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Selective growth of single phase VO$_2$(A, B, and M) polymorph thin films

Amar Srivastava,1,2 Helene Rotella,2,3 Surajit Saha,1,2 Banabir Pal,4 Gopinadhan Kalon,2 Sinu Mathew,2 Mallikarjuna Motapothula,2 Michal Dykas,2 Ping Yang,3 Eiji Okunishi,5 D. D. Sarma,4,6 and T. Venkatesan1,2,3,a

1Department of Physics, National University of Singapore, Singapore 117542
2NUSNNI-NanoCore, National University of Singapore, Singapore 117576
3Singapore Synchrotron Light Source, National University of Singapore, 5 Research Link, Singapore 117603
4Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India
5Electron Optics Division, JEOL Ltd., Tokyo 196-8558, Japan
6Council of Scientific and Industrial Research-Network of Institutes for Solar Energy (CSIR-NISE), New Delhi 110001, India

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We demonstrate the growth of high quality single phase films of VO$_2$(A, B, and M) on SrTiO$_3$ substrate by controlling the vanadium arrival rate (laser frequency) and oxidation of the V atoms. A phase diagram has been developed (oxygen pressure versus laser frequency) for various phases of VO$_2$ and their electronic properties are investigated. VO$_2$(A) phase is insulating VO$_2$(B) phase is semi-metallic, and VO$_2$(M) phase exhibits a metal-insulator transition, corroborated by photoelectron spectroscopic studies. The ability to control the growth of various polymorphs opens up the possibility for novel (hetero)structures promising new device functionalities. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4906880]

Transition metal oxides are used in a wide range of practical applications such as photocatalysts,1 cathode materials,2,3 gas sensors,4 optical switching devices,5 and intelligent thermo-chromic windows.6 They also exhibit various polymorphic structures, among which many are neither stable in ambient conditions nor can be easily synthesized. These metastable phases have been the subject of considerable interest due to their unique and superior physical and chemical properties. Among those functional complex oxides, vanadium oxides can adopt a wide range of V:O ratios, resulting in different structural motifs with various types of coordination polyhedra.7 In this class, vanadium dioxide (VO$_2$) exhibits a number of polymorphic forms, such as VO$_2$(M1), VO$_2$(M2), VO$_2$(M3), VO$_2$(R), VO$_2$(A), VO$_2$(B), and VO$_2$(C). The two layered polymorphs VO$_2$(A) and VO$_2$(B) are promising materials for science and technology. VO$_2$(A) is important for the study of strong electronic correlations resulting from structure and VO$_2$(B) is important for its use as electrode materials for batteries. Various preparation techniques have been used and developed to stabilize these phases in bulk and thin film forms.8,9 Using Pulsed Laser Deposition (PLD) technique, thin films of these polymorphs (M1, M2, M3, and R) have been stabilized by substrate engineering10,11 as well as by adding dopant, such as, Cr.12 In 1989, Oka et al.,13 reported for the first time the stabilization of polycrystalline powder of VO$_2$(A) using hydrothermal synthesis. They observed a weak metal-semiconductor transition at 162.8 °C. They related this behavior to a crystallographic transition between a low temperature phase (LTP, space group $P4/ncc$, No. 130) and a high temperature phase (HTP, space group...
In the later part of the paper dealing with the TEM cross section results indeed, this is seen to be
aligned with the substrate (A) and VO\(_2\) (B) phase thin films which can sit on the STO unit cell as follows:
\[ \text{a} = 8.44 \text{ Å}, \text{b} = 8.44 \text{ Å}, \text{ and } \text{c} = 7.666 \text{ Å} \]
with a space group P4/ncc (No. 130). VO\(_2\) (A) can sit on the STO unit cell with the following relation:
\[ \sqrt{2a_{\text{VO}_2\text{(A)}}} = 2a_{\text{STO}} = 7.810 \text{ Å}. \]
VO\(_2\) (B) bulk, on the other hand, has a monoclinic unit cell
\[ \text{a} = 12.093 \text{ Å}, \text{b} = 3.702 \text{ Å}, \text{ and } \text{c} = 6.433 \text{ Å} \]
with a space group C2\(_h\) (No. 15). This can sit on the STO unit cell as follows:
\[ a_{\text{VO}_2\text{(B)}} = 12.093 \text{ Å} \approx 3a_{\text{STO}} = 11.715 \text{ Å}, \]
\[ b_{\text{VO}_2\text{(B)}} = 3.702 \text{ Å} \approx a_{\text{STO}} = 3.905 \text{ Å}. \]
Thus, one expects a coincident lattice site model to apply here. In the later part of the paper dealing with the TEM cross section results indeed, this is seen to be true. The films of VO\(_2\) M, A, and B under investigation are of thicknesses 60 nm, 60 nm, 40 nm, respectively, confirmed by Rutherford back scattering (RBS) and TEM. The 2D XRD patterns are recorded for all samples of the series (see supplementary material for X-Ray reciprocal space map using 2D detector, Fig. S1\(^{15}\)). The 1D XRD patterns shown in Fig. 1(c) are extracted from 2D XRD patterns by integrating the intensity along the \( \chi \) direction. We observed that the VO\(_2\) phase reflections are not aligned in \( \chi \) with the substrate, while for VO\(_2\) (A) and VO\(_2\) (B), reflections are perfectly aligned with the substrate (\( \chi = 0 \)). At low pressure (1 \( \times 10^{-4} \) Torr), M phase is stabilized with the off-chi peaks at 20 = 27.89\(^{\circ}\), assigned to (011) crystallographic plane of VO\(_2\) (M). By increasing the pressure to 7.5 \( \times 10^{-4} \) Torr, we produced a mixture of M and A phases where the peak at 20 = 29.62\(^{\circ}\) is assigned to (220) plane of VO\(_2\) (A) phase,\(^{16}\) while a single phase VO\(_2\) (A) film is stabilized at and above a pressure of 5 \( \times 10^{-3} \) Torr. Intriguingly, at the same oxygen pressure, reduction of the laser frequency to 2 Hz gave rise to a single phase VO\(_2\) (B) film. A peak at 20 = 29.05\(^{\circ}\) in the XRD pattern is assigned to (002) plane of VO\(_2\) (B) phase.\(^{15}\) The effect of oxygen partial pressure and laser frequency on the stability of these polymorphs were explored and a phase diagram is established (Fig. 1(d)) for different phases of VO\(_2\). The rocking curves were recorded on each sample in order to check the crystallinity (see supplementary material for rocking curve, Fig. S2\(^{17}\)). VO\(_2\) (A) shows a high crystalline quality (FWHM = 0.1\(^{\circ}\)), while the crystal quality decreases for VO\(_2\) (B) (FWHM = 0.6\(^{\circ}\)) and VO\(_2\) (M) (FWHM = 0.9\(^{\circ}\)) phases (see supplementary material for comparison of the rocking curves and the calculated d spacings, Table S1\(^{15}\)). We have further verified the stoichiometry of VO\(_2\) (A) and VO\(_2\) (B)
FIG. 1. Schematic crystal structure representation of (a) 220 orientated VO$_2$(A), (b) 002 orientated VO$_2$(B) grown on (100) orientated STO substrate. (c) XRD $\theta$-2$\theta$ patterns showing different phases for VO$_2$ thin films. (d) Phase diagram for different polymorphs of VO$_2$ thin film grown by the PLD.

films using oxygen resonance Rutherford back scattering technique which confirms the composition to be VO$_{2s.o.}$ (see supplementary material for oxygen resonance Rutherford backscattering spectra, Fig. S3$^{17}$).

If we look at the various phases of VO$_2$, they all have different V–V inter-atomic distances.$^{18}$ One can empirically understand the type of bond length formed between the V–V due to V–V and V–O–V atomic interactions and its dependence on the influence of the surrounding oxygen. At lower oxygen growth pressures, the atomic interactions are likely to favor shorter V–V distances. At low oxygen pressures, VO$_2$(R) phase is preferred at the growth temperature which subsequently results in the M phase at room temperature due to the metal-insulator transition (MIT). When the oxygen pressure is increased, the A phase with a longer average V–V distance$^{19}$ may be favored. Further, by decreasing the V arrival rate (i.e., lowering the laser frequency), the B phase with the longest V–V distance is stabilized.$^{14}$ Moreover, the symmetry of the phases could also be an important factor for their stabilization. The relatively more symmetric structure of VO$_2$(A) over VO$_2$(B) suggests VO$_2$(A) to be more stable over a wide range of laser frequency. Our explanation is rather qualitative. The actual process can be much more complicated which might involve type of connectivity of the anion sublattice, e.g., number of corner, edge, or face sharing oxygen octahedra. Also, the high degree of structural imperfections suggests that defect formation at the interface (as seen in the TEM images in Fig. 2) might play a critical role as well.

Figs. 2(a)–2(e) and Figs. 2(h)–2(l) present the processed atomic resolution high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images of VO$_2$(A) and VO$_2$(B) thin films, respectively. The brighter spots represent V atoms, while the position of oxygen rows between the V rows is not resolved. For VO$_2$(A), the V atoms in 001 domains (Figs. 2(a) and 2(b)) are arranged in a square form separated by O planes aligned along [110] and $\overline{[110]}$ directions as depicted in Fig. 2(f). In the $\overline{110}$ domain (rotated by 90° with respect to 001 domain), shown in Figs. 2(a) and 2(c) and modeled in Fig. 2(g), V atoms are arranged in pair of chains separated by O planes
FIG. 2. Processed atomic resolution HAADF-STEM images of cross sectional (a) VO$_2$(A) and (h) VO$_2$(B) thin films. (b) and (c) are enlarged 001 and -110 domains, respectively, in VO$_2$(A), while (i) and (j) are zoomed 010 and 100 domains, respectively, in VO$_2$(B). (d), (e), (k), and (l) are the FFT patterns of the four respective domains, while (f), (g), (m), and (n) are sketching the epitaxial relations of VO$_2$(A) and VO$_2$(B) with respect to STO substrate.

aligned along [001] direction. Similarly, VO$_2$(B) contains 010 domains (Fig. 2(i)) where the V atoms are arranged in a parallelogram separated by O planes, consistent with the bulk structure oriented along [010] direction (Fig. 2(m)). Rotated by 90°, 100 domains show a pair of V atom chains separated by O plane, consistent with the bulk structure oriented along [100] direction (Fig. 2(n)). The processed FFT on each domain for the two films VO$_2$(A) (Figs. 2(d) and 2(e)) and VO$_2$(B) (Figs. 2(k) and 2(l))
FIG. 3. Temperature dependent resistivity for VO$_2$(M), VO$_2$(A), and VO$_2$(B) films deposited on SrTiO$_3$ substrate.
150 K, respectively. Room temperature carrier density of VO$_2$(A) ($1 \times 10^{17}$ cm$^{-3}$) is comparable to that of VO$_2$(B) at low temperature (150 K) which is 2 orders of magnitude less than the VO$_2$(M). The lower mobility for increased carrier density in VO$_2$ polymorphs indicates the role of carrier-carrier scattering in the electronic transport. No evidence of insulator to metal transition in VO$_2$(A) films at 162.8 °C was observed and this is not surprising as even in the bulk material, the observed transition was quite weak. On the contrary, the transport measurement of VO$_2$(B) films supports the previous low-temperature X-ray studies on VO$_2$(B) which revealed an evolution from a high temperature monoclinic metallic phase to another monoclinic insulating phase at low temperature.

Fig. 5 shows the valence band photo emission spectra of A, B, and M phases of VO$_2$ measured by hard X-ray photoelectron spectroscopy (HAXPES). The excitation energy and the Fermi level of VO$_2$ is calibrated using Au Fermi level spectra. Before measuring X-ray photo electron spectra of each of the samples, we have performed measurements on Au Fermi level and used this value of energy to calibrate the excitation energy. In Fig. 5(a), the broad and higher intensity feature between 2 eV and 9 eV binding energies arises primarily from O 2p states whereas the relatively lower intensity peaks nearer to the Fermi energy ($E_F$) are mainly contributed by V 3d-like states. We focus on the V 3d related states in the vicinity of the $E_F$, shown in Fig. 5(b), that control the low energy excitations in these systems. Spectra for both VO$_2$(M) and VO$_2$(A) phases exhibit a single peak structure with no spectral intensity at the Fermi energy, consistent with the insulating state of both these compounds. These spectral features correspond to the lower Hubbard band of these strongly correlated systems and often have been termed the incoherent feature. The band gaps estimated from these spectra are...
approximately 0.32 eV and 0.72 eV for the VO$_2$(M) and VO$_2$(A) phases, respectively. Band gaps are calculated based on the assumption that the conduction band is pinned close to the Fermi energy (i.e., the energy gap between the conduction band and the Fermi level is assumed to be very small.). In contrast, VO$_2$(B) phase V 3d spectral feature is relatively broad in nature. The broad spectral feature suggests two partially overlapping peaks in this case, with one peak position at about 1.6 eV, while the other at about 0.6 eV binding energy. The feature at the 1.6 eV binding energies appears between the spectral features of the lower Hubbard band in VO$_2$(M) and VO$_2$(A) phases, and can, therefore, be attributed to the incoherent spectral feature of the lower Hubbard band in VO$_2$(B) phase. The remaining feature, much closer to and with a finite intensity at the Fermi energy, clearly establishes the metallic nature of VO$_2$(B) phase at the room temperature; this low energy spectral feature is called the coherent peak in this case. Thus, the photoemission spectra for all three phases are consistent with the observed transport properties of VO$_2$ in these three phases.

In conclusion, we have shown that the three polymorphs of VO$_2$(A, B, and M) thin films can be prepared in single phase by controlling the vanadium arrival rate and the oxygen pressure both on SrTiO$_3$. The phase diagram for the growth of the various phases indicates that the VO$_2$(M/R) is the most stable phase, next is VO$_2$(A) followed by VO$_2$(B) as the least stable phase. The transport studies indicate that B is semi-metallic, A is insulating, while M is semiconducting which is corroborated by the HAXPES measurements. Thus, control of cationic and anionic atomic arrival rates is a powerful processing step for the growth of novel functional polymorphic materials.

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17. See supplementary material at http://dx.doi.org/10.1063/1.4906880 for X-Ray reciprocal space map and rocking curve using 2D detector for VO$_2$ thin films M, A, and B (Figs. S1 and S2, Table S1); stoichiometry of VO$_2$(A) and VO$_2$(B) thin films using oxygen resonance Rutherford backscattering spectra (Fig. S3); d(002)/d(T) versus temperature plot for VO$_2$ polymorphs (Fig. S4).