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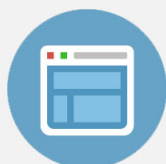Appl. Phys. Lett. **74**, 2286 (1999); 10.1063/1.123826

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Characterization and elimination of dry etching damaged layer in Pt/Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$/Pt ferroelectric capacitor

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The damage of Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ thin film due to dry etching process was characterized in terms of the microstructure and electrical properties. The damaged layer seems to be amorphous and the thickness of the damaged layer is about 10 nm. The existence of such a layer in Pt/Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$/Pt ferroelectric capacitor tends to increase the coercive voltage and the leakage current. The damaged layer was not fully reverted to perovskite phase by the thermal annealing. With the wet cleaning treatment, however, the damaged layer was successfully removed thereby revealing significantly improved electrical properties. © *1999 American Institute of Physics.*
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In the last decade, extensive studies have been carried out on ferroelectric thin films for the application in nonvolatile memories.[1] However, there are several problems that should be overcome to realize the integration of ferroelectric thin films to semiconductor devices. One of the associated issues is to establish dry etching process without producing the etching damage. In dry etching, reactive free radicals and ions in the plasma would change the physical and electrical properties of the etched films, which is called as the etching damage. In view of the functional point, the damaged layer in the ferroelectric capacitor is likely to play a parasitic role, which gives rise to a deteriorated performance. Up to now, it is not easy to find out etching process without the etching damage during dry etching process.[2–6] Recently, Torii *et al.* attempted the rf oxygen plasma treatment to reduce the etching damage. However, the etching damage was not completely removed by rf oxygen plasma treatment.[2] Due to the incomplete understanding about the damaged layer, no final conclusion can be drawn concerning to the minimization of the dry etching damaged layer. Therefore, in this study, we first characterized the damaged layer in terms of physical properties and electrical properties. Then, in next step, a wet cleaning approach was made to eliminate the damaged layer on the basis of the characterized properties about damaged layer.

Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ (PZT) thin films with the thickness of 240 nm were spin coated onto Pt/Ti/SiO$_2$/Si substrates by sol-gel method.[7] PZT and Pt films were etched by inductively coupled plasma (ICP) etcher with Ar–Cl$_2$–C$_2$F$_6$ gas mixtures.[3] For the study on the damaged layer, about 50 nm of PZT film was etched off without a photoresist protection, which eminently produced the damaged layer on the surface of PZT film. The physical properties of the damaged PZT film were characterized using x-ray diffraction (XRD), x-ray

photoelectron spectroscopy XPS, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [cross-sectional TEM (XTEM)]. Additionally, electrical properties including the ferroelectric property, were also evaluated using metal–ferroelectric–metal (MFM) capacitors that were fabricated by depositing top Pt electrodes on PZT/Pt films. The sizes of capacitors were about 1×10^{-4} cm^2. Along with the characterization about the damaged layer, an alternative approach utilizing a wet cleaning method was also examined.[8] The effectiveness of the wet cleaning treatment was determined by comparing the properties obtained from the damaged PZT films with those obtained from the wet cleaned PZT.

Figure 1(a) shows the surface morphology of as-deposited PZT thin film, and Fig. 1(b) shows the surface morphology of PZT film after about 50 nm of PZT was
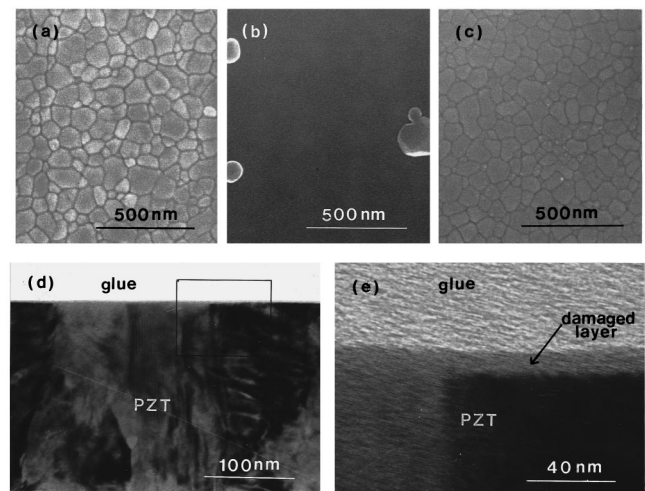

FIG. 1. (a) SEM pictures of as-deposited PZT thin film, (b) after dry etching process, and (c) surface wet cleaned PZT. The etching damaged layer is completely removed by the cleaning solution treatment. (c) Cross-sectional TEM images of dry etched PZT, (d) magnified image of inset region in (c).
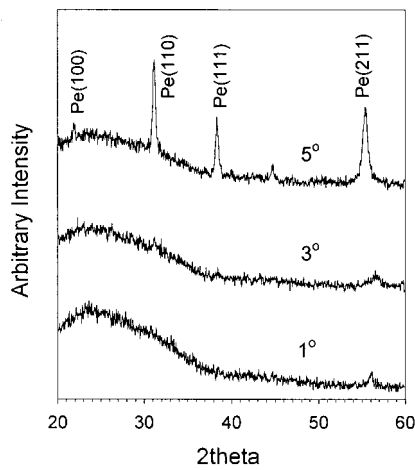
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FIG. 2. X-ray diffraction spectra of the dry etched PZT film with the glance angle of 1°, 3°, and 5°.

FIG. 4. X-ray photoelectron spectrum of the etching damaged layer. Solid lines: perovskite PZT, dashed lines: etching damaged layer.

etched off. The figures clearly illustrate the fact that well-defined perovskite grains are destroyed during dry etching process. Similarly, the cross-sectional TEM picture of Fig. 1(d) reveals that the surface of PZT film had a different contrast compared with that of perovskite grains. Moreover, the magnified image shown in Fig. 1(e) gives that the thickness of the damaged surface layer is about 10 nm. X-ray diffraction patterns with glance mode given in Fig. 2 clearly indicate that dry etching damaged layer does not have a crystallinity. Hysteresis loops obtained from the capacitors fabricated on PZT/Pt, where the surface of PZT film was damaged by the plasma, are given in Fig. 3(a). As shown in the figure, the distinct difference in the hysteresis loop is the coercive voltages (V_c). Capacitors that have the damaged layers on the PZT surface give higher coercive voltages compare to that of the damage free PZT film. The increase of the coercive voltage is attributed to the existence of the layer which cause the voltage drop, that is, the dry etching damaged layer. Up to the 550 °C annealing, which is considered as a typical temperature to recover dry etching damage, the shape of hysteresis loop was changed insignificantly. Even though it is annealed above the formation temperature, namely, 650 °C, the coercive voltage is still 0.3 V higher than that of as-deposited PZT. SEM and x-ray diffraction analysis indicate that the annealing at 650 °C yields only a partial recrystallization of the damaged layer.

The chemical composition of the dry etching damaged

layer was evaluated by using XPS analysis. As shown in Fig. 4, flourine and chlorine atoms were detected in XPS survey spectrum. The atomic percentage of fluorine and chlorine were 23.0% and 4.3%, respectively. Furthermore, the insets of Fig. 4 obviously show shifts of binding energy, such as lead (Pb $4f_{7/2}$), zirconium (Zr $3d_{5/2}$), and titanium (Ti $2p_{3/2}$) peaks. That is to say, in the etching damaged layer, Pb, Zr, and Ti peaks were shifted 2–4 eV toward higher binding energy compared to those obtained from the pure perovskite phase. Due to strongly electronegative fluorine atom, the peaks of metal components seems to be shifted to higher binding energy. This implies that metal components would make chemical bonds with halide atoms (Cl, F) as the result of the chemical reaction between reactive etching gas (Cl_2–C_2F_6) and PZT film. It is generally known that metal halides are hard to change into metal oxide below 800 °C. This is a main reason why 650 °C annealing could not completely revert the damaged layer to the crystallized perovskite layer. Since the thermal treatment was not sufficient to completely remove the dry etching damage, the approach utilizing the wet cleaning treatment was attempted. We prepared a specially designed cleaning solution, in which
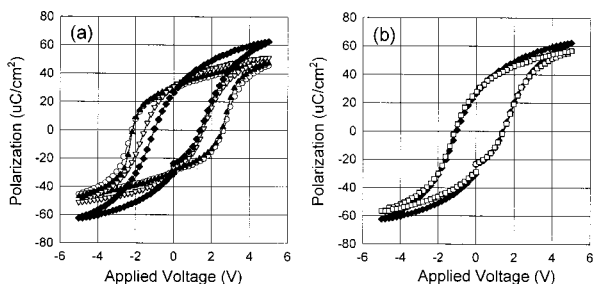
FIG. 3. (a) Hysteresis loops of Pt/PZT/Pt capacitors; (○) with the etching damaged layer on the PZT film surface, (▲) 550 °C annealed, (▽) 650 °C annealed, (♦) as-deposited PZT. (b) Hysteresis loops of Pt/PZT/Pt capacitors; (♦) as-deposited PZT, (□) after cleaning solution treatment.
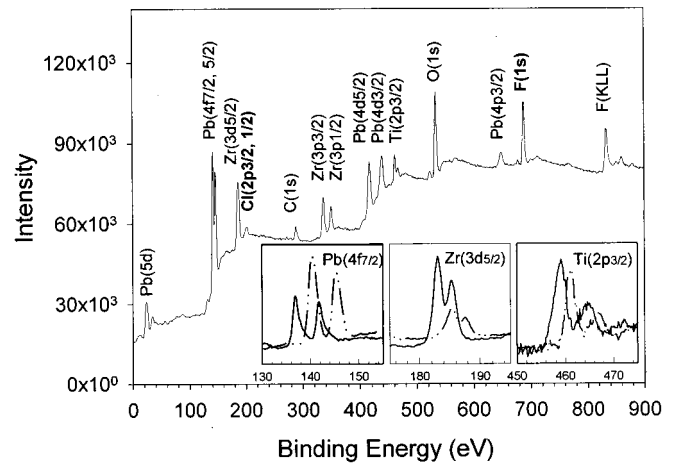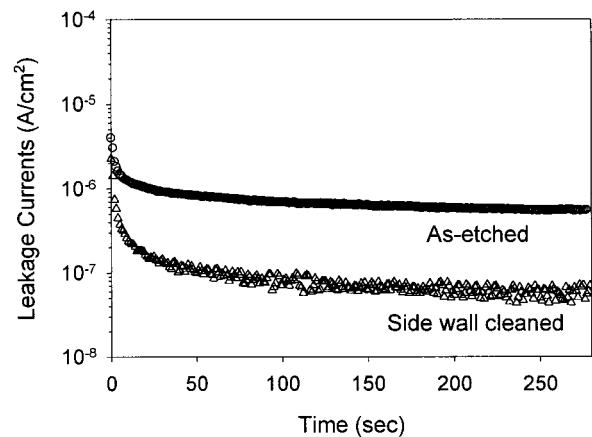
FIG. 5. Leakage current properties of PZT capacitors before and after cleaning solution treatment. Applied voltage: 5 V.

acetic acid, hydrofluoric acid, and ethanol were mixed with 10/5/85 volumetric ratio. The solution shows about 20 Å/min of etching rate to the dry etching damaged PZT thin film.[8] Figure 1(c) clearly shows that the damaged layer was fully removed by the wet cleaning treatment. In addition, as shown in Fig. 3(b), the shape of hysteresis loop obtained from the wet cleaned PZT is quite similar to that obtained from the damage free PZT except a minor difference in the slopes of the nonswitching cycles. This implies that the characteristic of Schottky contact would be changed by the cleaning of PZT surface. In fact, the etching damaged layer would be formed in the side wall of Pt/PZT/Pt capacitor during the fabrication of Pt/PZT/Pt capacitor. Thus, the effectiveness of the wet cleaning in patterned capacitors was evaluated by measuring the leakage current with TDDB mode. The TDDB characteristics given in Fig. 5 reveal that about one order (from 1×10^{-6} to 1×10^{-7} A/cm^2) improvement is achievable after the wet cleaning treatment. Such an improvement seems to be come from the elimination of the parasitic path which would be formed in the side wall of Pt/PZT/Pt capacitor.

The damaged layer in PZT thin film resulted from dry etching process is an amorphous layer with the thickness of about 10nm. It is thought that metals are bonded with halide atoms (Cl, F), which would require a sufficiently high temperature to convert it into metal oxides. The damaged layer seems to play a parasitic role in the current conduction, particularly when it is formed on the side region of the ferroelectric capacitor. Similarly, it acts as a voltage drop layer when it is formed on the surface of ferroelectric thin film thereby increasing the coercive voltage. The damaged layer could not be reverted to perovskite structure by the thermal annealing. However, it was completely removed by the treatment of the novel cleaning solution. After the treatment with the cleaning solution, the electrical properties, such as hysteretic characteristic and leakage currents are improved remarkably. Further studies are necessary to follow preliminary data.

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