

Epilayer control of photodeposited materials during UV photocatalysis

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(Received 29 January 2009; accepted 15 May 2009; published online 8 June 2009)

Epilayer control of photoassisted oxidation and reduction on the ferroelectric PbTiO₃ polar surface was investigated. Photo-oxidation of a AgNO₃ electrolyte resulting in formation of Ag₇NO₁₁ particles was observed on the PbTiO₃/Nb:SrTiO₃ film surface; whereas PbTiO₃/SrRuO₃/SrTiO₃ leads to AgNO₃ reduction under UV illumination. The oxidation reaction resulting in the formation of Ag₇NO₁₁ is explained in terms of a rectifying interface between PbTiO₃ and Nb:SrTiO₃, controlling the charge transport during UV photocatalysis. © 2009 American Institute of Physics. [DOI: 10.1063/1.3151820]

Photocatalysis has attracted considerably attention since the discovery of the Honda–Fujishima effect¹ due to the possibility of water splitting and photodeposition of various materials. In order to optimize the catalytic properties of a material, it is essential to understand the transport of electrons and holes under UV illumination. For example, NiO-loaded NaTaO₃ is a good photocatalytic material due to the separation of reduction and oxidation sites.² Also, Pt-loaded TiO₂ powders were reported to exhibit strong photocatalytic activity, explained in terms of transport rectification in the Schottky contact between the metal and the TiO₂.³ Moreover, it has been demonstrated that the ferroelectric polarity can be used to control photodeposition^{4–7} and hydrogen production⁸ with only one domain polarity contributing, explained by band bending at the ferroelectric surface. In keeping with this observation, a ferroelectric heteroepitaxial thin film structure might serve to tailor the photocatalytic process.

In this letter, we report on photodeposition of Ag₇NO₁₁ on the surface of ferroelectric PbTiO₃ thin films, heteroepitaxially deposited on conducting Nb:SrTiO₃ substrate. It is shown that the underlying layer of the ferroelectric may serve to promote either oxidation of the Ag⁺ ions in the AgNO₃ electrolyte to form Ag₇NO₁₁ on the PbTiO₃ surface or a reduction to Ag; thus opening for epilayer control of the photodeposited material.

Epitaxial PbTiO₃ and SrRuO₃ thin films were prepared on insulating SrTiO₃(001) and conducting Nb-doped SrTiO₃(001) (Nb: 0.5 wt %) substrates by off-axis rf magnetron sputtering.^{9,10} Typical film thicknesses were 10–40 nm for PbTiO₃ and 40 nm for the SrRuO₃ layer. X-ray diffraction (XRD) studies confirmed that all PbTiO₃ films used in this study display 180° domains.^{10,11} A 0.01 mol/l AgNO₃ solution was used as electrolyte. The immersion time was typically ~30–60 min. A high pressure Hg lamp (500 W,

20 mW/cm²) was used as UV source, and the electrolyte set-up was placed on an aluminum heat sink.^{12,13} During the reaction, bubbles were observed from the film surface as well as from the substrate edges. For electrical characterization, 20 nm thick e-beam evaporated Pt contacts with 400 μm diameter were defined on the PbTiO₃ film surface. Au/Ti thin film and Ag paste were used to contact the Nb:SrTiO₃ substrate and the SrRuO₃ layer, respectively. All electrical and ferroelectric characterization took place outside the AgNO₃ electrolyte.

Figures 1(a) and 1(b) show scanning electron microscope (SEM) images of the PbTiO₃ surface for samples grown on SrRuO₃ and Nb:SrTiO₃, respectively, after the photochemical treatment. Irregular precipitates were found for the PbTiO₃/SrRuO₃/SrTiO₃ system, in contrast to the octahedral particles obtained for PbTiO₃/Nb:SrTiO₃. X-ray

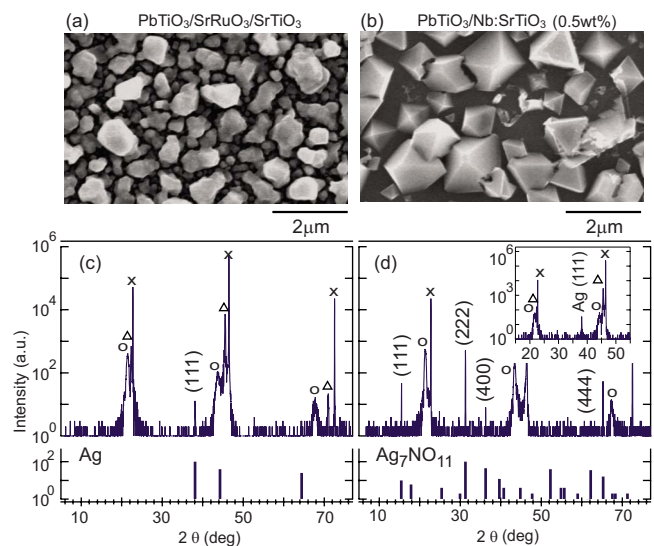


FIG. 1. (Color online) SEM image [(a) and (b)] and XRD patterns [(c) and (d)] after photochemical treatment on PbTiO₃/SrRuO₃ and PbTiO₃/Nb:SrTiO₃, respectively. The inset in (d) shows the XRD pattern after the photochemical treatment on PbTiO₃/SrRuO₃/Nb:SrTiO₃. A SrRuO₃ layer effectively changed the direction of the chemical reaction, turning oxidation to reduction. “x” refers to the substrate, “Δ” refers to SrRuO₃, and “o” refers to PbTiO₃.

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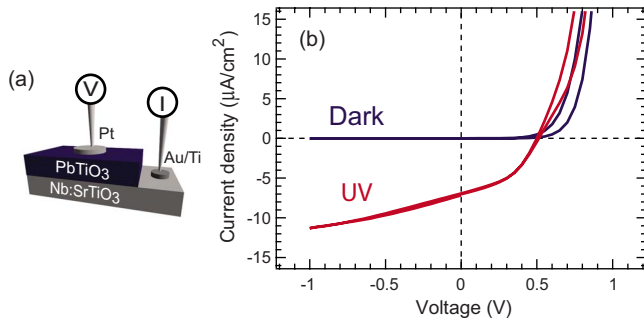


FIG. 2. (Color online) (a) Schematic illustration of the junction polarity defined as positive when a positive voltage is applied to the Pt top electrode. (b) The impact of UV illumination on the I - V characteristic properties of Pt/PbTiO₃/Nb:SrTiO₃/Ti/Au.

fluorescence and photoemission spectroscopy studies verified the presence of Ag at the PbTiO₃ surface. XRD measurements revealed that the precipitates were crystalline. For PbTiO₃/SrRuO₃/SrTiO₃ [Fig. 1(c)], a θ - 2θ Bragg reflection was observed at $2\theta=38.09^\circ$, corresponding to Ag(111).¹⁴ For PbTiO₃/Nb:SrTiO₃ [Fig. 1(d)], Bragg reflections were typically observed at $2\theta=15.50^\circ$, 31.28° , 36.27° , and 65.25° ; suggesting that (111)- and (100)-oriented silver oxide clathrate (Ag₇NO₁₁) was photodeposited.¹⁵ The octahedral shape of the Ag₇NO₁₁ crystals is consistent with previous reports on electrochemically deposited Ag₇NO₁₁.^{16,17} Ag₇NO₁₁ is reported to decompose both in air and at high temperature.¹⁶ XRD measurements of the Ag₇NO₁₁ crystallites, one year after photodeposition, revealed the presence of silver peroxide (Ag₂O₂) on the PbTiO₃ film surface. Silver was found at the substrate edges for samples where Ag₇NO₁₁ was observed.¹⁸

Photodeposition of Ag on PbTiO₃/SrRuO₃/SrTiO₃ is consistent with previous reports for Pb(Zr,Ti)O₃ (PZT) and BaTiO₃, showing reduction of Ag⁺ to silver.⁴⁻⁷ In Ag₇NO₁₁, silver takes on multiple valencies, including Ag⁺, Ag²⁺, and Ag³⁺, which implies oxidation of Ag⁺ to Ag²⁺ and Ag³⁺. In terms of charge transport, this corresponds to a flow of UV-excited holes in the thin film/substrate to the ferroelectric PbTiO₃ surface. Ag₇NO₁₁ precipitates were also observed on PbTiO₃/Nb:SrTiO₃ with lower doping (Nb: 0.05 wt %, 0.1 wt %) and on PbTiO₃/La:SrTiO₃ (La: 0.5 wt %).

This suggests the possibility of epilayer control of photocatalytic reduction versus oxidation. In order to put this hypothesis to test, a SrRuO₃ layer was inserted between PbTiO₃ and Nb:SrTiO₃. This effectively changed the direction of the reaction from oxidation to reduction, cf. the inset in Fig. 1(d).

I - V measurements were performed on both PbTiO₃/Nb:SrTiO₃ and PbTiO₃/SrRuO₃/SrTiO₃. The junction polarity was defined as illustrated in Fig. 2(a). Figure 2(b) shows the measured I - V characteristics of PbTiO₃/Nb:SrTiO₃ in the dark and under UV illumination. A distinct photovoltaic effect was found under UV illumination, in agreement with previous reports for Pt/PZT/Nb:SrTiO₃.¹⁹ A short-circuit current of $7.5 \mu\text{A}/\text{cm}^2$ and an open-circuit voltage of 0.5 V were obtained. The recorded shift in the I - V curve under UV illumination, as compared to dark current conditions, can be most readily explained by increased photogeneration of charge carriers in the depletion region of the PbTiO₃/Nb:SrTiO₃ interface. Similar I - V characteristics

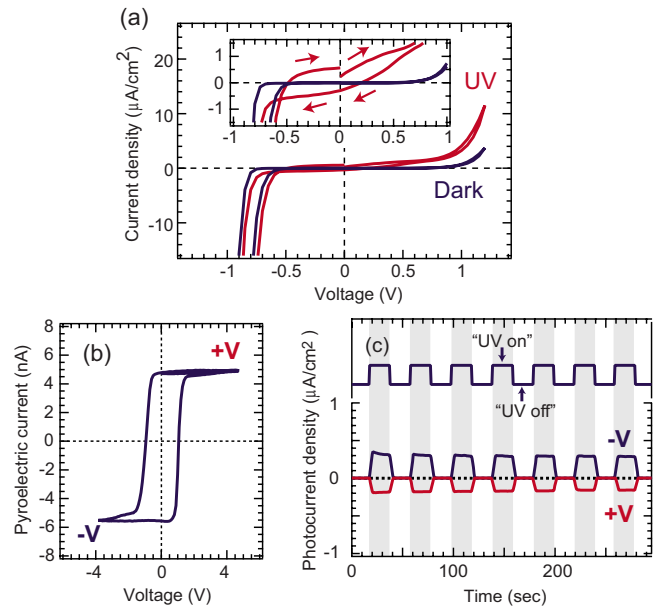


FIG. 3. (Color online) (a) I - V characteristic of Pt/PbTiO₃/SrRuO₃/Ag under and without UV illumination. (b) Pyroelectric hysteresis loop measured by the Chynoweth method. (c) Photoresponse of the short-circuit current for the Pt/PbTiO₃/SrRuO₃/Ag junction under intensity modulated UV illumination. The red and blue color refer to positively and negatively polarized ferroelectric domains, respectively.

were also obtained for the PbTiO₃/Nb:SrTiO₃ (Nb: 0.05 wt %) and PbTiO₃/La:SrTiO₃ (La: 0.5 wt %) systems.

Figure 3(a) displays the I - V characteristics of the PbTiO₃/SrRuO₃/SrTiO₃ system under and without UV illumination. At zero bias, the photovoltaic short-circuit current, I_{sc} , was found to depend on the direction of the voltage sweep (see inset). In Fig. 3(b), the pyroelectric hysteresis loop²⁰ suggests an effective switching between the two opposite polarization states at ± 1 V. Hence, the dependence of I_{sc} on the sweep direction is attributed to the actual ferroelectric polarization state of the PbTiO₃ film. Figure 3(c) shows the time response of the photocurrent at zero bias when the UV illumination is switched on and off repetitively. Red and blue refer to oppositely polarized ferroelectric domains. Thus, the direction of the photocurrent depends on the polarization state of the PbTiO₃ layer. A negatively polarized sample leads to a positive photocurrent, whereas a positively polarized sample leads to a negative photocurrent, in accord with previous reports.^{21,22}

Figure 4(a) shows the pyroelectric hysteresis loop of the PbTiO₃/Nb:SrTiO₃ system, which displays a partial switching between $+c$ and $-c$ domain states. The observed asymmetry of the pyroelectric hysteresis loop can be attributed to the presence of a depletion layer under negative bias, inhibiting complete negative polarization of the PbTiO₃ layer under dark conditions.²³ As seen in Fig. 4(b), a negative short-circuit current was always obtained. This is different from that of the PbTiO₃/SrRuO₃/SrTiO₃ system, having a domain polarity dependent photocurrent. Moreover, the amplitude of the photocurrent was approximately 30 times larger for the PbTiO₃/Nb:SrTiO₃ system, compared to that of the PbTiO₃/SrRuO₃/SrTiO₃ system. This suggests a photoexcited hole current from the Nb:SrTiO₃ substrate to the Pt electrode. In the present study, PbTiO₃/Nb:SrTiO₃ samples with either positive or negative net polarization were used,

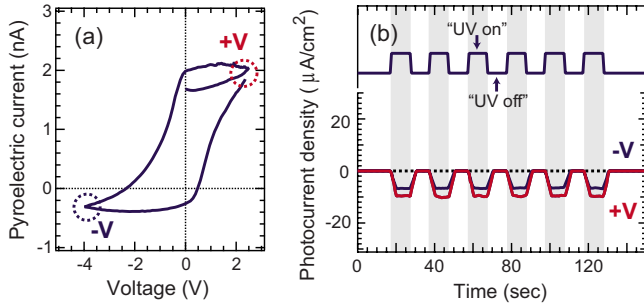


FIG. 4. (Color online) (a) Pyroelectric hysteresis loop of the Pt/PbTiO₃/Nb:SrTiO₃ junction. (b) The photoresponse of the short-circuit current from positively and negatively polarized domains under intensity modulated UV illumination.

and all samples showed Ag₇NO₁₁ precipitates on the PbTiO₃ surface after photodeposition.

For PbTiO₃/Nb:SrTiO₃, the interface between PbTiO₃ and Nb:SrTiO₃ forms a rectifying junction, hence a negative zero bias photocurrent is always obtained. This implies that only photoexcited holes in the Nb:SrTiO₃ layer will contribute to the charge transport from the substrate to the PbTiO₃ surface during photodeposition in agreement with oxidation of Ag⁺. The initial preferential polarization of the PbTiO₃ layer, positive or negative, did not affect the photodeposition of Ag₇NO₁₁. We note that a positive polarization, which would shrink the depletion layer in the Nb:SrTiO₃ substrate, is consistent with an internal field supporting hole transport to the surface and oxidation of Ag⁺. In contrast, the sign of the zero-bias current for the PbTiO₃/SrRuO₃ system depends on the domain polarity, thus facilitating transport of UV excited holes as well as electrons to the PbTiO₃ surface. Hence, both oxidation and reduction should be possible. However, from electrochemistry we know that reduction of silver, Ag⁺+e⁻→Ag, has a potential of +0.80 V versus the standard hydrogen electrode (SHE) potential,²⁴ whereas the oxidation reaction, 7Ag⁺+NO₃⁻+8H₂O→Ag₇NO₁₁+10e⁻+16H⁺, has a larger potential of +1.59 V versus SHE,¹⁷ which speaks in favor of a reduction at the PbTiO₃ film surface in agreement with the presence of Ag. Hence, a rectifying interface for thin PbTiO₃/Nb:SrTiO₃ films effectively separates the oxidation from reduction sites during UV photocatalysis and contributes to a substantial oxidation power.

In conclusion, we have demonstrated photoassisted oxidation of AgNO₃ to Ag₇NO₁₁ at the surface of ferroelectric

PbTiO₃/Nb:SrTiO₃. Introduction of a SrRuO₃ epilayer interposed between the ferroelectric film and the substrate was found to effectively change the oxidation reaction into a photocatalytic reduction of Ag⁺ to Ag. This possibility to tune the photocatalytic reaction to “reducing” or “oxidizing” conditions by insertion of an epilayer may enable photodeposition of chemical species beyond those which can be obtained in a standard reduction process.

The authors would like to thank the Research Council of Norway for funding via Contract No. 162874/V00 and the Core Research for Evolution of Science and Technology, Japan Science and Technology Agency (CREST-JST). H. Yamamoto and T. Ishii at Shinkosya are thankfully acknowledged for supplying the La:SrTiO₃ substrates. We also thank Dr. K. Itaka and S. Smistad for technical support.

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