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## LETTER TO THE EDITOR

## Efficient photocarrier injection in a transition metal oxide heterostructure

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### Abstract

An efficient method for doping a transition metal oxide (TMO) with hole carriers is presented: photocarrier injection (PCI) in an oxide heterostructure. It is shown that an insulating vanadium dioxide ( $\text{VO}_2$ ) film is rendered metallic under light irradiation by PCI from an n-type titanium dioxide ( $\text{TiO}_2$ ) substrate doped with Nb. Consequently, a large photoconductivity, which is exceptional for TMOs, is found in the  $\text{VO}_2/\text{TiO}_2:\text{Nb}$  heterostructure. We propose an electronic band structure where photoinduced holes created in  $\text{TiO}_2:\text{Nb}$  can be transferred into the filled V 3d band via the low-lying O 2p band of  $\text{VO}_2$ .

The strongly correlated electron system in transition metal oxides (TMOs) is one of the most interesting topics in solid-state chemistry and physics. It exists near the borderline between a Mott insulator based on strong electron correlations and a conventional metal. The recent discovery of many interesting phenomena in TMOs, such as colossal magnetoresistance in perovskite manganites [1], suggests that they may be useful as electronic device materials. Since such phenomena are attained by doping a Mott insulator with carriers [2], it is important for applications to establish an efficient and reliable method to control the carrier density of TMOs over a wide range under certain external conditions. For example, it would be useful if one could do it by using high electric fields produced by field-effect transistors [3]. Here we present an efficient method for achieving such dynamic carrier doping, using a photocarrier injection (PCI) technique on an oxide heterostructure.

Vanadium dioxide ( $\text{VO}_2$ ), with one 3d electron per  $\text{V}^{4+}$  ion, is a typical TMO. It undergoes a dramatic metal–insulator (MI) transition on cooling at a critical temperature  $T_{\text{MI}} = 340$  K, from a high-temperature rutile phase to a low-temperature monoclinic phase [4–6]. Although the compound has been studied extensively for more than 40 years, there is still hot debate regarding the origin of the MI transition [7, 8].

On the other hand, titanium dioxide ( $\text{TiO}_2$ ), also crystallizing in the rutile structure, is a typical insulator with a band gap of 3.0 eV [9]. The compound is technologically important because of its chemical stability and catalytic activity. In particular, the large

degree of sensitivity to ultraviolet (UV) light has made it useful as a photocell [10] and a photocatalyst [11]. It is known that nonstoichiometry in the chemical composition which occurs in a reducing atmosphere and intentional doping with Nb<sup>5+</sup> or Ta<sup>5+</sup> give rise to electron conductivity, as in n-type Si doped with P [12]. Recently, two of the authors (YM and ZH) have shown that a high-quality VO<sub>2</sub> film can be grown epitaxially on a TiO<sub>2</sub> substrate by using a pulsed laser deposition technique [13]. Moreover, they found that lattice matching at the interface gives rise to a large epitaxial stress which reduces  $T_{MI}$  to room temperature.

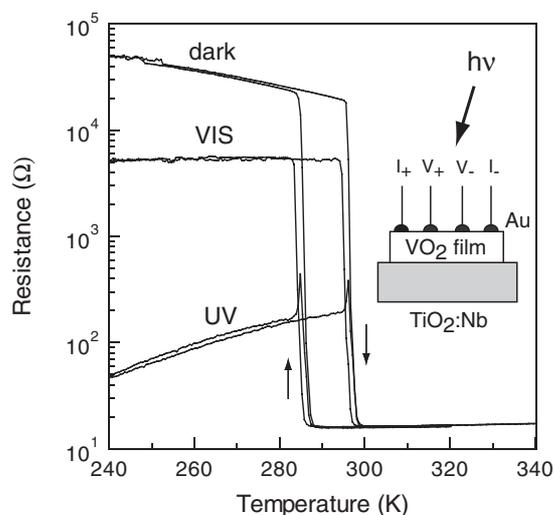
Photoconductivity provides one way of achieving photoelectric conversion. It is a general phenomenon for semiconductors, because absorbed photons can always create holes and electrons in the valence and conduction bands, respectively. However, the efficiency of photoconductivity depends on the lifetime of those photocarriers. A large photoconductivity is expected when certain impurity states in the band gap trap either type of photocarrier, which suppresses the recombination of holes and electrons. Cadmium sulfide is a typical, efficient photoconductor with dominant electron carriers and has been used to produce a light sensor [14].

In the last decade a lot of attempts have been made to control the electronic properties of TMOs such as manganese oxides and cupric oxide superconductors via photocarrier doping under light irradiation. However, the induced change was rather small in most cases [15, 16]. It would be of great advantage if one could control carrier density dynamically through photoelectric effects instead of chemical hole doping as in (La<sup>3+</sup>, Sr<sup>2+</sup>)<sub>2</sub>CuO<sub>4</sub> or (La<sup>3+</sup>, Sr<sup>2+</sup>)MnO<sub>3</sub>. The exceptionally marked effects of light irradiation reported so far are the light-induced insulator-to-metal transitions observed in Pr<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> [17] and in VO<sub>2</sub> [18] using a high-power pulsed laser beam. In the former the change of resistivity reached six orders of magnitude, but it was irreversible. It was reported for the latter that an insulator-to-metal transition took place reversibly on a subpicosecond scale, simultaneously with the structural transition, although the mechanism was not clear.

We have fabricated a 10 nm thick VO<sub>2</sub> film epitaxially grown on the (001) surface of a Nb-doped TiO<sub>2</sub> single-crystal substrate with a nominal Nb concentration of 0.05 wt%. The deposition was carried out in a vacuum chamber using a pulsed laser deposition technique with a KrF excimer laser ( $\lambda = 248$  nm) and a V<sub>2</sub>O<sub>3</sub> pellet as a target. The experimental conditions are nearly the same as those reported previously [13]. The structures of the film were characterized by means of x-ray diffraction, scanning electron microscopy, and atomic force microscopy, which confirmed that a high-quality, epitaxially grown film had been obtained.

Figure 1 shows the temperature dependence of the in-plane resistance measured in the dark and under light irradiation. In the dark, a large jump in resistance is observed at  $T = 297$  K on heating and  $T = 287$  K on cooling due to the MI transition:  $T_{MI}$  is lower by 40 K than that for a single crystal. The thermal hysteresis is due to the first-order nature of the phase transition. A large and sharp change in resistance observed at the transition indicates the high quality of the film. These results are in good agreement with our previous ones on a VO<sub>2</sub> film grown on a pure, insulating TiO<sub>2</sub>(001) substrate, where the decrease in  $T_{MI}$  is considered to be due to an in-plane tensile stress at the interface between the film and substrate [13]. The fact that we observed almost the same jump in resistance at  $T_{MI}$  for VO<sub>2</sub> films grown on insulating and on conducting TiO<sub>2</sub> substrates means that the current leak to the substrates can be ignored. In fact, the resistance of the junction measured across the interface was as high as 500 k $\Omega$ .

When the sample is irradiated by an UV light ( $\lambda = 300$ – $400$  nm), the resistance shows a small jump at almost the same  $T_{MI}$  as in the dark. Surprisingly, a dramatic reduction in resistance by more than two orders of magnitude is observed below  $T_{MI}$ . In addition, the resistance decreases gradually with decreasing temperature, indicating a metallic behaviour, in contrast to the insulating temperature dependence seen in the dark. We also detected a

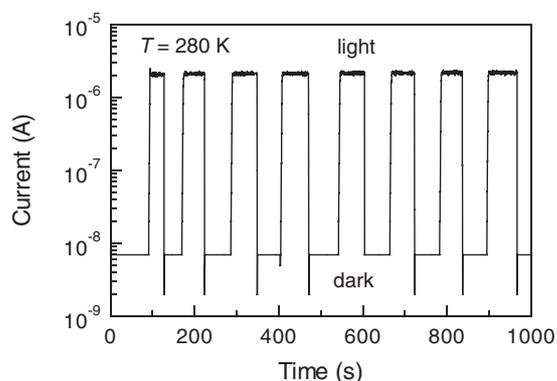


**Figure 1.** The temperature dependence of the in-plane resistance measured on cooling and heating, using a four-probe method in a Quantum Design physical property measurement system (PPMS). The sample is a 10 nm thick VO<sub>2</sub> film grown on an n-type TiO<sub>2</sub>:Nb (nominally 0.05 wt%) substrate with 0.5 mm thickness. Gold electrodes were put on the VO<sub>2</sub> film to obtain an ohmic contact. A current flow was measured at a constant voltage of 0.2 mV. An UV light (wavelength: 300–400 nm; irradiance: 140 mW cm<sup>-2</sup>) or a visible (VIS) light (wavelength: 400–700 nm; irradiance: 350 mW cm<sup>-2</sup>) from a xenon lamp was guided via an optical fibre into the PPMS to irradiate the sample during the measurements.

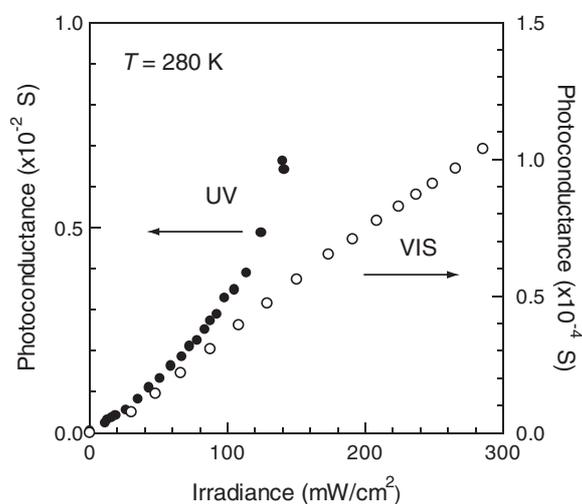
small reduction of about 4% in resistance above  $T_{MI}$ . On the other hand, a similar but smaller reduction is observed for visible light irradiation.  $T_{MI}$  now becomes slightly lower than that in the dark, which may be due to a heating effect of irradiation. As control experiments, we measured the resistivity of a VO<sub>2</sub> film grown on a pure TiO<sub>2</sub> substrate and of a TiO<sub>2</sub>:Nb substrate without films in the same experimental conditions. No photoconductive effect was detected in either case. Therefore, the combination of a VO<sub>2</sub> film and a TiO<sub>2</sub>:Nb substrate is crucial for the appearance of large photoconductance.

The photoconductivity occurs quite reversible upon light switching. Figure 2 shows the change of current measured at a constant voltage of 0.2 mV. Before irradiation, a very small current runs through the VO<sub>2</sub> film, while the current increases suddenly when an UV light is switched on. Then, the current decreases to the dark level immediately after the light is turned off. These changes occurred quite reproducibly, and no degradation was seen after switching thousands of times. A preliminary measurement to determine the decay time shows an order of milliseconds for  $T < T_{MI}$ , which is significantly smaller than those of other photoconducting materials such as CdS (30–100 ms) [14].

In general, the photoconductivity  $\Delta\sigma$  results when absorbed radiation creates hole–electron pairs in a semiconductor and increases the carrier density [14].  $\Delta\sigma$  is proportional to  $e(\Delta n \mu_n + \Delta p \mu_p)$ , where  $e$  is the elementary electric charge,  $\Delta n$  ( $\Delta p$ ) is the photoinduced electron-(hole-)carrier density, and  $\mu_n$  ( $\mu_p$ ) is electron (hole) mobility. Thus, it should depend on the light intensity and the band structure—that is, the band-gap energy and the density of traps or recombination centres, which determines the lifetime of carriers. Figure 3 shows photoconductance as a function of light intensity, which is superlinear and almost linear for UV and visible lights, respectively. The difference may come from the different photoexcitation processes. Moreover, the photoconductivity is larger by more than two orders of magnitude for



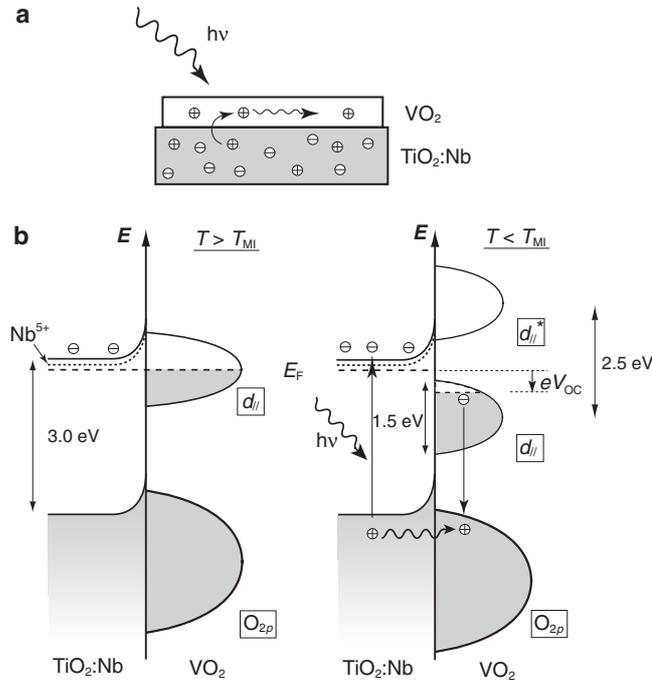
**Figure 2.** The reversible change in current upon UV light switching at  $T = 280$  K. The current was measured at a constant voltage of 0.2 mV. The light irradiance is  $140 \text{ mW cm}^{-2}$ . When the light is turned on, the current increases suddenly by more than two orders of magnitude, while it decreases to the dark level immediately after switching off.



**Figure 3.** Photoconductance as a function of irradiance for UV (left axis) and visible lights (right axis) at  $T = 280$  K. Measurements were carried out at a constant voltage of 0.2 mV for the former and of 5 mV for the latter. The response is nearly two orders of magnitude larger for the UV light than the visible light.

the former than the latter. This implies that majority photocarriers are created in  $\text{TiO}_2\text{:Nb}$  by photons with energy above the intrinsic absorption edge of  $\text{TiO}_2$  ( $\lambda \sim 380 \text{ nm}$ ), while minority ones may come from unknown deep impurity states in the band gap of  $\text{TiO}_2\text{:Nb}$ . In fact, we observed a broad light absorption peak in the visible light region for a  $\text{TiO}_2\text{:Nb}$  crystal.

However, the above indication seems to be in conflict with the fact that a  $\text{TiO}_2\text{:Nb}$  substrate itself does not show photoconductivity in our experimental conditions with a small voltage applied. The absence of photoconductivity means that the recombination process is too fast. This consideration leads us to conclude that the role of the covering  $\text{VO}_2$  film is to extract either photoinduced hole or electron carriers through the interface so as to suppress the recombination. Our preliminary experiments carried out to measure the transverse conductivity across the



**Figure 4.** Schematic drawings of PCI from a TiO<sub>2</sub>:Nb substrate into a VO<sub>2</sub> film under light irradiation (a) and of the electronic structure for the VO<sub>2</sub>/TiO<sub>2</sub>:Nb heterostructure (b). Small circles with bars and crosses represent electrons and holes, respectively. In (b) a possible band diagram at high temperature above  $T_{MI}$  in the dark is drawn on the left, and one for low temperature below  $T_{MI}$  under light irradiation on the right. TiO<sub>2</sub>:Nb possesses a band gap of 3.0 eV with Nb<sup>5+</sup> donor levels 0.09 eV below the bottom of the conduction band. Deep impurity states probably existing in the gap of TiO<sub>2</sub>:Nb are not shown. The band structure of VO<sub>2</sub> is depicted after the photoemission study by Shin *et al* [20]: in the insulating phase the bandwidth of the d<sub>||</sub> band is 1.5 eV, and the splitting of the d<sub>||</sub> and d<sub>||</sub><sup>\*</sup> bands is 2.5 eV. Thus, the band gap is about 1 eV, much smaller than that of TiO<sub>2</sub>:Nb. V<sub>OC</sub> is an open-circuit voltage associated with the hole-carrier injection under light irradiation. See the details in the text.

interface have indicated that a large photovoltage up to 0.5 V is induced upon irradiation, which is positive for the VO<sub>2</sub> film. This implies that hole carriers are transferred selectively to the VO<sub>2</sub> film, with electron carriers remaining in the TiO<sub>2</sub>:Nb crystal, as shown schematically in figure 4(a). We also confirmed this fact by observing a positive Hall voltage in the in-plane measurements under light irradiation.

Now we propose a simple picture for the electronic structure of the VO<sub>2</sub>/TiO<sub>2</sub>:Nb system to explain the experimental facts qualitatively. It is well established that TiO<sub>2</sub> possesses a valence band of nearly O 2p orbital character and a conduction band of Ti 3d character [19]. Nb<sup>5+</sup> donor levels exist just below the conduction band [12]. In fact, we determined the electron-carrier density and the activation energy at  $T = 280$  K to be  $2 \times 10^{18} \text{ cm}^{-3}$  and 0.09 eV, respectively, by means of Hall coefficient measurements on a TiO<sub>2</sub>:Nb crystal. Nb doping probably enhances light absorption near the band edge of TiO<sub>2</sub>. On the other hand, according to the photoemission study of VO<sub>2</sub> by Shin *et al* [20], the nearly half-filled d<sub>||</sub> band in the metallic phase splits into two (d<sub>||</sub> and d<sub>||</sub><sup>\*</sup> bands) in the insulating phase. Combining the two materials into a junction, assuming Fermi level matching, results almost uniquely in the energy diagrams shown in figure 4(b) for two situations; one at high temperature above  $T_{MI}$  in

the dark and the other at low temperature below  $T_{MI}$  under UV light irradiation. The V 3d and O 2p bands of VO<sub>2</sub> must be located close to the conduction and valence bands of TiO<sub>2</sub>:Nb, respectively. It is to be noted that the band structure of the junction would be completely different without donors in TiO<sub>2</sub>, because the Fermi level would lie in the middle of the gap of TiO<sub>2</sub> in that case.

Light absorption should occur mostly in the thick (0.5 mm) TiO<sub>2</sub>:Nb crystal, creating holes and electrons in the valence and conduction bands, respectively. Then, it is naturally expected from the energy diagram for the low-temperature case that only the holes can migrate into the O 2p band of VO<sub>2</sub>, because the top of the O 2p band of VO<sub>2</sub> is located slightly above that of the valence band of TiO<sub>2</sub>:Nb, while the bottom of the empty  $d_{||}^*$  band of VO<sub>2</sub> is considerably above that of the conduction band of TiO<sub>2</sub>:Nb. A possible upward bending of the TiO<sub>2</sub> bands near the interface may aid this electron–hole separation. In addition, small electron mobility [21] and relatively large hole mobility in TiO<sub>2</sub> must also be of advantage in that way. With increasing hole density in VO<sub>2</sub>, the VO<sub>2</sub> bands should shift downward by an induced open-circuit voltage  $V_{OC}$  which was in fact detected in our transverse voltage measurement across the interface, which will be reported elsewhere. The transferred holes in the O 2p band of VO<sub>2</sub> must find their counter-electrons located near the Fermi level to be combined, resulting in conducting hole carriers in the  $d_{||}$  band at low temperature below  $T_{MI}$ . As a result, the VO<sub>2</sub> film becomes a metal, exhibiting a large photoconductivity or an insulator-to-metal transition under light irradiation. Note that the carrier density is adjustable with light irradiance. A similar PCI is expected to occur at high temperature above  $T_{MI}$ , but the influence is minimal in the already metallic band structure, as actually observed in our experiments.

The two metallic states below and above  $T_{MI}$  must be discriminated from each other, because a signature for a phase transition between them still remains, as evidenced in the resistivity jump at  $T_{MI}$ , and also because the slopes of the resistance curves are quite different for the two metallic states. It is plausible that the structural phase transition is not suppressed under light irradiation. This means that the correlation gap between the  $d_{||}$  and  $d_{||}^*$  bands survives in the photocarrier-doped metallic phase. This scenario is apparently different from what one expects for a metallic phase obtained by doping a Mott insulator with carriers, where the correlation gap is destroyed by doping [2]. The origin of the MI transition in VO<sub>2</sub> may not be simple electron correlations, but is significantly related to the lattice degree of freedom.

In conclusion, efficient hole doping into a TMO using a PCI technique is demonstrated in the VO<sub>2</sub>/TiO<sub>2</sub>:Nb heterostructure. A dramatic insulator-to-metal change was observed with increasing light irradiance. The present PCI method would provide us with a convenient way for achieving dynamical carrier doping in many TMOs or other materials: neither the unusually high electric fields of the FET method nor a high-power laser is necessary. Other substrates such as SrTiO<sub>3</sub> can be used for perovskite oxides. In fact, we have already observed similar results with PCI for manganese perovskites and cupric oxides, which will be reported elsewhere [22]. PCI into cupric oxide superconductors would be especially interesting to test the effect of ‘clean’ hole doping on high- $T_c$  superconductivity. From the applications point of view, the present VO<sub>2</sub>/TiO<sub>2</sub>:Nb heterostructures will be potentially useful in light sensing devices, particularly for UV light. They also hold promise as regards other lights—after optimization of the sample geometry and other experimental factors.

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