RT, 473, 573 and 673 K

$$\alpha h\upsilon = B(h\upsilon - E_g)^r \quad (3)$$

where, B is the probability parameter. E_g is the optical band gap of the material, hυ is the incident photon energy and r is the transition coefficient. The value of r has taken as 1/2 for direct band gap transitions (Ashour and El-Sayed, 2009). The calculated values of the optical band gap E_g was found to be 2.29, 2.24, 2.22 and 2.18 eV for the as grown and annealed films at 473, 573 and 673 k, respectively. The variation of optical bandgap with increasing annealing temperature was plotted in Fig. 5. From this figure it was observed that with increasing annealing temperature, the optical bandgap was found to decrease. The decrease in optical

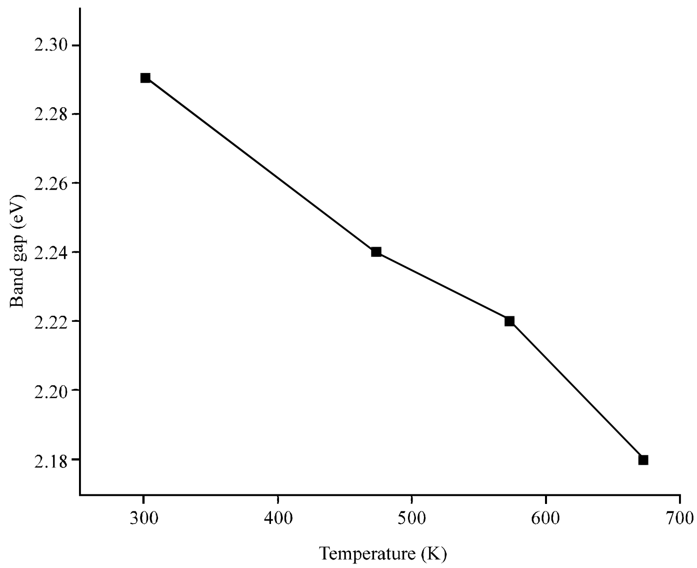

Fig. 5: Optical band gap vs. annealing temperature

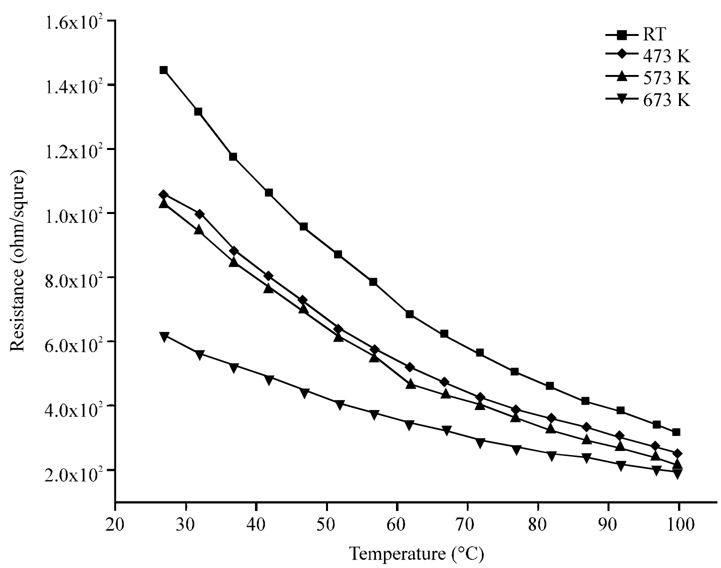

Fig. 6: Resistance vs. temperature

bandgap may be due to oxygen reduction in V_2O_5 which leads to creation of vacancies which may act as donor centers in band gap. This mechanism may leads to free flow of electrons to conduction band.

Electrical properties: The electrical resistance of the annealed films was measured in the temperature range 27-100°C as shown in Fig. 6. From the above graph, it was observed that the resistance was found to decrease with increase of temperature. It was further noticed from the above figure that as the annealing temperature increased, the resistance of films was decreasing and the R v/s temperature curves were maintained the same trend. The decrease in the resistance may be due to the reduction of V^{5+} to V^{4+} states. Increase in

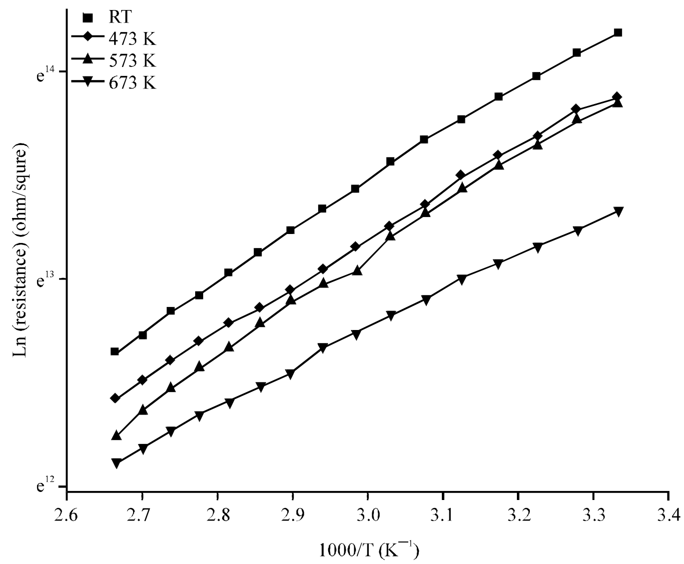

Fig. 7: Ln(resistance) vs. 1000/T

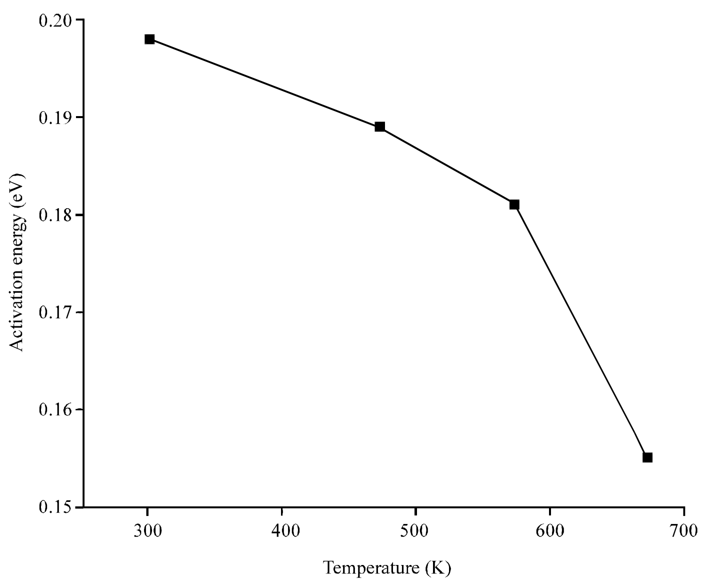

Fig. 8: Activation energy vs. annealing temperature

the content of V^{4+} ions results in increase of conductivity in V_2O_5 films. Activation energy (E_a) was calculated from Fig. 7 by using the relation (Oksuzoglu *et al.*, 2013):

$$R = R_0 \exp\left(\frac{E_\alpha}{kT}\right) \quad (4)$$

where, R is the resistance, R_0 is the constant, k is the Boltzmann constant and T is the absolute temperature. The activation energy (E_a) found to decrease with increasing annealing temperature as shown in Fig. 8. The decrease in electrical resistance and activation energy with increase of annealing temperature maybe due to the improvement in crystallinity of the films. Which was also confirmed with XRD data.

CONCLUSION

V_2O_5 thin films were synthesized by dip coating on quartz substrates at a constant withdrawn speed. XRD pattern of V_2O_5 thin films showed crystalline orthorhombic structure with a preferential (0 0 1) orientation. The films annealed at temperature 673 K shows good crystallinity and preferred orientation along c-axis. The optical band gaps of as grown and annealed films at different temperatures were found to be 2.29, 2.24, 2.22 and 2.18 eV, respectively. Electrical resistance and activation energies were decreasing with increasing annealing temperature, this may be due to formation of V^{4+} ions and increasing of crystallinity in the film structure. The annealing temperature significantly influences the structural, optical and electrical properties of V_2O_5 thin films.

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