Optoelectronic and all-optical multiple memory states in vanadium dioxide

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Vanadium dioxide exhibits a well-known insulator-to-metal transition during which several of its physical properties change significantly. A hysteresis loop develops for each of them as the material is heated and then cooled through the transition. In this work VO$_2$/SiO$_2$ samples were maintained—by heat sinking—at a selected temperature within the heating branch of the hysteresis loops for resistance and near-infrared transmittance, while brief thermal excursions of the VO$_2$ film were caused by either voltage pulses applied to the film or laser light pulses irradiating the film. These pulses had durations from milliseconds to a few seconds and the resulting drops in resistance or transmittance were easily and repeatedly measurable without appreciably affecting their new values. A sequence of equal-duration pulses (for either equal-voltage or equal-irradiation pulses) caused the resistance and infrared transmittance to continue to drop, each time by a smaller amount, and larger energy pulses were required in order to cause drops comparable with the initial one. The ability of the film to change the values of the measurands in this manner with additional pulses was maintained up to a limit defined by the outer hysteresis curve for the measurand in question. The results presented show that a plurality of memory “states” in VO$_2$ can be established or “written” either by voltage pulses or by light pulses applied to the material, and queried or “read” by resistance or transmittance readings, or both. These states were found to remain stable for at least several hours, as long as temperature was kept constant, and are expected to persist indefinitely under this condition. In the all-optical case, if the same light beam is used for writing and reading the memory state, the device is an optical analog of a memristor. © 2010 American Institute of Physics. [doi:10.1063/1.3518508]

I. INTRODUCTION

Vanadium dioxide exhibits an insulator-to-metal transition (IMT) first identified over half a century ago.1 The crystal structure of VO$_2$ is tetragonal in its metallic phase (rutile type, designated R). On cooling through the IMT, this changes to a monoclinic phase (designated M$_1$) by slight reordering of the vanadium ions, which causes a doubling of the unit cell.2 This ordered structural transition is responsible for a sharp resistivity change over several orders of magnitude which displays hysteresis during heating-cooling cycles. Very recently, this hysteretic characteristic was used to implement a memristor device in which consecutive voltage pulses causes a series of successively lower resistance states.3 The memristor, a fourth passive two-terminal circuit element—which would complement the resistor, capacitor, and inductor—was postulated almost four decades ago on formal grounds,4 and later generalized to cover systems in which the internal state of the device determines its resistance, capacitance or inductance.5 Practical memristive devices capable of working as passive memories were recently proposed exploiting the hysteretic current-voltage characteristics associated with nonlinearities caused by the high electric fields possible with low voltages in nanoscale structures, and demonstrated using TiO$_2$ thin film devices.6,7

In the present work, the infrared (IR) transmittance and electrical characteristics through the IMT of VO$_2$ are utilized to demonstrate passive device operation with multiple memory states. It is shown that each of these states may be reached by applying either voltage pulses to the film itself,3 or by light pulses. This suggests that a VO$_2$-based device can work as a passive electro-optical memory which is “written” by voltage pulses and optically “read,” optically written and electrically read, or optically written and read (that is, an all-optical memory). The use of VO$_2$ as an optical switch or memory has been explored before,8 but this was limited to on-off states. The present work instead exploits the multiplicity of states which can be addressed and passively maintained within the range of the IMT, and which are associated with the fraction of material transformed from the M$_1$ to the R phase. Whether by means of electric current pulses or light pulses, energy is conveyed to the film material and transformed into heat. Some of this thermal energy becomes part of the latent heat associated with the phase change. However, latent heat absorption occurs over a temperature range in VO$_2$ because insulating and metallic phases coexist throughout the transition region. As the temperature increases within the IMT range, metallic nuclei first form and grow through out the transition region. As the temperature increases within the IMT range, metallic nuclei first form and grow through the material, and then coalesce, eventually encompassing the full volume.9 Hence, electrical conduction and IR reflectivity increase rapidly and nonlinearly as temperature increases.

Naturally, operation with multiple distinguishable states requires that the device is maintained at a constant temperature. There will be a tradeoff between temperature sensitivity

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and the number of distinguishable states. For the purposes of interest here sharp hysteresis curves and large changes between the variables of interest on each side of the IMT are desirable, which are obtainable with highly crystalline VO₂. In contrast, for bi-stable memory applications very broad hysteresis curves, such as can be achieved in nanocrystalline VO₂, are desirable to avoid temperature sensitivity.

II. EXPERIMENTAL PROCEDURES

The experiments described were performed with two different samples coated with VO₂ thin films: a SiO₂ microbridge, used for experiments in which only resistance was measured (case 1), and a flat SiO₂ glass substrate, used for experiments in which IR optical transmittance was measured (cases 2 and 3). The SiO₂ bridge was fabricated by standard lithographic techniques, and had length, width, and thickness of 200 μm, 35 μm, and 3.3 μm, respectively. The VO₂ film growth was performed by pulsed laser deposition, following a similar procedure as that described elsewhere, but with an in situ annealing for 40 min in an oxidizing atmosphere with gas flows of 15 standard cubic centimeters per minute [SCCM (SCCM denotes cubic centimeter per minute at STP)] Ar and 50 SCCM O₂ and a total pressure of 330 mTorr. Annealing temperature was 350 °C for the bridge sample and film thickness was ~120 nm. For the flat sample, annealing temperature was 425 °C and film thickness was ~210 nm. Film composition was verified by x-ray diffraction with the sample on the glass substrate or, in the case of the sample with the micro bridge, using a companion test piece coated simultaneously. Film thicknesses were measured with a Tencor Alphasstep stylus profilometer using steps prepared on the samples.

For the three experiment groups performed, a hysteresis curve was first obtained by slowly taking the sample through a heating-cooling cycle starting and ending at room temperature, while measuring the variable of interest (resistance or IR transmittance). In each subsequent experiment, the sample was first “preparing” by bringing its temperature up slowly, using the heater, from room temperature up to a preselected temperature within the transition region, and taking care not to overshoot the target temperature in order to avoid hysteretic changes. This temperature was afterwards maintained by the heater controller. The heater plus sample stage essentially acted as a heat sink at this temperature on account of its large thermal capacity in comparison with the energy of the pulses absorbed by the sample.

All experiments were performed under vacuum (~10 mTorr or less) in order to reduce convective heat losses. Two different vacuum chambers were used, one of which had two parallel optical windows to allow transmittance measurements. In both cases the substrate side of the samples was cemented with silver-filled paste to a heater integrated in a sample holder. Thermocouples were directly attached to the samples, and read by temperature controllers feeding the heaters. For the transmittance measurements the sample was cemented first to a thin copper plate with a small (4 mm diameter) circular aperture. This copper plate was cemented in turn to the heater. To allow film resistance readings and application of voltage pulses, gold wires leading to the chamber electrical feedthroughs were attached directly to the VO₂ film. For the bridge sample these were placed in each of the two bridge anchors, so that a current could be passed along the bridge. For the flat sample the wires were placed just outside the area defined by the circular aperture. The light source for the transmittance measurements with the flat sample was a continuous IR laser diode (Mistubishi ML725B8F, 1.31 μm wavelength, 10 mW rated power) with collimating lens, mounted in a thermolectric cooler base and driven at constant temperature and power by a laser diode driver (Melles-Griot DLD203). A light detector with high IR sensitivity (Thorlabs PDA100CS) was positioned directly opposite the exit window. For the transmittance measurements the setup was calibrated with a similar uncoated substrate in place of the sample in the chamber. Because the area illuminated by the heating laser did not fill the area sampled by the IR laser, this procedure is adequate for measurements of changes in average transmittance in a fixed setup, which is sufficient for the purpose of this work, but would be inadequate for absolute measurements.

For the laser heating experiments, a current-controlled continuous diode laser with 672 nm wavelength and a maximum power output of 300 mW was used to illuminate the samples. Its output was calibrated with an optical power meter (Thorlabs MP100D). An electronic shutter (Uniblitz T-132) was used to control the duration of the pulses. The laser was focused to illuminate an area of the sample on which the resistance or transmittance measurements were performed. The average power density at the sample surface was estimated to be of order 100 W/cm², taking into consideration window losses, beam diameter at the sample, and beam inclination. High irradiance values of this order were required to cause sufficient heating of the sample with short enough pulses (down to few milliseconds). For the pulsed-voltage heating experiments rectangular constant-voltage pulses of the desired duration were applied using a Keithley 230 programmable voltage source. It is emphasized that the voltage or light pulses in these experiments are applied once the sample is at a preselected temperature within its hysteresis curve, and that the substrate and heater act as heat sinks at that temperature. While it is possible in principle to heat a sample with suitable geometry from room temperature up to the desired temperature either by irradiating it with a continuous light beam or passing a continuous current through the film, these options would complicate the temperature-control problem.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Case 1: Optical writing-electrical reading

Hysteresis curves for sample resistance were obtained through computer-controlled heating-cooling cycles as the breadth of the cycles was progressively narrowed in order to obtain a family of curves. The result for seven cycles is shown in Fig. 1. For each of the experiments described next, the sample was first “preparing” to 64 °C. The inset Fig. 1 shows the response in resistance due to a light pulse irradiating the sample for 2 s. The resistance drops rapidly while
the pulse lasts, then partially recovers more slowly, and stabilizes at a value an order of magnitude lower than the initial resistance. The dynamic is suggested by the highlighted hysteresis trace in the same figure, which was chosen because the starting, lowest, and ending resistance values approximately coincide with those actually measured in response to the light pulse. During illumination and recovery it is not meaningful to measure sample temperature with a single thermocouple, since there will be a changing distribution of values until equilibrium is reached and the material cannot be described by a single hysteresis curve. Nevertheless, comparison with the time behavior of sample resistance indicates that the film material undergoes a temperature excursion similar to that of the trace shown.

In the sequence shown in Fig. 2, all light pulses had the same intensity as before, but durations were chosen to produce roughly similar resistance drops, which can be achieved with successively longer pulses. In contrast, in a series of pulses with the same duration, those after the first one will produce much smaller resistance drops, as long as the delay between pulses is long enough to allow settling of the resistance value. This may be explained with reference to Fig. 1 again. After a first pulse, which would have caused a relatively large drop in resistance, the sample is again at the initial temperature (“end of excursion” in the figure). A second light pulse which causes a new temperature excursion will be associated with a partial hysteresis loop (not shown in the figure) starting at this point and ending at a point slightly below. Further additional pulses with the same energy will cause the system to end at points along the T =64 °C vertical line which are lower, but increasingly close to each other. After a sufficiently high number of equal pulses a limiting point is reached, which implies that the small hysteresis loops associated with these will be closed, that is: they will begin and end at this point. The resistance value for this point will not be lower than that corresponding to the same temperature for the cooling branch of the outer hysteresis curve. This limiting condition is expected as long as the energy absorbed by the film material from each light pulse is not high enough to cause permanent physical changes, such as oxidation, reduction, or recrystallization.

Starting from the initial condition, as shown in Fig. 2, pulses which are each time more energetic (i.e., longer in this case) are required to produce further substantial reductions in resistivity. It is noted that the single 2 s pulse (inset Fig. 1) causes nearly the same resistance drop as that due to the cumulative effect of all the pulses recorded in Fig. 2, of which the last pulse is also 2 s long. This seems counterintuitive, but can be understood realizing that the initial temperature of the sample for all pulses is the same, and that for the sequence of pulses in Fig. 2 only the last one produces as large a temperature excursion as that due to the single pulse in Fig. 1. The single 2 s pulse in the first case nearly exhausts the capability of the material to reduce its resistivity with temperature excursions of this magnitude, and only larger excursions will produce further reduction in the resistivity (as long as the end of the transition region is not reached first).

B. Case 2: Electrical writing-optical reading

The hysteresis curve for sample transmittance at \( \lambda =1.31 \) \( \mu \text{m} \) is shown in Fig. 3. For this particular sample the hysteresis loop is nearly double that of the sample used in case 1. For the following measurements the sample was first “prepared” to 70 °C using the heater. Voltage pulses were
then applied through the wires directly connected to the VO$_2$ film. As shown in Fig. 4, a sequence of pulses with increasing durations but equal voltages (80 V in this case) produces successive drops in sample transmittance. As in the previous case with the resistance measurements, there is some overshoot of the transmittance value just as the pulse ends, associated with thermal excursion in the region excited. The transmittance recovers rapidly, however, and remains at the new level when the local temperature stabilizes. The second trace in Fig. 4 was obtained by applying pulses of equal duration (1 s) but increasing voltage after the sample was again “prepared” to 70 °C.

C. Case 3: Optical writing-optical reading

The sample in this case was the same as for the previous one and the same hysteresis curve (Fig. 3) applies. The setup was modified only to be able to heat the sample with red light pulses instead of voltage pulses. The same laser and shutter as in case 1 were used, but the laser was focused to irradiate a small area exposed by the circular aperture in the sample holder. The measured initial sample transmittance value at 70 °C is somewhat higher than in the previous case. This is not attributed to a change in the sample material itself but to an artifact due to sample repositioning between the two setups. Figure 5 shows the effect of a sequence of pulses with equal irradiance and increasing duration, starting with a 0.6 s pulse and increasing by 0.6 s for each successive pulse. By the end of this sequence, even though the pulse energy continues to increase, the steps become smaller as the value of transmittance approaches the lower limit measured before. As in case 1, in which light pulses were used for heating the sample, it was found that approximately the same transmittance reduction can be caused with a succession of many pulses of increasing duration as with a single pulse with the same duration as the last in the sequence, as long as the device is allowed to “settle” between pulses and the lower transmittance limit has not been reached.

In order to verify the stability of the systems described, the setup for this last case was used to measure the IR transmittance continuously for 8 h, after the sample was brought up to 70 °C, subjected to a single light pulse—during which transmittance was lowered from 38.5% to 25.0%—and maintained at the same temperature. During this time the transmittance value slowly decreased to 24.8% by the time the experiment was ended. This slight reduction was attributed to instrumental drift in the temperature control or IR emission-detection system.

Although two separate light sources were used in the all-optical implementation presented in this third case, there would be no particular difficulty in using the same light beam for heating the film (with high intensity) and for light-intensity control through the film’s transmittance (with low intensity). In this case the device would be an optical analog of an electrical memristor. However, one would lose the flexibility afforded by choosing one wavelength with high absorbance (for writing) and another with high transmittance change through the IMT (for reading).

D. Device response for sequences of equal pulses

Figure 6 presents the result of applying a series of pulses of equal duration to the same sample, “prepared” at 70 °C. The upper trace is for equal irradiance light pulses and the lower one is for equal voltage pulses. The initial transmittance is different for the two traces, but this is again due to
sample repositioning between the two setups. In both cases, transmittance continues to drop after the first pulse, less noticeably each time. However, in the first case transmittance drops become smaller much more rapidly and clearly appear to approach a higher limit (i.e., lower transmittance reduction) than in the case of equal voltage pulses. This difference can be understood noting that while absorption characteristics for visible light by VO$_2$ do not change substantially through the IMT, resistivity does change drastically. Thus, subsequent light pulses with equal irradiance and durations deliver approximately equal energies to the sample. In contrast, subsequent equal-voltage pulses with equal duration deliver increasing energy due to the drop in resistance caused by the previous temperature excursions. In other words, the energy delivered to the VO$_2$ film by visible light at a constant irradiance increases approximately in a linear fashion with time, while that delivered by a current at constant voltage increases nonlinearly with time due to the simultaneous and abrupt resistance reduction. However, it is noted that while a light pulse with double duration will deliver approximately double the energy to the VO$_2$ film, it does not follow that twice the temperature increase will be produced. This is mainly due to the nonlinearity in latent heat requirement associated with the phase transition.

IV. CONCLUDING REMARKS

The present results extend those of Driscoll et al.,$^3$ which addressed the electrical (resistance) response to electrical (voltage) pulses of VO$_2$ samples maintained at a temperature within the IMT on its heating branch. It is noted that in that previous work as well as in the present one, the effect of the applied pulse is to momentarily increase the film temperature, so that the material advances along its hysteresis curve and, as its temperature returns to the initial value, the variable of interest (resistance, transmittance, etc.) has changed in value (as long as saturation has not been reached, as discussed above). Hence, the effects studied are entirely dependent on the hysteretic behavior of the material. In contrast, recent experiments by Gurvitch et al.,$^{13}$ show that by means of short backward excursions of temperature (i.e., cooling in the heating branch or heating in the cooling branch) nonhysteretic resistive response can be obtained from VO$_2$ within its transition region, which has the effect of linearizing its log (R) response as a function of temperature within the short excursion range. Interestingly, by correct operation, the thermal response of VO$_2$ may be employed for entirely different device applications depending on the sign of the limited temperature excursions it is subjected to within the transition region.

While the light or voltage pulses used for the experiments described here in all three cases were relatively long, it is possible to use shorter ones if higher irradiance or voltage values, respectively, are used. How high can these values be without damaging the device will in general depend on the crystal quality of the film. Because the VO$_2$ absorption coefficient is much higher for green and blue light than for red light, it is expected that similar results will be obtained at lower intensities or with shorter pulses if light with shorter wavelength is used for heating. However, it is noted that since irradiance decreases exponentially with penetration depth, if film thickness is comparable to or less than the material’s characteristic extinction length or “skin depth” then light absorption will be much higher in the film layer first exposed to the beam. While heat conduction will tend to equalize temperature rapidly, this effect can cause a spatial distribution in the film’s response along the beam path which can reduce its effectiveness for the purpose intended here. Hence, it may be advantageous to compromise between absorbance at the working wavelength for heating and film thickness in order to maximize performance.

As shown by the results presented, once a memory state is “written” either by an electric or light pulse in a VO$_2$ film otherwise kept at a constant temperature within the IMT region, it may be read either by its resistance or IR transmittance, or indeed both quantities could be read simultaneously. Clearly, IR reflectance could be used instead of transmittance, if preferred. These measurands can be monitored continuously without affecting the state as long as sufficiently low current or IR irradiance is utilized, so that the thermal load is negligible. Unfortunately, “erasing” the memory states requires reducing the temperature of the device below the IMT region values. While not attempted in the present work, it seems clear that the same light beam could be used in a VO$_2$-based device both to interrogate the transmittance state (using low irradiance) and to change the transmittance value (using high irradiance), in which case the device would be an optical analog of a memristor. These concepts can be extended to other properties which change hysteretically during the IMT. In addition, they are applicable to other IMT materials, although VO$_2$ is particularly convenient due to the accessibility of the transition temperature and the large changes in electrical and optical properties it exhibits. The responses observed in all cases here are due purely to thermal effects caused by the voltage or light pulses. Since ultrafast changes in optical properties of VO$_2$ have been demonstrated before,$^{14-16}$ it may be expected that sufficiently intense ultrashort light pulses can be similarly used to access different “states” of the material. However, the time evolution of the material’s response will be more complex in this case, as is known from previous work with VO$_2$,$^{17}$ and relaxation to a thermally determined condition should determine the final stable state.

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References