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Metal-insulator transition in nanocomposite VO_x films formed by anodic electrodeposition

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The ability to grow VO₂ films by electrochemical methods would open a low-cost, easily scalable production route to a number of electronic devices. We have synthesized VO_x films by anodic electrodeposition of V₂O₅, followed by partial reduction by annealing in Ar. The resulting films are heterogeneous, consisting of various metallic/oxide phases and including regions with VO₂ stoichiometry. A gradual metal insulator transition with a nearly two order of magnitude change in film resistance is observed between room temperature and 140 °C. In addition, the films exhibit a temperature coefficient of resistance of $\sim -2.4\%/^{\circ}\text{C}$ from 20 to 140 °C. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4829430>]

Metal-insulator transition (MIT) phenomena in transition metal oxides find potential application in solid state memories, ultra-fast two- or three-terminal electronic switches, memristive and optical storage devices.¹ Vanadium dioxide (VO₂) has been extensively studied in this context due to its sharp MIT at around 68 °C, originated by the phase transition from a low temperature monoclinic phase with a band gap of 0.6 eV to a metallic rutile phase.² Later studies have shown that ultra-fast MIT in VO₂ could also be triggered by electric fields³ or optical excitations.⁴ MIT transitions in VO₂ exhibit a change in resistivity of about five order of magnitude in single crystals,⁵ and about 3 orders of magnitude in thin films,⁶ sufficient to enable in principle MIT-based electronics.⁷ Amorphous VO₂ has also found application in bolometer devices for infrared detectors,⁸ where a high temperature coefficient of resistance (TCR)⁹ facilitates temperature determination from the measured resistance; values as high as $-2\%/^{\circ}\text{C}$ have been obtained by physical vapor deposition (PVD) methods for amorphous VO_x ($x \sim 1.8-2.0$) films.¹⁰⁻¹² In this case, a gradual change in resistance, allowing operation over a large temperature range, is required.

Thin films of VO₂ are grown by a variety of techniques, including pulse laser deposition or sputtering. High growth temperature ($T > 500^{\circ}\text{C}$) is generally required in order to form crystalline materials and achieve a large change in resistivity.^{13,14} Electrodeposition in contrast is capable to form highly crystalline transition metal oxide materials such as ZnO¹⁵ and Cu₂O¹⁶ at temperatures $< 100^{\circ}\text{C}$. The ability to electrodeposit VO₂ at such low temperatures would lead to significant advantages in the manufacture of electronic devices: by enabling additive filling of lithographic patterns, post-deposition etching processes could be avoided, leading to a low defect density and limiting preferential nucleation sites for phase transformations, which may degrade the quality of the MIT.¹⁴ Other potential advantages include the possibility to form films on non-planar and polymeric

substrates, of interest in flexible electronics. Two approaches have been reported on the electrochemical synthesis of VO₂; the first involves 45 days storage of a VO_x xerogel prior to annealing at 550 °C,¹⁷ while the second consists in the reduction of V⁵⁺ in triethanolamine solutions followed by annealing at 400 °C in an Ar atmosphere.¹⁸ These methods yield films exhibiting resistance changes of 2-5 times across the transition, much lower than the values observed in physically deposited films.

This Letter reports an electrochemical approach for the synthesis of VO_x films, which exhibit a resistance change of about two orders of magnitude across the MIT and TCR of $-2.4\%/^{\circ}\text{C}$. The method consists in the oxidation of V⁴⁺ to form V₂O₅, followed by thermal annealing in Ar atmosphere. Specifically, the first step involves the potentiostatic formation of dense, continuous V₂O₅ films via oxidation of V⁴⁺ at 1.5 V_{SCE} in an unstirred solution of 1M VOSO₄ and 0.1M Na₂SO₄ (pH = 1.5) at 40 °C.¹⁹ The current density at steady state during deposition was 40 mA/cm². The films, with a thickness varying between 200 and 600 nm, were deposited onto Si substrates coated with a 100 nm thick Ru seed layer. Deposition was followed by thermal annealing in a sealed glass capsule filled with an Ar atmosphere at 400 °C for 3 h. Sample imaging was performed by scanning electron microscopy (SEM) with a JEOL 6700F. Phase identification was performed with x-ray diffraction (XRD) using a PANalytical X'Pert Pro MPD X-ray diffractometer and Raman spectroscopy using a Tokyo Instruments Nanofinder 30 Raman Microscope with a 632 nm laser. Film composition and chemical states of vanadium and oxygen were investigated by X-ray photoelectron spectroscopy (XPS, PHI 5600, Al K_α source, 23.5 eV pass energy). The electrical transport properties were measured with a Micromanipulator Probe Station and an HP 4145 semiconductor parameter analyzer, using a two-terminal geometry at temperatures between 22 and 140 °C; a Au-coated W needle was connected to the film, the other to the Ru substrate. The current was swept between -2 mA and $+2\text{ mA}$, and the corresponding voltage recorded at five different locations per each temperature.

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FIG. 1. Cross sectional SEM showing different layers in electrodeposited VO_2 . Inset: Film thickness as a function of deposition time.

Figure 1 shows a cross sectional SEM image of a VO_2 film of 120 nm thickness, and the inset demonstrates a linear increase in film thickness with time, following the calibration curve: $t \text{ (nm)} = 4.96\tau \text{ (s)}$. A powdery debris layer—which can be selectively removed by rinsing in deionized (DI) water—forms on top of the compact layer, as seen in the upper portion of Figure 1. Films thicker than ~ 300 nm on the other hand tend to delaminate and are partly removed by rinsing.

FIG. 2. (a) XRD patterns of VO_2 films. Substrate peaks are indicated with (*). (b) Raman spectra show a broad peak centered at $1200\text{--}1500 \text{ cm}^{-1}$; no peaks associated with VO_2 are detected.

The as-deposited vanadium oxide film is amorphous: only the reflections associated with the substrate are detected by X-ray diffraction. Figure 2(a) shows the XRD patterns of VO_x films after annealing; only reflections from the VO_2 monoclinic structure are observed, suggesting the formation of VO_2 , possibly intermixed with nanocrystalline/amorphous phases. Raman spectra (Fig. 2(b)) exhibit only a wide maximum between 1200 and 1500 cm^{-1} , where no Raman-active modes for VO_2 are present; peaks associated with VO_2 and V_2O_5 are in fact reported only at wave numbers below 1000 cm^{-1} .^{20–22} This suggests the formation of a highly defected structure, consistent with the weak XRD reflections.

High resolution XPS spectra for vanadium recorded at different depths (Figure 3(a)) are all similar, showing broad $\text{V } 2p_{1/2}$ and $2p_{3/2}$ peaks encompassing the reference core levels for V^0 (512 eV), V^{2+} (513.7 eV), V^{3+} (515.2 eV), V^{4+} (515.8 eV), and V^{5+} (517.2 eV).²³ (Figure 3(b); Shirley background subtracted; deconvolution parameters according to Silversmit²³). The deconvolution indicates that V is present in various oxidation states, including the metallic state, sub-oxides, and partly in the 4+ and 5+ oxidation states. A compositional XPS depth profile down to a depth of 120 nm shows a constant V:O ratio of about 1:1.8.

Figure 4(a) shows the I-V characteristic of a VO_2 film (200 nm) at various temperatures; the I-V curves are non-linear, resulting in resistance switching behavior triggered by the electric field. The decrease in resistance at 40°C is

FIG. 3. (a) X-ray photoelectron spectra at various depths of a 200 nm VO_2 sample, showing a broad peak that encompasses various vanadium valence states but does not vary as a function of depth below the surface. (b) Deconvolution of the $\text{V}2p$ signal from higher resolution spectra taken below 120 nm.

assigned to local inhomogeneities of the film, as expected from a mixed oxide, but the remaining trend is consistent with our expectations of a decreasing resistance with temperature. The non-linear character of these curves is attenuated with increasing temperature, approaching a metallic behavior; this transition is clearly seen in the inset of Figure 4(a), which displays the differential resistance. Figure 4(b) shows the film resistance at low current (± 0.12 mA, circles) and high current (1.5 to 2 mA, squares) as a function of temperature, indicating the gradual occurrence of a MIT between 60 °C and 80 °C, with a resistance ratio of nearly two orders of magnitude. A temperature coefficient of resistance (TCR = $1/R \times dR/dT$)²⁴ of $-2.4\%/^{\circ}\text{C}$ was calculated by taking the slope of a linear fit to the natural logarithm of the resistance at low current as a function of temperature (Figure 4(b), inset). This performance compares favorably with that of VO₂ films prepared by vapor deposition methods.^{10–12}

The gradual change in resistivity is in contrast with the sharp MIT phenomena observed in sputtered, laser deposited, or PVD films¹² and is consistent with a multi-phasic film with high defect density, as suggested by structural data (Fig. 2). The presence of multiple oxidation states for vanadium on the other hand indicates that both metallic and various oxide phases are present, leading to complex transport phenomena, as shown by the observed I-V and differential

resistance data: metallic vanadium and V₂O₃ (Ref. 25) may short circuit the transport path through VO₂, and the presence of other oxides would attenuate the MIT intrinsic to VO₂. Such composite material on the other hand combines a resistance change of about 2 orders of magnitude, suggesting that the VO₂ volume fraction exhibits a significant resistance variation, with a high TCR, result of a gradual phase transformation. Improvements in the synthesis process, in particular, optimization of the annealing time, temperature profile, and of the annealing gas mixture, may lead to much improved materials that could possibly be synthesized at relatively low temperatures and optimized for either MIT or TCR applications.

In summary, we have demonstrated an electrochemical process for the synthesis of composite vanadium oxide films. As suggested by XRD data, the films are multi-phasic and consist of nanocrystalline/amorphous metallic as well as oxide phases, in particular, a VO₂ phase with high defect density. Due to their unusual microstructure, these films exhibit a resistance switching at room temperature (RT) triggered by an external electric field and a MIT between 60 and 80 °C with a change in resistance of about 2 orders of magnitude. In addition, these films also display a high TCR value of $-2.4\%/^{\circ}\text{C}$.

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FIG. 4. (a) Voltage-current curves collected on the 200 nm VO_x film in a temperature range from RT to 140 °C. Inset: Differential resistance as a function of applied current at various temperatures. (b) Resistance (*R*) of a 200 nm VO_x film measured at close to zero (squares) and close to ± 1.5 –2 mA (dots) current, as a function of temperature. Inset: A linear fit to $\ln(R)$ was used to calculate the thermal coefficient of resistance of 2.4%.

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