METAL–SEMICONDUCTOR TRANSITIONS IN NANOSCALE VANADIUM DIOXIDE—THIN FILMS, SUBWAVELENGTH HOLES, AND NANOPARTICLES

By

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APPENDIX A

VANADIUM SESQUIOXIDE (V_2O_3) THIN FILMS

Abstract

The following information is meant to provide some measure of continuity in our effort to make another material that undergoes a spectacular metal-insulator phase transition: vanadium sesquioxide, V_2O_3. A simple fabrication protocol is presented, along with some of the characterization data used to establish it. The two main steps are: **(i)** room-temperature PLD of amorphous V_xO_y with excess oxygen content, followed by **(ii)** high-temperature annealing in a reducing atmosphere and crystallization to stoichiometric V_2O_3.

1.1 Introduction

V_2O_3 is the other famous oxide of vanadium. First discovered by Föex in 1946, vanadium sesquioxide undergoes a metal-to-insulator transition upon cooling and the reverse transition upon heating through $T_c \approx 150$ K, accompanied by magnetic and crystallographic changes: at room temperature V_2O_3 is a paramagnetic metal with a rhombohedral (corundum) lattice, while the low-temperature phase is an antiferromagnetic monoclinic insulator with a 0.6-eV bandgap.[210] Resistivity jumps by up to 6–7 orders of magnitude,[21,211] infrared (IR) transmission also increases,[212–215] and the first-order nature of the transition gives rise to hysteresis. The V_2O_3 phase transition has long been regarded as a model for the Mott-Hubbard transition mechanism[59,210,216,217] (see also Section 1.1.3), with the monoclinic lattice distortion thought to originate simply from magnetostrictive forces[63] due to the peculiar magnetic ordering[23] below T_c. Unlike the structural transition of VO_2, the change in crystal structure of V_2O_3 is *not* associated with a Peierls instability and unit-cell doubling.[59] However, recent X-ray absorption measurements[218] of the temperature depen-

dence of the local structure have identified a structural *precursor* to the metal-to-insulator transition of V_2O_3, namely a continuous increase in the monoclinic tilt starting well before the onset of the electronic and magnetic transition. These findings suggest that it may be the orbital degrees of freedom that drive the metal-to-insulator transition via changes in hybridization, which are in turn triggered by the monoclinic distortion.[218] Here too, as in the case of VO_2, the web of cause-and-effect links in the transition mechanism of V_2O_3 is yet to be untangled.

Studies devoted to bulk single crystals or thin films of V_2O_3 abound in the scientific literature: according to Imada *et al.*,[23] more than 500 papers on V_2O_3 had been published as of 1998. Yet only a handful of articles[219–225] deal with nanocrystalline V_2O_3—all reporting exclusively on chemical synthesis and/or catalysis; I know of no studies on the phase transition of V_2O_3 nanoparticles (NPs). Observation of the optical switching of V_2O_3 NPs would be more than a scientific "first". Studying nanostructures of another system that behaves like VO_2 in terms of optical changes across the phase transition, and yet differs from VO_2 as regards the roles of the various degrees of freedom involved, can only improve our understanding of how one solid-state phase transforms into another at the nanoscale. In particular, experimental data from "switchable" V_2O_3 NPs would provide a new set of benchmarks for testing the "potent defect" model (see Section 1.3) of the microscopic origins of such solid-solid transformations.

1.2 A V_2O_3 "recipe"

The following deposition and annealing steps were found to yield good-quality V_2O_3 films (∼100 nm) on fused-silica substrates:

• Clean substrate: solvents (TCE, acetone, methanol/IPA, deionized water) and/or UV-ozone treatment.

• Deposit amorphous V_xO_y ($y/x \geq 1.5$) film by room-temperature PLD: V-metal or V_2O_3 pressed-powder target; 300-mJ pulses focused to ~ 0.1 cm^2 on target surface; 15-cm target-

to-substrate distance; 3–5 mtorr O_2.

• Reduce and crystallize deposited film by annealing in tube furnace, *one sample at a time*: **(i)** introduce 1 atm of flowing {4% H_2 + 96% Ar} into vacuum-tight quartz tube, pre-evacuated to 1–5 mtorr (use oil filter with the roughing pump); **(ii)** ramp up furnace temperature to 600 °C at 30 °C/min; **(iii)** dwell at 600 °C for 60 min; **(iv)** turn off heaters and let system cool down to (near) room temperature under flowing gas mix.

When viewed in transmission against white light, a "switchable" V_2O_3 film should look some shade of grey, depending on thickness, but without a tinge of green, brown, or yellow. The acid test, as it were, for good-quality V_2O_3 material is the optical switching in the vicinity of 150 K: sharpness, contrast, and hysteresis of the IR transmission across the metal-insulator transition. The transmission setup used here comprises: **(i)** fiber-coupled light source, either an IR laser at $\lambda = 1330$ nm or a white-light tungsten-halogen lamp; **(ii)** mechanical chopper connected to a lock-in amplifier through a frequency generator; **(iii)** beamsplitter and CDD camera for visual inspection of the interrogated area via reflected and scattered light from the sample surface; **(iv)** one focusing and one collection low-magnification micro-objectives, with the sample in-between; **(v)** pinhole aperture (∼0.5 mm) for stray-light rejection; **(vi)** InGaAs IR detector with responsivity (amp/watt) greater than 10 % for $\lambda = 800$–1700 nm; **(vii)** lock-in amplifier, with input signals from the chopper and the detector, and output of amplified and filtered DC signal proportional to the intensity of the transmitted light. The sample is mounted on a thin copper plate in contact with the heating/cooling pad of a micro-refrigerator assembly, which cools on the principle of expansion of highly pressurized dry N_2 gas inside a series of micrometer-sized capillaries (Joule-Thomson effect) and heats by means of a resistor coil. The assembly is housed in a small optical chamber, continuously pumped to maintain roughing vacuum. The sample temperature is scanned and maintained (±0.05 K) using a controller unit, which supplies power to the resistive heater based on the feedback from a temperature sensor under the heating plate.

1.3 Different annealing temperatures

The first three figures show the effect of annealing temperature on the IR transmission (Figures A.1 and A.3) and X-ray diffraction (XRD) (Figure A.2) of two sets of initially amorphous V_xO_y films on fused-silica (SiO_2) substrates. Upon visual inspection of these data, 600 °C was chosen for further experiments based on somewhat subjective criteria: **(i)** it is at the lower end of the temperature window that yielded films with "good switching", hence reducing the possibility that the (eventual) closely-spaced V_xO_y NPs would diffuse towards one another and coalesce during the anneal; **(ii)** unlike the 925-°C or 850-°C films, the film annealed at 600 °C has (nearly) completed its transition into the insulating state by the lowest measured temperature (85 K); **(iii)** switching contrast is larger for the 65-nm-thick 600-°C film than for its 700-°C counterpart; **(iv)** 600 °C has been popular processing temperature in previous V_2O_3 studies.[212–214]

1.4 Different annealing times and ramp rates

The interesting curve in Figure A.4 is the one for slow ramp-up (3 °C/min) to the final annealing temperature of 600 °C. That particular film likely became sub-stoichiometric ($V_2O_{y<3}$) before it had had a chance to crystallize into V_2O_3. A ramp-up rate of 30 °C/min and a dwell time of 1 hr were chosen for subsequent anneals, since dwell times of 0–4 hr had all produced switchable V_2O_3 films (Figures A.1 and A.4).

1.5 Different PLD target materials

Heeding an apropos observation by Schuler *et al.*[213] that V_2O_3 films grown by reactive e-beam evaporation from a V-metal target or from a sintered V_2O_3 powder exhibited "a drastic difference in quality", the former being the better, we performed depositions from four different PLD targets: V-metal disc from Cerac, inc. (http://www.cerac.com) and pressed-powder discs with nominal compositions of V_2O_3, VO_2, and V_2O_5 from Vin Karola Instruments (http://www.vinkarola.com). While the V and V_2O_3 targets did produce films

with steeper transmission hystereses than those from the other two targets, the differences in quality were hardly drastic (see Figure A.8).

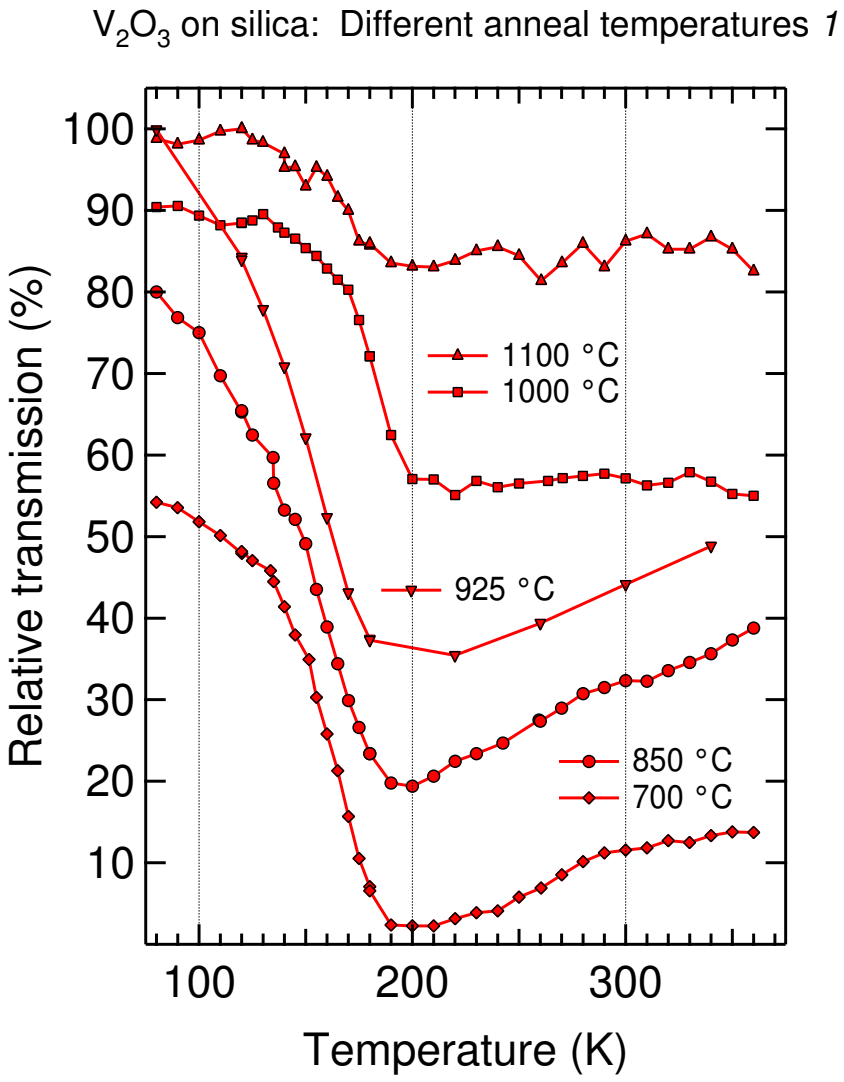

Figure A.1: Relative IR transmission as a function of temperature (heating part of hysteresis cycle) for 140-nm-thick V_2O_3 films on fused silica, H_2-annealed at the indicated temperatures: 1100, 1000, 925, 850, 700 °C. Dwell times: 2 hr, except for the 925-°C film, which was annealed for 4 hr. Illumination sources: white-light lamp for the 925-°C film, and IR laser (λ = 1330 nm) for the rest. The data for each film are normalized to the highest transmission in the low-temperature phase; the curves are offset vertically relative to one another for clarity.

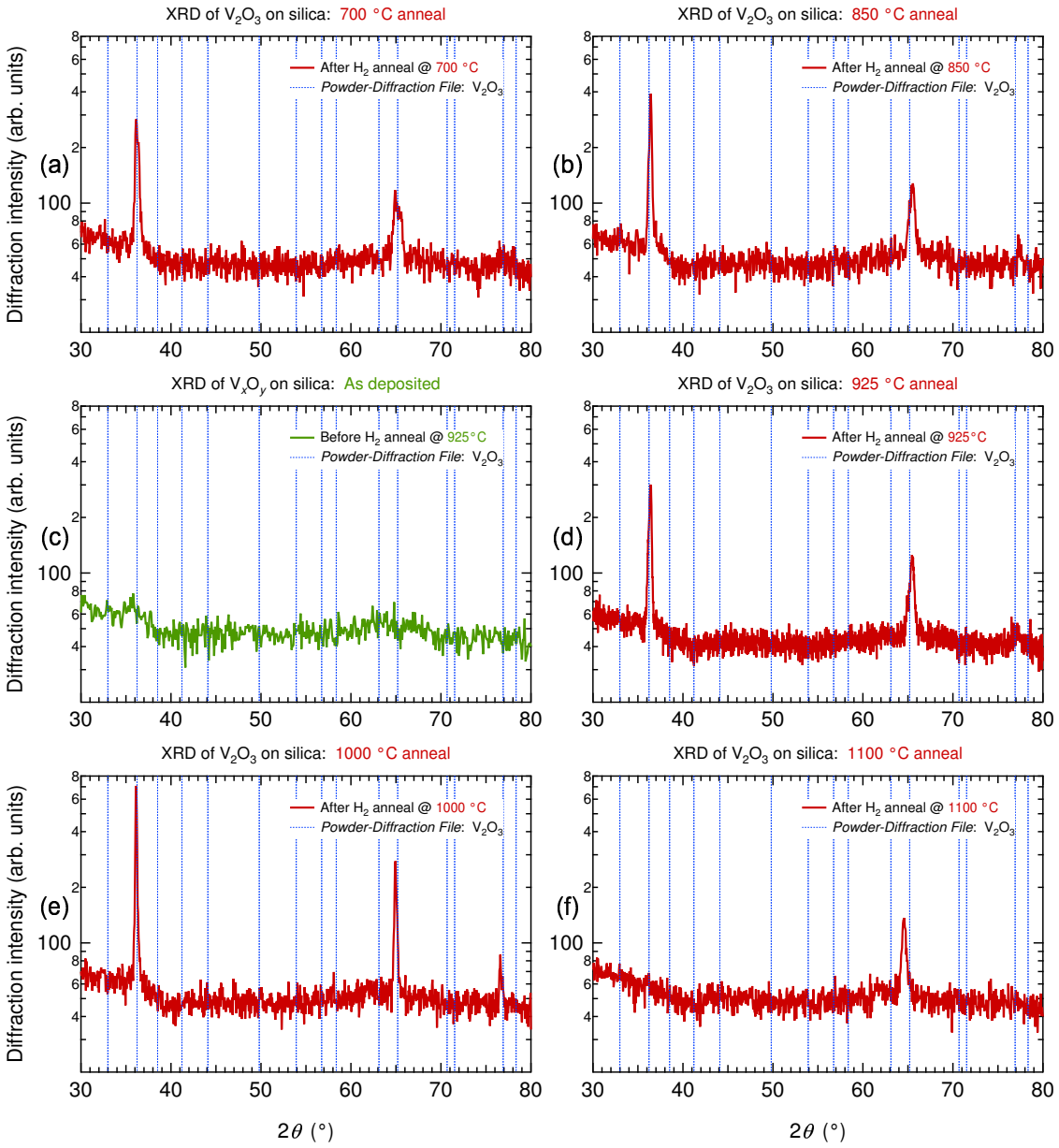

Figure A.2: Room-temperature X-ray diffraction (XRD) θ–2θ scans (Cu–K_α, $\lambda = 1.54$ Å), for the above 140-nm-thick V_2O_3 films on fused silica, H_2-annealed at the indicated temperatures: **(a)** 700 °C; **(b)** 850 °C; **(d)** 925 °C; **(e)** 1000 °C; **(f)** 1100 °C. Part **(c)** shows the XRD scan for the film in **(d)** as deposited, *i.e.*, before annealing at 925 °C. Peaks at the powder-diffraction values (PDF #34-0187) of $2\theta = 36.23°$, $65.193°$, and $76.914°$ correspond to reflections from V_2O_3 planes (1 1 0), (3 0 0), and (2 2 0), respectively.

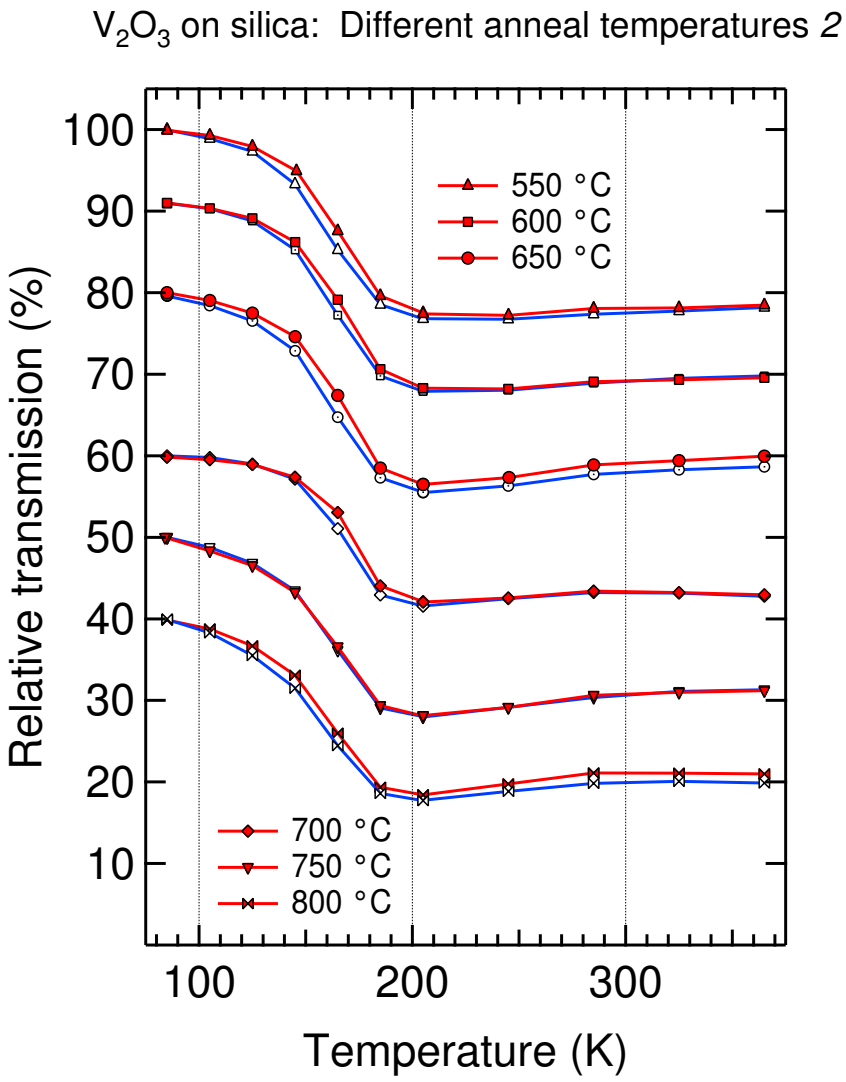

Figure A.3: Relative IR transmission as a function of temperature for 65-nm-thick V_2O_3 films, H_2-annealed at the indicated temperatures: 550, 600, 650, 700, 750, 800 °C. Dwell time: 1 hr. Illumination: white-light lamp. Data for each film are normalized to the highest transmission in the low-temperature phase; the curves are offset vertically relative to one another for clarity. Filled symbols (red lines) correspond to the heating part of the hysteresis cycle, and open symbols (blue lines) to the cooling part.

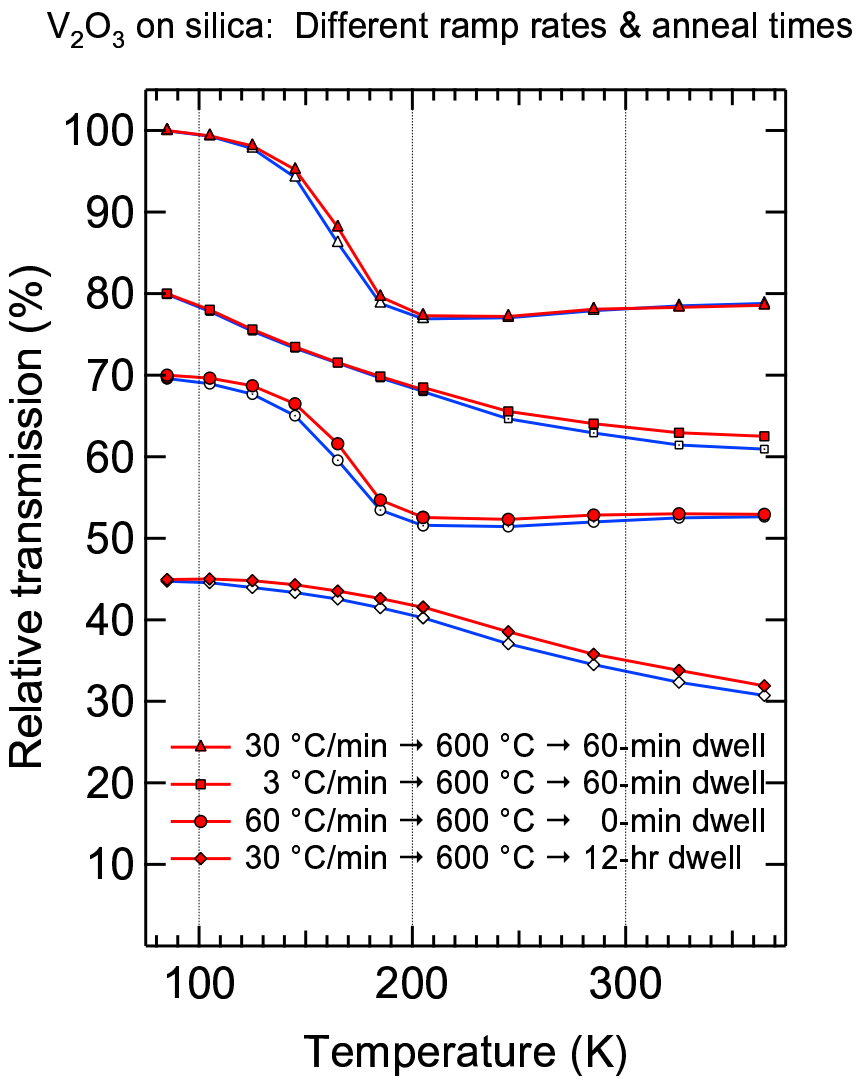

Figure A.4: Relative IR transmission as a function of temperature for 65-nm-thick V_2O_3 films (from the same initial batch as the films in Figure A.3), H_2-annealed by ramping up the temperature to 600 °C at the indicated rates and holding it constant thereafter for the indicated dwell times. Illumination source: white-light lamp. Data for each film are normalized to the highest transmission in the low-temperature phase; the curves are offset vertically relative to one another for clarity. Filled symbols (red lines) correspond to the heating part of the hysteresis cycle, and open symbols (blue lines) to the cooling part.

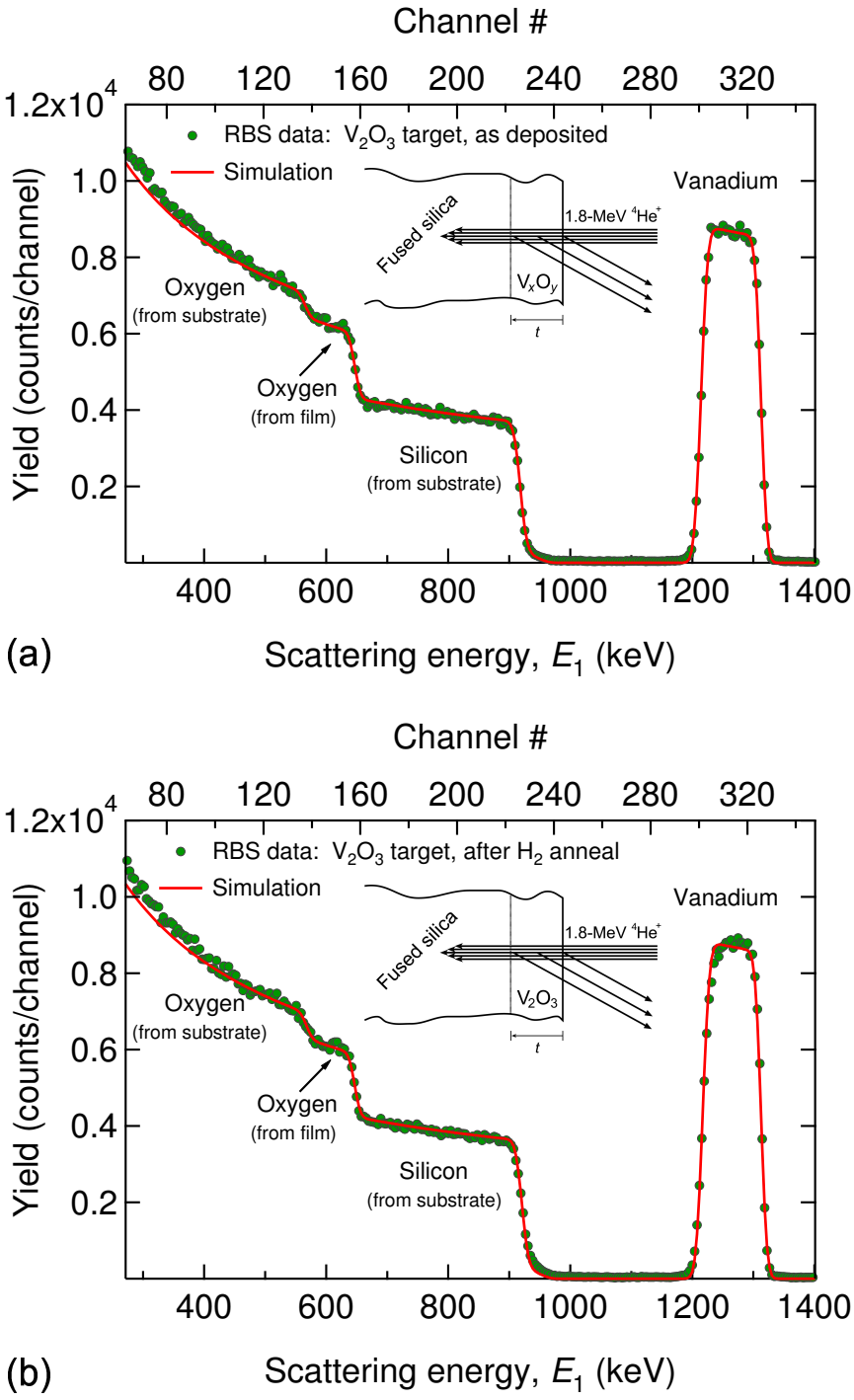

Figure A.5: Example of experimental (circles) and simulated (lines) RBS spectra for vanadium-oxide film on fused-silica (SiO_2) substrate: **(a)** before H_2 anneal (*i.e.*, as deposited); **(b)** after H_2 anneal for 1 hr at 600 °C. The film was grown by room-temperature PLD from a V_2O_3 target in 3 mtorr O_2 background gas. Simulations were performed using the SIMNRA program.[107] *Analysis*: **(a)** $V_2O_{3.12\pm0.01}$, $t \approx 101$ nm; **(b)** $V_2O_{3.03\pm0.01}$, $t \approx 99$ nm.

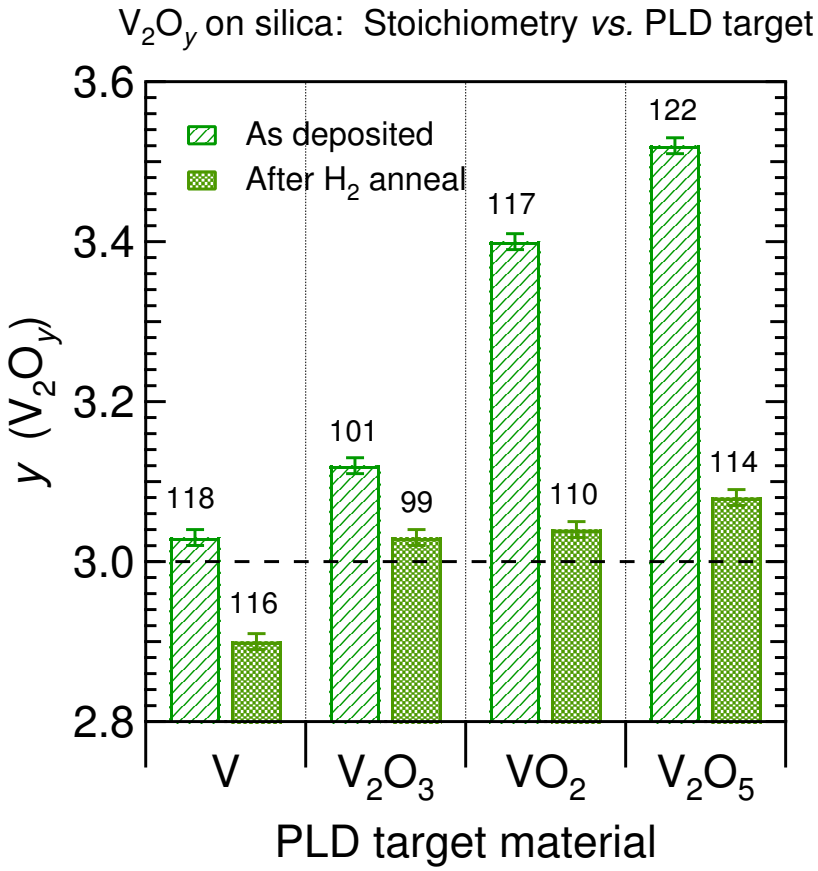

Figure A.6: RBS-measured stoichiometry (see example in Figure A.5), before and after H_2 anneal (1 hr at 600 °C), for vanadium-oxide films deposited from V-metal (in 3 mtorr O_2), V_2O_3 (in 3 mtorr O_2), VO_2 (in vacuum), and V_2O_5 (in vacuum) PLD targets. The number above each bar denotes the thickness in nanometers.

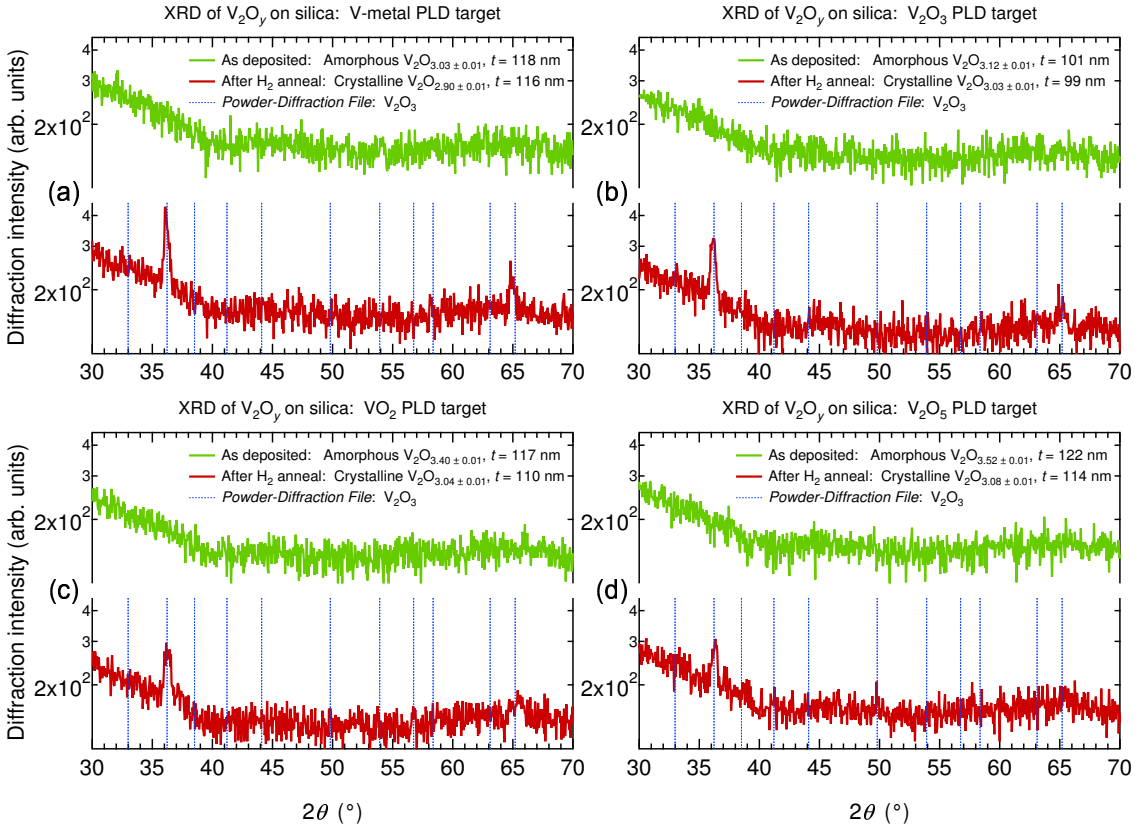

Figure A.7: Room-temperature XRD scans (Cu–K_α, $\lambda = 1.54$ Å), before and after H_2 anneal (1 hr at 600 °C), for vanadium-oxide films deposited from **(a)** V-metal (in 3 mtorr O_2), **(b)** V_2O_3 (in 3 mtorr O_2), **(c)** VO_2 (in vacuum), and **(d)** V_2O_5 (in vacuum) PLD targets. Peaks at the powder-diffraction values (PDF #34-0187) of $2\theta = 36.23°$ and 65.193° correspond to reflections from V_2O_3 planes (1 1 0) and (3 0 0), respectively.

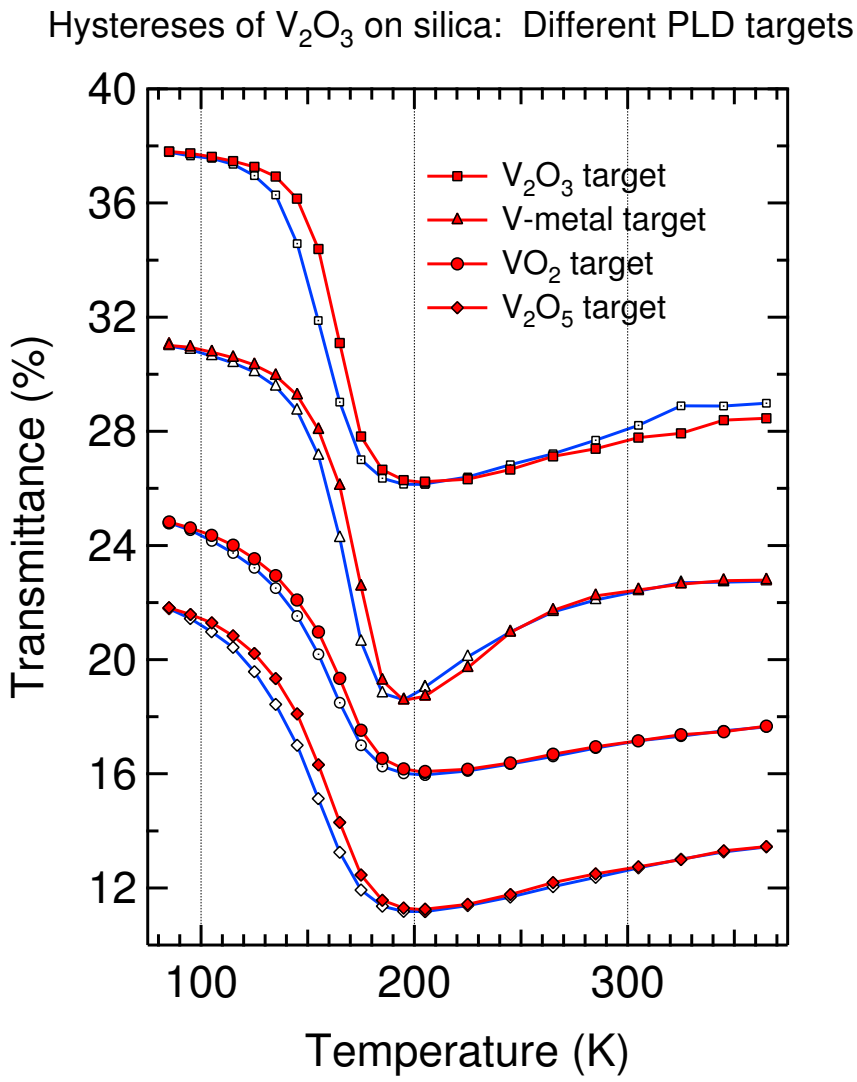

Figure A.8: Optical transmittance for H_2-annealed V_2O_3 films deposited from different PLD target materials. Anneal: 1 hr at 600 °C. Illumination source: white-light lamp. Data for each film are normalized at each temperature point to transmission through the bare fused-silica substrate; the curves are offset vertically relative to one another for clarity. Filled symbols (red lines) correspond to the heating part of the hysteresis cycle, and open symbols (blue lines) to the cooling part.

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