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Influence of deposition process and substrate on the phase transition of vanadium dioxide thin films

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Abstract—The abrupt changes in structural, electronic and optical properties that accompany the vanadium dioxide (VO_2) phase transition make it a promising material for a wide range of thin-film applications in electronics,photonics and plasmonics. Several physical vapor-deposition techniques are used by various research groups, but until now there has been no systematic comparison of the three most common methods – electron beam evaporation, pulsed-laser deposition and sputtering – covering the most common substrates. Here we explore the influence of substrate, deposition process and annealing time at 450 °C on the phase transition properties and morphology of thin VO_2 films. Films deposited by rf magnetron sputtering have the same structure on glass, silicon and sapphire substrates and are stable for 90 min of annealing. In contrast, the structure of films deposited by electron beam evaporation and pulsed laser deposition depends heavily on the substrate. Dewetting plays a prominent role in the evolution of film structure and the phase transition properties for films deposited on silicon and glass are unstable for 90 min annealing. The epitaxial relationship between VO_2 and sapphire stabilizes the phase transition contrast for all deposition processes and annealing times. Performance as measured by switching contrast is maximized for all deposition processes with 10 min of annealing.

Keywords: Vanadium dioxide; Pulsed laser deposition; Rf magnetron sputtering; Electron beam evaporation; Solid phase crystallization

1. Introduction

Vanadium dioxide (VO_2) is under active consideration world-wide for applications that range from large-area window coatings [1] to nanometer-scale plasmonics devices [2] and oxide electronics [3]. The metal-to-insulator transition (MIT) of VO_2 is the key property that makes this material technologically attractive. The phase transition in bulk single crystals occurs at 67 °C from the low temperature $P2_1/C$ [4] monoclinic phase to the high temperature $P4_2/mnm$ [5] rutile phase. The transition may be triggered thermally [6], optically by hole doping [7–10] or photoelectron injection [11], by strain [12] and by DC electric field [13], although the role of Joule heating in the last case is still under investigation [14]. The electronic and structural phase transitions are accompanied by a large change in electrical and optical properties: resistivity in high-quality single crystals [15] changes by five orders of magnitude, while the index of refraction at 1.5 μm changes by a factor of two [16], resulting in the optical hysteresis shown in Fig. 1A.

The abrupt change in optical, electrical and structural properties makes VO_2 interesting for a wide range of applications. For example, the ultrafast change in optical properties has prompted the development of silicon-based optical modulators [17–19], in which a patch of VO_2 is deposited in contact with an optical waveguide and used to modulate light propagation. The expansion of the unit cell along the *c*-axis that accompanies the structural phase transition has recently been employed to construct high-speed mechanical micromanipulators [20,21]. The integration of phase change materials (such as VO_2) with plasmonics and metamaterials will add indispensable functionality for device technologies [2,22].

The wide variety of VO_2 applications requires knowledge of film behavior on a variety of substrates, for different film thicknesses and across multiple deposition processes. However, to date there has been no systematic comparison of the influence of substrate and deposition process on VO_2 optical performance and morphology. Morphology, defects and strain are known to be critical for tuning the phase

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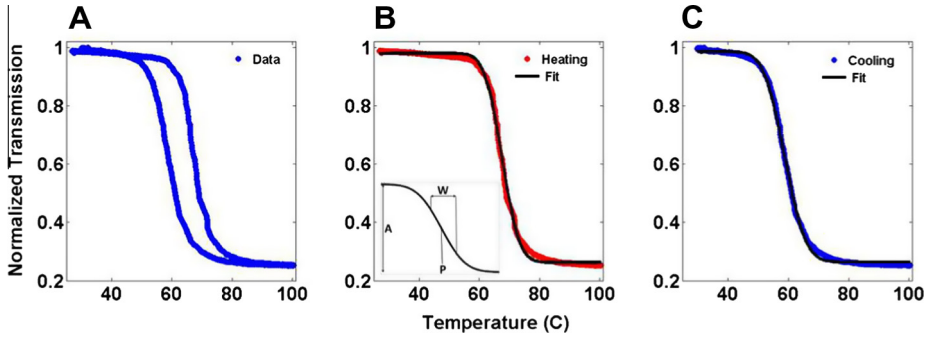

Fig. 1. (A) Optical hysteresis curve for VO_2 thin film (deposited by PLD on glass and annealed for five minutes) measured in transmission at 1550 nm. (B) Heating curve with sigmoidal fit and inset illustrating fit parameters. (C) Cooling curve with sigmoidal fit.

transition [23,24,12,25–28], highlighting the importance of understanding the influence of the substrate and deposition process.

In this paper we show how the film morphology and optical performance evolve as a function of annealing time for films deposited by pulsed laser deposition (PLD), electron beam evaporation and rf magnetron sputtering. In contrast to many other processes which deposit VO_2 at elevated temperature [29,23,30,31], we use post-deposition annealing to crystallize films deposited at room temperature, which makes this process compatible with PMMA based lithography and uses the lowest annealing temperature and shortest annealing time possible; for epitaxial thin films on sapphire, low-temperature growth produces higher quality films [32]. Our results show that grain growth in films deposited by rf magnetron sputtering is dominated by deposition-induced strain. In contrast, dewetting plays a critical role in the evolution of film morphology when films are deposited by pulsed laser deposition or electron beam evaporation. The importance of lattice matching between the VO_2 film and sapphire is evident, in that films deposited by all three techniques on sapphire remain stable even during prolonged annealing.

2. Experimental

2.1. Substrates

Amorphous VO_x films were deposited on three substrates: silicon (100) with an approximately 15 Å thick native oxide layer (as measured by ellipsometry), sapphire (0001) and glass; more detailed information is provided in Table 1.

2.2. Deposition processes

The deposition parameters for each physical vapor deposition (PVD) process were tuned such that the deposited film had the required 1:2 vanadium to oxygen atom stoichiometry, as verified by Rutherford backscattering spectrometry (RBS). All films were deposited at room temperature, as measured by a thermocouple in contact with the substrate holder and were deposited in a single run for each process type, eliminating run-to-run variations. As-deposited film thickness was confirmed using shadow mask lithography and a Dektak profilometer; all samples were determined to be 90 ± 5 nm thick. For X-ray reflectivity measurements, large (4 cm × 4 cm) substrates were required and deposited separately. Table 2 compares the deposition processes.

Pulsed-laser deposition was implemented in a Epion PLD-3000 system with a Lambda Physik (Coherernt COMPex) excimer laser operating at 248 nm (KrF), 4 J/cm^2 per pulse, 25 Hz repetition rate and 25 ns pulse duration. Prior to deposition the chamber was pumped down to 9×10^{-7} Torr. Ablation of a pure vanadium metal target was performed in ultra-high purity oxygen environment at 1.1×10^{-2} Torr with 2 sccm flow. The laser beam was rastered across the rotating target, while the substrate holder, located 8 cm above the target, also rotated. The average deposition rate was 0.3 Å/s.

An Ångstrom Engineering Inc. deposition system was used for rf magnetron sputtering and electron beam evaporation; both depositions were carried out in the same vacuum chamber. For sputtering, a 5 cm diameter vanadium metal target was sputtered at 270 W, 6.0×10^{-3} Torr pressure, 20 sccm Ar and 1 sccm O_2. The chamber was conditioned under these parameters for 45 min prior to opening the sample shutter and beginning deposition. The deposition rate remained constant at 1 Å/s, as measured by quartz crystal microbalance. Electron beam evaporation was carried out at 5×10^{-6} Torr. The electron beam was rastered across the VO_2 powder precursor (Materion) while increasing the power until the evaporation rate stabilized at 1 Å/s, at which point the sample shutter was opened and the deposition initiated.

2.3. Annealing

The deposited films were annealed in sets of nine (three substrates and three deposition processes) inside a tube furnace for 2,5,10,30 and 90 min at 450 °C. The tube was pumped down to ~1 mTorr before annealing at 250 mTorr O_2. After annealing for the specified time, the samples were moved out of the heated zone and allowed to cool in the tube before exposing them to ambient conditions. The labeling scheme used to identify the 45 different samples produced in this work is presented in Table 3. Without annealing films do not exhibit a phase transition.

2.4. Rutherford backscattering spectrometry

The stoichiometry of the as-deposited films was measured by Rutherford backscattering spectrometry (RBS) using a NEC 6SDH pelletron accelerator equipped with