Characterization of pulsed laser deposition grown V_2O_3 converted VO_2

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Abstract. Controllable tuning of Metal-insulator transition in V_xO_y thin film has been a field of extensive research. However controlled synthesis of desired Vanadium oxide phase is a challenging task. We have successfully achieved VO_2 phase on Silicon substrate after post deposition annealing treatment to the PLD grown as deposited V_2O_3 thin films. The annealed thin film was characterized by x-ray diffraction (XRD), resistivity, Raman spectroscopy, X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) measurements. XRD confirms the crystalline nature and growth of VO_2 phase in thin film. The characteristic MIT was observed from resistivity measurements and transition temperature appeared at lower value around 336 K, compared to bulk VO_2. The structural transition accompanied with MIT from lower temperature monoclinic phase to higher temperature Rutile phase became evident from temperature dependent Raman measurements. Chemical state of vanadium was examined using XAS and XPS measurements which confirm the presence of +4 oxidation state of vanadium in thin film.

1. Introduction

Vanadium exhibits variable oxidation states towards oxygen, hence results in the formation of different number compound with oxygen. Among all the vanadium oxide phases, Vanadium Dioxide (VO_2) has been extensively studied because of its near room temperature metal-insulator (MIT) transition (T_t = 341 K), transition from high temperature metallic phase to low temperature insulating phase. The MIT in VO_2 is accompanied by the structural transition from high-temperature tetragonal (Rutile) structure to low temperature monoclinic (M1) structure [1]. The MIT in VO_2 is of both fundamental and technical interest, the former due to the important questions about its origin while the latter due to the possible applications in electronic devices such as electrical switches and field effect transistors [2]. The mechanism of the metal-insulator transition in VO_2 is considered to be of Peierls type or Mott-Hubbard type involving the electron-phonon and electron-electron interactions respectively [2].

The tendency of Vanadium to form different compounds with oxygen poses a stiff challenge on synthesis of high purity single phase of vanadium oxides. Various deposition methods including molecular beam epitaxy, chemical vapour deposition, R-F sputter deposition, sol-gel, ion implantation and pulsed laser deposition have been utilised for the deposition of vanadium dioxide thin films [3].

In this paper, we report the attempt of the growth of VO_2 thin film using pulsed laser deposition technique on the [0 0 1] Silicon substrate using V_2O_5 as the target material. The VO_2 phase was obtained after the annealing treatment to the as grown Vanadium sesquioxide (V_2O_3) thin film. The annealed thin film was using X-ray diffraction (XRD), Raman, Resistivity, X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron spectroscopy (XAS) measurements.

2. Experimental details

KrF excimer laser (λ = 248 nm, repetition rate of 5Hz and pulse laser energy of 210mJ) was focussed onto a target (pressed V_2O_5 with purity > 99.9%) with a fluence of 3 J/cm^2. The angle between the incident laser beam and normal to the target surface was 45˚. The base pressure during the deposition was 3.6×10^{-6} Torr. 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 a uniform thin film V_2O_3 was deposited on ultrasonically cleaned Si (001) substrate. The substrate temperature was maintained at 650°C during the deposition of 50 minutes. The V_2O_3 phase was confirmed through X-ray diffraction measurements (not shown here). The thickness of the film as measured by the stylus profilometer comes out to be 70 nm. The as grown thin film was annealed at 650^0C for 2 hours in presence of 100 mTorr oxygen partial pressure. X-ray diffraction (XRD) was carried out by Bruker D8 X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å). Temperature dependent resistivity measurements were performed using four-probe resistivity setup. Temperature dependent Raman spectra were collected in backscattering geometry using a 10 mW Ar (488 nm) laser as an excitation source coupled with a Labram-HR800 micro-Raman spectrometer equipped with a 50X objective. All the spectra were corrected in frequency by using a silicon substrate. The X-ray photoelectron spectroscopy (XPS) measurement was performed using Omicron energy analyzer (EA-125) with Al K_{α} (1486.6eV) X-ray lab source. Room temperature soft X-ray absorption spectroscopy across V $L_{3,2}$ and O K edges were carried out at the beam line BL-01 (soft X-ray absorption spectroscopy beamline) at Indus-2 Raja Ramana centre for Advanced Technologies Indore. SXAS measurements were performed in total electron yield mode (TEY). Energy resolution during SXAS measurements at oxygen Kedge energy was better than $\sim$ 250 meV energy.

3. Results and discussion

Figure 1(a) shows the θ-2θ XRD patterns of annealed thin film grown on silicon substrate along with XRD of Si substrate. The XRD pattern of thin film shows peaks at 2θ = 29.15, 39.85, 41.50 and 85.88. The peak at 2θ= 29.15 correspond to the reflection from the (0 0 2) plane of metastable monoclinic VO_2 (B) phase which is one of the polymorphic structures of VO_2 with space group C2/m [4], while as the peak at 2θ=39.85 can be indexed to the reflection from the planes (0 0 2) of insulating monoclinic phase of VO_2 (M) with the space group P2$_1$/c [JCPDS card no 82-0661], which is one of the stable phases of VO_2. The third peak at 2θ= 41.50 can be assigned to the reflection from the (1 1 3) plane that belongs to the rhombohedral phase of V_2O_3 with space group R$\overline{3}$C [JCPDS card no 85-1411], while all the other remaining peaks are from the substrate Si. Fig 1(b) represents the characteristic metal-insulator transition in VO_2 thin film obtained from the temperature dependent resistivity measurements. The observation of thermal hysteresis confirms the first order nature of this transition. From the graph, it is clear that the change in the magnitude of resistivity across the metal-insulator transition is not large. The reason behind this may be the presence of V_2O_3 phase which does not undergo change in the resistivity [5]. More over the presence of VO_2 (B) polymorphous also affect the MIT [4]. The phase transition temperature defined as T_t = ($T_{c,h}$ + $T_{c,c}$) /2 (Where $T_{c,h}$ and $T_{c,c}$ correspond to the phase transition temperature of heating and cooling branch respectively) has been calculated as 336.1 K. The transition temperature ($\sim$ 336.1 K) is appearing at the lower temperature compared to bulk VO_2 ($\sim$ 341 K). This may be because of substrate induced stress present in the thin film due to substrate [ref]. The metal-insulator transition of the compound is characterized by transition temperature (T_t), hysteresis width (ΔH = 7.07 K) and transition sharpness (ΔT = 5.04
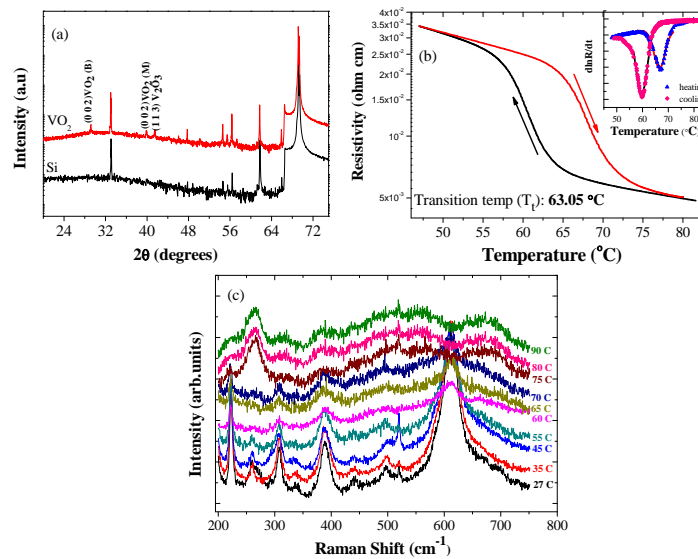
Figure 1. (a) X-ray diffraction pattern of annealed thin film. (b) Temperature dependent resistivity of annealed thin film. Inset: Gaussian fitting of the differential curves of resistivity Vs temperature. (c)Temperature dependent Raman measurements of annealed thin film in heating cycle only.

(heating) and 5.42 K (cooling)).All these parameters are calculated from the Gaussian fittings of the differential curves of lnR-T plots shown in the inset of Fig 1b.

To investigate the structural transition accompanying with MIT in the annealed thin film, temperature dependent Raman scattering measurements were performed from room temperature up to 363 K, shown in Figure 1(c). The structural transition from the low temperature monoclinic structure to higher temperature tetragonal structure is quite visible and occurs around the MIT of VO_2 thin film signifying the importance of periels nature to the transition. In our spectrum we have observed 8 Raman modes in low-temperature monoclinic insulating phase at 222.1, 259.9, 308.8, 334.9, 388.8, 439.9, 497.5, 611.8 cm^{-1} with A$_g$ symmetry [6]. The low intensity Raman mode around 520 cm^{-1} is from the Si substrate. The peaks at 194 and 223cm^{-1} were assigned to V–V vibration modes, whereas those in the high-frequency region 300–700 cm^{-1} were assigned to V–O vibration modes [7]. The Ag phonon mode at 221 cm^{-1} appears to be at lower wave number compared to that observed in single crystal VO_2 [8] which signifies the decrease in V-V distance hence an increase in the direct overlapping of V- 3d orbitals that results in the strain induced decrease of MIT in annealed thin film.
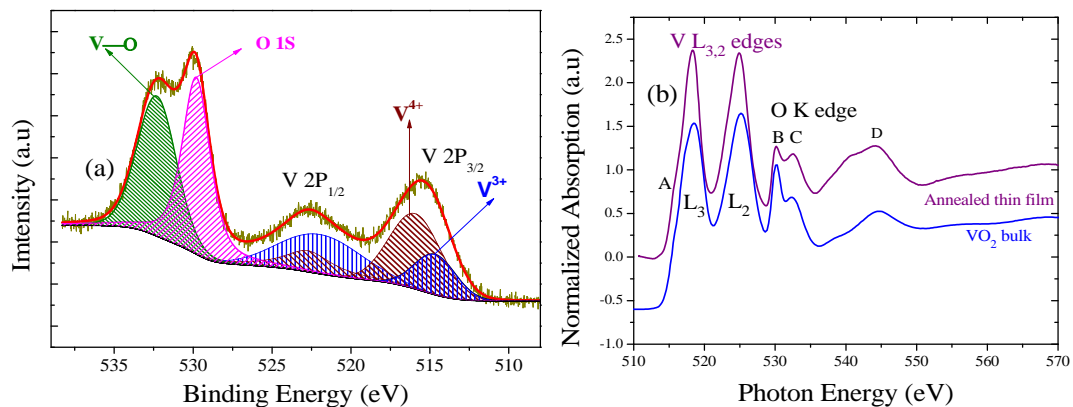

Figure 2. (a) XAS of annealed thin film along with pure bulk VO_2. (b) XPS of annealed thin film

The correct chemical composition of thin film was confirmed from XPS measurements as shown in Fig 2(a). The graph shows that annealed thin film is composed of both +3 and +4 oxidation states of Vanadium [9]. X-ray absorption spectroscopy XAS has proven to be a valuable tool to study the unoccupied conduction bands of VO_2 and improve the understanding of this system. We have performed the XAS measurements across the V $L_{3,2}$ and O-K edges of annealed thin film and pure VO_2 bulk (99.9% purity) shown in Fig 2(b). V $L_{2,3}$ edges correspond to the transition from V $2p_{1/2}$ (L_2) and $2p_{3/2}$ to empty V $3d$ states while O K-edge involves the transition from O $1s$ to O $2p$ state hybridised with V $3d$ orbitals. The fine feature A for V L portion corresponds to the transition to t_{2g} band obtained because of the octahedral crystal field splitting of V $3d$ orbitals. In the O-K edge the features B and C emerge from the the transition to π and sigma bands which result from the hybridization of O 2p with t_{2g} and e_g orbitals of V 3d band respectively, The broad feature D around ~544.1 eV is attributed to V4sp bands formed by V4sp-O2p antibonding interactions [10]. The magnitude of relative intensity of O K edge features reflects the amount of hybridization among metal ligand orbitals [ref]. The magnitude of the relative intensity (B/C = 1.08) in thin film is found to be smaller compared to bulk VO_2 (~ 1.54). This magnitude difference is attributed to the presence of V_2O_3 impurity phase which has different strength of hybridization with O 2p orbitals compared to VO_2.

4. Conclusion

We have been successful in obtaining a significant VO_2 phase from as deposited V2O3 thin film. XRD confirm the presence of VO2 polymorphic phase along with small secondary phase of V2O3in annealed thin film. The effect of strain and impurity phase on the MIT was observed from resistivity measurements. Raman measurements confirm structural transition accompanying with MIT dominated by VO_2. XPS reveal the +3 and +4 oxidation states of Vanadium. Presence of +3 Vanadium observed here from XPS in annealed film is in agreement to XRD data. The effect of impurity phase on the magnitude of hybridization among V $3d$ and O 2p orbitals was observed from XAS measurements.

References
[1]   Tan X, Yao T, Long R, Sun Z, Feng Y, Cheng H, Yuan X, Zhang W, Liu Q, Wu C, Xie Y and Wei S 2012 *Scientific Reports* **2** 466
[2]   Laverock J, Preston A R H, Newby Jr. D, Smith K.E, Sallis S, Piper L F J, Kittiwatanakul S, Lu J W, Wolf S A, Leandtrsson M, and Balasubramanian T 2012 *Phys Rev B* **86** 195124
[3]   Fu D, Liu K, Tao T, Lo K, Cheng C, Liu B, Zhang R, Bechtel H, and Wu J 2013 *Journal of Applied Physics* **113** 043707
[4]   Wang Y L, Li M C, Zhao, L C 2006 *Science Direct* **201** 6772–6776
[5]   Yang Z, Ko C and Ramanathan S 2010 *Journal of applied physics* **108** 073708
[6]   Petrov G I, Yakovleva V V, Squier J 2002 *Applied Physics Letters* **81** 1023
[7]   Shibuya K, Tsutsumi J, Hasegawa T and Sawa A 2013 *Applied Physics Letters* **103** 021604
[8]   P. Schilbe 2002 *Physica B* 316, 600
[9]   Zimmerman R, Claessen R, Reinert F, Steiner P, and Hfner S 1998 *J. Phys. Condens. Matter* **10** 5697.
[10]   Abbate M, Pen H, Czyzyk M T, de Groot F M F, Fuggle J C, Ma Y J, Chen C T, Sette F, Fujimori A, Ueda Y, and Kosuge K 1993 *J. Electron Spectrosc. Relat. Phenom.* **62** 185