

## Photoemission Study of $\text{YBa}_2\text{Cu}_3\text{O}_y$ Thin Films under Light Illumination

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Heterojunctions of Nb-doped  $\text{SrTiO}_3$  substrate and  $\text{YBa}_2\text{Cu}_3\text{O}_y$  thin films show photoconductivity and photovoltaic effects due to photocarrier injection. Photocarrier injection is expected to be a new carrier doping method in strongly correlated systems instead of chemical substitution. We have studied the nature of photocarrier injection in  $\text{YBa}_2\text{Cu}_3\text{O}_y/\text{SrTiO}_3\text{:Nb}$  using x-ray photoemission spectroscopy with pulsed laser excitation. The core-level spectra shift to higher binding energy by 0.78 eV under pulsed laser illumination at 30 Hz. The energy shift corresponds to the photovoltage, which arises at the interface. In addition, we have observed that the energy shift strongly depends on the frequency of the laser. The lifetime of the injected photoholes has been estimated to be 40 ms by analyzing the frequency dependence.

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Photoinduced phenomena, which appear in the  $p$ - $n$  junction of semiconductors under light illumination such as the photovoltaic effect and photoconductivity, have been extensively investigated [1,2]. The understanding of photoinduced phenomena contributes to technologies such as switching devices, photocells, and so on. Recently, Muraoka *et al.* discovered photovoltage and photoconductivity in heterojunctions of transition-metal oxide (TMO) thin films and Nb-doped titanium oxide substrate under light illumination [3–8]. Nb-doped  $\text{TiO}_2$  and  $\text{SrTiO}_3$  (STO:Nb), which are employed as substrates, have band gaps about 3.0 and 3.2 eV, and behave like  $n$ -type semiconductors against the  $p$ -type TMO films. There are many interesting issues in TMO films and titanium oxide under light illumination [9–11]. Since the valence band of TMOs is composed of strongly correlated electronic states, it is expected to show different behavior from conventional semiconductors. It is therefore highly important to study the nature of these heterojunctions under light illumination. Since the TMO films exhibit rich physical properties, such as superconductivity, ferromagnetism, and a metal-insulator transition, the nature of the TMO-based heterojunction is very interesting and important in relation to basic physics as well as applications.

Various TMO thin films show different phenomena such as  $\text{VO}_2$  [3,5,12] with a metal-insulator transition near room temperature,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  [8] with a ferromagnetic transition, and  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (YBCO) [6,7] with high- $T_c$  superconductivity. Although the TMOs have different properties, in all cases those resistivities are reduced by illumination with the light of photon energy larger than the band gap of the Nb-doped titanium oxide substrate. In all cases, the photovoltage induced by the light illumination is always positive. These results show that the photoinduced electron-hole pairs are generated in

the Nb-doped titanium oxide by illumination and that photoholes are dominantly injected into the TMO film, lowering the whole TMO band [see Figs. 1(a) and 1(b)]. Band bending in the depletion layer accelerates injection of photoholes into the  $p$ -type TMO film and acts as a potential barrier for photoinduced electrons at the junction. This phenomenon, called photocarrier injection (PCI), is reversible and has a quick response to light switching. In addition, the doping level of holes is tunable by varying the light irradiance. PCI has the potential to

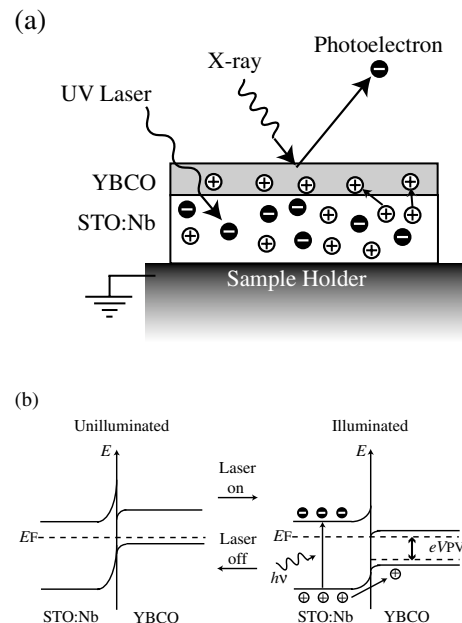


FIG. 1. (a) Setup of the XPS measurement for PCI effect. (b) Schematic picture of the band structure of the YBCO/STO:Nb heterojunction. The horizontal axis is the depth from the interface.

become a new carrier doping method, instead of the conventional chemical substitution, for control of the physical properties of TMOs. For example, in a YBCO film on STO:Nb (YBCO/STO:Nb) not only does the resistivity decrease but also the superconducting critical temperature  $T_c$  increases due to the light illumination [6]. In the present work, we have investigated the YBCO/STO:Nb by using x-ray photoemission spectroscopy (XPS) combined with pulsed laser excitation.

The STO substrate included 0.05 wt % niobium. The YBCO film was grown at 973 K by the pulsed laser deposition technique with a KrF excimer laser ( $\lambda = 248$  nm) under oxygen pressure at 13 Pa. Measurement of the x-ray reflectivity indicated that the thickness of the YBCO film was 24 nm. Although we could not exactly evaluate the oxygen content in the film, transport measurements showed a  $T_c$  of 84 K, near the optimum level. To clean the surface before the XPS measurements, we annealed the sample under oxygen pressure of  $8 \times 10^{-3}$  Pa at 593 K for 30 min. We used a JEOL JPS-9200 hemispherical analyzer with monochromatized Al  $K\alpha$  x-ray source of photon energy of 1486.6 eV to measure the XPS spectra. The total energy resolution was 0.6 eV. A Nd:YAG pulse laser was the light source for photoexcitation, the third harmonic of the laser giving photon energies of 3.5 eV ( $\lambda = 355$  nm). In the STO:Nb substrate, 3.5 eV is large enough to excite the electrons from the valence band to the conduction band. The frequency of the laser  $f$  is tunable up to 30 Hz, and the pulse width  $\gamma$  is about 10 ns. The laser beam spot size  $S$  was  $0.2$  cm<sup>2</sup> for  $f = 30$  Hz and  $0.8$  cm<sup>2</sup> for  $f \leq 15$  Hz, and shines onto the sample via a mirror and quartz window. Another important parameter of the laser is the energy per pulse  $P$  with the unit of mJ. As shown in Fig. 1(a), the substrate was contacted to the ground in order to observe the photovoltage generated at the junction.

Figure 2 shows the laser switching properties of the Ba 3d, Ba 4d, Cu 2p, and O 1s core-level spectra at 130 K. The laser conditions were  $f = 30$  Hz,  $P = 1$  mJ, and  $S = 0.2$  cm<sup>2</sup>. In all the spectra, the energy shift of 0.78 eV caused by the light illumination was observed by XPS. The laser illumination shifted the whole YBCO band by 0.78 eV towards higher binding energy. The energy shift rapidly vanished after the laser was turned off, and the spectrum returned to the same position as before the laser illumination. Therefore we can assign the energy shift  $eV_{PV}$  to the photovoltage due to the PCI effect, and we can exclude some other effects such as charge up, thermal effect, and surface decomposition. The photovoltage  $V_{PV} = 0.78$  V observed in the XPS spectra is smaller than the open circuit voltage of 1.2 V by Muraoka *et al.* at room temperature [6,7]. The disagreement could be caused by differences in experimental conditions such as the thickness of the YBCO films, measurement temperature, and light source. In particular, we note that

Muraoka *et al.* used a continuous UV light source while we employed a pulsed laser, and that their UV light included wavelengths  $300 \leq \lambda \leq 400$  nm while the pulsed laser is monochromatic at 355 nm.

As reported by Muraoka *et al.*, the photovoltage increases linearly for light power density per unit time  $L < 1 \times 10^{-2}$  mW/cm<sup>2</sup>. For  $L > 1 \times 10^{-2}$  mW/cm<sup>2</sup> the photovoltage tends to saturate, because the injection of photo-induced electrons is promoted by reduction of the potential barrier in the conduction band, and the recombination with the photoholes is enhanced. We have investigated the laser power density dependence with  $P = 1$  and 2 mJ at 130 K. Using the above-mentioned parameters, the averaged power density per pulse  $P/\gamma S$  is of the order of  $10^5$  W/cm<sup>2</sup>. Since the averaged power density per pulse is huge compared to that of the previous study using continuous light, it is reasonable to consider that the photovoltage reaches the maximum value. Actually, in the results shown in Fig. 3, the energy shift is pinned at about 0.78 eV with  $P = 2$  mJ. We have also observed the same energy shift limit with higher  $P$ . Therefore, the

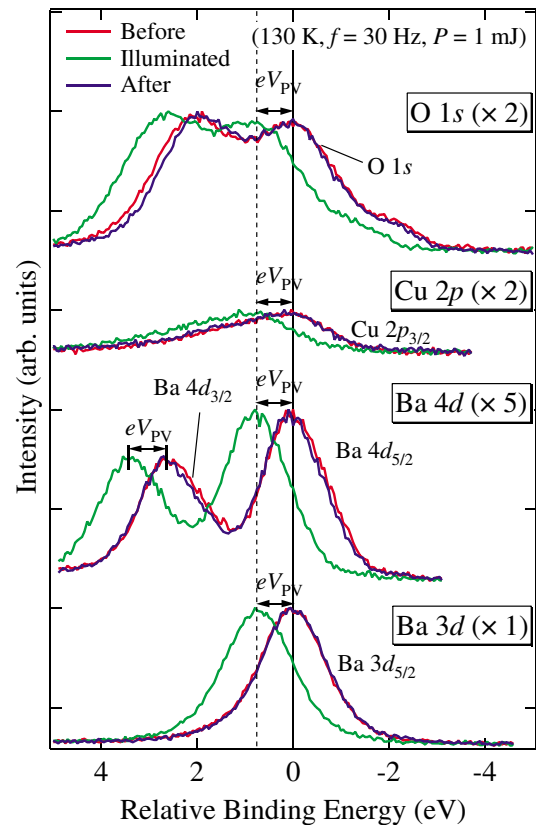


FIG. 2 (color online). Switching properties of the Ba 3d, Ba 4d, Cu 2p, and O 1s core-level spectra of YBCO/STO:Nb. The spectra are plotted using binding energies relative to the main peaks at 779.78 eV (Ba  $3d_{5/2}$ ), 89.28 eV (Ba  $4d_{5/2}$ ), 932.90 eV (Cu  $2p_{3/2}$ ), and 531.13 eV (O 1s). The energy shift  $eV_{PV}$  of the core-level spectra corresponds to the shift of the whole YBCO band as indicated in Fig. 1(b).

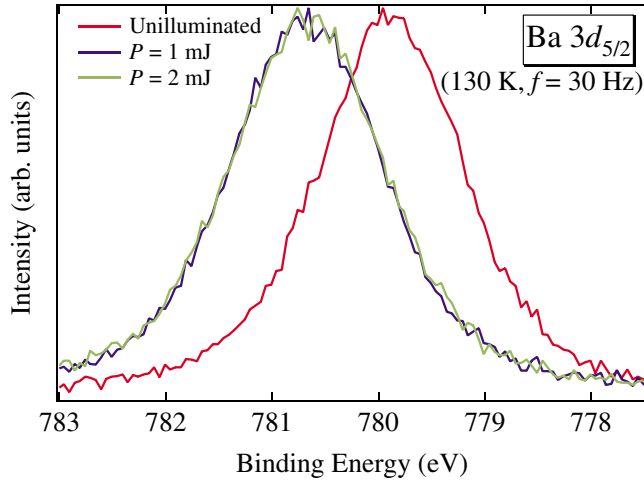


FIG. 3 (color online). Laser power dependence of the Ba  $3d_{5/2}$  core-level spectra of YBCO/STO:Nb.

photovoltage is always saturated with the pulse energy in the present measurement. However, the observed energy shift of 0.78 eV is reduced from that reported in the paper by Muraoka *et al.*

We present the laser frequency dependence of the energy shift at 130 K in Fig. 4. The spectra were measured with  $P = 1$  mJ. One can see that the shift is strongly dependent on the frequency. On the other hand, we have also confirmed the dependences were almost the same for both  $P = 1$  and 2 mJ cases, indicating that the photovoltage was already saturated with the photon flux density. Therefore, we do not need to consider the laser power density dependence of the photovoltage for any cases. The energy shift is plotted as a function of laser frequency in Fig. 5. The frequency dependence reveals that the photovoltage tends to saturate with higher laser frequency. Accordingly, we assume that the original photovoltage

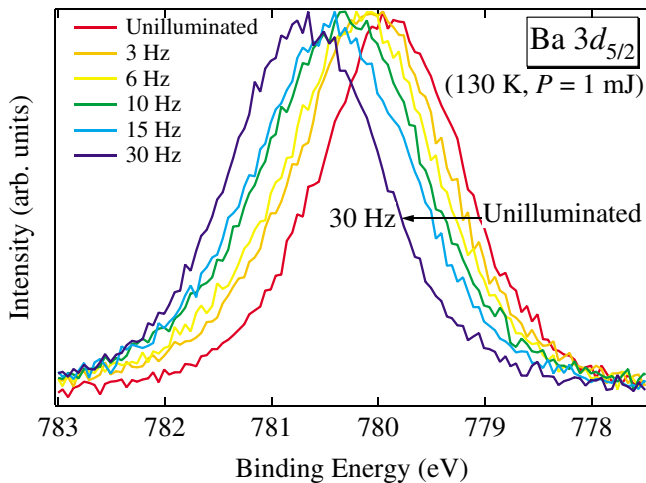


FIG. 4 (color online). Frequency dependences of the Ba  $3d_{5/2}$  core-level spectra of YBCO/STO:Nb.

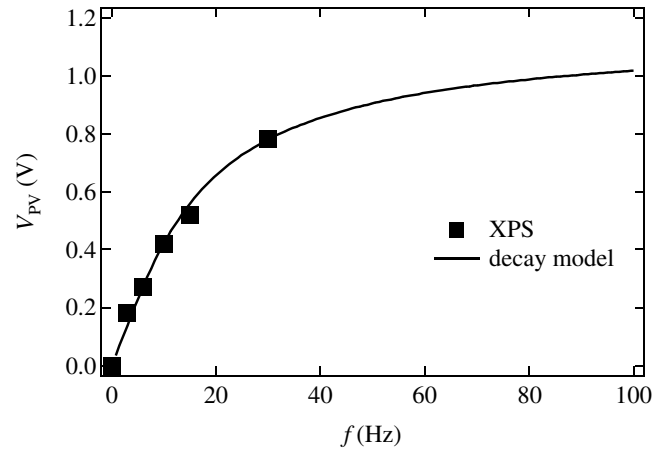


FIG. 5. Photovoltage as a function of laser frequency. The fitting curve is given by the exponential decay model.

decays with the relaxation time  $\tau$  after every laser pulse (Fig. 6). The photovoltage  $V_{PV}$  observed in the XPS spectra should be a time average of the integral of the decay curves.  $V_{PV}$  is expressed as

$$\begin{aligned} V_{PV} &= f \int_0^{1/f} V_{\max} \exp(-t/\tau) dt \\ &= f V_{\max} \tau [1 - \exp(-1/f\tau)]. \end{aligned} \quad (1)$$

Here,  $V_{\max}$  is the height of the exponential curve at  $t = 0$  and is equal to the maximum photovoltage in the high frequency limit. In other words,  $V_{\max}$  is the saturated photovoltage under continuous light. Since the laser power density per pulse is huge compared to that of the previous report with the continuous light, it is reasonable to assume that  $V_{\max}$  is independent of the frequency.

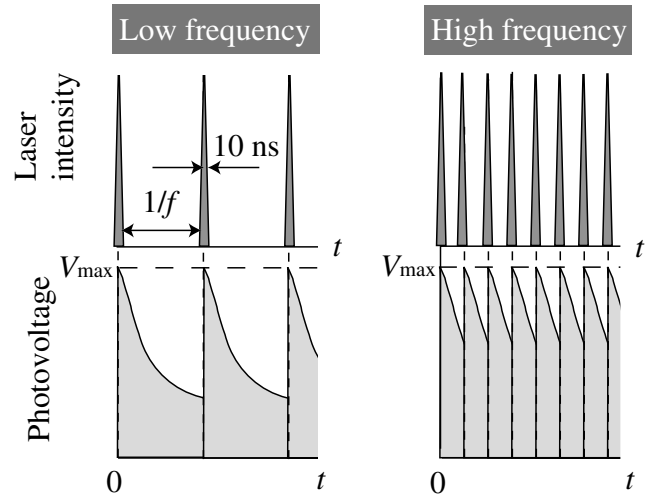


FIG. 6. Schematics of the decay model. The horizontal axis is time. In this picture, we assume that  $V_{\max}$  is independent of the laser frequency because the intensity of each laser pulse is high enough to suppress the laser power dependence.

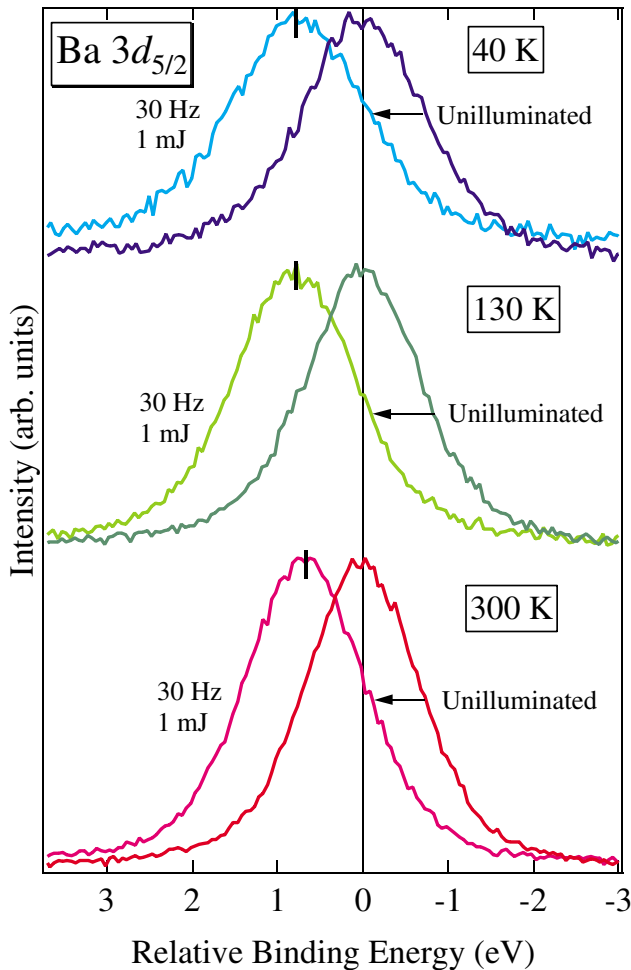


FIG. 7 (color online). Temperature dependence of the photovoltage observed in Ba  $3d$  spectra. The peaks of the unilluminated spectra taken at each temperature are fixed to zero.

Using Eq. (1) and adjusting  $V_{\max}$  and  $\tau$ , we have obtained the fitted curve shown in Fig. 5.  $V_{\max}$  is 1.15 V for  $P = 1$  mJ. The relaxation time of the photovoltage,  $\tau$  is 40 ms. While this phenomenological model analysis does not include complex mechanisms such as carrier trapping due to the impurity levels at the interface and recombination processes of the photoholes with electrons, the results are reasonable compared to the previous report by Muraoka *et al.*, which concludes that the photovoltage is around 1.2 V at room temperature, and the relaxation time of the YBCO film is relatively longer than the other TMO films [6,7].

It is expected that the photovoltage increases with decreasing temperature since the thermal excitation of the electrons at the interface is suppressed with cooling. As shown in Fig. 7, the Ba  $3d$  spectra taken at 300, 130, and 40 K with  $f = 30$  Hz and  $P = 1$  mJ showed temperature dependence. The shifts were 0.67 eV for 300 K, 0.78 eV for 130 K, and 0.78 eV for 40 K. The photovoltage was slightly enhanced at 130 K compared with 300 K and

almost saturated below 130 K. While 40 K is certainly below the  $T_c = 84$  K, the core-level spectra did not show any significant difference between 40 and 130 K. At both 40 and 300 K, the laser switching properties, the saturation of the photovoltage with the laser power, and the laser frequency dependence reproduced the same behavior as those at 130 K while the amount of the energy shift changes a little. In the future, high-energy resolution ultraviolet photoemission spectroscopy should be performed to investigate how the valence band spectra changes above and below  $T_c$  and how the PCI affects the valence band in terms of hole doping.

In conclusion, we have observed the photovoltage due to the PCI effect at the heterojunction of YBCO/STO:Nb using XPS combined with the pulsed laser source. The magnitude of the photovoltaic-induced shift in the core level is 0.78 V at a laser frequency of 30 Hz at 130 K. The energy shift is not dependent on the power density. On the other hand, the energy shift is dependent on the laser frequency. From the laser frequency dependence, we have estimated the relaxation time of the photovoltage and maximum photovoltage. The maximum photovoltage, which corresponds to the photovoltage with a continuous wave light, is 1.15 V for  $P = 1$  mJ. The lifetime of the injected holes is estimated to be 40 ms. The photovoltage is slightly enhanced with cooling from 300 to 130 K and saturated below 130 K.

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