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Electron back-scattered diffraction of crystallized vanadium dioxide thin films on amorphous silicon dioxide

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ABSTRACT

Crystalline films and isolated particles of vanadium dioxide (VO_2) were obtained through solid phase crystallization of amorphous vanadium oxide thin films sputtered on silicon dioxide. Electron back-scattered diffraction (EBSD) was used to study the crystals obtained in the thin films, to differentiate them from different vanadium oxide stoichiometries that may have formed during the annealing process, and to study their phase and orientation. EBSD showed that the crystallization process yielded crystalline vanadium dioxide thin films, semi-continuous thin films, and films of isolated particles, and did not show evidence of other vanadium oxide stoichiometries present. Indexing of the crystals for the orientation study was performed using EBSD patterns for the tetragonal phase of vanadium dioxide, since it was observed that EBSD patterns for the monoclinic and tetragonal phases of vanadium dioxide are not distinguishable by computer automated indexing. Using the EBSD patterns for the tetragonal phase of vanadium dioxide, orientation maps showed that all VO_2 crystals that were measurable (approximately the thickness of the film) had a preferred orientation with the c-axis of the tetragonal phase parallel to the plane of the specimen.

1. Introduction

Vanadium is a transition metal whose oxides undergo a semiconductor-to-metal transition at some characteristic temperature [1–6]. Vanadium dioxide (VO_2) has been extensively studied because its transition temperature occurs near room temperature, 68 °C [1,3,6,7]. In single crystals, vanadium dioxide undergoes several drastic, abrupt, and reversible changes in its properties during its phase transition. These changes to its properties include: 1) A structural change from a low temperature semi-conducting monoclinic phase to a high-temperature tetragonal metallic phase; 2) a resistivity change of several orders of magnitude; and 3) a sharp change in optical transmittance in the infrared region. These optical and electronic properties that vanadium dioxide exhibits due to its phase transition increase the potential use of this material for various technical applications [5,8–15]. Several studies have focused on deposition and characterization of VO_2 thin films on various substrates, however, the nature of the phase transition and its mechanism are still under debate [4,6,16–24]. Changes in transition temperature, hysteresis, and sharpness of the transition have been attributed to variations in stoichiometry, particle size, stress, misorientations between grains, morphological faults, and other "imperfections." However, while specific bulk properties of the reported films are well characterized, characterization of their microstructure is often limited to particle size and morphology [8,9,11,14,25–28]. We add here a detailed study of the microstructure of VO_2 thin films on SiO_2 surfaces formed by solid phase crystallization.

During the transition from the high-temperature tetragonal phase to the low-temperature monoclinic phase, the atomic arrangements undergo both subtle changes in position as well as a break in symmetry. The reference structure to this discussion is the higher symmetry tetragonal phase and the phase transition described is then from high to low temperature (see Fig. 1). Along the c-axis of the tetragonal phase, there is a 0.88% expansion; the vanadium atoms move from being collinear with a spacing of 2.85 Å to being staggered with alternating spacings of 3.2 Å and 2.6 Å with a 166.7° angle. Along the a-axis, there is a 0.44% contraction; the vanadium atoms again move from their collinear state to a staggered one with alternating spacings of 4.3 Å and 4.8 Å at an angle of 171.5°. Due to the staggering of the atoms along the a- and c-axes, the unit cell doubles along these directions. There is also a 0.44% contraction along the b-axis (to greater precision, this is a slightly larger contraction than in the a-axis), however the vanadium atoms remain lined up and there is no doubling of the unit cell in this direction.

Externally applied stress on crystal grains can have impact on the observed properties of the crystal. Phase transitions are one clear case where, for instance, externally applied pressures can significantly impact the temperature of a transition. Recent work with single-crystal beams of vanadium dioxide suggests structural phase changes due to external stresses [8,15,19,29–31]. In the case of thin films, the

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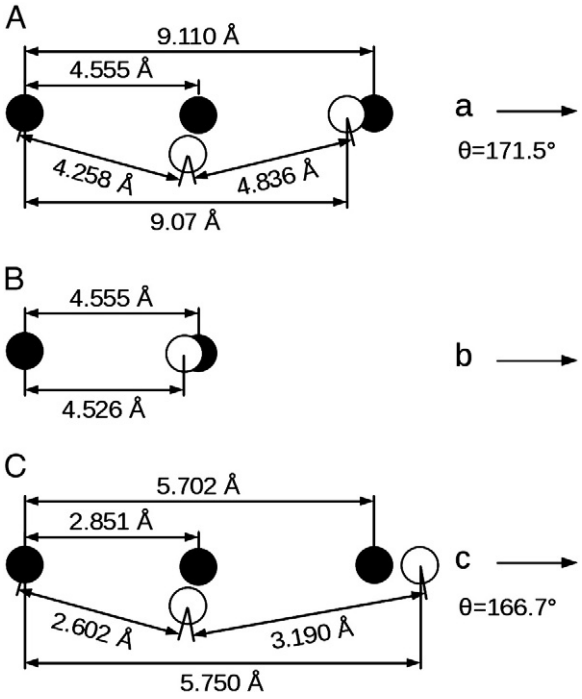

Fig. 1. Diagram of the structural changes during the phase transition (not to scale) along the respective (A,B,C) crystal directions of the tetragonal phase. The solid circles represent the positions of the vanadium atoms in the high-temperature tetragonal structure, and the white circles represent the new positions in the low-temperature monoclinic structure. The axis labels correspond to the tetragonal phase.

interactions between grains and with the substrate could either aid or hinder the changes expected from the phase transition and thus potentially shift the temperature of the local phase transition. In the case of VO_2 where each crystal axis has its own direction (expansion or contraction) of change, the relative alignment of the grains may have impact on the observed properties.

Knowing the microstructure of the thin films may aid in understanding the phase transition in VO_2 thin films. Vanadium dioxide is often deposited and studied on amorphous SiO_2-type substrates, such as silica or glass, but no detailed studies of crystal orientation have been done [5,9,10,13,25,27]. Preferred orientations of the grains on these type of substrates may create the type of stresses that affect the phase transition of individual vanadium dioxide grains within the film. In this work, solid phase crystallization conditions of VO_2 thin films were explored and film morphology and grain orientation were characterized by scanning electron microscopy and electron back-scattered diffraction.

2. VO_2 film formation and morphology

The samples consisted of a silicon wafer with a thermally grown amorphous silicon dioxide layer approximately 380 nm in thickness. A layer of amorphous vanadium oxide (VO_x), approximately 50 nm in thickness, was sputtered on top of the thermally grown oxide by means of reactive DC magnetron sputtering. Smaller pieces of this wafer were then cleaved and annealed under various conditions. A Lindberg-Blue 800 W tube furnace with a 1 in tube diameter was used to perform the anneals. Individual samples were annealed at temperatures ranging from 200 °C up to 1000 °C under argon gas flow at approximately 600 sccm. The annealing times ranged from 17 h down to 5 min. All the anneals were performed under atmospheric pressure and given 10 min before heating for the argon to purge the furnace.

A Philips XL30 S-FEG scanning electron microscope (SEM) was employed to determine the morphology of the films after each anneal. Using micrographs obtained from the SEM the particles were measured. Due to the irregular shape of most grains, the longest dimension was measured and used to compare grain sizes. Surface scanning electron micrographs were obtained with accelerating voltages ranging from 10 kV up to 25 kV.

After annealing, granular crystalline thin films, crystalline semi-continuous thin films, and crystalline isolated particles were observed (Fig. 2). Enough surface mobility and VO_2 crystal growth atop the silicon dioxide layer were observed at temperatures above 500 °C such that isolated grains taller than the original film were formed. Temperatures ranging from 400 °C to 500 °C also showed nucleation and growth of crystals, but the films were more continuous. In this latter range, higher temperatures again showed higher mobility on the SiO_2 surface forming semi-continuous thin films as low as 440 °C, while temperatures below 440 °C produced continuous crystalline thin films.

A summary of the annealing results is shown in Table 1. There were no electron back-scattered diffraction patterns observed with temperatures lower than 400 °C with the use of the SEM. However, work with a FEI Technai F20 (200 kV field-emission) transmission electron microscope (TEM) shows nano-crystallites beginning to form for anneals as low as 350 °C.

3. Sample characterization through electron back-scattered diffraction

The annealed samples were identified and differentiated using electron back-scatter diffraction. The EBSD system consisted of a TSL/OIM detector with a 1024 by 1024 pixel CCD camera. The patterns acquired by the CCD are automatically indexed with the OIM software (TSL OIM Data Collection V. 4.6). The EBSD patterns corresponding to the crystal structures of different vanadium oxides (VO, V_2O_3, VO_2 monoclinic, VO_2 tetragonal, V_2O_5) were calculated by the OIM software from the material's known structural parameters. Differentiation among the different vanadium oxides was initially performed as a test of this technique. Commercial powder samples of VO_2 and V_2O_5, obtained from Alfa Aesar, were used as control samples. EBSD patterns were acquired from these control samples and compared to calculated patterns. The OIM software correctly indexed and identified the structures for the commercial powders. This was performed to verify that the patterns calculated from the known materials' structures would match those patterns acquired from the actual samples.

Using a scanning electron microscope, with an accelerating voltage of 25 kV, and a 70° incident angle, EBSD patterns were obtained from the individual particles and thin films produced from the annealed samples described above. A representative EBSD pattern obtained from the films is shown in Fig. 3A. The diffuse bands shown in the pattern indicate the crystallinity of the spot being probed and the symmetry of those bands reveal the structure and orientation of the crystal. The degraded aspect of the EBSD pattern shown in Fig. 3A can be attributed to the low signal to noise ratio from probing a small grain (approximately 300 nm long, and 60 nm deep), and with it, associated problems such as grain boundaries, twinning, sub-grain boundaries, and other various strains in the lattice [32–34]. It was observed that the monoclinic and tetragonal EBSD patterns are too symmetrically similar for the software to distinguish between them. Fig. 3B–D shows the same diffraction pattern overlaid with the calculated patterns from the tetragonal and two (M1 and M3 structures) of the monoclinic phases of vanadium dioxide. As observed from Fig. 3a–d, the bands shown in the acquired EBSD pattern are present in all three phases (tetragonal, M1, and M3) of VO_2.

The locations of the calculated bands, their widths, and the angles between these three phases of VO_2, are too close to the acquired EBSD pattern that the OIM software cannot accurately differentiate among