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Polarization-induced Photovoltaic Effect in Er-doped $BiFeO_3$ Ferroelectric Films

Er添加$BiFeO_3$強誘電体薄膜における分極誘起光起電力効果

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Ferroelectric hysteresis behavior was observed in Er-doped $BiFe_{0.97}Mn_{0.03}O_3$ capacitor using Au top and $SrRuO_3$ bottom electrodes. A photovoltaic effect was observed in the current density vs. voltage measurement under a light irradiation onto the sample. This photovoltaic effect is ascribed to the ferroelectric polarizations.

1. Introduction

Novel solar cells are studied for achievement of a low cost and a high conversion efficiency while Si solar cell is the major one. For example, the photovoltaic effect caused by the polarization reversal is different from well-known photovoltaic effect, because the photo-generated carriers in ferroelectric materials are not separated by the built-in field of the conventional p-n junction. However, the photovoltaic conversion efficiencies in ferroelectric capacitors are limited by the small current density (around 10^{-6}mA/cm^2) and the large band gap energy (around 3.5 eV). Therefore, recently, polarization-induced photovoltaic effect in $BiFeO_3$ (BFO) has attracted much attention[1,2] due to a huge remnant polarization and a small band gap (E_g = 2.67eV) of BFO among ferroelectric perovskite materials. The latter feature suggests a high absorption coefficient in visible light region, leading to a promising material for solar cell application.

So far, we tried to dope Er atoms, emitting light in the optical communication band, into ferroelectric $LiNbO_3$ and BFO films for developing a novel optical switches using the piezoelectric effect. However, the electrical conductivity of BFO films varied depending on the Er content. Therefore, this result led us to polarization-induced photovoltaic effect of Er-doped BFO films for obtaining a synergistic effect of the semiconducting feature and the ferroelectric feature in Er-doped BFO films. In addition, it is attracting our attention that the photoluminescence (PL) spectrum and the PL intensity vary with the local crystallographic symmetry of Er in various host materials[3], leading to clarifying the local environment of Er atoms in oxides .

In the present study, we fabricated Er-doped BFO thin film using the pulsed laser deposition (PLD) method. As a result, we have observed a photovoltaic effect depending on the ferroelectric polarization reversal in Er-doped BFO films.

2. Experimental

The conductivity of non-doped BFO films is known to be governed by deviation of the Bi content from stoichiometry and the valence fluctuation of Fe ion. We reported a leakage current reduction, or a conductivity reduction, by substituting the Bi and Fe sites by rare-earth and transition metals, respectively[4]. Here, we substituted Fe site with Mn atom to obtain a low conductivity sample as a starting host material. Er atoms are incorporated into the host material, resulting in $BiEr_{0.01}Fe_{0.97}Mn_{0.03}O_3$ (Er:BFM) thin film. For sample preparation, firstly, the surface of Nb(0.05wt.%)-doped $SrTiO_3$(001) (Nb:STO) was treated with buffered hydrofluoric acid solution. Then, Er:BFM thin film of 170nm thickness was deposited on it by PLD using bottom electrode of 100nm thick $SrRuO_3$ (SRO) film. Finally, using vacuum evaporation method Au top electrodes were deposited on it. The X-ray diffraction (XRD), the ferroelectric and the electrical transport measurements were performed. For characterization of the photovoltaic property, Ar^+ laser (488nm in the wave length) was employed with an irradiation intensity around 1-3 W/cm^2.

3. Results and Discussion

XRD result showed no Bi deficiencies and (001) preferential orientation of Er:BFM on the

SRO-coated Nb:STO substrate. The electric field dependences of the electric polarization (P-E property) for various maximum applied fields at a frequency of 10 kHz were shown in Fig.1. The hysteresis caused by ferroelectricity was observed, indicating the existence of the polarization reversal although rounded P-E hysteresis curves due to some leakage current can be seen.

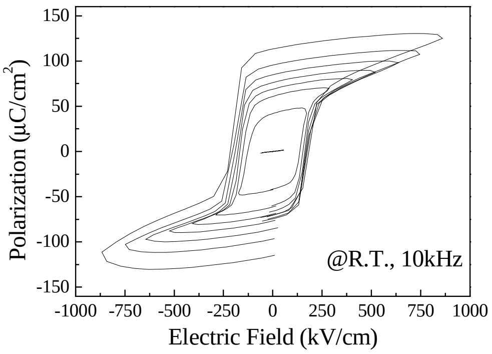

Fig.1 Polarization vs. electric field (P-E) hysteresis loops with measurement frequency of 10 kHz at R.T.

Figures 2 shows the photo- and dark current densities vs. applied voltage (*J-V*) characteristics. Figure 3 shows the expanded one of Fig.2. The voltage was applied to the top electrode against the bottom one. The *J-V* measurements under the irradiation were done with both the sweep directions, that is, the forward voltage sweep from minus to plus and the reverse one from plus to minus. As shown in Fig.2 asymmetric pattern was observed in dark, indicating a rectification behavior. Under the irradiation the short-circuit current density J_{sc} and the open-circuit voltage V_{oc} are +0.04 mA/cm^2 and -0.07 V, respectively, for the forward voltage sweep, and are -0.15 mA/cm^2 and +0.24 V, respectively, for the reverse voltage sweep. The hysteresis behavior in the *J-V* curve of the present Er:BFM film under the illumination is ascribed to a photovoltaic effect caused by the polarization reversal as proposed by Yang *et al.* for non-doped BFO film[2]. It should be noted that the polarization-dependent photovoltaic effect does not necessarily require the conventional built-in potential, which is essential for the separation of photo-generated carriers in the normal p-n or Schottky junctions.

So far, conductivity changes with the Er content have been observed in our previous experiments. The small short-circuit current density in the present ferroelectric sample is expected to turn to large one by optimizing the Er content or improving the Er incorporation scheme. The future PL measurement for these materials will give us valuable knowledge in materials design for improvement of the photovoltaic effect because Er atoms can be used as probes for knowing the local environment.

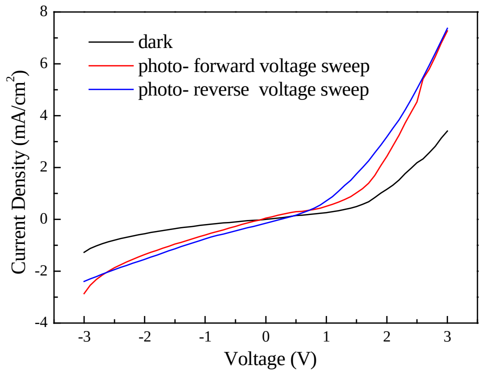

Fig.2 Photo- and dark current density vs. voltage (*J-V*) characteristics

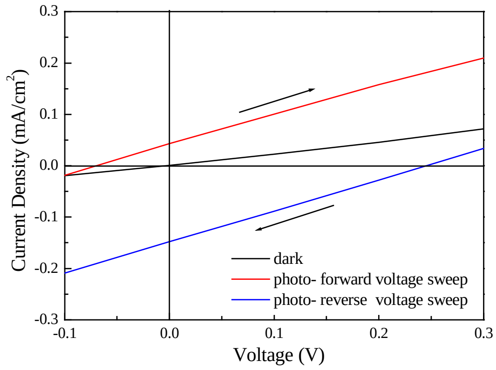

Fig.3 Expanded view of the current density vs. voltage curves in Fig.3 near zero bias field (V=0)

4. Summary

Ferroelectric hysteresis behavior originating from the polarization reversal was observed in Er:BFM capacitor with Au top and SRO bottom electrodes. A photovoltaic effect was also observed in the current density vs. voltage measurement under a light irradiation. This photovoltaic effect is ascribed to the ferroelectric polarization.

References

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