

Oxidation State Discrimination in the Atomic Layer Deposition of Vanadium Oxides

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Tunable control over the oxidation state of transition metal oxides (or sulfides) remains a significant challenge in ALD. Traditionally, the oxidation state of the metal precursor or strength of oxidant dictates the final oxidation state of the metal, and stoichiometry of elements, in the resulting film. In this work, a single vanadium 3⁺ precursor performs self-limiting growth of thin films that span common oxidation states of vanadium, 3⁺, 4⁺, and 5⁺. ALD of V₂O₃, VO₂, and V₂O₅ are realized via *four* distinct reaction mechanisms accessed at the same temperature by judicious choice of oxygen sources and co-reactants. Saturation behavior in all cases, the O₃, H₂O₂, H₂O/O₂, and H₂O₂/H₂ processes, is observed by *in situ* quartz crystal microbalance (QCM) and surface chemistry is studied with quadrupole mass spectrometry. As expected O₃ oxidizes vanadium fully to the 5⁺ state to grow crystalline V₂O₅. Growth with O₂ has not observed and self-termination with H₂O occurs after less than 250 cycles corresponding to film growth of ~ 5 nm as measured by spectroscopic ellipsometry. When H₂O and O₂ are introduced in sequence, synergistic growth of amorphous V₂O₅ occurs. In this synergistic process, a clear distinction between non-oxidative protic ligand exchange, the H₂O reaction, and metal oxidation, the O₂ reaction, is demonstrated in either reaction order. In addition, it is apparent from these results that this vanadium precursor requires an oxidation mechanism in sustained ALD film growth.

In an extension of this approach, we can produce films with the intermediate vanadium 4⁺ oxidation state, VO₂, through reducing equivalents – H₂ gas. In traditional A/B-type ALD, H₂O₂ produces an amorphous mixed 4⁺/5⁺ oxide that is easily reduced to vanadium 3⁺ oxide, V₂O₃, or oxidized to vanadium 5⁺ oxide, V₂O₅, by varying the atmosphere of a low temperature anneal. Phase pure VO₂ is not readily accessible. When H₂ is dosed after H₂O₂ during growth, amorphous films of VO₂ are grown that can be crystallized with a low temperature, 350 °C, anneal. These VO₂ films show the characteristic temperature dependent Raman spectroscopy response in the expected temperature range, Figure 1, of the well-known insulator to metal transition (IMT) for VO₂. Conformal films of VO₂ were grown on indium-tin oxide (ITO) nanorods in this method, Figure 1, in order to modify the phonon response of the ITO nanorods. A distinct blue-shift of the wavelength of all absorption spectral features above the IMT transition temperature is observed and can be modulated through VO₂ film thickness.

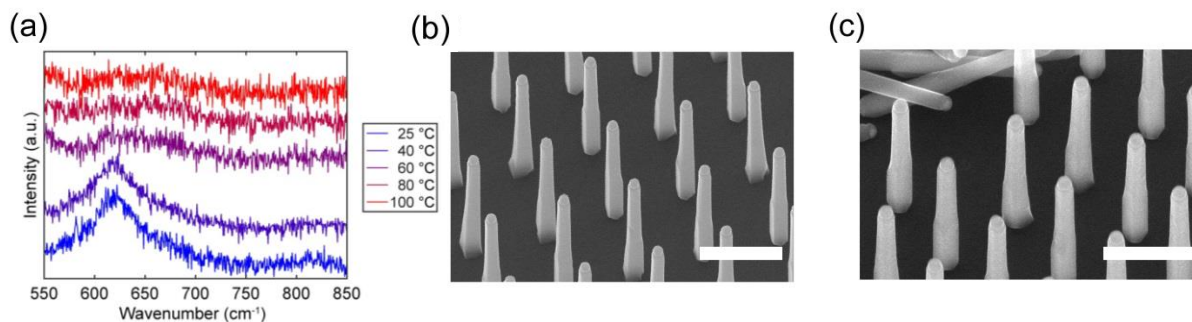


Figure 1. (a) Temperature dependent Raman spectroscopic (473 nm laser) data taken from 25 to 100 °C for a 12.5 nm VO₂ films grown on native oxide Si at 200 °C. (b) SEM image of uncoated indium-tin oxide (ITO) nanorods and (c) SEM image of ITO nanorods coated with 12.5 nm of ALD VO₂ film. Scale bars are 1 μm in (b) and (c).