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Imprinting of Local Metallic States into VO_2 with Ultraviolet Light

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Materials exhibiting electronic phase transitions have attracted widespread attention. By switching between metallic and insulating states under external stimuli, the accompanying changes in the electrical and optical properties can be harnessed in novel electronic and optical applications. In this work, a laterally confined conductive pattern is inscribed into an otherwise insulating VO_2 thin film using ultraviolet light, inducing an almost four orders of magnitude decrease in electrical resistivity of the exposed area. The metallic imprint remains in VO_2 after ultraviolet light exposure and can be completely erased by a short low temperature anneal. The ability to optically pattern confined metallic structures provides new opportunities for reconfigurable photonic and plasmonic structures, as well as re-writable electric circuitry.

1. Introduction

Strongly correlated materials exhibit exotic properties for future optical and electronic applications, one of the most interesting phenomena being the metal to insulator transitions (MITs). These transitions are of great scientific as well as technological interest in developing the next generation of power efficient electrical and optical devices with ultrafast response.[1,2] VO_2 is a particularly attractive MIT system because it exhibits a first-order phase transition from an insulating to a metallic state near room temperature with a decrease in resistivity by more than four orders of magnitude in bulk single crystals, accompanied by a structural change from a monoclinic M1 (space group $P2_1/c$) structure to a high temperature rutile structure (space group $P4_2/mnm$).[2] Even though the mechanism of this phenomenon is still under debate,[3–7] sustained advances in synthesis and fabrication techniques have enabled the generation of VO_2-based devices for infrared imaging,[8] fast computing,[9,10] and memory applications,[11,12] taking advantage of the MIT behavior.

One of the most exciting possibilities is to use optical excitation to manipulate the MIT behavior.[1,11,13] The ability to optically induce reversible electronic phase changes in VO_2 whereby the electrical conductivity changes by orders of magnitude, which is local and persists when the optical source is turned off, is highly desirable to enable novel optical and electrical applications, such as reconfigurable optical elements[14,15] and utilizing VO_2 for re-writable electronic circuitry, e.g., as bottom electrode material, allowing to imprint and erase metallic pattern and to write different "contacting schemes." This capability has tremendous potential for studying novel electronic materials, such as exfoliated 2D layered materials or topological insulators, where traditional device fabrication schemes have been found incompatible and therefore detrimental to the targeted material properties.[16–18]

Recent experiments on ultrafast time scales have shown that a metallic state can be induced into otherwise insulating VO_2 through optical pumping, but these states were unstable and relaxed back to the insulating state on picosecond time scale, indicating that a structural and electronic reconfiguration

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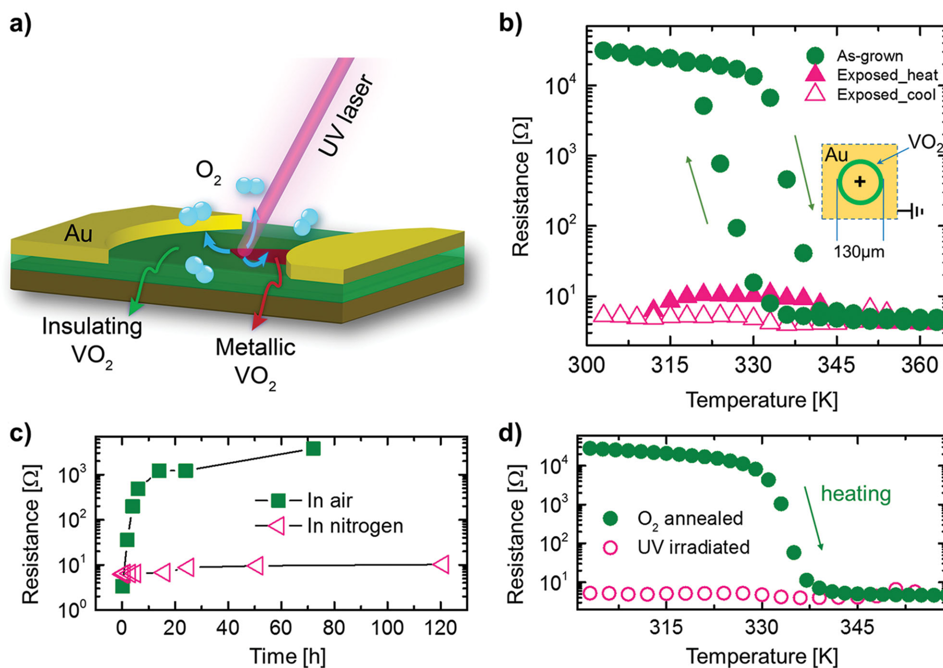

Figure 1. VO_2 thin films under UV laser irradiation and recovery of the MIT. a) A schematic figure of the optical fabrication process, where a focused UV laser beam can be used to write local conductive patterns on VO_2 thin films. b) Temperature-dependent resistance measurements of a VO_2 device before and after UV light irradiation in nitrogen. The inset pattern on the right shows the schematics of an exposed device. The UV spot was focused to be around 1 mm in diameter. c) Recovery time measurements of MIT suppressed VO_2 devices in different atmospheres at room temperature. d) Comparison of the resistance between a suppressed VO_2 device and the suppressed device annealed in oxygen at 480 K for 5 min.

toward a permanent metallic state was not achieved.[19] On the other hand, recent results have suggested that the electronic transport properties of VO_2 can be altered through exposure to electromagnetic waves.[20–23] Persistent photocurrents were induced when VO_2 samples were irradiated by X-ray or ultraviolet (UV) light.[20–22] Furthermore, it was also found that exposure to UV light can play a critical role in modifying the stoichiometry, i.e., the vanadium to oxygen ratio in VO_2 films,[23] suggesting the possibility to optically control the MIT.

Here, we report a method to optically imprint conductive areas into an otherwise insulating VO_2 film, as schematically depicted in **Figure 1**a. The pattern is permanent at room temperature, and can be quickly erased at moderately elevated temperatures. In contrast to conventional thin-film patterning techniques, which require chemical etching of patterns defined through lithography steps, the optical imprint is performed by irradiating single crystalline VO_2 films with UV light in nitrogen atmosphere. A metallic pattern is sketched into the electrically poorly conducting VO_2 matrix, with 3.7 orders of magnitude change in resistivity (see Figure 1b). The metallic pattern created this way can be completely erased by a 5 min anneal at 480 K in oxygen atmosphere. The stabilization of the metallic state at temperatures much lower than the phase transition temperature is demonstrated, independent of the strain state in VO_2 films. The formation of oxygen vacancies in areas exposed to UV light irradiation is proposed as the underlying mechanism. Following the concept of chemistry driven MIT,[24,25] we show that optically induced oxygen vacancies can be a key knob to tune the MIT behavior for optoelectronic applications.

2. Results and Discussion

To rule out the role of strain and the type of deposition technique employed, two sets of samples have been synthesized and investigated. A 10 nm thick coherently strained VO_2 film was grown on (001) TiO_2 using reactive molecular beam epitaxy,[26] while a 30 nm thick fully relaxed VO_2 film was grown on $(1\bar{1}0)$ Al_2O_3 (*m*-plane sapphire) using a co-deposition growth approach.[27] For both sets of samples, an abrupt hysteretic change in electrical resistance was observed. A transition temperature close to that of bulk single crystal VO_2 (≈340 K) was observed for the relaxed VO_2 on Al_2O_3, while it shifted to a lower temperature by ≈50 K for VO_2 grown on TiO_2 due to a tensile strain in the film.[28,29] A hysteresis width of around 15 K and a resistivity of the high temperature metallic phase of 10^{-3} Ω cm was measured for both the VO_2 films, which resulted in a resistance of ≈10 Ω (see Figure 1b, **Figure 2**a). The lower resistance of the low temperature semiconducting phase in case of VO_2 on TiO_2 was possibly attributed to a sizable parallel conduction of the TiO_2 substrate.

Before UV light irradiation, the as-grown VO_2 thin film on *m*-plane (10-10) sapphire showed a typical MIT transition with ≈3.7 orders of magnitude (see Figure 1b). The inset of Figure 1b shows the test devices for probing the resistance of a 5 µm wide VO_2 ring. The contacts were ohmic and the contact resistance was found negligible. After UV light irradiation at room temperature, the resistance of the exposed VO_2 device decreased by several orders of magnitude, comparable to that of the metallic state, and it remained almost constant throughout the MIT transition. To test the long-term stability of the conductive

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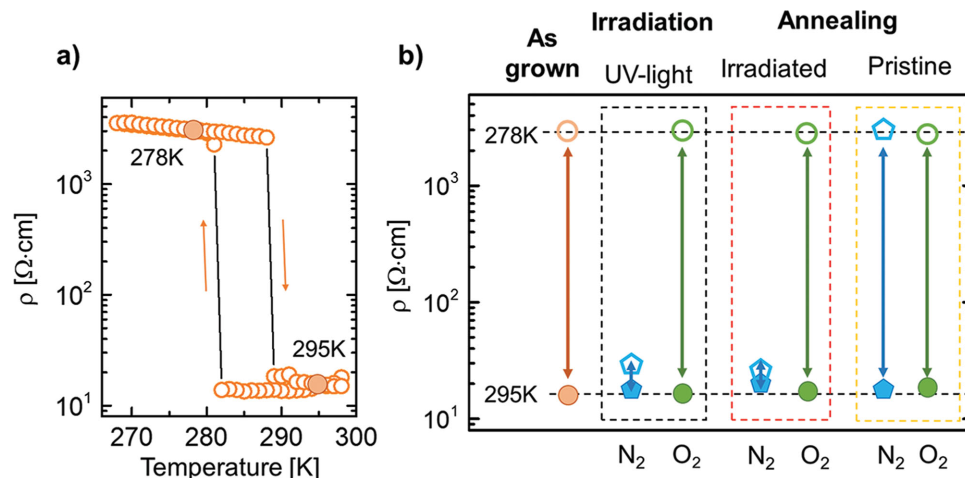

Figure 2. Atmosphere effects on the MIT suppression. a) Temperature-dependent resistance of a 10 nm thick VO_2 film on TiO_2 (001). b) Resistance comparison between 278 K (insulating) and 295 K (metallic) for films irradiated/annealed in different atmospheres. The measurement temperatures are also indicated as filled dots in (a). Left black-dashed column: VO_2 thin films irradiated in nitrogen (blue pentagon) or oxygen (green circle). Middle red-dashed column: MIT suppressed VO_2 thin films annealed in nitrogen or oxygen. Right orange-dashed column: pristine VO_2 thin films annealed in nitrogen or oxygen.

path inscribed into the VO_2 matrix, a recovery experiment was carried out in nitrogen and ambient atmospheres (see Figure 1c). For the devices left in nitrogen atmosphere at room temperature, the VO_2 remained conductive, while the devices kept in ambient atmosphere recovered back to a high resistance state within hours. The recovery process can be accelerated by annealing the UV-light-exposed devices in oxygen for 5 min at 480 K (see Figure 1d). Local conductive paths can be inscribed into VO_2 thin films using UV light irradiation, which remained stable when kept under nitrogen. In addition, this conductive path could be easily erased by low temperature annealing in air or oxygen. This apparent suppression of MIT behavior arises from band filling resulting from oxygen vacancy formation as discussed in detail further below.

To further study the effect of atmosphere on the MIT modification, VO_2 films on TiO_2 were irradiated and annealed in different atmospheres. The as-grown VO_2 films exhibited a typical MIT transition, with critical temperature $T_c \approx 290$ K upon heating, as shown in Figure 2a. The irradiation was performed in nitrogen or oxygen atmosphere, respectively. During the irradiation, the temperature of the sample was maintained at 278 K, about 10 K below the transition temperature. Figure 2b shows the resistance of VO_2 films on (001) TiO_2 measured at 278 K and 295 K. On the left, the insulating and metallic state of the "as-grown" VO_2 on TiO_2 films are shown for comparison, while results after UV light irradiation in different atmospheres are shown to its right, enclosed by a black box. After UV light irradiation in N_2, the MIT behavior of VO_2 was suppressed, with only ≈1.5 times change in resistance between 278 K and 295 K. On the contrary, VO_2 films irradiated in O_2 atmosphere showed no significant change in the MIT ratio. The MIT suppression by UV light irradiation required an oxygen deficient atmosphere.

The role of atmosphere on the MIT suppression was further verified by annealing UV exposed VO_2 films in nitrogen and oxygen atmospheres at 480 K for 5 min (see Figure 2b) (red box, middle). While annealing in N_2 barely affected the MIT suppression, leaving the resistance at low temperature unaltered, the MIT behavior completely recovered after annealing in O_2. In comparison to the pristine sample, an almost identical resistance ratio was obtained. Annealing in an oxygen atmosphere completely reversed the MIT suppression induced by UV light exposure in reducing atmosphere. The behavior is consistent with previous reports about the role of O-stoichiometry and resistivity change across the MIT in VO_2,[23,28,30,31] indicating that exposure to UV light plays a critical role in the formation of oxygen vacancies in VO_2, ultimately causing the MIT suppression. To further substantiate the hypothesis that exposure of VO_2 to UV light was essential to induce oxygen vacancies in VO_2, a control experiment was performed in which pristine VO_2 films were annealed in N_2 or O_2 at 480 K for 5 min, shown in the right yellow column of Figure 2b. Insignificant changes in the MIT behavior were observed, further corroborating the critical role of UV light irradiation.

To study the electronic band structure change of UV-exposed VO_2 film, and to rule out the possibility of catalytic effects from the nearby Au contacts, in situ temperature-dependent spectroscopic ellipsometry (SE) measurements were performed on VO_2 films without metal contacts. **Figure 3**a shows a simplified schematic of the VO_2 band structure around the Fermi level derived from the t_{2g} orbitals upon transition from insulating state to metallic state. Crystal field splitting separates the vanadium d orbitals into a higher e_g^σ and a lower t_{2g} band. In the high temperature metallic state, the delocalized electron per vanadium atom populates the t_{2g} bands that overlap with a higher lying e_g^π and a lower lying a_{1g} band. Upon symmetry lowering through V pair formation and associated monoclinic distortion, the a_{1g} band splits into an upper and a lower part, while the e_g^π band shifts up, opening a fundamental gap between the lower a_{1g} and the e_g^π band,[5,6] which is associated with a dramatic change of the extinction coefficient, plotted in Figure 3b. The characteristic feature of the VO_2 insulating state is a peak at ≈1.3 eV due to optical transitions from the occupied lower a_{1g} bands to the unoccupied states of the e_g^π band.[5] This

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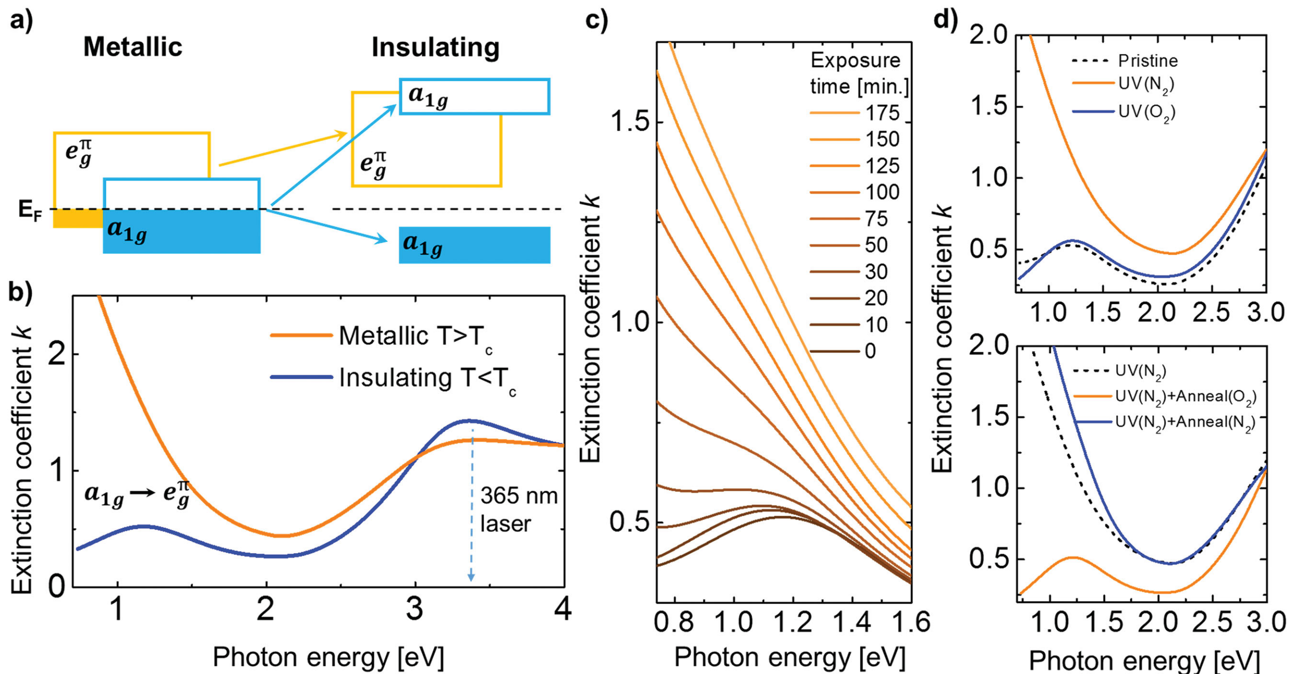

Figure 3. Optical responses upon UV-light irradiation and annealing. a) Schematic diagram of vanadium t_{2g} band change during MIT. b) The extinction coefficient k of a pristine VO_2 film below T_c (insulating) and above T_c (metallic) measured by spectroscopic ellipsometry. c) Time-dependent extinction coefficient measurements under UV light irradiation in nitrogen. d) The extinction coefficient k of a pristine VO_2 film and films irradiated in nitrogen or oxygen (upper panel). The extinction coefficient k of an MIT suppressed VO_2 film and MIT suppressed films annealed in nitrogen or oxygen (lower panel).

transition was absent in the metallic state, and its low energy optical absorption spectrum was dominated by a pronounced Drude tail. The suppression of the interband transition peak at ≈1.3 eV reflected a merge of lower a_{1g} bands and e_g^π bands in the metallic phase. Figure 3c shows the in situ evolution of the extinction coefficient of the VO_2 film under UV light exposure in nitrogen at 278 K (insulating phase). Upon exposure to UV light irradiation, the peak at ≈1.3 eV gradually disappeared and a Drude response from free carrier reflection emerged, suggesting a progressing transition from the insulating to the metallic state. Note that the interband transition shoulder was still seen as the film turned more conducting with UV exposure, and eventually got buried under the Drude peak, indicating band filling and the rise of the Fermi level, instead of a sudden collapse of the bandgap. For comparison, SE measurements were carried out after the VO_2 films were irradiated in different atmospheres. In agreement with the resistance measurements, optical experiments shown in Figure 3d (upper panel) confirmed that VO_2 films exposed to UV light in nitrogen atmosphere turned metallic, but remained insulating when irradiated in oxygen. In addition, annealing in oxygen after UV exposure in nitrogen recovered the insulating state, while the irradiated film remained metallic when annealed in nitrogen (see Figure 3d) (lower panel).

The irradiation and annealing experiments indicated that oxygen stoichiometry level played a critical role in suppressing the MIT in VO_2 thin films. The formation of oxygen vacancies in the film when stimulated by UV light irradiation under nitrogen atmosphere and the subsequent removal of the vacancies in the film by thermal annealing in an oxygen atmosphere is hypothesized as the underlying mechanism of the persistent photoconductivity changes observed. The O-vacancy generation can be described by the following defect chemistry equation:

$$O_o^X \rightleftharpoons V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2 \uparrow \quad (1)$$

During UV light irradiation in O_2, the high O_2 partial pressure would limit the formation of O vacancies, shifting the reaction balance to the left. In contrast, a nonoxidizing atmosphere such as N_2, promoted the oxygen vacancy formation, suppressing the MIT. Consistently, MIT recovery was achieved by thermal annealing under oxygen atmospheres through backfilling oxygen into the previously formed oxygen vacancy sites. The activation energy for creating oxygen vacancies was calculated to be in the range of 3 to 3.5 eV.[32,33] Such a large energy barrier would prevent oxygen vacancy formation even in oxygen deficient atmospheres, as observed in Figure 3b. However, 365 nm UV light (3.4 eV) provided enough activation energy to form oxygen vacancies, thus resulting in the MIT suppression in VO_2.

To further investigate whether UV light is necessary for the MIT suppression or if this process mainly results from a photo-thermal effect, i.e., local heating due to light absorption, another irradiation experiment was carried out by choosing a laser with a photon energy (of 2.4 eV) smaller than the oxygen vacancy formation energy. The exposure time was kept the same as the previous UV-light irradiation experiments, while

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the intensity was four times higher than the UV light. No suppression of the MIT was observed after exposure to visible light, and the resistance of insulating VO_2 decreased only by 0.7%, suggesting that a photon energy higher than the oxygen vacancy formation energy is required for the MIT suppression. Furthermore, heat generation and heat transport in the VO_2/TiO_2 samples during UV-light exposure have been simulated using a finite element approach.[13] The VO_2 surface temperature during UV-light irradiation was found to be ≈286 K. As observed in the anneal experiment (Figure 2b, right column), the MIT behavior was not suppressed by annealing VO_2 samples in nitrogen at 480 K. Therefore a surface heating effect during UV light irradiation is negligible, and hence cannot be responsible for the observed MIT suppression (see Figure 1 and Note 1, Supporting Information for simulation details).

In order to characterize the formation of oxygen vacancies during UV-light irradiation, X-ray photoelectron spectroscopy (XPS) was performed at room temperature on as-grown films and films exposed to UV light in a nitrogen atmosphere (without metal electrodes). High-resolution XPS spectra of the V 2p and O 1s core levels along with peak fitting of the corresponding individual components are presented in **Figure 4**a. O 1s peak was used as reference in both XPS spectra. Figure 4b shows quantitative fitting results of the V valence state, determined from the integrated area of the individual component giving rise to the measured intensity of the V $2p_{3/2}$ peak. The presence of V^{5+} state was attributed to the pronounced surface oxidation of VO_2 when kept in ambient atmosphere.[29] This surface effect, even though it dominated the XPS results, was limited to be within ≈1.0 nm of the outermost surface,[31] as estimated using inelastic electron mean free path of 1.6 nm reported earlier.[34] Before UV-light irradiation, negligible V^{3+} signal was found in the film, which increased to ≈10% after the exposure to UV light. During this process, the chemical environment of some vanadium cations became oxygen deficient due to oxygen vacancy formation and thus the led to the V^{3+} signal increase. Both signals from V^{4+} and V^{5+} slightly decreased, directly suggesting the increase of oxygen deficiencies in the film (lower average bonding energy).[35] If the signal from the V^{5+} peak is considered as surface effect, i.e., extrinsic to the VO_2 thin film, the concentration of oxygen vacancy formed during UV-light irradiation can be estimated. Normalizing the V^{3+} signal by the total intensity of V^{3+} and V^{4+} (the total V signal from the film), the chemical environment of ≈25% vanadium cations was affected due to oxygen vacancy formation under UV-light irradiation. Since the formation of each oxygen vacancy breaks two oxygen-vanadium bonds, there is a ratio of 1:2 between the concentration of oxygen vacancy and that of vanadium cations with an oxygen deficient environment. The concentration of vanadium cations in VO_2 is 3.4×10^{22} cm^{-3}, and thus the concentration of oxygen vacancies is ≈5×10^{21} cm^{-3}, which gives rise to a free electron concentration of 1×10^{22} cm^{-3} because each oxygen vacancy donates two free electrons. Such a high carrier concentration is similar to that of the metallic state of as-grown VO_2 films (see Figure 2, Supporting Information), and therefore suppresses the MIT behavior of the VO_2 films. Room temperature XRD measurements were carried out before and after UV-light irradiation (see Figure 3, Supporting Information). Negligible changes of the film peak position, width, and intensity were observed indicating that only minute changes of

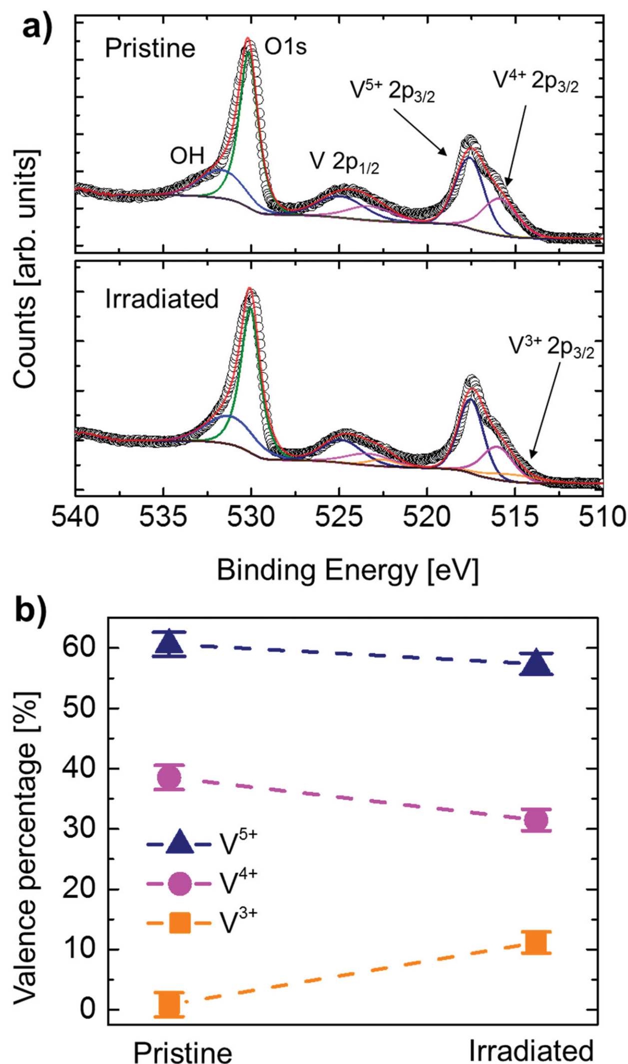

Figure 4. X-ray photoelectron spectroscopy (XPS) measurements before and after UV light irradiation. a) XPS spectra measured around V 2p peaks. After MIT suppression, the V 2p peak shifted to lower energy by 0.3 eV. b) Integrated area percentage of vanadium valence peaks before and after UV light irradiation. The ubiquitous presence of V^{5+} peak is due to an ultrathin surface layer (≈1 nm) over-oxidized by atmosphere. The fitting error bars were calculated to be ≈2% and 1.7% for before and after UV light irradiation results, respectively.

the form factor were induced. The films retained their crystal structure upon UV light irradiation.

3. Conclusion

We have demonstrated a simple optical sketching method to inscribe local metallic pattern into an otherwise insulating VO_2 matrix by exposure to UV light in a nonoxidizing atmosphere. The insulating state of the previously UV-exposed areas can be recovered by a short annealing in an oxidizing atmosphere at low temperatures. The formation of oxygen vacancies was proposed as the origin of the induced conductive phase. It would

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be interesting to explore this phase in the future on the nanoscale with other probes such as spatially resolved in situ XRD, Raman and infrared spectroscopy techniques. Here, the minimum feature size was limited by the UV beam intensity profile (spot size ≈ 500 µm). Next neighbor devices ≈1000 µm away from the exposed structure did not show any change in their resistivity. Since MIT suppression in VO_2 has been proved to be a photon-induced defect reaction, extreme UV lithography or focused X-rays can be used to write nanoscale pattern with a much smaller feature size. The ability to locally suppress and recover the MIT property of VO_2 film by UV light, especially the low temperature writing and erasing of arbitrary spatial circuitry, provides a novel route to build next generation reconfigurable electronic circuits using strongly correlated materials.

4. Experimental Section

Film Growth and Device Fabrication: The 30 nm VO_2 film on m-plane (10-10) sapphire[27] and 10 nm VO_2 on TiO_2 (001) plane[26] was grown by a co-deposition method and molecular beam epitaxy (MBE), respectively. Devices with a circular transmission line model (CTLM) geometry are fabricated on the sample by standard lithography techniques. Electrodes made of 15 nm Pt and 50 nm Au were deposited via electron-beam evaporation.

UV-Light Irradiation, Transport, and Spectroscopic Ellipsometry (SE) Measurements: The devices on 10 nm VO_2 were uniformly exposed under a UV lamp (HOYA-SCHOTT, HLS210U, 150 W mercury xenon lamp) with 365 nm (3.4 eV) light at 278 K for one hour, under a light intensity of 1.1 W cm^{-2}. The devices on 30 nm VO_2 were irradiated by a 257 nm (4.8 eV) Coherent FRED intracavity frequency-doubled argon ion laser with a intensity of 5.9 W cm^{-2}. The samples were exposed to UV light at room temperature for 4 h. All annealing experiments were performed at 480 K for 5 min via a rapid thermal annealler (RTA). Two-terminal measurements were performed on irradiated and annealed samples using a CASCADE probe station, which was purged by nitrogen or oxygen by 60 min prior to laser irradiation. A rectangular wave with a sweeping voltage from –0.5 V to 0.5 V was applied and generated current was measured to determine the resistance of the device. RC2 Ellipsometer was used to monitor optical properties VO_2 thin film under UV-light irradiation. Experimental and fitting details are provided in Note 2 (Supporting Information).

X-ray Photoemission Spectroscopy (XPS): XPS measurements were performed on Kratos Ultra XPS under Aluminum Kα radiation with a pass energy of 20 eV and the fitting procedure was reported in previous work.[31,35]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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