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Photogenerated hole carrier injection to $YBa_2Cu_3O_{7-x}$ in an oxide heterostructure

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We have fabricated a $YBa_2Cu_3O_{7-x}/SrTiO_3:Nb$ heterostructure and measured the current–voltage and photovoltaic properties under ultraviolet light irradiation at room temperature. A large photovoltage of 0.8 V is observed and is positive to the film. The photovoltage appears under illumination of light with photon energy larger than 3.2 eV. These results indicate that photogenerated hole carriers in the $SrTiO_3:Nb$ substrate are injected to the film. The maximum surface hole density is attained to be 3.5×10^{13} cm^{-2} at a light power of 44 mW/cm^2. The present photocarrier injection technique could apply to many transition metal oxides to control the hole carrier density externally. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1803616]

It is well-known that many transition metal oxides (TMOs) exhibit dramatic phase transitions as a function of carrier concentration. In order to control these properties such as superconducting and metal–insulator transitions, there has been a great interest in manipulating the carrier concentration by using external fields, for example, electric field or light.[1–3] Concerning superconductivity, for example, Ahn *et al.* prepared an ultrathin film of $GdBa_2Cu_3O_{7-x}$ on a ferroelectric oxide $Pb(Zr_xTi_{1-x})O_3$ and demonstrated an electrostatic modulation of superconductivity by using the polarization field of the ferroelectric oxide.[3] Nieva *et al.* observed a small enhancement in the superconducting transition temperature T_c of a $YBa_2Cu_3O_x$ thin film after a long time laser illumination.[4]

Recently, we reported an alternative way for hole doping, which is a photocarrier injection (PCI) method in TMO heterostructures.[5,6] We prepared an insulating thin film of vanadium dioxide (VO_2) on an *n*-type TiO_2 substrate doped with Nb, and observed a remarkable decrease in resistance under ultraviolet (UV) light irradiation. We also observed a positive photovoltage of 0.5 V to the film. To explain these observations, we have proposed a simple band picture where only hole carriers created by absorbing a light in $TiO_2:Nb$ are injected to the film through the interface, resulting in the reduced resistance of the VO_2 film. In this letter, we apply this PCI method to $YBa_2Cu_3O_{7-x}$ (YBCO) in a $YBCO/SrTiO_3:Nb$ heterostructure and study the current–voltage and photovoltaic properties under UV light illumination.

A $YBa_2Cu_3O_{7-x}$ thin film was prepared on a $SrTiO_3$ (100) single crystal substrate doped with 0.05 wt % Nb (STO:Nb) with donor concentration $N_d=1.7\times10^{19}$ cm^{-3}. The film deposition was carried out by using the pulsed laser deposition technique with a KrF excimer laser ($\lambda=248$ nm). A YBCO film was grown in an O_2 atmosphere of 100 mTorr and at a substrate temperature of 700 °C. The film thickness was 400 Å. The structure of the film was characterized by means of x-ray diffraction and atomic force microscopy, which confirmed the epitaxial growth of the film. As the source of a UV light ($\lambda=300–400$ nm), a Xe lamp was used. The light irradiance was changed by using variable neutral density filters. The current–voltage curve and open-circuit photovoltage V_{OC} were measured with electrodes of Ag and Ti deposited on the film and substrate, respectively, in order to prevent a Schottky barrier from being formed at the interface. All the measurements were carried out at room temperature.

Figure 1(a) shows the current density (J)–voltage (V) curves of the YBCO/STO:Nb heterostructure measured in the dark and under UV light irradiation ($L=44$ mW/cm^2). In the dark, the $J-V$ curve exhibits marked rectifying behavior: the current increases steeply around a positive bias voltage of 0.6 V. A small leakage current of 5×10^{-6} A/cm^2 at $V=-2$ V indicates the uniform heterojunction with a negli-

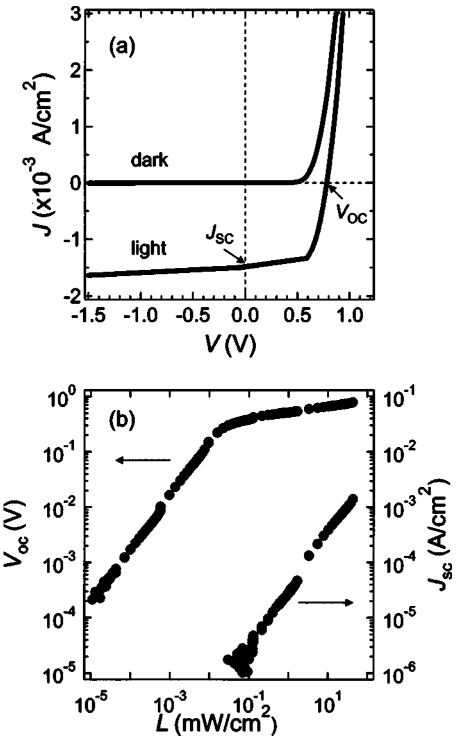

FIG. 1. (a) Current–voltage characteristics of a $YBa_2Cu_3O_{7-x}/SrTiO_3:Nb$ heterostructure measured at room temperature in the dark and under UV light irradiation with a light power of $L=44$ mW/cm^2; (b) UV light irradiance dependence of the open-circuit voltage V_{OC} (left) and the short-circuit current density J_{SC} (right).

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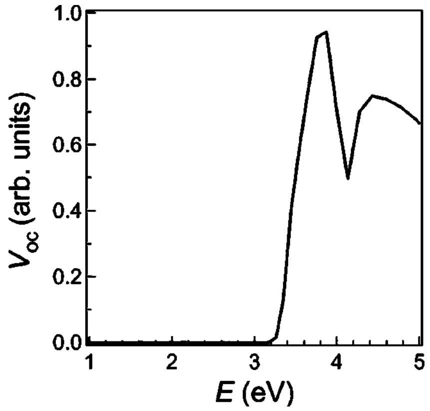

FIG. 2. Spectral response of V_{OC}.

gibly small number of interface states. Under UV light irradiation, the $J-V$ curve shifts downward with an open-circuit voltage V_{OC} of 0.78 V and a short-circuit current density J_{SC} of 1.5 mA/cm^2, as in a conventional semiconductor photodiode. The external quantum efficiency is calculated to be 12.1%, which is given by $(J_{SC}/e)/(L/h\nu)$, where $L/h\nu$ is the number of photons arriving and is $\sim 7.7 \times 10^{16}$ photons/ cm^2 s, assuming that the incident light has a wavelength of 350 nm.

The observed V_{OC} is positive to the YBCO film as in the VO_2/TiO_2:Nb heterostructure, implying that hole carriers are injected to the film. Figure 1(b) shows the V_{OC} as a function of UV light irradiance. Note that the V_{OC} increases linearly with light irradiance in a wide range of $10^{-5} < L < 10^{-2}$ mW/cm^2. At higher irradiance, it tends to saturate toward 0.8 V. The J_{SC} is also proportional to the light irradiance in a wide range. The sensitivity at zero bias for the UV light with $L = 1$ mW/cm^2 is 0.02 A/W, which is comparable to that of AlGaN-based heterojunctions.[7]

Figure 2 shows the incident photon energy dependence of the V_{OC}. The V_{OC} can be detected only under light irradiation with the photon energy larger than 3.2 eV, which corresponds to the band gap energy of $SrTiO_3$. This means that photocarriers generated only in the substrate are responsible for the appearance of photovoltage. The result demonstrates the possibility to use the present oxide heterojunction as a UV-selective photodetector.

In order to interpret the obtained results, we propose a simple band picture as shown in Fig. 3. This energy-level diagram for YBCO/STO:Nb is essentially the same as that of a *p-n* heterojunction with a positive reverse barrier made of ordinary semiconductors, and is obtained by combining two band diagrams from YBCO and STO:Nb, taking into account the Fermi level matching. Near the interface, the band bending should occur mostly in the STO:Nb substrate, because of the large dielectric constant of STO. The formed barrier height, which corresponds to the diffusion voltage V_D, is determined by the difference in the Fermi energy between the two materials. The thickness of the depletion layer in STO:Nb is approximately calculated to be 600 Å at zero bias by using the dielectric constant of $\varepsilon_s = 380$ estimated from our capacitance measurements shown in Fig. 4(a) and the impurity density of $N_d = 1.7 \times 10^{19}$ cm^{-3}. This means that there is a large electric field gradient of $\sim 10^5$ V/cm for holes. Under UV light irradiation, STO:Nb absorbs the light to create holes and electrons in the valence and conduction bands, respectively. Among them, holes can be transferred to the YBCO film across the interface, while electrons cannot be due to the large barrier at the interface. As a result, photoexcited holes and electrons in STO:Nb are separated spatially to have a sufficiently long lifetime and then a photovoltage is generated. A similar band diagram was proposed for VO_2/TiO_2:Nb heterostructure, as described in Ref. 5.

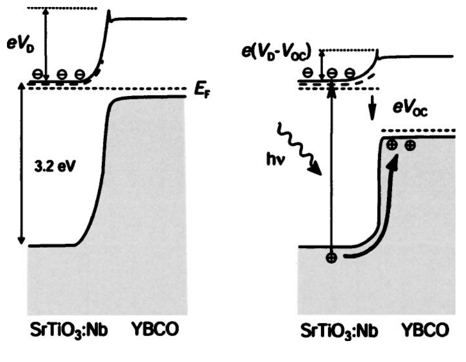

FIG. 3. Possible energy-level diagrams for the $YBa_2Cu_3O_{7-x}/SrTiO_3$:Nb heterostructure in the dark (left) and under UV light irradiation (right).

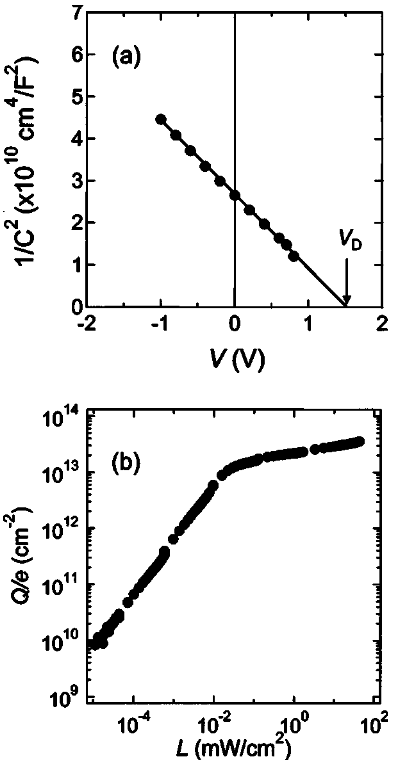

FIG. 4. (a) Bias voltage dependence of $1/C^2$ in the dark, measure at an ac frequency of 20 Hz; (b) injected surface charge density Q/e as a function of UV light irradiance.

On the basis of the band diagram, we try to estimate the surface carrier density Q/e of injected holes. A photodiode is generally considered to be a condenser to accumulate photogenerated charges in an open-circuit voltage condition. Therefore, the surface density can be obtained from a simple relation of $dQ = CdV$, where C is the capacitance of the depletion layer given by $C = \varepsilon_0 \varepsilon_s / w = [e\varepsilon_0 \varepsilon_s N_d / 2(V_D - V_{OC})]^{1/2}$. Here, w and ε_s is the width and dielectric constant of the depletion layer, respectively. We measured the bias voltage dependence of the capacitance of the junction in the dark, and found that $1/C^2$ changes linearly with bias voltage, as shown in Fig. 4(a). The C at

$V = 0$ is 6.2 μF/cm^2. A voltage where $1/C^2$ intercepts the V axis corresponds to the diffusion voltage of the heterojunction and is determined to be 1.5 V. This indicates that the original difference of the Fermi energy between the film and substrate is 1.5 eV. The dielectric constant ε_s of the depletion layer is estimated to be 380 from the slope of the $1/C^2 - V$ plot, which is nearly equal to that of a $SrTiO_3$ single crystal ($\varepsilon_s = 330$).[8]

Figure 4(b) shows injected surface hole density Q/e plotted against the light irradiance. The Q/e at the maximum light power of $L = 44$ mW/cm^2 is 3.5×10^{13} cm^{-2}. This is nearly the same value as that reported for the VO_2/TiO_2:Nb heterostructure under UV light.[9] It is to be noted that the surface charge density of the present oxide heterojunction is much larger than that of conventional semiconductor photodiodes ($\sim 10^{12}$ cm^{-2}). The major reason is presumably the large dielectric constant of STO, compared with that of conventional semiconductors ($\varepsilon_s < 10$). Assuming the uniform distribution of holes in the 400-Å-thick film, the obtained Q/e corresponds to the increase of hole carrier density Δp by 0.002 holes per Cu atom. This increase seems to be too small to change the physical properties of the film. However, an enhancement of T_c has been observed in underdoed YBCO films grown on STO:Nb substrates under UV light irradiation,[10] where the Δp deduced from the increase of T_c is about 0.02 holes per Cu atom. This value is ten times larger than that obtained assuming the uniform distribution of holes in the film. Therefore, we believe that most of the injected hole carriers exist near the interface, giving rise to a hole-rich thin layer with an enhanced T_c. A similar conclusion has been obtained in a photoemission study on a VO_2/TiO_2:Nb heterostructure under UV light irradiation.[11]

In conclusion, efficient hole doping into a YBCO film using the photocarrier injection technique is demonstrated in a YBCO/STO:Nb heterostructure. The maximum injected surface hole carrier density is attained to be 3.5×10^{13} cm^{-2} at $L = 44$ mW/cm^2. The present PCI technique would apply to many TMOs or other materials such as organic compounds[12] as a way for achieving dynamical hole doping to control a phase transition.

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[1] K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, Appl. Phys. Lett. **78**, 4257 (1997).
[2] H. Katsu, H. Tanaka, and T. Kawai, Appl. Phys. Lett. **76**, 3245 (2000).
[3] C. H. Ahn, S. Gariglio, P. Paruch, T. Tybell, L. Antognazza, and J.-M. Triscone, Science **284**, 1152 (1999).
[4] G. Nieva, E. Osquiguil, J. Guimpel, M. Maenhoudt, B. Wuyts, Y. Bruynseraede, M. B. Maple, and I. K. Schuller, Appl. Phys. Lett. **60**, 2159 (1992).
[5] Y. Muraoka, T. Yamauchi, Y. Ueda, and Z. Hiroi, J. Phys.: Condens. Matter **14**, L757 (2002).
[6] Y. Muraoka and Z. Hiroi, J. Phys. Soc. Jpn. **72**, 781 (2003).
[7] C. J. Collins, U. Chowdhury, M. M. Wong, B. Yang, A. L. Beck, R. D. Dupuis, and J. C. Campbell, Appl. Phys. Lett. **80**, 3754 (2002).
[8] K. A. Müller and H. Burkard, Phys. Rev. B **19**, 3593 (1979).
[9] Z. Hiroi, T. Yamauchi, Y. Muraoka, T. Muramatsu, and J. Yamaura, J. Phys. Soc. Jpn. **72**, 3049 (2003).
[10] Y. Muraoka, T. Yamauchi, T. Muramatsu, J. Yamaura, and Z. Hiroi, J. Magn. Magn. Mater. **272–276**, 448 (2004).
[11] R. Eguchi, Ph. D. thesis, University of Tokyo, 2003.
[12] J. Yamaura, Y. Muraoka, T. Yamauchi, T. Muramatsu, and Z. Hiroi, Appl. Phys. Lett. **83**, 2097 (2003).