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Description	

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Fine-patterning of sol-gel derived PZT film by a novel lift-off process using solution-processed metal oxide as a sacrificial layer

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Abstract

Sub-5μm pattern of sol-gel derived lead-zirconium-titanate (PZT) film with a thickness of 80-390 nm was successfully prepared on $Pt(111)/TiO_x/SiO_2/Si$ (100) substrate by a novel lift-off process using solution-processed metal oxides as a sacrificial layer. The process is simply divided into three steps: In-Zn-O (IZO) sacrificial layer spin-coating and patterning, PZT film formation followed by lift-off process. The results suggested that the IZO layer is effective in preventing PZT crystallization because of its thermal stability during PZT post-annealing, and its barrier-effects between the spin-coated PZT precursor and the Pt/TiO_x substrate. Consequently, the micro-pattern of lift-off PZT exhibited better properties than that formed by wet-etching. In particular, the lift-off PZT films possessed better ferroelectric properties, higher break-down voltage, and more well-defined shape than those of films patterned by conventional wet-etching. This lift-off process shows great promise for highly integrated devices due to its fine pattern-ability.

Keywords: PZT film; Micro-patterning; Lift-off; In-Zn-O metal oxide

Introduction

Lead-zirconium-titanate (PZT) films have been drawing much attention for applying to sensor, actuator, generator, and non-volatile memory devices due to their high piezoelectric and ferroelectric properties [1-5]. As an alternative processing to vacuum-based depositions, solution deposition has emerged as one of the most promising methods of ferroelectric films with perovskite structure because of low processing temperature, high simplicity of composition control, and large-area [6, 7]. In order to apply this functional film to micro-devices, a micro-patterning process is inevitably introduced. As a key patterning technique of PZT film, reactive ion etching (RIE) requires expensive equipment, and is accompanied by physical defect generation, properties degradation, and pollution due to hazard materials usage [8-11]. On the other hand, the current wet-etching process has been inevitably accompanied by lateral etching and the etching solution includes HF, HCl which may infiltrate and damage PZT properties and other films, especially Ti electrode [12-18]. Lift-off process is an ideal patterning method, whereas PZT thick films cannot be patterned using conventional lift-off processes for failure of resist stripping caused by high deposition temperature of PZT films. So far, the pattern-ability of PZT film by lift-off process was already proved, however the feature size was limited above 50 μm, and also PZT films exhibited random crystalline structure, large leakage current, and rather poor ferroelectric properties [19-21]. In particular, Zhao reported a fabrication of PZT film using 100-μm-thick photoresist SU-8 [19]. The fabricated PZT film had perovskite structure; however it exhibited random crystalline structure which is not ideal for electronic device application. Further, such a thick resist might result in deformation, and hence cracking of coated PZT gel. Lu proposed the use of a hydrophobic self-assembled monolayer as sacrificial layer for lift-off process of PZT film [20]. Even though the lift-off process was successful, the film showed random crystalline structure and the feature size was limited above 50 μm. Fabrication and properties controllability of the self-assembled monolayer might be critical leading to a narrow fabrication process window. Recently, Li reported micro-patterning of PZT thick film by lift-off using ZnO as a sacrificial layer [21]. The film with feature size larger than several tens of micrometer exhibited rather poor ferroelectric properties (low remnant polarization and large leakage current) due to its random crystalline structure. In addition, the use of ZnO sacrificial layer maybe not preferable for scaling down owing to its crystallized structure.

This work demonstrates the preparation of fine-patterned PZT films by sol-gel method and a novel lift-off. In this process, solution-processed In-Zn-O (IZO, In:Zn=1:1) instead of photoresist employed in a conventional lift-off was used as a sacrificial layer. The reasons why IZO was selected as the sacrificial material are as follows: IZO is high temperature resistant, while photoresist can be carbonized during deposition of PZT films leading to failure of resist stripping in lift-off. In addition, IZO is easy to be etched thus stripping process can be conducted smoothly. Furthermore, due to amorphous nature of IZO material it is effective in preventing PZT film from crystallization, resulting in a loosen structure above IZO layer for feasible lift-off. Comparing to ZnO, the IZO film possesses stable amorphous structure up to 400 ºC annealing while that of the ZnO is limited below 250 ºC. In addition, the IZO film is easily to be formed uniformly by spin-coating while that is hard for the ZnO due to de-wetting property of the ZnO precursor solution.

Experimental

0.6 mol/kg In_2O_3 precursor solution was synthesized by dissolving indium nitrate trihydrate ($In(NO_3)_3.3H_2O$, 99.0 % purity, Kanto Chemical) in 2-methoxyethanol. 0.6 mol/kg ZnO precursor solution was synthesized by dissolving zinc nitrate dehydrate ($Zn(NO_3)_2$, Wako Chemical) in 2-methoxyethanol. These solutions were stirred at 1000 rpm for 30 min on a hot plate (110 ºC) to form transparent and homogeneous solutions. Then, In_2O_3 and ZnO solution was mixed with 1:1 ratio to

form IZO precursor solution. Prior to use, the IZO solution was filtered through a 0.2 μm syringe filter [poly(tetrafluoroethylene), GE)].

The whole processes were illustrated in Fig. 1. As for the platinized silicon substrate, 100-nm-thick platinum film was deposited onto a SiO_2 (500 nm)/Si substrate using RF-sputtering technique at a RF power of 30 W, Ar gas flow of 3.8 sccm, and substrate temperature of 100 °C [22]. An IZO sacrificial layer was first deposited by spin-coating IZO solution at 3000 rpm for 30 sec on the platinized silicon substrate followed by drying at 400 °C for 5 min. Thickness of a single IZO layer was approximately 80 nm. Multilayer IZO film was formed by repeating this process to get desired thickness. The IZO film was patterned using the standard photolithography techniques and wet-etching process. In particular, the OMR-85 negative resist (Tokyo Ohka Kogyo Co., Ltd.) was used to pattern IZO film. The sample was dipped into 50% (v/v) ITO-02 etchant solution (KANTO Chemical Co., Inc.) for 30 second at room temperature. Therefore, a negative pattern of the final PZT layer was created on the IZO sacrificial layer as shown in Fig. 1 (b). After that, PZT film was deposited by spin-coating PZT precursor solution (Pb:Zr:Ti=120:40:60, 25wt%, Mitsubishi Materials) at 5000 rpm for 60 sec on the substrate, followed by drying at 150 °C for 30 sec and 250 °C for 5 min to remove the organic components. This process was repeated to get desired thickness of PZT film (80-390 nm) (Fig. 1(c)). Finally, the PZT gel film was annealed at 600 °C for 20 min in air ambient using rapid thermal annealing to develop perovskite structure. The wafer was immersed in 99% (v/v) H_3PO_4 etchant solution (WAKO Pure Chemical Industries, Ltd.) under ultra-sonication at room temperature for 18-35 min depending on the thickness of PZT film. As a result, the IZO film under PZT layer was etched leading to lift-off of above PZT layer. As a result, the PZT films were patterned as shown in Fig. 1(d). In order to compare wet-etching and the novel lift-off process, the PZT film was also patterned by wet-etching using conventional buffered hydrofluoric etchant solution and its properties were evaluated.

Surface topology of PZT patterns was characterized by optical microscopy and atomic force microscope (AFM) using a NanoNavi/S-image Probe station (SII NanoTechnology Corporation). X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert system with CuKα radiation. Leakage current, hysteresis loop and capacitance-voltage characteristics were measured at room temperature by Ferroelectric Characterization Evaluation System (TOYO Corporation Model FCE-1). Ferroelectric domain switching behavior was analyzed by piezo-response microscope (PRM) image using the NanoNavi/S-image Probe station.

Results and discussion

Figure 2 shows optical microscope images of PZT patterned by novel lift-off and wet-etching processes, respectively. We can see that the edges of PZT patterned by the lift-off (Fig. 2(a)) were clear and sharp at the magnification, and the residual PZT film was not almost observed on non-patterned area, which led to that the substrate was smooth after patterning. On the contrary, the lateral etching was found to be more than 10 μm, which was so serious that some electrode's area designed to be covered by PZT was exposed after the wet-etching, and lots of residual remained on electrodes. Consequently, the substrate became rough as shown in Fig. 2(b).

Figure 3 shows optical microscope images of lift-off PZT films fabricated using the sacrificial IZO layers with different thicknesses. As the thickness of the IZO layer was thin (Fig. 3(a), (b)), even though the lift-off could be performed, size and shape of PZT patterns were not faithful to the designed ones. In conventional lift-off process, normally the deposited film which is nearby edges of thick-resist patterns would be either deformed or broken, resulting in feasible lift-off. Thin IZO layer might have not deformed the above PZT film sufficiently leading to hard lift-off, and hence, degradation of patterns quality. On the contrary, the spin-coated PZT film might be thinned and

broken around the thick IZO pattern similar to the case of conventional Photoresist (Fig. 3(c), (d)). This would make the lift-off easier resulting in fine patterns without residual at the edges. It was found that in order to fabricate well-defined lift-off pattern the thickness of the sacrificial layer should be equal or larger than that of PZT.

Furthermore, fine-patterns of approximately 3.8 μm could be achieved by the lift-off without residual "rabbit-ear" at the edges as observed by AFM (Fig. 4(a), (b)). AFM image at higher resolution (Fig. 4(c)) reveals that a smooth surface with roughness mean square of 0.86 nm was obtained, which is similar to the surface morphology of non-patterned PZT film (data not shown). Therefore, the lift-off using IZO as a sacrificial layer can get better and smaller PZT film patterns by avoiding lateral etching and powder residual. So far, such fine patterns are not accessible by conventional wet-etching process. The successful patterning by the lift-off was due mainly to the fact that the IZO layer is easy to be etched and high temperature resistance. Furthermore, it is well known that the crystallization and growth of PZT film is dominated by perovskite nucleation [23]. Therefore, interaction between PZT precursor and the Pt/TiO_x bottom electrode during spin-coating, post-baking and rapid thermal annealing determines whether the PZT film can be well-crystallized with the preferred orientation [24]. In this regard, the amorphous nature of the IZO is effective in preventing PZT crystallization because of its thermal stability during PZT post-annealing, and its barrier-effects between the spin-coated PZT precursor and the Pt/TiO_x substrate. This fact makes the PZT deposited on IZO layer rather easily etched and loosen during the etching under ultra-sonication. Confirmation of amorphous structure of the PZT layer deposited on the IZO was done by XRD measurement (not shown)

Figure 5 (a) shows the X-ray diffraction (XRD) patterns of the lift-off and wet-etch PZT films. Both films exhibited same crystalline structure. The peaks were indexed as per the crystalline structure of PZT films. The lift-off film was well-crystallized with pure perovskite phase and highly (111)-preferential orientation indicating that the fabrication process is appropriate for good phase structure. The growth of highly (111)-oriented PZT film was inherited from the device-quality (111)-oriented Pt substrate [22].

Figure 5 (b) illustrates the *P-V* hysteresis loops of PZT film patterned by different techniques. The obtained remnant polarization (P_r) were approximately 34 $\mu C/cm^2$ and 27 $\mu C/cm^2$ for lift-off and wet-etch PZT films, respectively. The lower remnant polarization indicates degraded piezoelectric properties of the wet-etch PZT compared to the lift-off ones. The leakage current of the lift-off PZT was less than 10^{-5} A/cm^2 at 550 kV/cm, indicating that there is no enhanced leakage behavior due to the lift-off process and scaling down of PZT film to several tens of μm size (Fig. 5(c)). The breakdown electrical field of the film patterned by lift-off was more than 550 kV/cm, while that of the film patterned by wet-etching was about 250 kV/cm, which is more than two times lower than that of the lift-off film.

Figure 5 (d) shows a capacitance-voltage (*C-V*) characteristic of the PZT films measured at 1.0 kHz within a range of ±7 V. The *C-V* curves displayed a symmetric butterfly shapes at room temperature indicating ferroelectric nature of the PZT films. Peaks were observed at -0.8 and 1.1 V, corresponding to negative and positive coercive voltages, respectively. The dielectric constants of the lift-off and wet-etch films at the maximum capacitance were calculated as 630 and 490, respectively. As mentioned above, the lateral etching was serious in the wet-etch film leading to degradation of film performance by further infiltration of corrosive etchant liquid. As a result, the wet-etch PZT film exhibited lower remnant polarization, breakdown field, and dielectric constant.

In order to evaluate piezoelectric properties of the fine PZT pattern (< 5 μm), piezo-response force microscope (PRM) image was measured and shown in Fig. 6. Figure 6(a) shows the PRM image measured before voltage applied. Obviously, no contrast was observed as expected. Positive and negative voltages of 10 V in the continuous and pulse forms (f = 0.1 kHz) were sequentially applied

on the area of 500 nm ×500 nm marked as number 1, 2, 3 and 4, respectively, as shown in Fig. 6(a) using an AFM mode with a SI-DF40 cantilever (Hitachi High-Tech Corp.). After that, the PRM images were recorded on the area of 2.0 μm × 2.0 μm, which covered the pre-polarized areas, using a PRM mode without voltage application. As for the morphology (Fig. 5(b)), there was no change in contrast among the areas with voltage application. However in the PRM image, apparent contrast (bright and dark) were observed between the areas with positive (areas 1 and 3) and negative (areas 2 and 4) applied voltages indicating good piezoelectric response of the patterned PZT (Fig. 6(c)). Uniform polarization switching of ferroelectric domains was confirmed as the applied voltage was switched from positive voltage to negative ones. Vertical displacement (d_{31}) as a function of applied voltage is shown in Fig. 6(d). The observed butterfly shape further ensures native ferroelectric property of the patterned area. The d_{31} was approximately 112 pm/V, which is consistent with the values reported previously [25, 26]. These results indicate that the lift-off process is capable of down scaling PZT film to less than 5 μm size while preserving good structural and electrical properties.

Conclusion

A novel lift-off using solution-processed metal oxide IZO thin film as a sacrificial layer for fine-patterning PZT film was successfully demonstrated. The PZT patterns have feature sizes of 3.8 μm in width and 80-390 nm in thickness. The PZT pattern's shape, structural and electrical properties were confirmed which is better than those of the conventional wet-etch PZT films. The successful lift-off process is mainly attributed to native characteristics of the IZO film such as high-temperature resistance, easily etched, and amorphous structure preventing PZT from crystallization. This work enables the use of sol-gel derived PZT film for high-performance highly-integrated electronic devices.

Acknowledgement

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Figure captions

Fig. 1. (Color online) A schematic lift-off process using IZO film as a sacrificial layer.

Fig. 2. (Color online) PZT patterns prepared by (a) Lift-off and (b) Wet-etching process.

Fig. 3. (Color online) Lift-off PZT patterns as a function of thickness of the IZO layer: (a) 80 nm, (b) 170 nm, (c) 330 nm, and (d) 415 nm.

Fig. 4. (Color online) AFM image of fine PZT pattern: (a) 2D morphology, (b) 3D morphology, and (c) local surface morphology.

Fig. 5. (Color online) (a) XRD patterns; (b) Hysteresis loops; (c) Leakage currents; and (d) capacitance-voltage characteristic of lift-off and wet-etch PZT films.

Fig. 6. (Color online) (a) PRM before applying voltage; (b) Surface morphology; (c) PRM image after applying voltage; and (d) Displacement versus applied voltage of lift-off fine-patterned PZT.

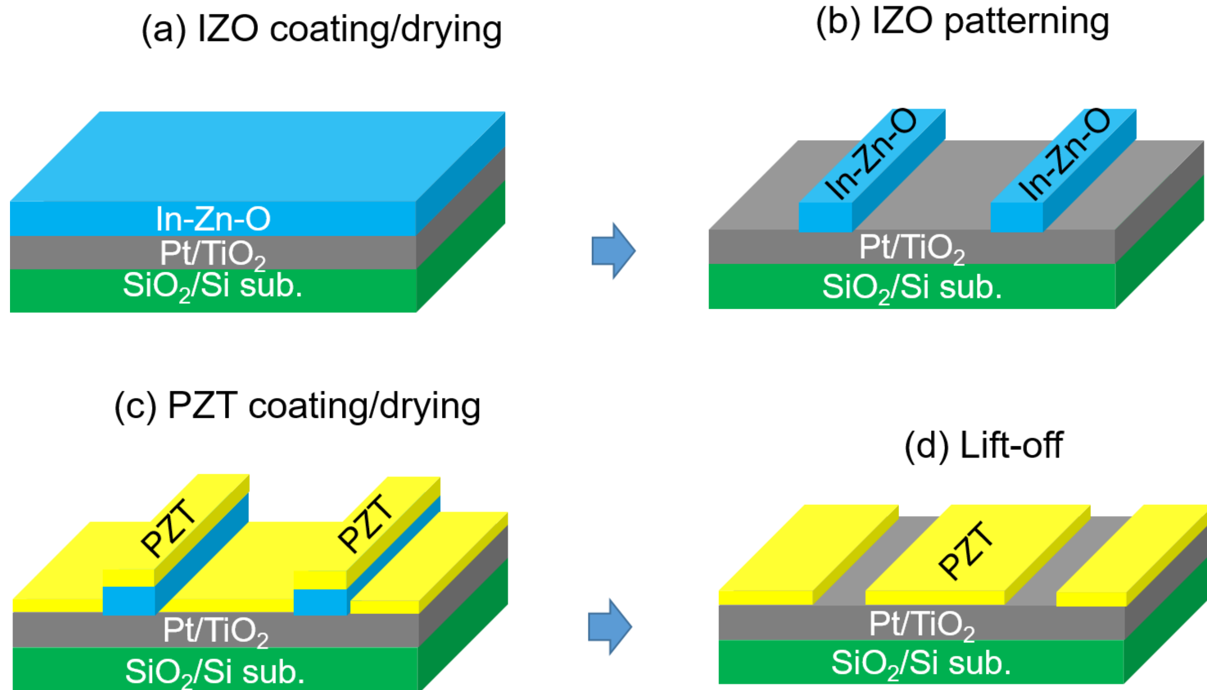
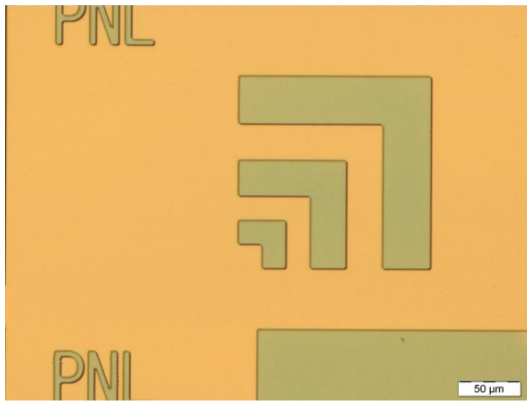


Fig. 1

(a) Lift-off



(b) Wet-etching

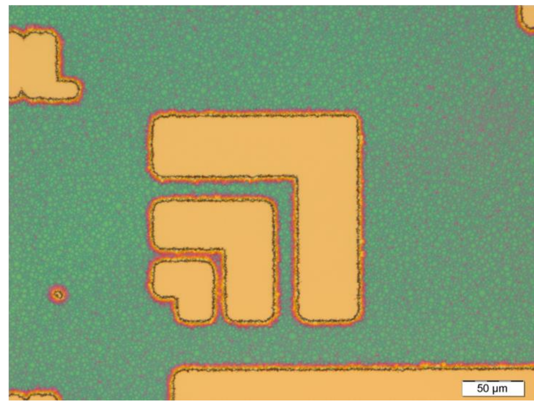
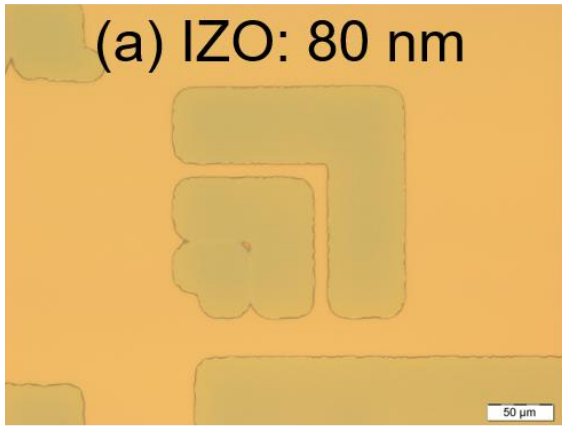
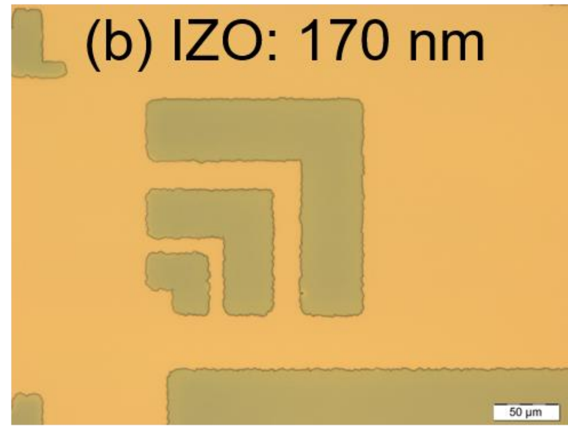
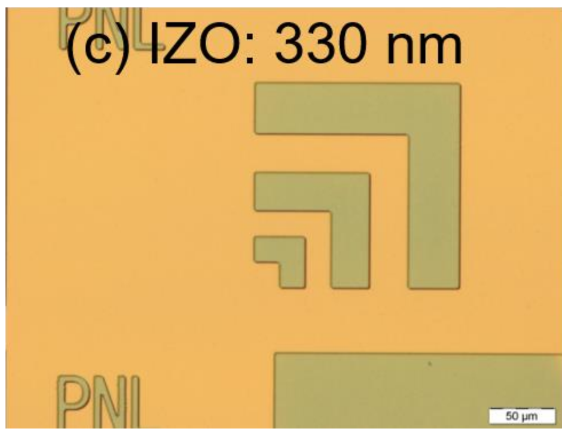


Fig. 2







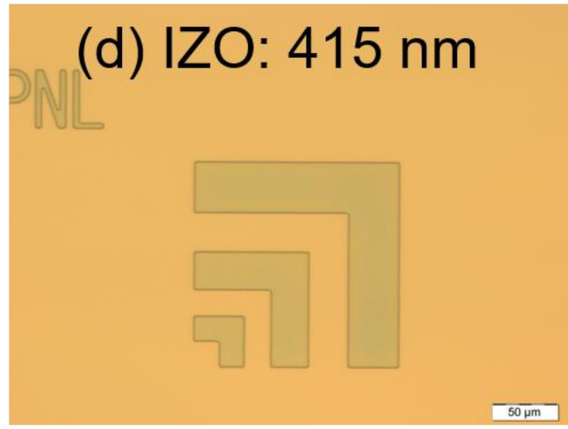


Fig. 3

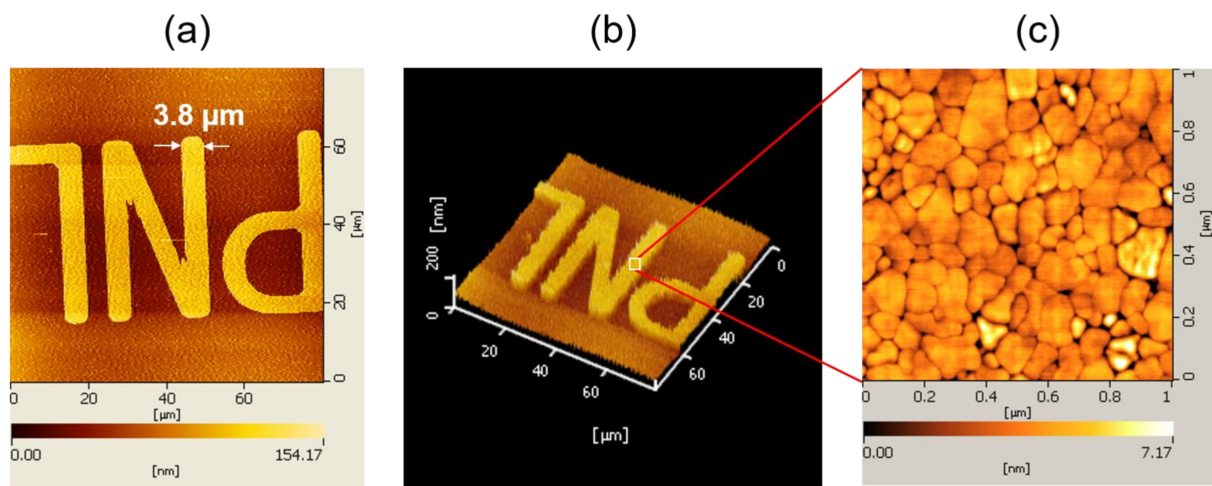


Fig. 4.

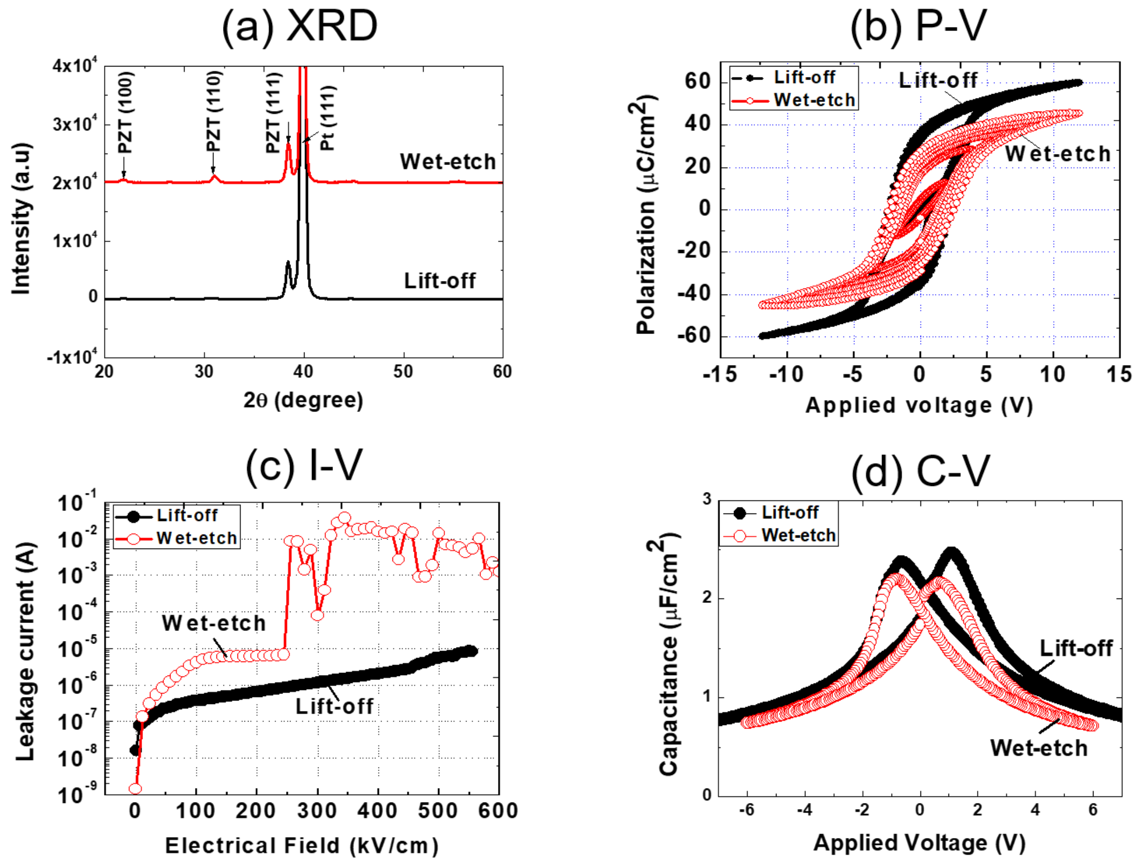


Fig. 5.

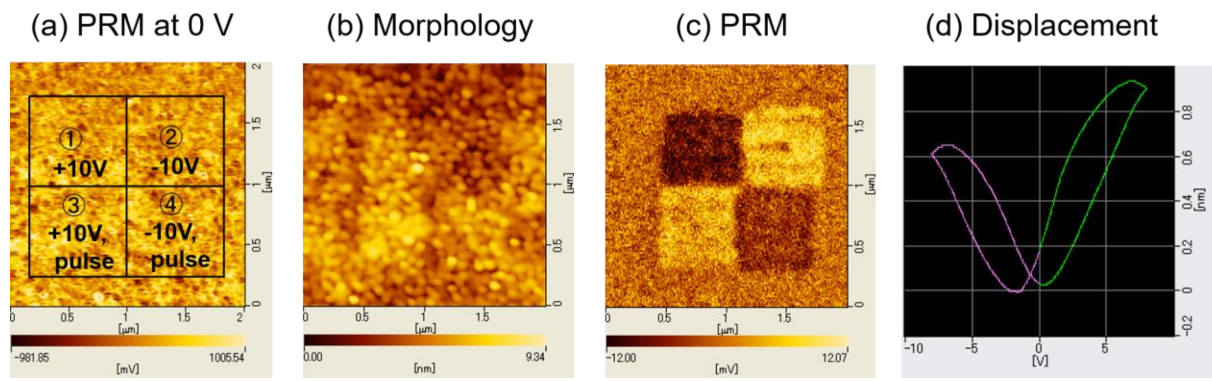


Fig. 6.