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Correlation between Growth Conditions, Microstructure, and Optical Properties in Pulsed-Laser-Deposited V_2O_5 Thin Films

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V_2O_5 thin films were prepared by pulsed laser deposition (PLD) over a wide substrate temperature range, 30−500 °C, and were characterized by studying their microstructure and optical properties. Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and UV−vis−NIR spectral measurements were made on the PLD V_2O_5 films to understand the effect of substrate temperature on the chemical composition, elemental distribution, surface morphology, and optical properties. The substrate temperature strongly influences the structure and optical properties of PLD V_2O_5 films and a correlation exists between the growth conditions, grain structure, and optical characteristics. The grain size increased, associated with a change in surface morphology, with increasing substrate temperature. The optical energy band gap of PLD V_2O_5 films is strongly dependent on the substrate temperature and decreased from 2.47 to 2.12 eV with the increase in temperature from 30 to 500 °C.

I. Introduction

There has been tremendous interest in transition-metal oxide thin films for a wide range of applications in microelectronics, optoelectronics, and solid-state ionics.[1,2] Vanadium pentoxide (V_2O_5) has been widely studied in recent years in view of its novel material characteristics, which can be readily integrated into many scientific and technological applications. V_2O_5 has high potential for the development of electrochromic devices, electronic information displays, and color memory devices.[2−5] The ability to incorporate large amounts of lithium ions coupled with its peculiar optical properties ranks vanadium oxides among the most studied materials for electrochemical applications in general, and in particular for applications in high-energy density solid-state batteries and information displays.[5−7] The variable optical properties of V_2O_5 films find application in the development of smart windows.[7] V_2O_5 films can also be integrated in other technological applications where the typical functions of these films include chemical sensing, photochromism, catalysis, and optical and electrical switching.[8−11]

One of the major problems encountered during the preparation of vanadium oxides in thin-film form is tuning the process parameters for controlled growth and desired properties because the window of processing over which these oxides occur as a *stable single-phase material* is relatively small. Vanadium forms a large number of oxides each of which is stable over a certain composition range. Particularly, oxides in the $V_2O_5-V_2O_3$ system are complex and many intermediate oxide phases exist within this compositional range.[8] The composition and phase stability of grown films is highly important for all practical applications. V_2O_5 films can be obtained by thermal evaporation,[10] flash evaporation,[12] electron-beam evaporation,[13] sol−gel growth methods,[2,14] chemical vapor deposition,[15,16] and sputtering.[7,8] The removal of oxygen from the V_2O_5 lattice, when heated above its melting point in a vacuum or a reducing atmosphere, causes the formation of defects or reduced phases, which could eventually lead to the fading or poor electrochromic/electrochemical performance.[8,13]

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(1) Granqvist, C. G. *Handbook of Inorganic Electrochromic Materials*; Elseveier: Amsterdam, 1995.
(2) Lakshmi, B. B.; Patrissi, C. J.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 2544.
(3) Nagase, K.; Shimuzu, Y.; Miura, N.; Yamazoe, N. *Appl. Phys. Lett.* **1992**, *61*, 243.
(4) Cogan, S. F.; Nguyen, N. M.; Perrotti, S. J.; Rauh, R. D. *J. Appl. Phys.* **1989**, *66*, 1333.
(5) Benmoussa, M.; Outzourhit, A.; Bennouna, A.; Ameziane, E. L. *Thin Solid Films* **2002**, *405*, 11.
(6) Lee, S. H.; Liu, P.; Tracy, C. E.; Benson, D.K., *Electrochem. Soild-State Lett.* **1999**, *2*, 425.
(7) Talledo, A.; Granqvist, C. G. *J. Appl. Phys.* **1995**, *77*, 4655.
(8) Moshfegh, A. Z.; Ignatiev, A. *Thin Solid Films* **1991**, *198*, 253.
(9) Legrouri, A.; Baird, T.; Fryer, J. R. *J. Catal.* **1993**, *40*, 173.
(10) Nadkarni, G. S.; Shirodkar, V. S. *Thin Solid Films* **1983**, *105*, 115.
(11) Nishio, S.; Kakahana. *Chem. Mater.* **2002**, *14*, 3730.
(12) Julien, C.; Guesdon, J. P.; Gorenstein, A.; Khelfa, A.; Ivanov, I. *Appl. Surf. Sci.* **1995**, *90*, 389.
(13) Ramana, C. V.; Hussain, O. M.; Naidu, B. S.; Reddy, P. J. *Thin Solid Films* **1997**, *305*, 219.
(14) Be, B. N. T.; Minh, T. P.; Simona, B. *J. Appl. Phys.* **1996**, *80*, 7041.
(15) Barreca, D. L.; Caccavale, A. F.; Noto, V. D.; Gregori, A.; Rizzi, G. A.; Tondello, E. *Chem. Mater.* **2000**, *12*, 98.
(16) Chen, H. L. M.; You, H.; Guo, J. *Appl. Surf. Sci.* **1991**, 48−49, 12.

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Recently, extensive and successful efforts have been undertaken for thin-film processing of vanadium oxides using pulsed laser deposition (PLD) since it is an attractive choice for the preparation of stoichiometric and high-quality metal−oxide films.[17−23] PLD is a flexible and powerful technique and has been successfully employed in the past for the deposition of a wide variety of materials.[24] The excellent capability of PLD for reactive deposition and to transfer the original stoichiometry of the bulk target to the deposited film makes it suitable for the fabrication of simple and complex metal−oxide films.[24] In this context, we have made an attempt to prepare V_2O_5 films by PLD. The growth of crystalline V_2O_5 films at a relatively low temperature (200 °C) even onto amorphous glass substrates using PLD has been reported elsewhere.[21] Since the properties and application of the resulting V_2O_5 films are sensitive to the growth conditions employed for the film deposition, improved understanding of the relationship between growth conditions, structure, and physical properties are essential to produce the films to meet the requirements of a given technological application. For this reason, in this present investigation, we have focused our attention on the study of growth, structure, and optical properties of PLD V_2O_5 thin films produced over a wide substrate temperature range. The size effects on the optical properties of PLD V_2O_5 thin films have been already reported in a research note.[25]

The surface/interface features of V_2O_5 films have been examined using Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). RBS, a nondestructive technique for surface/interface analysis, provides a direct means to determine the absolute concentration of elements as a function of thickness. It can also be used to determine the thickness of the films. XPS provides the composition and chemical state of the elements present in the films. SEM measurements allow us to probe the film surface morphology. Characterization of V_2O_5 films by spectrophotometric measurements permits probing the optical properties. Using the results obtained, we show that the substrate temperature strongly influences the growth, microstructure, and optical properties of PLD V_2O_5 films. Correlations between the growth conditions with structure and optical properties in PLD V_2O_5 films were noted. To the best of our knowledge, this is the first detailed report on the influence of growth temperature on the optical properties of PLD V_2O_5 thin films.

Table 1. Details of V_2O_5 Thin-Film Fabrication Process Parameters

experimental parameter	value
wavelength	248 nm
energy	300 mJ
pulse repetition rate	10 Hz
power density	10 Jcm^{-2}
V_2O_5 target dimensions	20 mm × 2 mm
target-to-substrate distance	4 cm
base pressure	2×10^{-6} Torr
oxygen partial pressure	100 mTorr
deposition temperature	30−500 °C
film thickness	300 nm

II. Experimental Section

A. Deposition of V_2O_5 Thin Films. Thin V_2O_5 films were produced by PLD. The targets for PLD were prepared from pure (99.99%) V_2O_5 powder (M/s Merck, Germany). The diameter and thickness of the targets are 20 mm and 2 mm, respectively. The pressed V_2O_5 target was heated at a rate of 10° C/min and sintered at 650° C for about 10 h. The target was examined and confirmed for its composition and structure before introducing it into the chamber for laser ablation to produce V_2O_5 thin films. The structural details of the target using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) are reported elsewhere.[23]

A KrF excimer laser (Lumonics PM 882) with a wavelength of 248 nm was used to ablate the V_2O_5 target. The UV laser beam focused by the lens passes through the quartz window to scan the target surface. The angle between the incident laser beam and normal to the target surface was 45°. The energy and the repetition rate of the pulse were 300 mJ and 10 Hz, respectively. The laser fluence produced (after focusing) at the target surface was 10 Jcm^{-2}. During ablation, the target was rotated at the rate of 10 rotations per minute to avoid the depletion of the material at the same spot continuously and to obtain uniform thin films. The deposition process parameters along with the details of laser are presented in Table 1. The deposition was made onto well-cleaned Pyrex glass substrates. The substrates were heated and maintained in the temperature range of 30−500 °C. The target-to-substrate distance was 4 cm. The chamber was evacuated to a base pressure of 2×10^{-6} Torr prior to film deposition. For reactive deposition, pure oxygen gas was introduced (using flow controller) into the chamber, and the oxygen partial pressure (pO_2) maintained during the deposition was 100 mTorr, the optimum value to obtain stoichiometric V_2O_5 films. The thickness of all the PLD V_2O_5 films was 300 nm.

B. Characterization of V_2O_5 Thin Films. The grown V_2O_5 thin films were characterized by studying their surface/interface composition using Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS), their surface morphology using scanning electron microscopy (SEM), and their optical properties using UV−vis−NIR spectrophotometric measurements. These measurements were made at room temperature and as a function of growth temperature. The RBS experiments were performed in an analysis chamber connected to a 2 MV van de Graff accelerator via a differentially pumped beam line. The samples were mounted on a carousel with freedom for *x*, *y*, and *z* translation, continuous rotation about the carousel axis. The He^+ probe ion beam was incident on the sample at normal incidence and the backscattered ions were detected using a silicon barrier detector. The detector position was set at a scattering angle of 165° for these experiments with a solid angle of 0.978 msr. XPS measurements were made using Leybold, AG to determine the film composition. The spectra were recorded using the AlK_α X-rays (1486.6 eV) as the excitation source. Core level binding energies of V 2p and O 1s have been used to characterize the V_2O_5 film composition and

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(17) Zhang, J. G.; McGraw, J. M.; Ginley, D. *J. Electrochem. Soc.* **1997**, *144*, 1630.

(18) Julien, C.; Haro-Poniatowski, E.; Hussain, O. M.; Ramana, C. V. *Ionics* **2001**, *7*, 165.

(19) McGraw, J. M.; Perkins, J. D.; Hasoon, F.; Parilla, P. A.; Warmsingh, C.; Ginley, D. S. *J. Mater. Res.* **2000**, *15*, 2249.

(20) Fang, G. J.; Yao, K.L.; Liu, Z. L. *Thin Solid Films* **2001**, *394*, 64.

(21) Ramana, C. V.; Naidu, B. S.; Hussain, O. M.; Pinto, R. *J. Phys. D: Appl. Phys.* **2001**, *34*, L35.

(22) Chu, Y. Q.; Qin, Q. Z. *Chem. Mater.* **2002**, *14*, 3152.

(23) Ramana, C. V.; Hussain, O. M.; Naidu, B. S.; Pinto, R.; Julien, C. *Appl. Surf. Sci.* **2003**, *207*, 135.

(24) *Pulsed Laser Deposition of Thin Films*; Chrisey, D. G., Hubler, G. K., Eds.; Wiley Publications: New York, 1994.

(25) Ramana, C. V.; Smith, R. J.; Hussain, O. M. *Phys. Status Solidi A* **2003**, *199*, R4.

chemical oxidation state of vanadium using the standard procedures reported elsewhere.[13] The SEM measurements were made using a JEOL (Model 6150) scanning electron microscope. The optical transmittance and reflectance of the V_2O_5 films were recorded in the wavelength range of 300−1500 nm using a Hitachi U3400 UV−vis−NIR double-beam spectrophotometer. To obtain the spectrum, a V_2O_5 film on the glass substrate was placed in the source beam, and an uncoated substrate was placed in the reference beam. The transmittance was measured at normal incidence and reflectance was recorded at near normal incidence.

III. Results

A. RBS and XPS Measurements—Chemical Composition Analysis. Chemical compositional analyses using RBS and XPS measurements indicated the growth of compositionally stoichiometric V_2O_5 films in the substrate temperature range of 30−500° C with oxygen partial pressure fixed at 100 mTorr. Figure 2 shows the experimental Rutherford backscattering (RBS) spectrum of vanadium oxide film deposited at 200 °C (circles) along with the simulation curves (lines) calculated using SIMNRA code.[26] The experimental RBS spectrum was obtained using 1 MeV He^+ ions incident in the direction normal to the surface of the vanadium oxide film and collecting the backscattered ions. The simulated curves were calculated using SIMNRA code for the fixed set of experimental parameters: (1) incident He^+ ion energy, (2) integrated charge, (3) energy resolution of the detector, and (4) scattering geometry. The backscattered ions observed were due to various elements, and the positions are indicated by arrows for the experimental spectrum. The scattering from vanadium, the heaviest among the elements present either in the film or substrate, occurs at higher backscattered energy as shown in the figure. The measured height and width of this peak is related to the concentration and thickness distribution of vanadium in the oxide film and serves as a calibration check for composition and thickness since known Rutherford scattering cross section and experimental parameters can be used to calculate this height and width. The cutoff of the spectrum at 765 keV corresponds to those ions backscattered from the vanadium surface atoms at the set scattering angle of 165°.

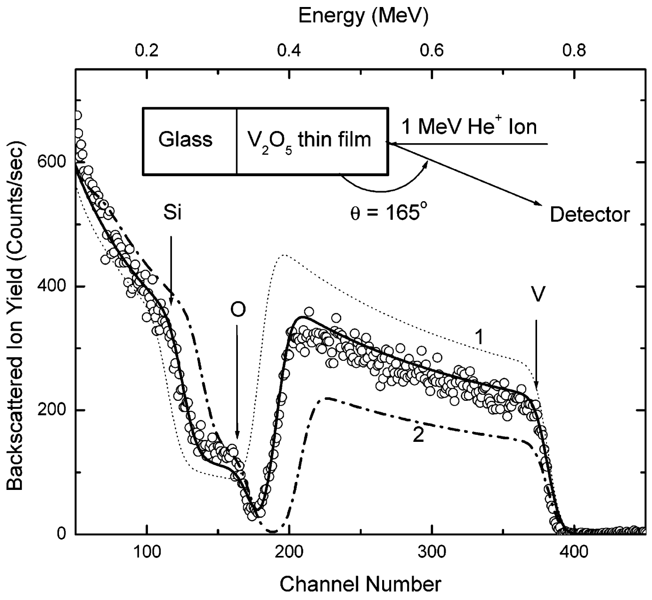

Figure 1. Rutherford backscattering (RBS) spectrum of 1 MeV He^+ ions backscattered from PLD V_2O_5 thin film grown at T_s = 200 °C. The experimental RBS spectrum is shown with circles. The simulation RBS curves are shown with lines. The simulation curves were calculated using SIMNRA code for the fixed set of experimental parameters, incident He^+ ion energy, integrated charge, energy resolution of the detector, and scattering geometry. The energy position of the peaks because of ion scattering from vanadium, oxygen, and silicon atoms are indicated with arrows for the experimental RBS spectrum. It can be seen in the figure that the simulation (thick solid line) using experimental parameters and a target composition of the film the same as the starting material can only produce the curve identical to the experimental RBS spectrum. The curves 1 and 2, calculated for lower oxide and oxygen-rich phases, are not identical to the experimental RBS and rules out these possibilities.

It is hard to evaluate the oxygen concentration of the film for a couple of reasons. The oxygen signal overlaps the silicon signal, and it is difficult to separate ion scattering contribution from oxygen in the film and in the substrate. However, the simulation of the RBS spectrum using experimental parameters in the SIMNRA code allows us to obtain the composition of the film since the target composition can become variable for fixed experimental parameters in the fitting procedure. For a fixed set of experimental parameters, the composition and thickness of the film should essentially produce the experimental RBS spectrum. It can be seen in Figure 1 that the simulated curve (thick solid line) calculated using the experimental parameters for a film of 300-nm thickness using the bulk target composition is in good agreement with the experimental RBS spectrum. This observation indicates that film had a stoichiometic V_2O_5 composition over a thickness of 300 nm. Since the composition estimate is completely based on the fitting procedure, we have also made calculations for other possibilities: (a) lower oxide phase formation and (b) oxygen-rich phase formation with vanadium metal deficiency. These two cases are represented by the simulation curves 1 and 2, respectively. The RBS spectrum should look like or very close to curve 1, which is calculated for VO_2 phase, if the film had a compositional deviation with the formation of lower oxide phases (e.g., VO_2, V_2O_3, etc.). On the other hand, if the sample had vanadium-metal deficiency and oxygen-rich phase, the experimental RBS spectrum would be similar to the curve shown in 2. Since the simulation curve corresponding to stoichiometric V_2O_5 phase for a 300-nm film is the only one in good agreement with the experimental RBS spectrum, we conclude that the films produced by PLD are stoichiometric. Further evidence for the formation of stoichiometric V_2O_5 films over the entire temperature range was provided by XPS measurements reported elsewhere in detail.[21,23] The detailed analysis of O 1s and V 2p core level photoemission peaks indicated that the films maintained O/V ratio as expected from the chemical formula (2.45−2.50) and existence of vanadium in its highest oxidation state (V^{5+}).

B. SEM Measurements—Morphological Characteristics. The morphological characteristics of PLD V_2O_5 thin films have been studied using SEM measurements. We show the SEM images for V_2O_5 films in Figure 2 as a function of growth temperature. The SEM data (image A of Figure 2) does not show any features, even at higher magnification,

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(26) Mayer, M. Technical Report IPP 9/113; Max-Planck-Institut fur Plasmaphysik: Garching, Germany, 1997.

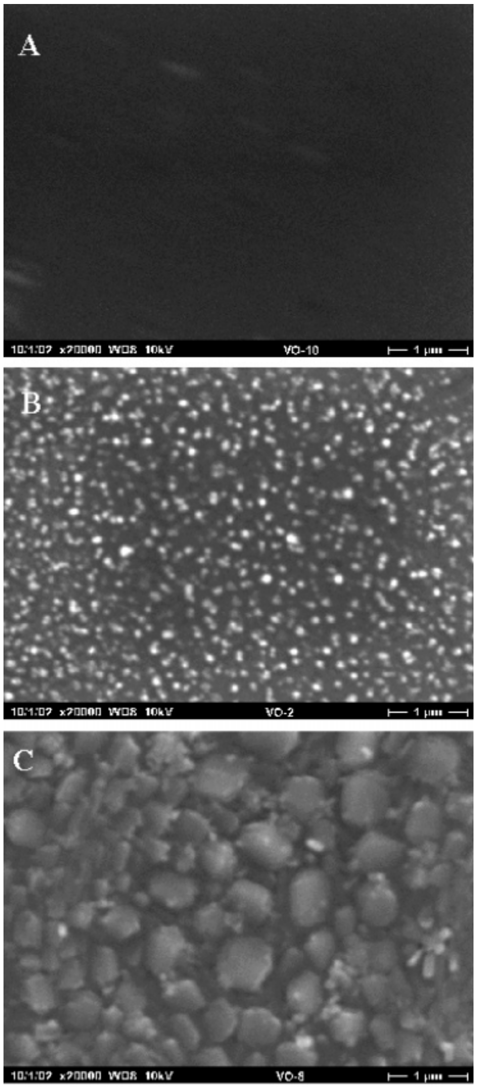

Figure 2. SEM images of V_2O_5 thin films deposited at various growth temperatures. (a) V_2O_5 films grown at $T_s = 30$ °C. (b) V_2O_5 films grown at $T_s = 200$ °C. (c) V_2O_5 films grown at $T_s = 500$ °C.

for PLD V_2O_5 films grown at temperatures less than 200 °C. These films are amorphous as determined by X-ray diffraction (XRD), FTIR, and Raman scattering (RS) measurements.[21,23] For growth at 200 °C, the SEM data (image B of Figure 2) revealed the onset of grain growth for the V_2O_5 films. It can be seen in the SEM image (B) in Figure 2 that the V_2O_5 films have a fine microstructure with nanosized grains nearly spherical in shape spreading on the substrate surface uniformly. The average grain size is about 50 nm. The grain size measurements using SEM are in good agreement with the results of AFM measurements.[27]

The other notable characteristic feature in the present study is the change in surface morphology of the PLD V_2O_5 films with increasing temperature. The morphological changes are dominant at temperatures above 300 °C. The significant changes seen are in the grain size and shape associated with their distribution. AFM data also confirmed that these films roughened considerably with increasing temperature; a more detailed discussion of the growth mechanism that includes a phase diagram for microstructure evolution is described elsewhere.[27] The grain size increased with increasing growth temperature. The grains are much larger in size for V_2O_5 thin films grown at the highest temperature of 500 °C as shown in SEM (image C, Figure 2). The variation of average grain size with growth temperature is shown in Figure 3, where it is evident that the higher the growth temperature the higher the grain size. The films deposited at room temperature are completely amorphous and therefore represented with zero grain size. The grain size increased from 50 to 300 nm with the increase in substrate temperature from 200 to 500 °C. Furthermore, the exponential dependence of grain size on the temperature as shown in the figure (solid line) suggests thermally activated growth mechanism of PLD V_2O_5 films. The SEM images in Figure 2 indicate that the grains are becoming closely compact, with increased density at higher temperatures. This could be due to enhanced surface diffusion of the species leading to smaller grains joining together to grow into larger grains. The activation energy obtained from the data is 0.45 eV, which is in good agreement with the value of 0.43 eV obtained using AFM measurements.[27] However, the grain morphology is associated with a random grain distribution with increasing substrate temperature. The evidence for increased surface roughness was provided by AFM measurements as shown in the inset of Figure 3.

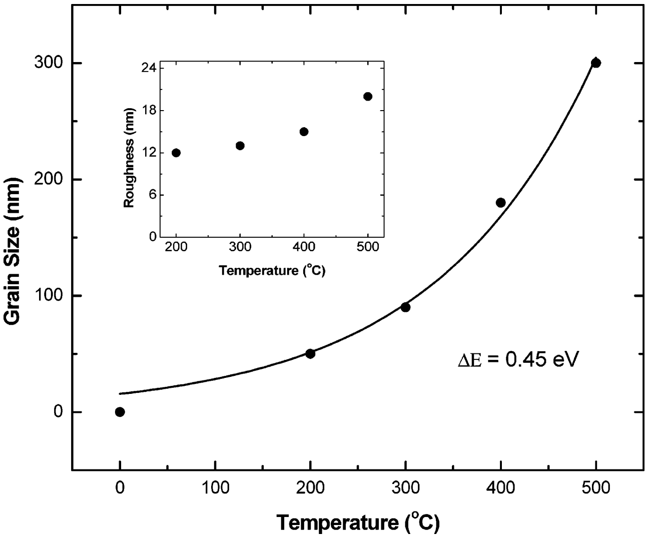

Figure 3. Variation of grain size with growth temperature of PLD V_2O_5 films. The circles and line represent the experimental data and fit to exponential growth, respectively. The data fit to the exponential function suggests thermally activated growth of pulsed-laser-deposited vanadium oxide films. The activation energy obtained using the data is 0.45 eV. The inset shows the film roughness as a function of growth temperature and provides evidence for film roughening at higher temperatures.

C. Spectrophotometric Measurements—Optical Properties. The spectral transmittance characteristics of V_2O_5 thin films deposited at different temperatures are shown in Figure 4. The curves indicate that the films deposited at lower temperatures show a relatively high degree of optical transmission, while the spectral transmittance of the films decreases with the increase in temperature. The spectral characteristic curves indicate that the optical absorption increases monotonically with the wavelength toward the UV region. The sharp decrease in transmittance with most of

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(27) Ramana, C. V.; Smith, R. J.; Hussain, O. M.; Julien, C. M. *J. Vac. Sci. Technol., A* **2004**, *22*, 2453.

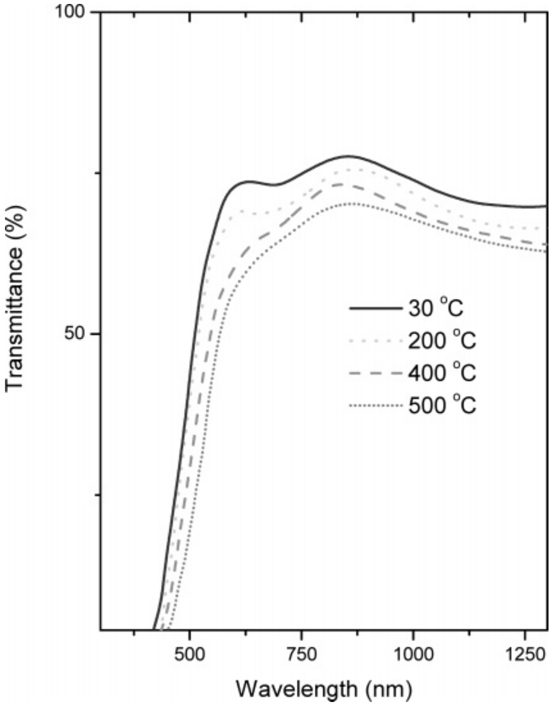

Figure 4. Optical transmittance curves of vanadium oxide thin films as a function of growth temperature.

the radiation absorbed for incident photons in the wavelength range 500−600 nm is associated with the fundamental absorption. This region of fundamental absorption edge for PLD V_2O_5 thin films is in good agreement with the reported values in the visible range of 480−600 nm, on the basis of synthesis conditions, for films obtained by other methods.[3−5,7,8,13−15] It is evident from the spectra that the fundamental absorption edge shows a positive shift in the wavelength (red shift) with increasing grain size, which indicates a shift in the optical band gap to lower energy. Furthermore, the shift in the fundamental absorption edge is associated with a slight decrease in the spectral transmittance above and below the absorption edge with increasing temperature. This observation, and also on the basis of the microstructure data, leads to the first speculation that the optical properties of these V_2O_5 thin films are varying in relation to the growth conditions and microstructure of the films. However, the relatively high spectral transmission above the fundamental absorption edge ($\lambda > 600$ nm) reveals that these oxide films, in general, are *weakly absorbing* in the spectral range of investigation.

The optical absorption coefficient, α, of the films is evaluated from the optical transmittance of the films using the relation[28]

$$\alpha = [t^{-1}]\ln[T/(1 - R)^2] \qquad (1)$$

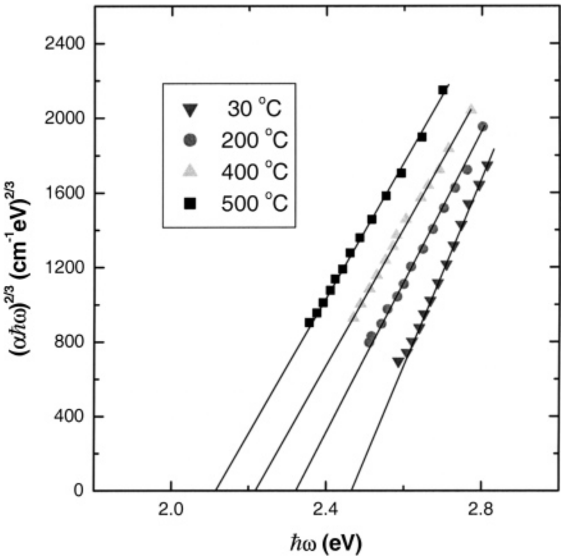

Figure 5. Fit of the optical absorption data to the direct-forbidden transitions. The optical band gap is determined by extrapolating the linear region of the plots to zero absorption, as indicated by the lines.

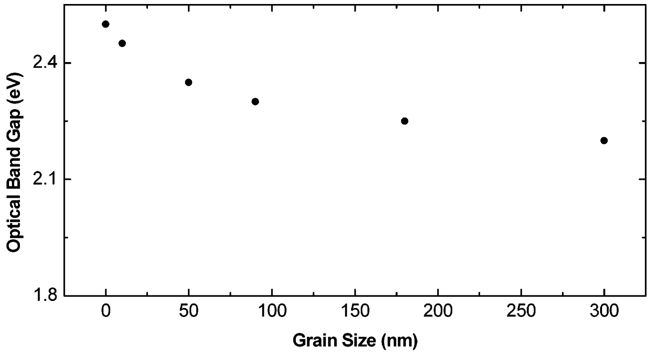

Figure 6. Variation of the optical energy band gap with grain size.

where T is the transmittance, R the reflectance, and t the thickness of the oxide film. The consideration of reflection losses, although they are not very significant, is to measure the dependence of optical absorption on energy accurately and to determine the nature of optically induced transition. The optical absorption coefficient determined experimentally from the measured transmittance and reflectance spectra for V_2O_5 films gives a better fit when $(\alpha\hbar\omega)^{2/3}$ is plotted against the incident photon energy ($\hbar\omega$). This suggests direct forbidden transitions across the energy band gap of the material, which is in good agreement with recent reports on V_2O_5 thin films.[13,15] The plots obtained from optical absorption data are shown in Figure 5 as a function of growth temperature. The optical band gap was evaluated by extrapolating the linear region of the curve to zero absorption. The films deposited at room temperature exhibited a higher energy band gap. The band gap decreases with the increase in growth temperature of the oxide film. However, the variation in the optical band gap energy is very small for growth temperatures >300 °C. The optical energy band gap evaluated from the absorption data for PLD V_2O_5 films in the present work was in the range 2.12−2.47 eV, which is in good agreement with the reported values for V_2O_5 thin films obtained by various deposition methods in the range 2.0−2.6 eV on the basis of the growth conditions of the films.[3−5,7,8,13−15] The noteworthy feature is a direct relationship between the grain size of the films and optical band gap. Figure 6 shows the variation in optical band gap with grain size. The optical band gap decreases with the increase in grain size; however, the changes are not very significant for grain size >100 nm.

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(28) Chopra, K. L. *Thin Film Phenomena*; McGraw-Hill Book Company: New York, 1969; p 734.

IV. Discussion

The emphasis in this work is to characterize the growth behavior, microstructure, and optical properties of PLD V_2O_5 thin films as a function of growth temperature. For this purpose, first we discuss the RBS and XPS results to show the compositional phase stability of V_2O_5 films. Subsequently, we focus on SEM data to discuss the effect temperature has on the grain structure and morphology. Finally, we explain the observed dependence of optical properties on the growth temperature on the basis of the relative structural changes in the oxide films and make an attempt to establish a correlation between growth conditions, structure, and optical properties of V_2O_5 films.

Chemical composition analysis using RBS and XPS measurements indicated that the films are stoichiometric with vanadium-to-oxygen ratio well maintained. This is mainly due to the optimum partial pressure of oxygen maintained during the growth of films. The RBS and XPS measurements indicate that the stoichiometric V_2O_5 films can be grown successfully in the wide range of temperature, 30−500 °C, keeping the oxygen partial pressure at 100 mTorr. The observed dependence of growth and morphology on the substrate temperature can be explained as follows. The substrate temperature plays an important role, in addition to the oxygen partial pressure, in governing the structure as well as properties of films resulting from vapor deposition. The SEM data indicated that the V_2O_5 films grown at temperatures lower than 200 °C are amorphous. If the substrate temperature is very low such that the period of the atomic jump process of adatoms on the substrate surface is very large, then the condensed species may stay stuck to the regions where they are landing thus leading to an amorphous film. From SEM results, it is very clear for V_2O_5 films deposited at room temperature that the impinging flux may be just sticking to the substrate surface at its place of hitting with almost no surface diffusion and hence the formation of amorphous V_2O_5 films. This conclusion was also supported by the absence of reflections in the XRD, broad and diffuse spectra in FTIR and Raman measurements, and absence of features in AFM.[21,23,27] With an increase in substrate temperature, the adatom mobility on the surface increases.[21] The small-size grains spherical in shape observed in SEM along with our previous XRD and AFM results clearly indicate that the substrate temperature of 200 °C is the critical temperature to promote the growth of nanocrystalline phase V_2O_5 films. The increase in grain size as well as their distribution characteristics in general can be attributed to the enhanced mobility of ablated species impinging on the substrate surface with the increase in substrate temperature. At higher substrate temperatures, the impinging flux on the surface acquires higher energy and hence a large mobility. As a result, the diffusion distance of the adatom on the surface increases and the collision process initiates the nucleation for more adatoms joining to form larger grains. It is clearly evident from Figure 3 that the thermally activated process of surface diffusion is responsible for the microstructure changes.

The optical characterization of PLD V_2O_5 films indicates that the substrate temperature has a strong influence on the optical properties. First, we consider the nature of optical-induced transitions across the energy band gap of the material and then focus on the dependence of various optical characteristics on the growth conditions and microstructure of the films. It is well known that the optical absorption below the fundamental absorption edge or optical energy band gap follows exponential behavior.[29] Therefore, the absorption is exponentially dependent on the energy of incident photons in that region. In the energy band gap region (high absorption) or above the fundamental absorption edge, the optical absorption follows a power law of the form[30]

$$(\alpha\hbar\omega) = B(\hbar\omega - E_g)^n \tag{2}$$

where $\hbar\omega$ is the energy of the incident photon, B the absorption edge width parameter, E_g the optical band gap, and n the exponent. It has been well established that the exponent n determines the type of electronic transition causing the optical absorption and can take values $^1/_2$, $^3/_2$, 2, and 3 for direct-allowed, direct-forbidden, indirect-allowed, and indirect-forbidden transitions, respectively. The linear fit of the optical absorption data, when $(\alpha\hbar\omega)^{2/3}$ is plotted against $\hbar\omega$, suggests direct-forbidden transitions across the energy band gap of V_2O_5 films. The validity of exponent $^3/_2$ (direct-forbidden transitions) for V_2O_5 films has been examined recently[31,32] and is in good agreement with the reports for V_2O_5 films obtained by other deposition methods.

The effect of growth temperature is significant on the optical band gap and transmittance of the films. The observed variation of the optical band gap as a function of substrate temperature is mainly due to changes in growth behavior and morphology of the PLD V_2O_5 films. The observed effects as a function of growth temperature can be explained on the basis of the electronic band structure of V_2O_5. The electronic band structure of V_2O_5 has been studied several times using theoretical and experimental investigations.[33−35] The complicated layered structure of the material leads to many bands with low dispersion. In general, the conduction band in V_2O_5 is formed by V 3d bands and the valence band by O 2p bands. In crystalline V_2O_5, the fundamental absorption is mainly due to transitions from the O p-type wave function to the 3d-type V wave functions. Therefore, the band gap corresponds to the energy between the top of the O 2p band and the bottom of the V 3d band. The band gap widening (blue shift in the absorption edge) in the films with relatively low grain size is mainly due to quantum-size effects. In the amorphous films, where there is a considerable blue shift in the absorption edge, there exists very small particles, grain boundaries, and imperfections, which lead to larger free

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(29) Urbach, F. *Phys. Rev.* **1966**, *92*, 627,

(30) Tauc, J. *Optical Properties of Solids*; Abeles, F., Ed.; North-Holland: Amsterdam, 1972.

(31) Ramana, C. V.; Hussain, O. M. *Adv. Mater. Opt. Electron.* **1997**, *7*, 225.

(32) Ramana, C. V.; Hussain, O. M.; Uthanna, S.; Naidu, B. S. *Opt. Mater.* **1998**, *101*, 1998.

(33) Parker, J. C.; Lam, D. J.; Xu, Y. N.; Ching, W. Y. *Phys. Rev. B* **1990**, *42*, 5289.

(34) Bachmann, H. G.; Ahmed, F. R.; Barnes, W. H. *Z. Kristallogr.* **1961**, *115*, 110.

(35) Murphy, D. W.; Christian, P. A.; Disalvo, F. J.; Waszczak, J. V. *Inorg. Chem.* **1979**, *18*, 2800.

carrier concentrations and the existence of potential barriers. The electric fields arising from these factors in the disordered state result in an increase in the optical band gap. It is very clear (Figure 6) that the optical energy band gap is much higher for films at lower growth temperatures, where the grain size is relatively low ($\leq$50 nm). When the average crystal dimension becomes small, the quantum-size effect results in a dramatic increase in the band gap. Recently, Allan et al. reported[36] the blue shift in the absorption edge for amorphous silicon nanoclusters, where the band gap shifts to the higher energy with reduction in size. The shift in the band gap to higher energy in the disordered state was also reported for several other transition-metal−oxide films.[1,36−39] Further decrease in the optical band gap (red shift in the absorption edge) observed for V_2O_5 films is attributed to (a) transition from amorphous to polycrystalline state as observed in our previous XRD measurements[23] and (b) an increase in the grain size. In addition, there may be a contribution from internal stress developed in the polycrystalline film and effective decrease in the imperfections at grain-boundary regions.[27] However, further decrease in the band gap for a grain size >100 nm (temperatures $\geq$300 °C) is very small. This suggests that the effects due to increase in the average grain size after certain critical dimensions are not very significant. AFM and SEM measurements indicated that the increase in grain size is associated with a random distribution of the grains on the film surface. The random distribution of the grains makes the film surface rough and results in the increased light-scattering losses at the interface. This accounts for the observed decrease in the transmittance with increasing growth temperature. Furthermore, an increase in the scattering coefficient (generally with the square of the grain radius) would decrease the optical transmittance in the UV region.[37] This feature was also clearly observed in the transmittance curves (Figure 5) with increasing growth temperature and supports the idea of scattering losses due to random distribution of grains. However, it is worth to consider the absence of near-infrared bands, found in the literature for oxygen-deficient films,[31] which are direct evidence for the high quality of PLD V_2O_5 films. On the basis of electron paramagnetic study of as-grown single crystals[40] and optical absorption measurements of thin films,[31,32] the defect centers in the lattice V_2O_5 involve an oxygen vacancy in the O layer between two V−O layers and cause the near-infrared optical absorption bands. The absence of near-infrared bands is mainly attributed to the deposition of V_2O_5 films at an optimum oxygen partial pressure and to the advantage of PLD, where the original stoichiometry of the starting material is retained in the films, otherwise, the oxygen vacancies would have resulted in the atomic disorder.

V. Summary and Conclusion

V_2O_5 thin films were prepared by pulsed laser deposition over a wide substrate temperature range (30−500 °C) at an oxygen partial pressure of 100 mTorr. Chemical composition analysis by RBS and XPS indicated the stoichiometric V_2O_5 film growth in the entire range of temperature. Characterization of V_2O_5 films by SEM studies revealed that the substrate temperature plays a key role in deciding the growth and morphology of the films. The results indicated the V_2O_5 film growth process was thermally activated with an activation energy of 0.45 ± 0.2 eV. The grains are compact and dense, and the average grain size increases with the increase in growth temperature. The increase in grain size is associated with the random distribution of grains, which is effective at higher temperatures, and results in the decrease of spectral transmittance of the films. The optical band gap of V_2O_5 films deposited at room temperature is 2.47 eV and decreased to 2.12 eV with the increase in growth temperature to 500 °C. A higher energy shift observed in the optical band gap for low-temperature-deposited films in comparison with films deposited at high temperature is attributed mainly to the quantum-size effects due to very low grain size. The changes in optical properties with growth temperature can be attributed to the increase in grain size and structural modification of the material in the films. Electrochemical measurements on the pulsed-laser-deposited V_2O_5 films to test their applicability in solid-state microbatteries are under progress and will be reported separately.

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(36) Allan, G.; Delerue, C.; Lannoo, M. *Phys. Rev. Lett.* **1997**, *78*, 3161.
(37) Zhang, L.; Ouyang, D.; Mo, C. *Nanostruct. Mater*. **1997**, *8*, 1991.
(38) Lu, X. M.; Zhu, J. S.; Zhang, W. Y.; Ma, G. Q.; Wang, Y. N. *Thin Solid Films* **1996**, *274*, 165.
(39) Tang X. G. et al. *Solid State Commun*. **2000**, *116*, 507.
(40) Clauws, P.; Vennik, J. *Phys. Status Solidi B* **1974**, *66*, 553.