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Growth And Characterization Of Activated Reflective Evaporated V_2o_5

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ABSTRACT:

V_2O_5 with orthorhombic layered structure. The importance of ARE technique an attempt was made to prepare V_2O_5 thin film at various oxygen partial pressures and substrate temperatures keeping the glow power at 6W. Activated reactive evaporated V_2O_5 thin films are found to be uniform and well adherent to the substrate surface. It is observed that stoichiometric V_2O_5 thin films with better crystalline nature and optical properties can be obtained by a proper control of deposition parameters such as substrate temperature and oxygen partial pressure.

The X-ray diffraction pattern of the films deposited in an oxygen partial pressure of $5x10^{-4}$ Torr, andat substrate temperature 523 K, exhibited predominantly (001) orientation with a grain size of about 200 nm. For the films deposited at lower oxygen partial pressures the intensity of (001) peak slightly reduced with a relative growth of hexagonal (h00) orientations. The effect of substrate temperature on the structure of V_2O_5 films was also studied by keeping oxygen partial pressure at $5x10^{-4}$ Torr. The V_2O_5 films formed at $Ts < 423$ K were found to be amorphous in nature. The grain size was observed to be increased with increase of substrate temperature.

The IR absorption bands were broad and poorly resolved for the films deposited at a substrate temperature < 473 K. The high frequency IR bands corresponding to symmetric and anti-symmetric vibrations of V=O are observed at1020 $cm^{-1,}$ 992 cm^{-1} respectively for the films deposited at Ts= 523 K. The IR active modes correspond to V-O-V stretching vibration appeared at 815 cm^{-1} The effect of oxygen partial pressure and substrate temperature on the optical properties of V_2O_5 thin films were studied from the optical transmission and reflection data in the wavelength range 350-2500 nm. $5x\ 10^{-4}$ Torr is 2.35 eV. The films prepared at lower oxygen partial pressures ($5x\ 10^{-4}$ Torr) exhibited a significant broad band absorption in the near infrared region and the optical absorption edge shifted towards lower energy region indicating the sub stoichiometric nature of the films. There is no significant variation in the optical band gap of V_2O_5 thin films with substrate temperature.

INTRODUCTION

Transition metal oxides constitute an enormous and interesting group of solids exhibiting a variety of novel properties, useful for advanced technological applications [1-5]. They exhibit structural phase transformations, sub-stoichiometry and electronic properties arising from electron hopping through the mixed valence oxide network as well as ionic properties arising from proton diffusion in the aqueous phase [6-8]. Thin films of these oxides can be easily deposited by various physical and chemical methods and have attracted the attention of researchers over the past few years owing to their application in the fields of microelectronics, micro-Ionics and display systems [8-11].They are semiconductors, which exhibit photochromism and electrochromic, utilized in multicolorelectro chromic devices, color filters, switchable mirrors, energy efficient windows and other optical devices [12,131. These oxides with either two-dimensional van der Waal's bonded-layered structure or three dimensional frame work tunnel structures are also investigated for their use as positive electrodematerials in the fabrication of solid-state lithium micro-batteries [14, 15].

Vanadium Pentoxide (V_2O_5), one among these transition metal oxides, is an interesting material for scientific and technological applications [16-18]. It is a low mobility semiconductor with predominantly n-type conductivity [19]. V_2O_5 exhibits an orthorhombic layered structure and can be prepared in thin film form by a variety of deposition techniques [20-22]. As a thin film, it exhibits multicolored electrochromic, and has high potential for use in electrochromic display devices, color filters and other optical devices [12]. Bulk and thin film V_2O_5 with vanadyloxygen vacancies have been used as an oxidation catalyst [l l]. As a functional inorganic material, V_2O_5 can be used in gas sensors and electrochromic cells. High values of its electrochemical potential difference with lithium and its specific energy density made it suitable as a cathode material in solid state lithium micro batteries [23].

In view of multifarious characteristics and applications of these vanadium pentoxide thin films, it has been aimed to investigate the growth and physical properties

Structure:

Vanadium oxide system exhibits interesting electrical and optical properties because of the various valence states of vanadium cations. Vanadium oxides especially in the $V_2O_5 - V_2O_3$ system, are complex and within this compositional range many stable intermediate oxide phases have beenreported [24,25].

$V_n O_{2n-1}$ where $2 \leq n \leq 8$ (Magneli phases)

$V_n O_{2n}$ where n = 2 V_2O_{2n+1} where n=2,4,6

Among the family of vanadium oxides, vanadium pentoxide is the most stable compoundwith the highest oxygen concentration and it can be built from corner sharing and edge-sharing V_2O_6 Octahedra. V_2O_5 crystallizes with an orthorhombic unit cell and belongs to P_{mnm} space group with lattice parameters a = 1 1.510 A^0 b = 3.563 A^0 and c = 4.369 A^0, where the b and c axes areoften interchanged [26].

The structure of V_2O_5 is shown in Fig. I. l.

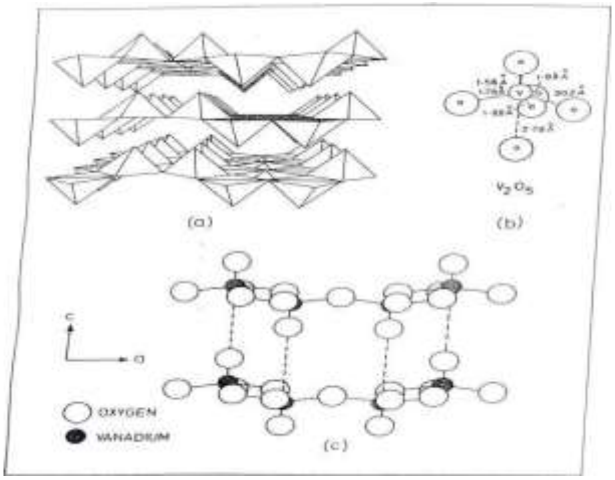


Fig. 1.1 (a) The perspective lamellar structure ofV205.
(b) The fivefold coordination of vanadium with oxygen in V205. (c)The

projection ofV205 structure off-to (010) plane

Fig. l. I (a) illustrate the perspective lamellar structure. Fig. 1.1 (c) represents the projection of the structure on the (010) plane of V_2O_5. The fivefold coordination of vanadiumwith oxygen in V_2O_5 with V-O bonds is shown in

Fig. l. I (b). One with 01 atoms, one with 02 atoms and three with the 03 atoms. From the structural figure of V_2O_5, it is evident that the $V\text{-}O_3$ bonds form puckered chains in the b-direction, which are linked to each other in the a-direction by the bridging oxygen 02. The layers so formed areheld together by weak V-O bonds. The shortest vanadium-oxygen bond length corresponds to a double vanadyl bond (V=O). As such the oxygen in crystalline V_2O_5 is divided into three types. According to infrared and Raman spectroscopic studies [27] a bond at 992 cm- was characterized as a stretching vibrational mode of the V-O, bond; a second vibrational mode at about 765 cm- has been assigned tothe V-2-V bond; and the third type at about 702 cm- was characteristic of the stretching vibration ofthe $V\ \text{-}O_3<$ bond. The stoichiometry of V_2O_5 is considered as a deformed octahedra VO_6 which serves as the building block of the V_2O_5 structure. The octahedra are irregular in V_2O_5 with five V-O distances between 1.585 and 2.021 A^O and a sixth distance as large as 2.79 A^o. The deformed V06 octahedra form wrapped layers in which oxide anions are shared by adjacent octahedra. From this structure, itis assumed that only weak van der Waal's type interaction exists between the layers. Thus, the crystalstructure of V205 is a layered structure (the layers are 4.4 A^O apart) with an easy cleavage along (001) plane.

The way in which V_2O_5 crystal structure evolves to an amorphous structure is explained as follows. Starting from a crystal model of double chains of trigonal prisms, the reorganization in double chains of tetrahedra by small displacements of the oxygen atoms placed at the apexes of the trigonal prisms, new partial chain of tetrahedra with some vacant symmetry which allow connection with other smaller tetrahedra units. The final model of a V205 proposed by Mosset et al [28] is shown inFig. 1.2. Fig. 1.3 illustrates the schematic representation of O(2P) and V(3d) bonds in V_2O_5. Generally, the conduction band in V_2O_5 is formed by vanadium 3d bonds and the valence band is formed by 2P bonds of oxygen. In crystalline V_2O_5, the fundamental absorption is mainly dueto thetransition from oxygen p-type wave functions to 3d-type vanadium wave functions following the direct forbidden transitions [l l].

Vanadium pentoxide is a low mobility n-type semiconductor. The semiconducting properties of V_2O_5 arises from the hopping of unpaired electrons between vanadium metal ions of variable valency (V^4+--> V^5+). The electron hopping process is schematically represented in Fig.

1.4. The lower valence vanadium sites are assumed to form as a result of thermally excited electronsfrom the trapping centers [23].

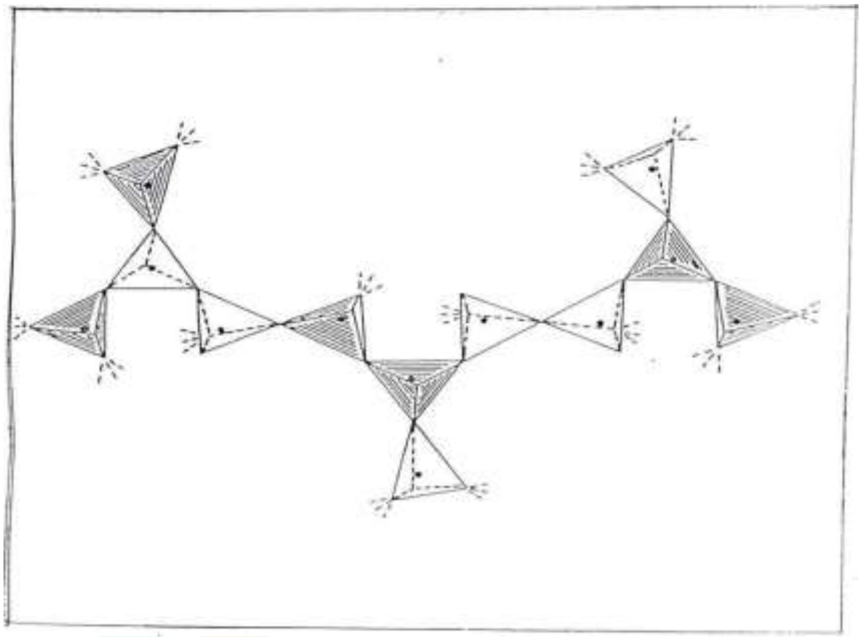


Fig. 1.2 The final model of amorphous V_2O_5proposed by Mosset et al. Fig.Schematic representation of O(2p) and V(3d) bonds in

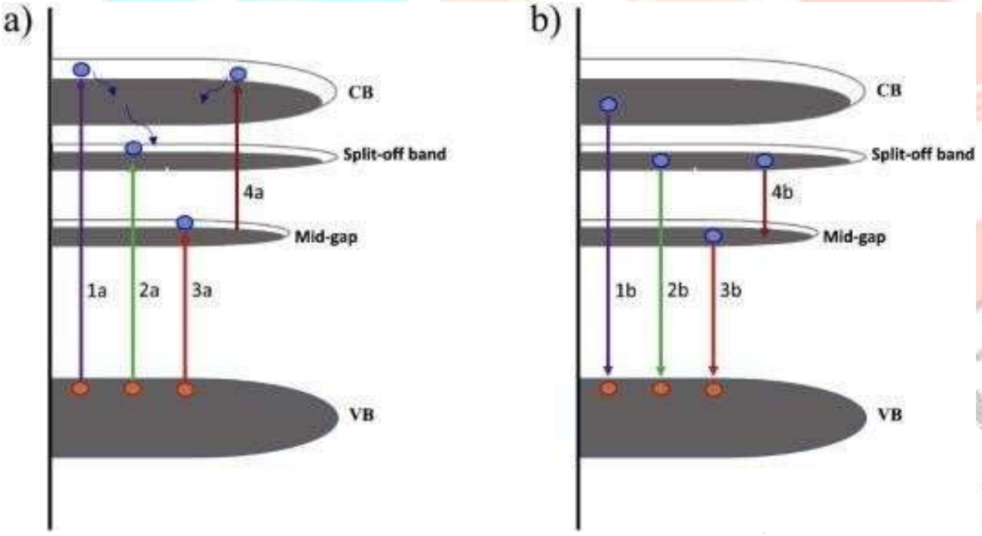
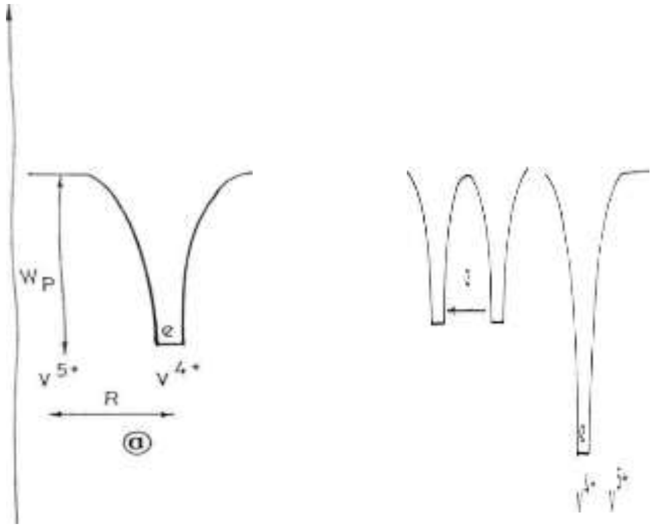


fig 1.3



(b) (c)

fig.l. 4 Schematic representation of electron hopping by phonon assisted tunnelling process in V_2O_5 (a) before hopping, (b) activated transition state, and (c) after hopping. Fig. 1.3 Schematic representation of O(2p) and V(3d) bonds in V_2O_5.

EXPERIMEINTAL:

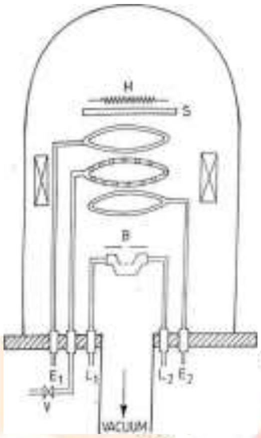
Activated Reactive Evaporation (ARE) is a plasma deposition method used to deposit refractory compounds such as oxides, carbides, nitrides, sulphides. The advantage of Activated reactive evaporation process are: (l) the reaction occurs predominantly in plasma (2) the chemical composition of the film can be controlled by changing the ratio of reacting species and (3) high melting point inorganic compounds can be synthesized at low substrate temperatures. Presently the ARE technique has different names like low pressure plasma, cold plasma, non-equilibrium plasma and glow discharge deposition. In this technique, the evaporated material (either by resistive heating or by the electron beam evaporation) is transported through the reactive gas plasma. The reaction between the evaporated material and the gas is activated by establishing a thermionically assisted plasma in the reaction zone. The main difference between the reactive evaporation and activated reactive evaporation is the presence of plasma in the ARE. As a result, in activated reactive evaporation process the vapor no longer consists of neutral atoms or molecules in their low energy state, but contains in addition, positive and negative ions as well as energetic neutrals of both the metal and constituents. The plasma can be generated by applying a high voltage between two electrodes. The plasma density is enhanced by applying a magnetic field with a field strength of 500 Gauss between the two electrodes. The reaction kinetics involved in reactive evaporation can be treated exactly in the same manner as the reaction in heterogeneous systems of condensed phases. The heterogeneous reactions involve the transport of the reactants to the reaction interface, occurrence of the chemical reaction at the reaction interface, transport of any reaction biproducts away from the reaction interface, the nucleation and growth of the film and transfer of heat to (or) away from the reaction interface. The deposition rate in activated reactive evaporation can be controlled by using the following steps: (i) the adequate supply of reactants, (ii) adequate collision frequency between reactants, (iii) the rate of chemical reaction at the reaction interface and (iv) the rate of removal of any undesired products away from the reaction interface. Considering the technical advantages and flexibility of controlling the deposition parameters, the investigations are aimed to prepared thin films of V_2O_5 by activated reactive evaporation technique.

System Details:

The activated reactive evaporation setup fabricated in a Hind Hivac vacuum coating unit in our thin film laboratory [19] is employed for the deposition of V_2O_5 thin films. The system consists of a stainless steel beljar mounted on a base plate provided with suitable electrical feed- throughs. The schematic diagram of activated reactive system is shown in Fig.

2.1. A circular plane target is kept in between the circular electrodes. The electrodes are externally connected to a high voltage d.c. power supply with a current rating of IA at 2000 V.A dense plasma can be generated by applying a high voltage between two circular electrodes in a controlled oxygen partial pressure.

The vacuum chamber can be evacuated to a base pressure of $2x10^{-6}$ Torr using a conventional three stage water cooled oil diffusion pump backed by two stage rotary pumps. Two Pirani gauges and one cold cathode ionization gauge (penning gauge) are used to measure the pressure in the chamber. The mass flow rate of oxygen is accurately controlled and measured by mass flow controller. The substrate temperature is controlled by a Eurotherm temperature controller.



B-M0 Boat M-Magnet El; E2- Electrodes V- Needle Valve H – Heater S- Substrate

Deposition of V205 thin films by ARE Technique:

pure vanadium pentoxide (99.99% obtained from Merk) powder is sintered in an oxygen atmosphere at 573 K and charged in a specially designed molybdenum boat with a small orifice. The boat is connected between two electrodes. The important deposition parameters which play an important role in defining the properties of the films are ultimate vacuum, substrate temperature, rate of deposition, oxygen partial pressure glow power etc. The substrates are chemically and ultrasonically cleaned and mounted of to substrate holder along with suitable masks. The source to substrate distance is fixed at 10cm. The substrates are maintained in the temperature range 300 K — 600 K. After attaining the ultimate vacuum of $5x10^{-6}$ Torr, pure oxygen is admitted into the chamber through mass flow controllers and controlled to a required oxygen partial pressure in the chamber. Then the high voltage is applied between the circular electrodes. A sustained high dense plasma is obtained by controlling the voltage and oxygen partial pressure. The oxygen partial pressure is varied in the range 10^{-2} - 10^{-4} Torr. The glow power is fixed at 6 W. V_2O_5 thin films are deposited by activated reactive evaporation process in which the V_2O_5 is resistively evaporated at low rates from an electrically heated molybdenum boat and transported on the substrates through a high dense plasma.

RESULT AND DISCUSSION:

The properties of Vanadium pentoxide (V_2O_5) thin films are generally generated by the deposition technique and deposition parameters used for the growth of thin films. In the present investigation V_2O_5 thin films were prepared by activated reactive evaporation technique. The influence of oxygen partial pressure and substrate temperature on the composition, structure, Optical and electrical properties of thin films were studied.

Thin films of V_2O_5 were deposited at different oxygen partial pressures ranging from $1x10^{-2}$ Torr to $1x10^{-4}$ Torr keeping the substrate temperature at 523K. The films formed in an oxygen partial pressure of $5x10^{-4}$ Torr were found to be transparent with pale yellow colour. The colour of the films varied from pale yellow to orange yellow and then the honey gray with the decrease of oxygen partial pressure. The glow was not sustained by decreasing the pressure below $1x10^{4}$ Torr. The films grown at higher oxygen partial pressures (> $5x10^{-3}$ Torr) were found to have poor adhesion.

The X-ray photoelectron spectroscopic measurements were made on V_2O_5 thin films deposited on Pyrex glass substrates to identify the chemical state of the constituent elements present in the films. The sample was irradiated with soft monochromatic X-rays and detailed scans were taken in the binding energy range 510 - 540 eV. The binding energies were calibrated with Au $4f_{1/2}$(E_B = 83.9 eV) and Cu $2P_{3/2}$ (E_B = 932.7 eV). As an Internal reference for the peak position, the C(ls)peak occurredat the binding energy of 284.6 eV. The X-ray photoelectron spectra of the films deposited at various oxygen partial pressures keeping the substrate temperature at 523 K are shown in Fig. (a). The spectra exhibited two intense peaks corresponding to vanadium (2p) and oxygen (1s) core level. The 2p levels of vanadium in V_2O_5 gives rise to the characteristics double of V($2p_{3/2}$) and V($2p_{1/2}$) peaks in the XPS spectrum prepared by a small amount of energy, which is the consequence of the electron spin [2]. The XPS spectra of V_2O_5 films deposited in an oxygen partial pressure of $5x10^{-4}$ Torr displayed core level binding energy peaks of V($2P_{3/2}$) at 517.1 eV and V($2P_{l/2}$) at 524.4 eV with an energy separation of 7.3eV due to spin orbit splitting of vanadium 2p levels. The oxygen(ls) level is observed at 530.2 eV. The peak positions and energy separations are in good agreement with that of V2O5 powder [3] suggesting that the films prepared in an oxygen partial pressure of

$5xl0^{-4}$ Torr -$1x10^{-3}$ Torr are nearly stoichiometric with vanadium in its highest oxidation state i.e. V^{5+}.The position of core level binding energy peak of V($2p_{3/2}$) for the films deposited in an oxygenpartial pressure <$5x10^{-4}$Torr was found to be shifted slightly towards lower binding energy with a decrease inthe O(1s): V($2p_{3/2}$) ratio. The V($2p_{3/2}$) and V($2p_{l/2}$) emission peaks for the films depositedin an oxygen partial pressure of $2x10^{-4}$ Torr was observed at 516.4 eV and 524.1 eV respectively. These results indicate that the films formed at lower oxygen partial pressures (<$5xl 0^{-4}$ Torr) were sub-stoichiometric V_2O_{5-x} where x is a small fraction. At lower oxygen partial pressures, the degreeof ionization is low since the availability of reacting oxygen atoms are low [4]. The glow is not sustained if the pressure isdecreased below $1x10^{-4}$ Torr. When the oxygen partial pressure increases to $5x10^{-4}$ Torr or above, the degree of ionization also increases and hence the reactivity of oxygen ions with decomposed vanadium atoms increases and leads to the formation of stoichiometric films. The influence of substrate temperature on the composition of V_2O_5 thin films deposited at a constant oxygen partial pressure of $5x10^{-4}$ Torr was also studied. There was no significant change in the peak positions of V($2p_{3/2}$) and V($2p_{l/2}$) for the films deposited in the substrate temperature range 303K-573K. However, the corresponding full width at half maximum was observed to be broadened forthe films deposited at lower substrate temperature.

Structure analysis:

The X-ray diffraction patterns of the V_2O_5 films were recorded in the scanning anglerange 10^0-60^0. The X-ray diffraction spectra of V_2O_5 films deposited at various oxygen partial pressures and at a fixed substrate temperature of 523 K are shown in Fig. (d). The X-ray diffractionpattern of the films deposited in an oxygen partial pressure of $5x10^{-4}$ Torr exhibited predominantly

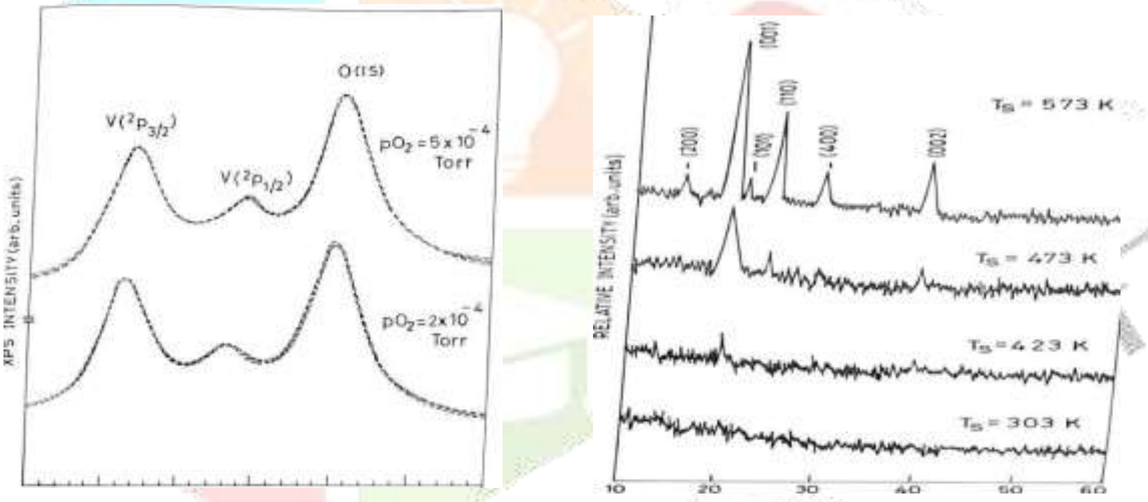
(01) orientation along with the subsequent appearance of characteristic orientations such as (200), (101), (110), (400) and (002). The intensity ratios (I/I_0) for (001) and (400) lines were 100 and 14respectively. The evaluated lattice parameters a=1 1.532 A ^{o},

b = 3.553A^0, c = 4.385A^O are in good agreement with the reported values [5]. The X-ray diffractionpattern of the films formed in an oxygen partial pressure of $2x10^{-4}$ Torr is also shown in Fig. (d). It is observed that the intensity of (001) peak slightly reduced with a relative growth of hexagonal (h00) orientations. The intensity ratios (I/I_0) for (001) and (400) were found to be 100 and 34. Thissuggest that the films formed at lower oxygen partial pressure are sub stoichiometric with oxygendeficiency exhibiting mixed phases in the films. With the increase of oxygen partial pressure up to5x 10^{-4} Torr, the intensity of (h00) phases decreased with a relative increase of (001) phase representing the growth of the in a single-phase orthorhombic structure. Further increase of oxygenpartial pressure (> $2xl0^{-3}$ Torr) leads to the decrease of mean free path which in turn enhances the scattering of evaporating species resulting a decrease in the crystallinity and adhesion of the films.

The effect of substrate temperature on the growth of V_2O_5 thin films was also studiedby keeping oxygen partial pressure at $5x10^{-4}$ Torr. The substrate temperature was varied in the range 303 K - 603 K. Fig. 3.3 shows the X-ray diffraction spectra of V_2O_5 films deposited at various substrate temperatures. The effect of substrate temperature on the degree of crystallinity isclearly observed from diffractograms.

The V_2O_5 films formed at Ts<423 K were found to be amorphous in nature. It is observed that the crystallinity of the films increases on increasing the substrate temperature. The X- ray diffraction pattern of the films grown at Ts=423K show a very small peak at 20.3^0 which is attributed to the Bragg reflection from the (001) lattice planes of orthorhombic V_2O_5 [6]. The subsequent appearance of the characteristic orientation such as (200), (101), (110), (400) and (002)along with the predominant (001) orientation in the XRD spectra of the films deposited at higher substrate temperatures is related to the in-plane organization of V-O-V chains. As the deposition temperature increases, the atomic rearrangement takes place due to the increase of adatom mobility leading to the V_2O_5 films in orthorhombic structure. Another feature is that the grain size increases with the increases of substrate temperature. At the higher temperature the atomic, molecular or ionic species of V_2O_5 impinged on the substrate surface acquire a large thermal energy resulting the growth of continuous film with large grains [7]. However, the films deposited at a substrate temperature ≥573K were found to be sub-stoichiometric and the subsequent growth of (h00) phase increased resulting a mixed phase film. It may be assumed that the substrate temperature is too high to break the bonds of V-O and to re-evaporate the deposited films, rather than to move their stable sites [8].

The surface morphology of the films has been studied by atomic force microscopy (AFM). Fig. (c) shows the surface morphology of V_2O_5 thin films deposited on Pyrex glass substrates maintained at different temperatures. The AFM data demonstrate that the activated reactive evaporated V_2O_5 thin films are homogeneous and uniform with regard to surface topography and thickness. The films exhibited dense layers with fine grains at lower substrate temperatures and the grain size increases with increase of substrate temperatures. The AFM image of the film deposited at Ts = 473 K reveals that the film is composed of roughly spherical grains of varying sizes. The calculated average grain size and root mean square surface roughness of the films were 70 nm and 10 nm respectively. The grain size was about 200 nm for the films deposited at 523 K with a root mean square surface roughness of 12 nm. This indicates that the film growth process is thermally activated. The evaporated species interact with plasma and reach on to the substrate surface which is high temperature required a large thermal energy and have a large mobility. This enhances the diffusion distance and as a result, the collision process initiates the nucleation and enhances the island formation to grow a continuous film with large grains.[8].

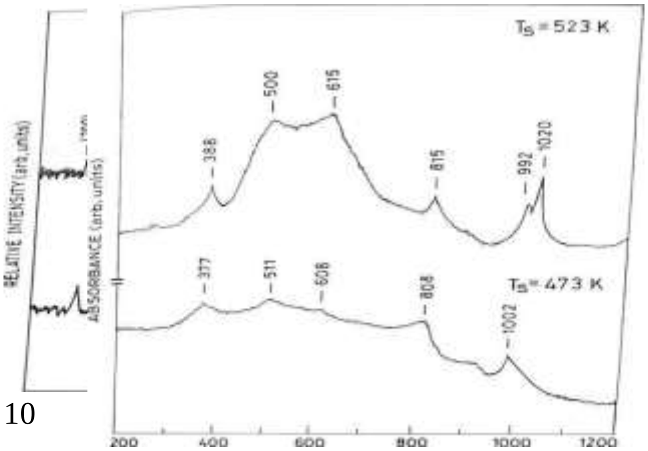


510 515 520 525 530 535 540

(a) BINDING ENERGY (eV) (b) 2θ(degree)

The vibrational infrared spectroscopic studies provide information with regard to the basic structural units present in the molecule, the binding energy configuration of the atoms and the internal vibrational motion of the molecule of the normal vibrations of the constituent elements. The infrared spectroscopic measurements were made on V_2O_5 thin film deposited on monocrystalline Si wafers. The IR absorbance was recorded using Pye Unicam SP3 300 spectrometer in the wavenumber range 200-1200 cm^{-1}. The IR absorbance spectra of activated reactive evaporated V_2O_5 thin films deposited at different substrate temperatures are shown in Fig. (e). The observed spectral features are due to internal and external vibrations with respect to structural units, however the separation cannot be done in a unique way. The internal modes can be described in terms of stretching and bending of V-O bonds. The external modes can normally lie in the low frequency region and are represented as relative motions of structural units with respect to translations and liberations [8].

The IR absorption bands were broad and poorly resolved for V_2O_5 thin films deposited at a substrate temperatures of Ts = 473 K. The band width is observed to be much larger due to random potential fluctuations arising from the amorphous state. However, the short-range order nevertheless appears to be similar to that of bulk V_2O_5 [9] suggests that the vanadium coordinate is not strongly modified. The vanadyl mode corresponding to the symmetric stretching of the shortest V=O double bond is observed at 1002 cm^{-1}. The angular deformation mode appeared at 377 cm^{-1} and 511 cm^{-1}. The effect of substrate temperature is clearly observed in the infrared spectra which supports the structural data. The high frequency IR bands corresponding to symmetric and antisymmetric vibrations of V=O double bond is observed at 1020 cm^{-1} and 992 cm^{-1} respectively for the films deposited at Ts=523 K. The splitting of infrared active modes corresponds to vibrations along zigzag rows which is the characteristic of layered orthorhombic structure of V2O5 thin films [10] as evidenced by XRD. The infrared active mode corresponds to V-O-V stretching vibration appeared at 815 cm^{-1}. The angular deformation modes, which are related to the V-O bonds, mainly contributing to the edge sharing between square pyramids of VO_5 were observed at 388 cm^{-1} and 500 cm^{-1}. These IR results suggest that the structural symmetry is maintained in V2O5 thin films without a significant change in the vanadium co-ordination. These results are in good agreement with those reported for bulk V_2O_5 [9, 10].

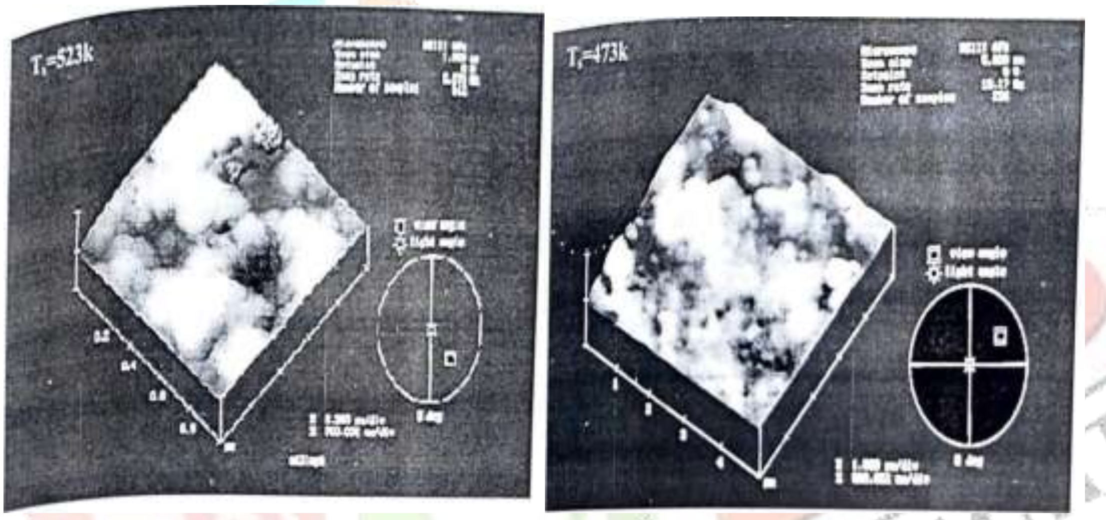


10

(c) Wavenumber(cm-1)

20 30 40 50 60

(d) 2θ(degree)



(e)

(a) The X-ray photoelectron spectra of the films deposited at various oxygen partial pressures.

(b) The x-ray diffraction spectra of V_2O_5 films deposited at various substrate temperatures.

(c) The IR absorbance spectra of V_2O_5 thin films deposited at different substrate temperatures.

(d) The X-ray diffraction spectra of V_2O_5 films deposited at various oxygen partial pressures.

(e) The surface morphology of V_2O_5 thin films deposited on Pyrex substrates maintained at different temperatures.

Optical properties:

The study of optical properties of V_2O_5 thin films particularly the optical absorption edge has proved to be very useful for elucidation of the electronic structure. It is possible to determine whether the optically induced transitions are direct or indirect and allowed or forbidden by the analysis of optical absorption edge. In the present investigation, the optical characterization of V_2O_5 thin films has been carried out by recording the optical transmittance and reflectance using Hitachi- U 3400. UV-VIS-NIR double beam spectrophotometer in the wavelength range 350-2500 nm. The influence of oxygen partial pressure and substrate temperature on the optical properties of V_2O_5 thin film was studied.

Fig. (f)shows the optical transmittance and reflectance spectra of V_2O_5 thin deposited at various oxygen partial pressures and at a fixed substrate temperature 523 K. The transmittance spectra can be classified into two parts. The first part is concerned with the optical absorption edgeat around 550 nm and the second part deals with the broad band absorption in the near infrared region. A relatively high transmission reveals the fact that the films are weakly absorbing. The opticaltransmission was found to increase with increase of oxygen partial pressure. The fundamental absorption edge was found to be shifting towards lower wavelengths with increasing oxygen partial pressure.

The optical absorption coefficient was evaluated from the optical transmittance data, where reflection losses were taken into consideration, using the relation α where $\alpha=1/t \ln [T/ (1-R)^2]$ where 'T' is the transmittance, R is the reflectance and 't' is the film thickness. For the incident photon energy (hν) greater than the optical band gap, the optical absorption follows a power law of the form [12]. $\alpha h\nu= B (h\nu -E_g)^n$, where 'B' is a constant, Eg is the optical band gap and 'n' is the exponent, which determines the type of the electronic transitions causing the absorption. The optical band gap of the film deposited at different oxygen partial pressures is evaluated by extrapolating the straight-line portion of the $(\alpha h\nu)^{1/n}$ versus hν plots. Theexperimental optical absorption data for V2O5 thin films was found to give a better fit for the direct forbidden transitions i.e. with an exponent n=3/2. Fig (g) shows the plot of $(\alpha h\nu)^{2/3}$ versus hν incident photon energy for V2O5 thin film deposited at different oxygen partial pressures and at a substrate temperature 523 K. The optical band gap is evaluated by extrapolating the linear region of the plot to zero. The evaluated optical band gapof V2O5 thin films deposited in an oxygen partial pressure of $5\text{x}10^{-4}$ Torr is 2.35 eV and is in good agreement with the reported value by several authors [13-14]. The optical band gap is decreased withdecreasing oxygen partial pressure and found to be 2.28 eV for the films deposited in an oxygen partial pressure of $2\text{x}10^{-4}$ Torr. The decrease in the optical band gap and the increase of absorption innear IR region of V_2O_5 thin films formed at lower oxygen partial pressure (< $5\text{x}10^{-4}$ Torr) may be due to the formation of sub-stoichiometric V_2O_{5-x} thin films where x is a small fraction. The sub- stoichiometric V_2O_{5-x} contains a large number of vacancies. These vacancies can be considered as positively charged structural defects capable of capturing one or two electrons. The oxygen vacanciesoccupied by these electrons act as donor centers. These donor centers form an energy level and existsin the forbidden below the conduction band [15]. Generally, the oxygen in vanadyl

-oxygen is removed more easily. Empty 3d - orbitals of vanadium atoms adjacent to a vacancy are able to localize excess electrons. This leads to the formation of V^{+4} in the vicinity of a vacancy. The broad band absorption in the near IR region is observed from the spectra is due to the transitions from these levels [10]. The optical transmission above the fundamental absorption edge is increasedwith Increasing oxygen partial pressure with a slight shift in the edge towards lower wavelengths region. When the oxygen partial pressure increases towards $5\text{x}10^{-4}$ Torr the degree of ionization alsoIncreases and as such the reactivity of oxygen ions with decomposed vanadium atoms improves. This leads to the formation near stoichiometric V_2O_5 thin films. Theseresults are in consistent with the XPS data. The influence of substrate temperature on the optical properties of V2O5 thin films deposited at various substrate temperatures and at a constant oxygenpartial pressure of 5x10-4 Torr was studied. The optical transmittance and reflectance spectra of V2O5 thin films deposited at various substrate temperatures are shown in Fig. 3.8. The films showed a high transmission above fundamental absorption and a sharp fall at around 550 nm. The optical absorption coefficient near the fundamentalabsorption edge is observed to be exponentially dependent on the photon energy. The exponential dependence of a on photon energy may arise from the random potential fluctuation of the internal fields associated with the structural disorder in many amorphous/fine grained polycrystalline materials. This behavior can be represented by Urbach rule [l l]. $\alpha = \alpha_0 e^{h\nu/Ee}$ where α is the absorption coefficient,α_0 a constant and Ee often interpreted as the width of localized state. In the present study, the exponentialbehavior of optical absorption coefficient may be due to the electronic transitions between the localized states which have tailed off in the band gap. The density of these states falls offexponentially with the energy. This is in consistence with the theory of Tauc [16]. The width ofthe localized states (Ee) is estimated from the slope of the lnα versus hν plot. From the fig(h) shows the ln α versus hν plots for the V_2O_5 films deposited at different substrate temperatures.The values of width of localized states and the optical band gap for V_2O_5 thin films deposited at different substrate temperatures. From below table the Ee values were found to decreased with the increase of substrate temperature. This may be due to the increase in the structural order ofthe films as revealed from the structural data. The Ee values are in good agreement with those Table 3.1: Optical band gap, width of localized states thin films deposited at various substrate temperatures

Substrate temperature(Ts) (K)	Optical band gap (Eg) Eg(eV) (±0.02)	Width of localizedstates (Ee) (eV) (±0.002)
423	2.34	0.42
473	2.32	0.31
523	2.35	0.28
573	2.28	0.30

reported for V_2O_5. There is no significant variation in the optical band gap of V_2O_5 thin filmwith the substrate temperature up to 523 K. A slight decrease of the optical bandgap was observed for V_2O_5 films prepared at Ts ≥ 573K.

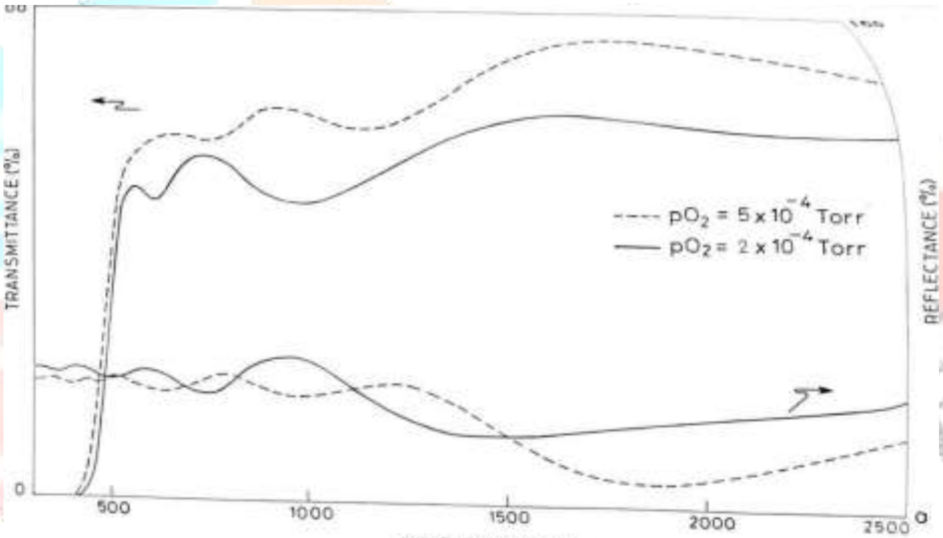
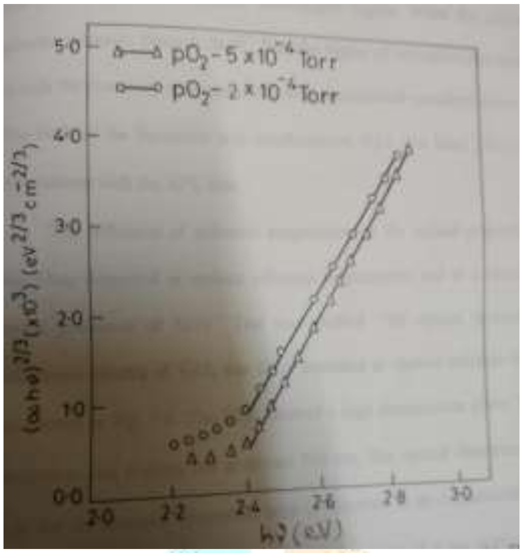
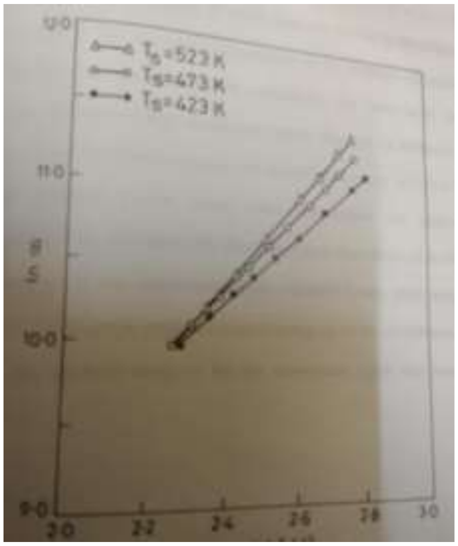


Fig. 3.6 The optical transmittance and reflectance spectra of V_2O_5 thin films deposited at various oxygen partial pressures.





0

The plot of $(\alpha h\nu)^{2/3}$ vs hν incident photon energy (hν) thin films different oxygen partial

Fig (h) The ln α versus hν plots for the V_2O_5 deposited at for V_2O_5 thin films depositedpressures at different substrate temperature.

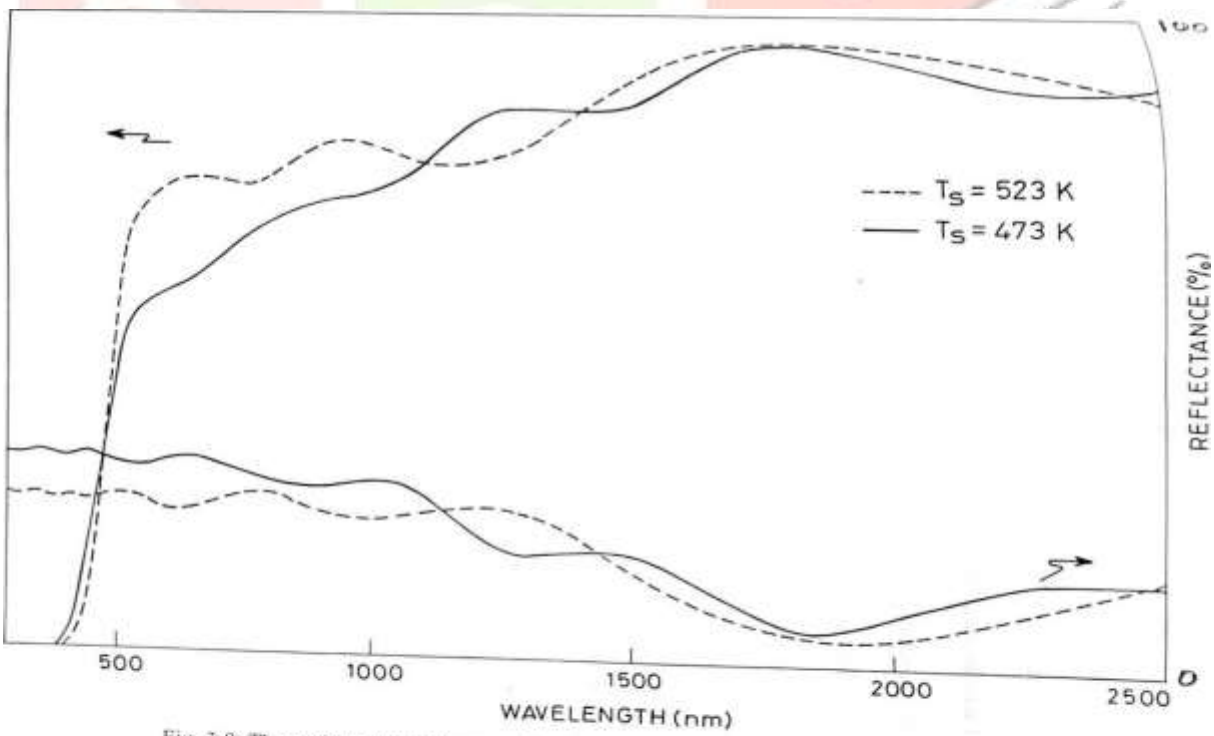
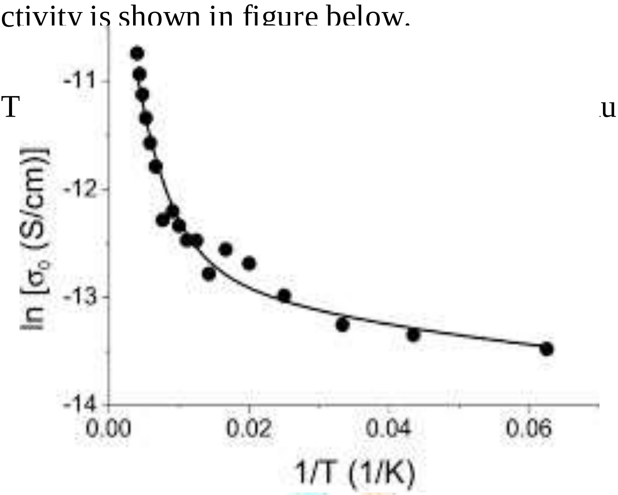


Fig. 3.8. The optical transmittance and reflectance spectra of V_2O_5 thin films deposited at various substrate temperatures.

Electrical Properties:
The dc electrical conductivity of V_2O_5 thin films deposited at Ts=523 K and in an oxygen partialpressure of $5x10^{-4}$ Torr was studied in the temperature range 120-500K. The temperature dependence of dc electrical conductivity is shown in figure below.



Fig(i) T uctivity.

The dc electric conductivity was found to be strongly temperature dependent in high temperature region. This is may be attributed to the multiphoton assisted polaron hopping with an activation energy of 0.43 eV. Such thermally activated process above room temperature was observed in polycrystalline V_2O_5 thin films [19]. The temperature dependence of dc electrical conductivity in the low temperature region exhibited a very weak temperature dependence which can be attributedto the freezing out of the multiphoton optical process. The activation region was found to be 0.03eV.

CONCLUSIONS:

Thin films of V_2O_5were prepared by activated reactive evaporation technique atvarious oxygen partial pressures and substrate temperatures keeping the glow power at 6W. The XPS, XRD and IR measurements revealed that the V_2O_5thin films prepared in an oxygen partial pressure of $5x10^{-4}$ Torr and at a substrate temperature of 523 K were nearly stoichiometric with predominant (001) orientation representing the orthorhombic layered structure. The films were found to be uniform with regard to the thickness and surface topography as revealed from AFM data. The average grain size of the films was found to be 200 nm. The films also exhibited a relatively high transmittance with an optical band gap of 2.35 eV.
These V_2O_5 films deposited by activated reactive evaporation technique may be highly useful in the fabrication of solid-state micro batteries, gas sensors and electrochromic devices.

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