Evidence of Fermi level tuning in multiferroic $BiFeO_3$ thin films by Mn doping for high photovoltage generation

A bulk photovoltaic effect (BPVE) is a recently refocused mechanism for novel solar cells that are expected to have power conversion efficiencies exceeding those of conventional p-n junction solar cells. The BPVE is due to a quantum mechanical effect called shift current, which can generate a high open-circuit voltage (V_{OC}) exceeding the band gap (E_g) by irradiating light to noncentrosymmetric crystals. Among the noncentrosymmetric crystals, a ferroelectric material with a polar crystal structure shows the BPVE and a converse piezoelectric effect simultaneously, realizing optically induced strain. However, high electric field generation by the BPVE in the material itself is necessary for inducing optical strain. The multiferroic $BiFeO_3$ (BFO) is one of the best candidates for optical actuator application because of its excellent ferroelectric properties and environmentally friendly lead-free composition. In addition, the bandgap of BFO is in the visible wavelength region of 2.5–2.8 eV, realizing visible-light-driven devices. Indeed, the ultrafast response of the optical strain under femtosecond laser irradiation [1] and the magnetic field modulation [2] of the optical strain in bulk single crystals have already been reported. However, the optical strain is still small at *ca.* 0.0002% even in bulk BFO single crystals. To enhance the optical strain, the enhancement of the photovoltage is required; therefore, a highly insulating BFO thin film is necessary. We have generated 852 V generation in a multiferroic Mn 0.5-at% doped $BiFeO_3$ (BFMO) thin-film coplanar capacitor at 80 K under blue-violet laser (λ = 405 nm) irradiation, as shown in Figs. 1(a) and 1(b) [3]. The interelectrode distance was 260 μm, indicating that such a high voltage can generate an electric field of 32.7 kV/cm to the BFMO thin film itself, which is a sufficiently high electric field for inducing the converse piezoelectric effect. In addition, by investigating the dependence of V_{OC} in the BFMO thin films on the amount of doped Mn, the maximum V_{OC} of 280 V at RT was found to be obtained in the Mn 1-at% doped BFMO thin film, as shown in Fig. 1(c). This indicates electronic structural evolution upon Mn doping because high voltage generation can be induced in a highly insulating medium.

In the present work [3], we investigated the Fermi level tuning of BFO by Mn doping to clarify the electronic structure evolution. For the precise evaluation of Fermi level shift in ferroelectrics, the hard X-ray photoemission spectroscopy (HAXPES) of ultrathin metal-film-capped surfaces is suitable, because ferroelectrics are insulators with spontaneous polarization charges at the surface. The charged surface is partly terminated by adsorbed molecules, causing an unstable surface potential. Therefore, it is difficult to evaluate the chemical shifts of the charged surface by photoemission spectroscopy. On the other hand, at the ultrathin metal-film-capped ferroelectric surface, the spontaneous polarization charges are terminated by the capped metal layer, stabilizing the potential at the metal/ferroelectric interface. In other words, the Fermi level of the ferroelectric at the interface is pinned by the Fermi level of the metal layer; however, this means that band bending in the ferroelectric layer should be evaluated. HAXPES can be used to evaluate the ferroelectric layer through the ultrathin metal layer because of the deep penetration of high energy photoelectrons (>20 nm). Therefore, Au (9 nm)/BFMO (150 nm)/$SrRuO_3$ (SRO) (30 nm)/$SrTiO_3$(001) structures were used for the measurements. The

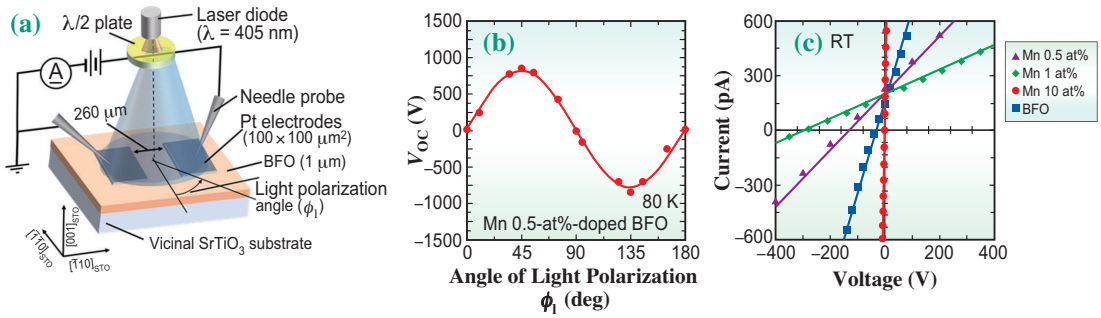

Fig. 1. **(a)** Schematic illustration of the sample structure and setup for photovoltaic property measurements. **(b)** Dependence of the light polarization angle (ϕ_l) on the open circuit voltage (V_{OC}) defined as the voltage at I = 0 A in Mn-0.5-at%-doped BFO thin film at 80 K. **(c)** I–V characteristics of BFMO thin films with various amounts of doped Mn measured at RT. The measurements were performed under blue violet laser (λ = 405 nm) irradiation with a power density of 17 W/cm^2. The light polarization angle (ϕ_l) was fixed at 45° in (c). The double sinusoidal dependence of V_{OC} in (b) means that the photovoltage is due to the BPVE, and the maximum V_{OC} of 852 V was confirmed at ϕ_l = 45°.

HAXPES measurements were performed at SPring-8 **BL47XU**. For exciting Bi 4*f*, Au 4*f* and valence band electrons in the samples, synchrotron X-rays with an energy of 7.94 keV were used. The measurements were performed at RT, and the excited photoelectrons were detected using the R4000 photoelectron analyzer (VG-Scienta Co.) equipped with a wide-acceptance-angle electrostatic lens with an acceptance angle of about ±32° [4,5]. During the measurements, both Au and SRO electrodes were grounded.

Figures 2(a) and 2(b) show Au 4*f* and Bi 4*f* HAXPES spectra, respectively, for the Au-capped Mn-1-at%-doped BFO/SRO/STO structure. For the measurements, photoelectron take-off angles (TOAs) are fixed at 85° (TOA85) and 5° (TOA5). The lower TOA corresponds to surface-sensitive conditions, whereby the electronic structures at the Au/BFMO interface might be evaluated. In contrast, the higher TOA corresponds to bulk sensitive conditions owing to the deep penetration of hard X-rays. From the Bi 4*f* spectra, slightly lower binding energies can be obtained at a TOA of 5° than at a TOA of 85°, revealing that the energy bands of BFMO were bent up near the Au/BFMO interface. In contrast, from the Au 4*f* spectra, almost the same binding energies can be detected under any TOA condition, confirming stable surface potentials. Thus, the Bi 4*f* spectral shifts are due not to the surface potential fluctuations but to the energy band bending in the BFMO. Figures 2(c) and 2(d) show the change of the Bi 4*f* and Au 4*f* binding energies of the Au/BFMO/SRO/STO structures as a function of amount of Mn doping. With increasing amount of Mn, the shift to lower binding energies were confirmed in the Bi 4*f* spectra. In contrast, the binding energies of Au 4*f* remained almost the same. These results reveal Fermi level lowering upon Mn doping into BFO, indicating that the doped Mn acts as acceptors. In addition, the difference between the binding energies of Bi 4*f* spectra obtained at TOAs of 85° and 5° also increased clearly with the amount of doped Mn despite an almost constant binding energy of the Au 4*f* spectra. These results indicate a larger energy band bending with a higher amount of doped Mn, in agreement with Fermi level lowering upon Mn doping.

In conclusion, we have demonstrated high voltage generation by the BPVE in Mn-doped BFO single crystal thin films. In addition, the evidence of Fermi level lowering in BFO upon Mn doping has been found through HAXPES spectral measurements, revealing that Mn doped into the BFO acts as acceptors. These indicate that the photoconductance of BFO can be modulated by Fermi level tuning by Mn doping, resulting in photovoltage enhancement. These results provide important information for ferroelectric material design by impurity doping for optical actuator applications.

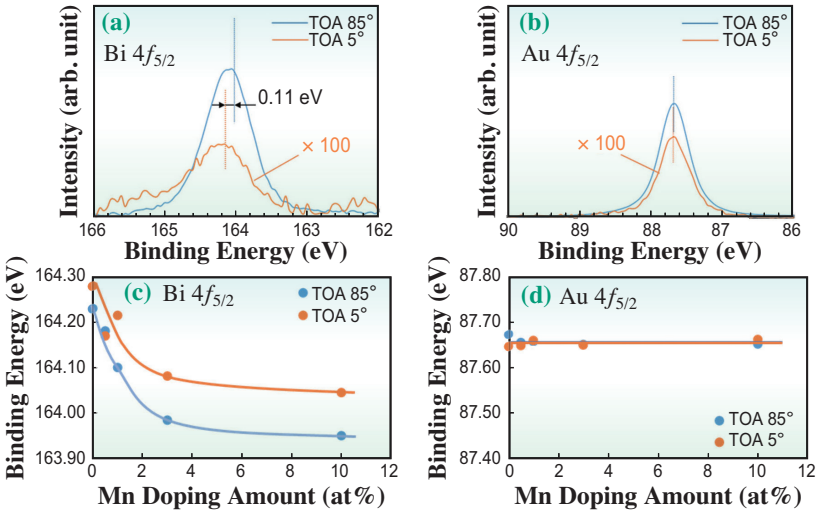

Fig. 2. **(a)** Bi $4f_{5/2}$ and **(b)** Au $4f_{5/2}$ HAXPES spectra at TOAs of 5° (orange line) and 85° (blue line) in the Au-capped Mn-1-at%-doped BFO thin film. Doped Mn amount dependence of **(c)** Bi $4f_{5/2}$ and **(d)** Au $4f_{5/2}$ binding energies measured at TOAs of 5° (orange line) and 85° (blue line) in the Au-capped BFMO thin films.

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