First publ. in: Applied Physics Letters 91 (2007), 091907

Transmission increase upon switching of VO_2 thin films on microstructured surfaces

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The authors compare transmission measurements of near-infrared light through VO_2 thin films on smooth substrates and on ordered arrays of silica microspheres. When the samples are heated above the critical temperature for the semiconductor-metallic phase transition, smooth thin films show reduced transmission independent of thickness; however, the VO_2 film deposited on the microspheres may show either reduced or enhanced transmission, depending on VO_2 film thickness. They show that this at a first glance, unexpected behavior is directly related to the change of scattering efficiency upon the phase transition. This suggests that optical transmission through thin-film microstructures could be tuned by an appropriate combination of microsphere ordering and VO_2 film thickness.

Vanadium dioxide is one of the most-studied transition metal oxides due to its reversible thermochromism, evident in a semiconductor-to-metal phase transition (SMPT) occurring at a critical temperature T_c of 68 °C.[1–3] The electrical properties of the oxide change markedly upon completion of the structural SMPT; near-to midinfrared transmission through VO_2 films likewise decreases dramatically in the metallic state. Moreover, the SMPT can be induced by a pulsed laser on picosecond time scales.[4] Optical switching in VO_2 has extensively been studied in thin films,[5] nanoparticles,[6] nanoparticle arrays,[7] and subwavelength nanohole arrays.[8] However, relatively little attention has been paid to thin-film micro-or nanostructures of VO_2, even though optically switchable nanostructures are attractive for photonic applications. In this letter, we use transmission measurements through VO_2 thin films and thin films deposited on ordered arrays of spherical silica (SiO_2) microspheres to show how the zeroth-order ("straight through") transmission can be altered by substrate microstructure.

The microstructured thin-film samples were prepared in two steps. First, drops of colloidal solutions of SiO_2 particles with a diameter of 1.54 μm were deposited by micropipette onto clean glass substrates under ambient conditions. Upon evaporation of the solvent, compact structures including monolayers of hexagonal-close-packed (hcp) silica microspheres formed on parts of the substrates.[9–12] Next, thin films of VO_2 were deposited on the microsphere arrays by pulsed laser deposition followed by thermal oxidation at 450 °C,[13] to create samples like those shown schematically in Fig. 1. The hcp microspheres covered only part of the substrate, so that each sample had a region of unstructured film for comparative study. The two samples tested differed only in thickness with samples 1 and 2 capped by 100 and 140 nm thick VO_2 films, respectively.

In our preparation, the VO_2 film is expected to be equally thick on the bare glass area and near the center of the microspheres, but film thickness decreases at increasing angles θ with respect to the deposition axis.[14] The switching behavior of witness samples prepared at the time of deposition was confirmed using a diode laser at 980 nm, while the stoichiometry was verified using Rutherford backscattering spectrometry.

The oxide layers were switched either by resistive heating of the substrate holder or by a Nd:YAG (yttrium aluminum garnet) laser at 532 nm wavelength. The Nd:YAG laser had a circular beam spot about 5 mm in diameter, its pulse duration was 10 ns, and the fluence of the heating pulse was of the order of 10 mJ/cm^2. The optical transmission was measured using a 980 nm laser diode with a Gaussian spatial profile, beam radius of approximately 1 mm, and power less than 10 mW. As shown in Fig. 1, the beams were incident on the sample perpendicular to the glass substrate and were adjusted to be collinear with the probe beam centered on the

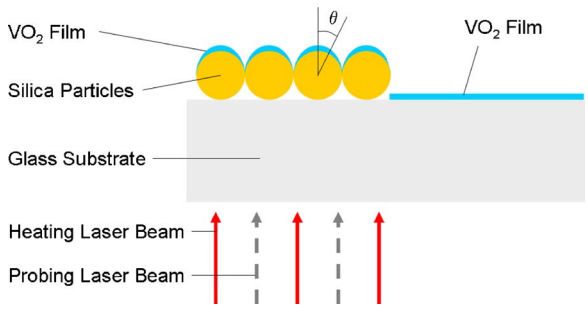

FIG. 1. (Color online) Schematic diagram of the samples used in the study: plane VO_2 thin films deposited on the bare substrate and thin films deposited on colloidal microspheres of fused silica.

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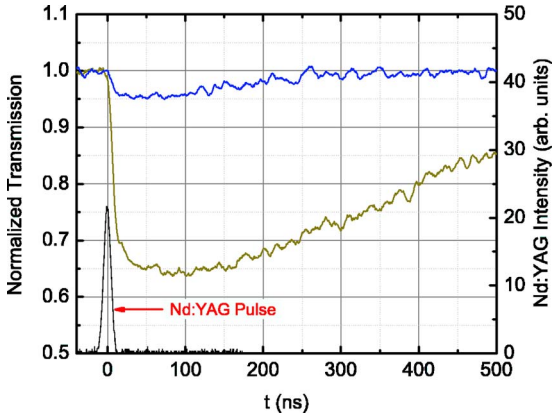

FIG. 2. (Color online) Normalized transmission through VO_2 bulk films as a function of time at 980 nm. The upper curve represents the transmission through 100 nm thick film (sample 1); the lower curve is for the 140 nm thick film (sample 2).

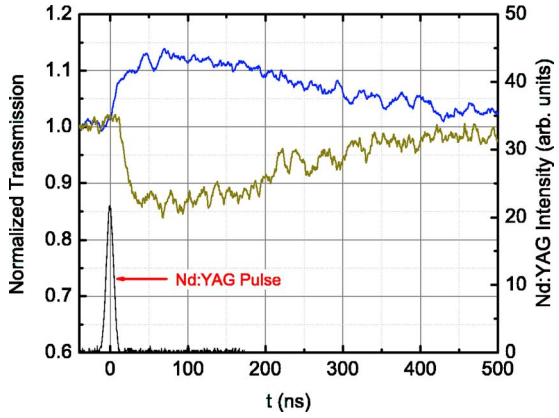

FIG. 3. (Color online) Normalized transmissions through VO_2 films deposited on 1.54 μm silica particles as a function of time at 980 nm. The upper curve represents the transmission through 100 nm thick film (sample 1); the lower curve is for the 140 nm thick film (sample 2).

heating beam. Sample heating by the probe beam was found to be negligible. Filters and polarizers in front of the photodiode blocked the Nd:YAG beam in order to prevent any contribution of the Nd:YAG light to the transmission signal. The data were saved in a fast digital oscilloscope, transferred to a computer, and subsequently normalized by the transmitted intensities in the semiconducting state.

In Fig. 2, we show the time-resolved normalized transmission measurements through VO_2 thin films on the two samples. When the Nd:YAG pulse was used to initiate the SMPT in the samples, the 980 nm probe beam experienced a transient decrease in transmission. The upper curve in the figure represents the transmission change through the bulk film on sample 1, while the lower curve is for the bulk film on sample 2. As expected from the optical constants, the decrease is larger for the case of the 140 nm thick film. After cooling, the transmission of both samples returned to their original values.

The observed maximum decreases in fractional transmissions were 0.05 for sample 1 and 0.35 for sample 2. For both samples, a plateau in minimum transmission lasting about 50 ns indicates persistence in the metallic state for a brief time after the heating pulse. Recovery to the semiconducting state, as indicated by a return to the initial transmission level, occurs in about 300 ns in sample 1 and 1 μs in sample 2.

Expecting a similar behavior, we repeated the transmission measurements on thin films deposited on monolayers of 1.54 μm silica particles. The results are shown in Fig. 3. The data in the figure were again normalized by the transmitted intensities in the semiconducting state. To our surprise, we observed an *increase* in the transmitted intensity through the VO_2:silica microstructured film on sample 1. Although transmission also decreased through the microstructured VO_2:silica film on sample 2, the magnitude of the decrease was reduced from 0.35 for the bulk film down to 0.15 on the microstructures.

The increased transmission for sample 1, on first glance, seems to be inconsistent with a SMPT in which both absorption and reflectivity are enhanced in the metallic state. This unexpected behavior is partly due to the lateral ordering of the microspheres since the hcp microsphere array with a nominal interparticle distance of 1.54 μm constitutes a diffraction grating. For the probe wavelength of 980 nm, diffraction will only appear in the zeroth and first orders. To ascertain the effect of diffraction by this grating, we monitored the intensities in these two diffracted orders. Due to the polycrystallinity of the hcp colloidal monolayers, the first-order diffracted light appears not in the sixfold symmetry for crystalline monolayers, but as a ring surrounding the central bright spot. A detector subtending a solid angle corresponding to approximately one-tenth of this ring was monitored and the measured intensity was then multiplied by 10 to obtain the total first-order amplitude.

In Fig. 4, we display the intensities of the diffracted beams in zeroth and first orders as a function of the sample-holder temperature, normalized to the zeroth-order intensities at 25 °C. The temperatures were recorded while the sample holder was continuously heated starting at ambient temperature, with a dwell time of approximately 1 s at each point, and thus were not taken in equilibrium. Hysteresis curves for the metal-to-semiconductor (cooling) transition (not shown) showed mid-SMPT temperatures at 72 °C for sample 1 and 67 °C for sample 2. From Fig. 4, in the semiconducting state (at 25 °C), the first-order fractional transmissions are 0.8 and 0.6 of the zeroth order signals for samples and, respectively. Switching the VO_2:microsphere structures through the SMPT results in decreased first order intensity by a factor 1.75 in sample 1 and a factor 10 in sample 2. In the metallic state 0.75 of the intensity is in the zeroth order in sample 1

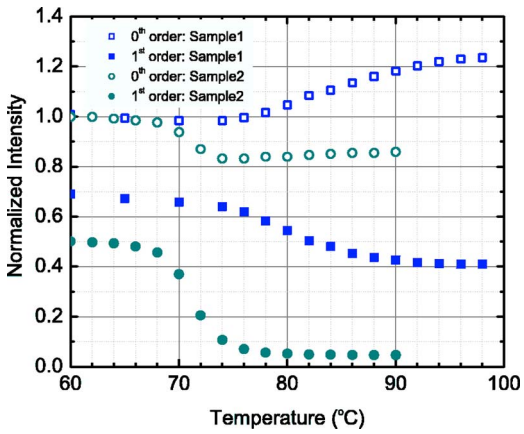

FIG. 4. (Color online) Normalized intensity of the light at 980 nm diffracted into the zeroth and first orders, for sample 1 and sample 2, as a function of sample holder temperature.

compared to 0.95 in sample 2. In fact, almost the entire decrease in first-order transmitted intensity in sample 1 appears in the increased zeroth-order signal.

In conclusion, the near-infrared optical transmission through VO_2 films deposited on a hcp array of SiO_2 microspheres shows an unexpected dependence on the thickness of the deposited oxide. The measured differences in zeroth-order transmission efficiency in both samples is explained by the interplay between the diffracted orders. The SMPT changes the refractive index and thus the diffraction efficiency of the grating, thus shifting intensity from the first-order to the zeroth-order beam. The net increase or decrease in the zeroth order depends on whether this transferred intensity is larger or smaller than the characteristic decrease in the transmission due to film thickness alone. The intensity of the first diffraction order is reduced by an order of magnitude in the thinner VO_2 film and this signal appears in the zeroth-order beam. In sample 2, on the other hand, the increased zeroth-order intensity is insufficient to compensate for the decreased transmission due to film thickness alone. Thus the combination of VO_2 films of varying thicknesses and microsphere gratings may make it possible to tune the transmission behavior of thin film micro- and nanostructures.

Two of the authors (I.K. and R.F.H.) gratefully acknowledge the support of the Alexander von Humboldt Foundation through Research Fellowship and Senior Scientist Award, respectively. Vanadium dioxide research at Vanderbilt was supported by the National Science Foundation through a Nanoscience Interdisciplinary Research Team Grant No. (DMR-0210785) and a Major Research Instrumentation Grant No. (DMR-9871234).

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