



Generation of oxygen vacancies in the surface of ferroelectric $\text{Pb}(\text{Nb,Zr,Ti})\text{O}_3$

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ABSTRACT

Controlled generation of oxygen vacancies in the surface of ferroelectric thin films is crucial to study how surface reduction affects molecular adsorption and catalysis of gas–surface phenomena. We demonstrate the effective reduction in the surface of 4% niobium doped 20/80 PZT (PNZT) thin films. The sample was characterized by X-ray diffraction (XRD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), and heated at 200, 250 and 300 °C in a high vacuum system at 10^{-5} T of H_2 . Auger peak-to-peak intensities was used to study the elemental concentrations during the reduction experiment. High-resolution XPS spectra were acquired before and after reduction process for detecting the changes of the oxygen signal. Vacancies production rates as slow as 0.21% per minute were achieved and the temperature was not a key parameter in the process. Experiments at higher hydrogen pressures and lower temperatures might improve the control of the vacancies production.

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1. Introduction

It is well known that the chemical composition and the structure of the surface are crucial to control the properties of thin ferroelectric films such as domain distribution, polarization reversal and retention [1]. Moreover, the ability to manipulate the domains has recently motivated several studies that explore surface reactivity for applications in ultra sensitive sensors and controlled catalysis. In particular, several studies have pointed out the influence of the structural and ferroelectric phase transition in the adsorption of gas molecules on bulk samples [2–4] and, more recently, on thin films [5–7]. The physical explanation of this interesting effect relies on the change of the physisorption and chemisorption potential well due to different ferroelectric domains orientation. In oxides, chemisorption is mediated mainly by vacancies and defects present in the surface, thus polarization reversal may induce preferred pathways of adsorption. Moreover, density functional theory (DFT) calculations predict that dissociation of CO_2 predominates at oxygen vacancies on c^+ domains in BaTiO_3 thin films, while molecular adsorption at defect sites would be the most energetically favorable mode of adsorption on c^- domains [5]. The study of H_2 annealing in PZT thin films have shown that the ferroelectric properties are strongly affected due to the damage of electrodes caused by the catalytic activity of the incorporated H_2 at the surface and bulk [8,9].

In this work, a reduction of the oxide surface was performed in order to study the generation of oxygen vacancies in the PNZT film surface. The sample was first characterized by X-ray diffraction (XRD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Then was heated at 200, 250 and 300 °C in a high vacuum system under a H_2 atmosphere, and the elemental concentrations were analyzed using AES.

2. Materials and methods

The substrates used in this study consisted of 4% niobium doped 20/80 PZT (PNZT) thin films provided by Radiant Technologies Inc. The film thickness was 200 ± 15 nm and was grown at 650 °C by metal–organic deposition on the substrate $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$. Before to carry out the heat treatments in reducing atmosphere of H_2 , the sample was annealed at 650 °C during 2 h by using O_2 flux in ambient conditions in order to allow the filling of the oxygen vacancies. Then the reduction experiments were carried out in a HV surface analysis system equipped with a double-pass cylindrical mirror analyzer (DESA 100 from STAIB Instruments) for Auger electron spectroscopy (AES). The energy of the electron beam was 3 keV, the emission current was in the range from -0.7 to $-1 \mu\text{A}$, and the area of analysis was 1 mm^2 . The base pressure of the chamber was 10^{-8} T, and a specially designed manipulator was built to provide a heating of the sample. The surface chemical information was obtained from X-ray photoelectron spectroscopy (XPS) using a Physical Electronics system model 1257. The X-ray source was $\text{Mg K}\alpha$ at 1253.6 eV. The binding energies were obtained

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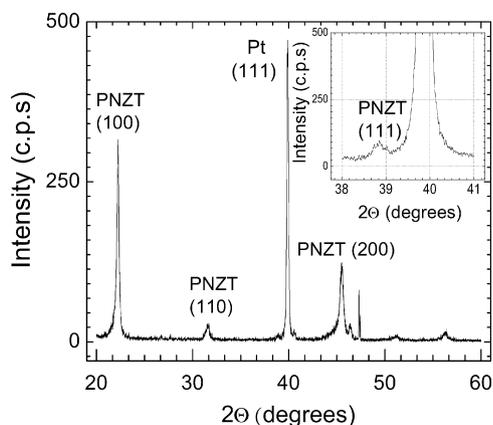


Fig. 1. XRD pattern of the PNZT film after annealing at 650°C and before the reduction experiment. The exposure time was 1 s.p.s and 9 s.p.s for the inset.

from high-resolution scans, and the energy scale was calibrated by assigning 284.8 eV to the C1s peak. X-ray diffraction patterns were taken at room temperature with a Bruker D-8 Advanced Diffractometer, using a tube with a copper anode ($\lambda(\text{CuK}\alpha) = 0.154 \text{ nm}$). The diffraction patterns were obtained in the usual $\theta - 2\theta$ geometry and the diffracted X-rays were detected with a scintillation detector. Atomic force microscopy (AFM) was performed in order to study the surface topography of the thin film. The measurements were carried using the equipment Omicron model Scala in contact mode, at room conditions. We used ultra pure H_2 gas (99.9999%) from Indura S.A. to perform the reduction experiment.

3. Results and discussion

3.1. Sample characterization

After annealing in oxygen, the PNZT film was characterized using XRD, AFM and XPS analysis. The XRD pattern showed the PNZT (100) (110) and (111) diffraction planes at the angles $2\theta = 22.26^\circ$, 31.59° and 38.94° , respectively (Fig. 1). These peaks correspond to the Pervoskite structure in the tetragonal (ferroelectric) phase, and have been observed in similar PZT-based compounds [10,11]. The Pt (111) peak at $2\theta = 39.92^\circ$ and the peaks at angles higher than $2\theta = 46^\circ$ corresponds to the substrate.

Independent of the in-plane direction in which the sample was measured, the diffraction peaks maintained the same angular positions. The diffraction planes (100) and (111) were used to calculate the lattice parameters a ($3.99 \pm 0.06 \text{ \AA}$) and c ($4.0 \pm 0.5 \text{ \AA}$). The AFM topographic images showed a well-texturized surface composed by grains of no uniform sizes (Fig. 2).

The measured root mean square (RMS) roughness measured in a $1500 \text{ nm} \times 1500 \text{ nm}$ area was 6.7 nm, while 6.6 nm in a $500 \text{ nm} \times 500 \text{ nm}$, showing a very homogeneous surface with well-faceted grains, some of them exceeding $100 \text{ nm} \times 100 \text{ nm}$. The Fig. 3 shows a XPS survey spectrum of the PNZT film after the annealing at 650°C in oxygen atmosphere.

This spectrum reveals the chemical composition of the sample surface, which shows only the photoelectron peaks of Pb (Pb4p, Pb4d, Pb4f, Pb5d), O (O1s), Ti (Ti2p, Ti3p), Zr (Zr3s, Zr3p, Zr3d) and Nb (Nb 3d) as well as the Auger signals of the oxygen (O-KLL) and titanium (Ti-LMM). The C1s photoelectron peak corresponds to the adventitious carbon on the surface. No impurities were detected in the film.

The Auger spectrum of Fig. 4 showed the presence of Pb, Ti and O, corresponding to the ferroelectric surface. We observed that

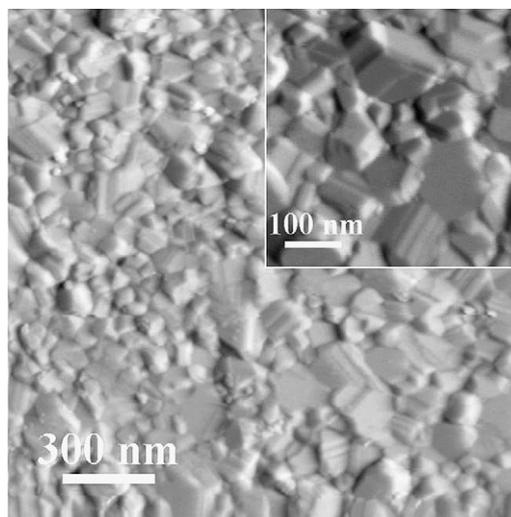


Fig. 2. AFM images of the PNZT film after annealing at 650°C and before the reduction experiment.

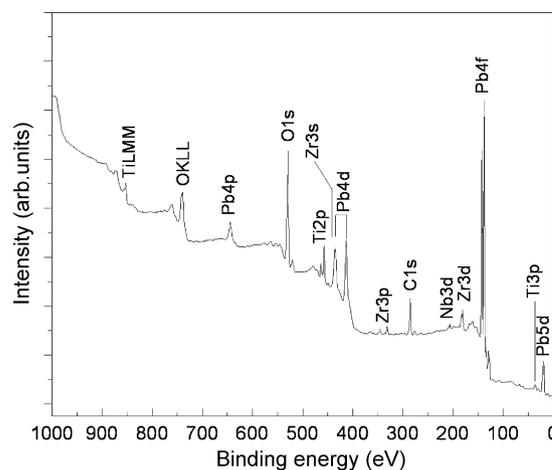


Fig. 3. XPS spectrum of the PNZT film after the annealing at 650°C and before the reduction experiment.

adventitious C attenuated the Auger signals, but helped to decrease charge effects. On the other hand, the Pb–NOO transitions showed a high intensity and were shifted to higher kinetic energies due to charge effects at low energies. Because no Zr was detected by

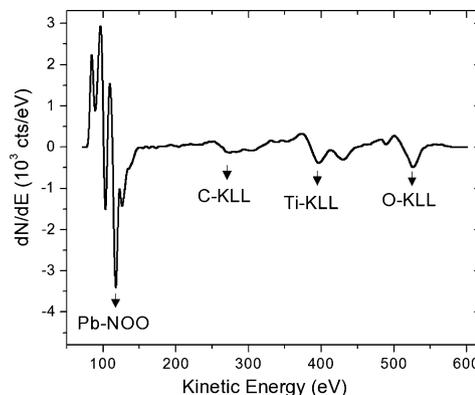


Fig. 4. Auger spectrum of the PNZT film after annealing at 650°C and before the reduction experiment.

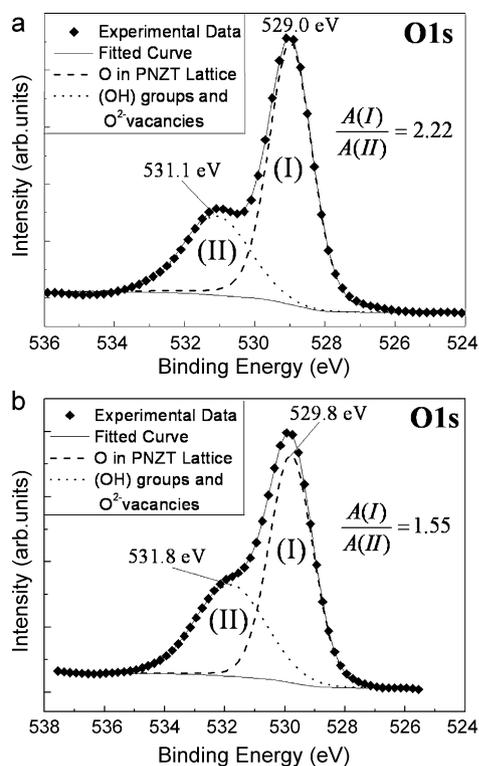


Fig. 5. High-resolution XPS spectra of the O1s level corresponding to the PNZT film (a) before and (b) after the reduction experiment.

AES, we claim that the Auger electrons depth was less than a PNZT monolayer (4 Å), instead XPS detected a small signal of 3s, 3p and 3d levels (Fig. 3).

4. Reduction experiment

In order to generate oxygen vacancies in the PNZT film surface, we performed a reduction experiment. The sample was heated at 200, 250 and 300 °C in the HV system under a H₂ atmosphere (10⁻⁵ T). Before measuring each Auger spectrum, the H₂ flux to the system was stopped and the electron emission current was stable (5 min). The same parameters of range, resolution, energy step and dwell time, were used to measure each spectrum. This is a very important issue, since the intensity of the peaks might change when changing any of these parameters. Before each experiment, the same Auger spectrum was taken 5 times to measure reproducibility, which corresponds to the error bars. Although the relative signals change with the electron beam exposure time [12], the error was smaller than the changes in the Auger peak-to-peak high (APPH), which is commonly used to measure the elemental abundance [13].

Fig. 5 shows high resolution XPS spectra of the O1s level and its corresponding curve fitting of the PNZT film before and after the reduction experiment under hydrogen at 250 °C, Fig. 5(a) and (b), respectively. In both spectra the fit was resolved using two peaks where the binding energy of the highest intensity (dashed line of curve I) corresponds to oxygen in the PNZT lattice, including Pb–O, Ti–O, Zr–O and Nb–O bonding whereas the binding energy of the lower intensity (dotted line of curve II) was attributed to the presence of hydroxyl (OH) groups on the film surface and oxygen vacancies [14,15].

A fit for distinguishing between peaks corresponding to OH groups and oxygen vacancies was not possible. The fit of Fig. 5(a) assigned a binding energy of 529.0 ± 0.1 eV and a full width at half

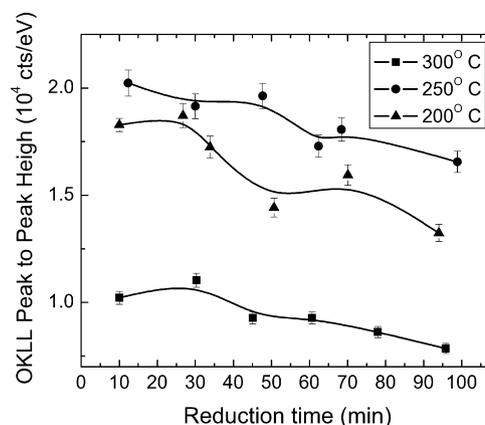


Fig. 6. Auger peak-to-peak height of the KLL transition in oxygen in function of the reduction time.

maximum (FWHM) of 1.4 eV to oxygen in the PNZT lattice and 531.1 ± 0.1 eV and a FWHM of 2.2 eV to the OH groups and oxygen vacancies. These same chemical states of oxygen were observed at 529.8 ± 0.1 eV (FWHM ~1.7 eV) and 531.8 ± 0.1 eV (FWHM ~2.7 eV) for the film exposed to reducing atmosphere, as shown in Fig. 5(b). In both figures, the binding energy values are close to reported values of 529.0 eV for oxygen in PNZT and 532.0 eV for OH groups and oxygen vacancies [16]. Whereas the ratio between the areas below the curves I and II, A(I)/A(II), was of 2.22 and 1.55 for the film without and with the reduction experiment, respectively. The decrease in the ratio of the areas is attributed to the increase in the oxygen vacancies concentration in the PNZT film surface after the heat treatment under hydrogen.

As shown in Fig. 6, for all the annealing temperatures, the oxygen abundance in the surface decreases, which is attributed to the increase in the oxygen vacancies concentration in the PNZT film surface during the reduction. Also, the APPH is lower for higher temperatures, probably due to the dispersion of the Auger electrons when interacting with the oscillating atoms of the surface. The rate of reduction were calculated by adjusting linear fit, resulting in a decrease of 0.29%, 0.21% and 0.33% per minute, when reducing at 300, 250 and 200 °C, respectively. Thus no considerable differences were found when reducing in the 200–300 °C range.

For all the reduction temperatures we observe a higher decrease rate for O than for Ti and Pb due to the reduction experiment that is mediated by the O–H hydroxyl groups generated in the surface and then desorbed (Fig. 7). Nevertheless, Pb concentration slightly decreases at 300 and 200 °C, and match with the increment of Ti concentration at the same reduction time. This is probably due to desorption of Pb atoms from the surface, which leads to lower Pb and higher Ti intensities. The inverse effect is observed at 250 °C. The Auger intensities ratios Pb/O and Ti/O at 200 and 300 °C, showed that the oxygen linked to Pb was more likely to be desorbed, because of the strong Pb–O bonding. We claim that by decreasing the reduction temperature and increasing the H₂ pressure, the desorption of heavier atoms than oxygen would decrease and the generation of oxygen vacancies could be even more controlled.

The presumable lost of Pb at this range of temperatures, as far as we know, have never been reported before. If detaches from the surface under the influence of hydrogen, the electrical properties of the PNZT/electrode interface would be affected, considering that Pb vacancies are essentially electronic traps. This observation may impact our understanding of electrical reliability and needs further study.

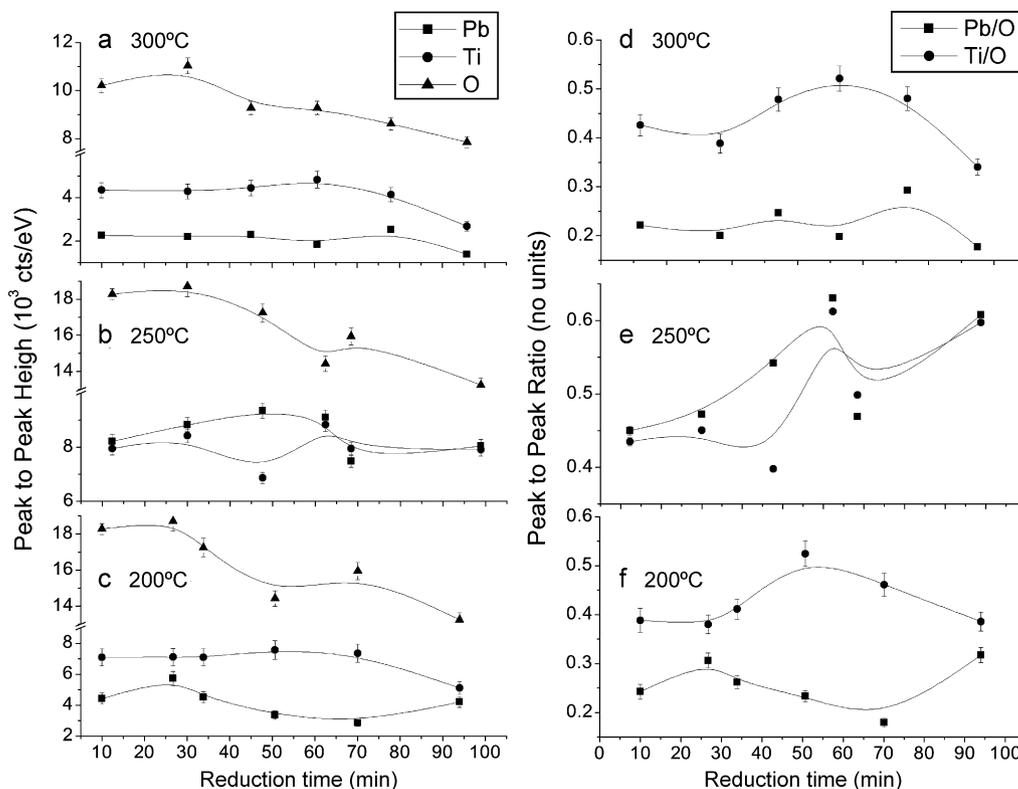


Fig. 7. Auger peak-to-peak height of the KLL transition in O, KLL in Ti and ONN in Pb, in function of the reduction time at (a) 300, (b) 250 and (c) 200 °C. Intensity ratio Pb/O and Ti/O at (d) 300, (e) 250 and (f) 200 °C.

5. Conclusions

The results obtained in this study demonstrate that it is possible to control the generation of oxygen vacancies in the surface of PNZT ferroelectric thin films by means of a thermal process under H_2 atmosphere. Reduction rates as slow as 0.21% per minute can be performed and the temperature does not sensibly affect the process in the range of 200–300 °C. Further experiments at lower temperatures and higher hydrogen pressures might avoid the desorption of heavy atoms from the surface. The effective and highly controlled generation of oxygen vacancies in ferroelectric thin films opens the possibility to study how different levels of surface reduction might affect the molecular adsorption and catalysis of gases such as CO_2 , CO and NO.

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