



Efficient Photocarrier Injection to Transition Metal Oxides

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Abstract

We have fabricated transition metal oxide (TMO) films on n-type titanium oxide substrates, and measured in-plane resistance under ultraviolet light irradiation. A dramatic decrease in the resistance and enhancement of the superconducting critical temperature are observed for $\text{VO}_2/\text{TiO}_2\text{:Nb}$ and $\text{YBa}_2\text{Cu}_3\text{O}_x/\text{SrTiO}_3\text{:Nb}$, respectively. Out-of-plane voltage measurements under light irradiation indicate hole-carrier injection from the substrate to the film in both the cases. The present photocarrier injection technique could apply to many TMOs to control the hole carrier density externally. © 2001 Elsevier Science. All rights reserved

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1. Main text

Transition metal oxides (TMOs) exhibit drastic phase transitions such as a metal-to-insulator transition as a function of carrier concentration. One of recent interesting topics is to control the carrier concentration by using external fields such as electric field or light, which is fascinating from both scientific and application point of views. Although there have been reported a few examples to control the electronic properties of TMOs by using light, the observed change in resistance was small or irreversible [1,2]. In our recent work, we presented a highly efficient and tunable photocarrier injection (PCI) method by using TMO heterostructures [3,4]. Here we apply the PCI method to two heterostructures, $\text{VO}_2/\text{TiO}_2\text{:Nb}$ and $\text{YBa}_2\text{Cu}_3\text{O}_x/\text{SrTiO}_3\text{:Nb}$.

We fabricated $\text{VO}_2/\text{TiO}_2\text{:Nb}$ (001) and $\text{YBa}_2\text{Cu}_3\text{O}_x/\text{SrTiO}_3\text{:Nb}$ (100) (Nb: 0.05 wt%) by using a pulsed laser deposition technique with a KrF excimer laser ($\lambda = 248$ nm). The film thickness was 100 Å and

400 Å, respectively. The detail experimental conditions are reported previously [3].

Inset to Fig. 1 shows the temperature dependence of in-plane resistance for $\text{VO}_2/\text{TiO}_2\text{:Nb}$, measured in the dark and under light irradiation. Large jumps in resistance observed in the dark at $T_{\text{MI}} = 297$ K on heating and at $T_{\text{MI}} = 287$ K on cooling are due to a metal-to-insulator transition, as reported previously [5]. Under ultraviolet light (UV: $\lambda = 300 - 400$ nm) irradiation from a xenon lamp, the resistance shows a smaller jump at almost the same T_{MI} as in the dark, but below T_{MI} it is decreased by more than three orders of magnitude from the dark level. The magnitude of reduction increases gradually with increasing light irradiance. Since a resistance of VO_2 film on pure TiO_2 substrate and also of $\text{TiO}_2\text{:Nb}$ substrate itself show no comparable photoconductive effect, the combination of a VO_2 film and a $\text{TiO}_2\text{:Nb}$ substrate is crucial for the appearance of the large photoconductance.

Figure 1 shows the out-of-plane open-circuit voltage, V_{OC} , of the $\text{VO}_2/\text{TiO}_2\text{:Nb}$ heterostructure as a function of light irradiance. Interestingly, a large photovoltage up to 0.5 V is observed, implying a well-

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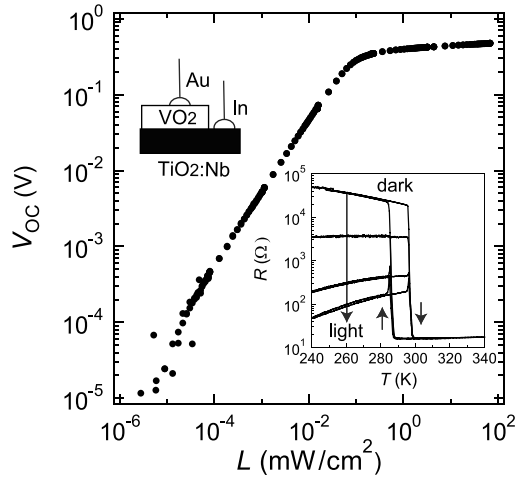


Fig. 1 Light irradiance dependence of out-of-plane open-circuit voltage for $\text{VO}_2/\text{TiO}_2\text{:Nb}$ (001), measured at $T = 270$ K. The inset to Fig. 1 shows the temperature dependence of in-plane resistance. The measurements were carried out on heating and cooling, using a four-probe method in a Quantum Design Physical Property Measurement System (PPMS). An UV light (UV: $\lambda = 300 - 400$ nm) from a xenon lamp was guided via an optical fiber into the PPMS to irradiate the sample during measurements.

defined heterojunction formation between the VO_2 film and the $\text{TiO}_2\text{:Nb}$ substrate. The most important fact is the observation of a *positive* photovoltage to the VO_2 film, implying that hole carriers are injected to the film. The photovoltage can be detected only under light irradiation with the photon energy more than 3 eV, which corresponds to the band gap of TiO_2 . This means that hole carriers generated by light irradiation in the $\text{TiO}_2\text{:Nb}$ substrate are injected into the VO_2 film through the interface. Notice that the V_{OC} increases linearly with increasing light irradiance L in a wide range of $10^{-5} \leq L \leq 10^{-1} \text{ mW/cm}^2$, which indicates that the injected hole carrier density can be tunable by light irradiance.

We then applied the present photocarrier injection method to another system, i.e., a $\text{YBa}_2\text{Cu}_3\text{O}_x$ film grown on an n-type $\text{SrTiO}_3\text{:Nb}$ (100) substrate. $\text{YBa}_2\text{Cu}_3\text{O}_x$ is well-known as a high- T_c superconductor. Figure 2 shows the temperature dependence of in-plane resistance measured in the dark and under light irradiation. In the dark, the film exhibits superconductivity below a critical temperature $T_c = 25$ K. The T_c is lower than the optimum value ($T_c = 90$ K) of this material, suggesting that the film is underdoped with certain amount of oxygen vacancies. Under an UV light irradiation, the enhancement of T_c is observed up to $T_c = 30$ K with increasing light irradiance, accompanied with a decrease in resistance. These changes can be

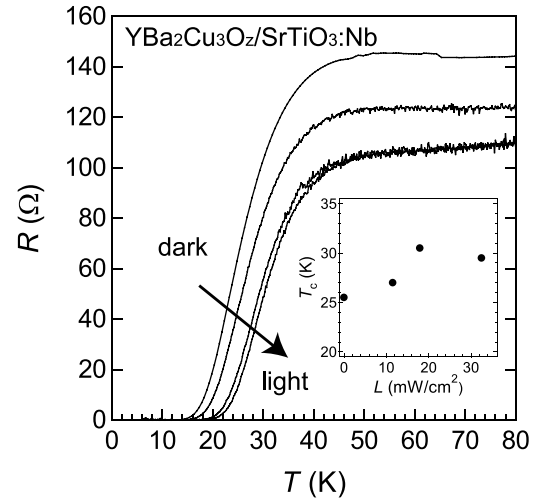


Fig. 2 Temperature dependence of the in-plane resistance of $\text{YBa}_2\text{Cu}_3\text{O}_x/\text{SrTiO}_3\text{:Nb}$ (100). The inset displays the dependence of T_c on light irradiance. The T_c stands for the midpoint temperature of the superconducting transition.

understood as a result of hole carrier injection to the film in the underdoping state by light irradiation. In fact, out-of-plane voltage measurements upon light irradiation reveal a large photovoltage of 1.2 V at room temperature, indicating that hole carriers are injected from the substrate to the film. The number of injected hole carriers into the film is estimated from the change of T_c to be 0.02 per Cu in $\text{YBa}_2\text{Cu}_3\text{O}_x$.

In conclusion, efficient hole doping into TMOs using the photocarrier injection technique is demonstrated in the $\text{VO}_2/\text{TiO}_2\text{:Nb}$ and $\text{YBa}_2\text{Cu}_3\text{O}_x/\text{SrTiO}_3\text{:Nb}$ heterostructures. A dramatic decrease in resistance in the former and enhancement of T_c in the latter are observed by UV light irradiation. The present PCI method would apply to many TMOs or other materials as a novel way for achieving dynamical hole doping or controlling phase transitions.

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