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Generation of oxygen vacancies in the surface of ferroelectric $Pb(Nb,Zr,Ti)O_3$

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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.

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 $Pt/TiO_2/SiO_2/Si$. 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 μA, 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 Mg K_α at 1253.6 eV. The binding energies were obtained

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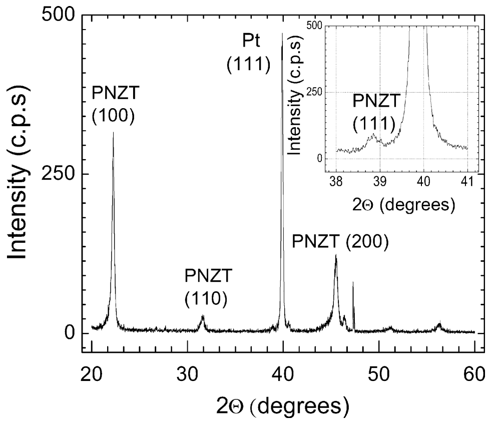

Fig. 1. XRD pattern of the PNZT film after annealing at 650 °C and before the reduction experiment. The exposure time was 1 s.p.s and 9 s.p.s for the inset.

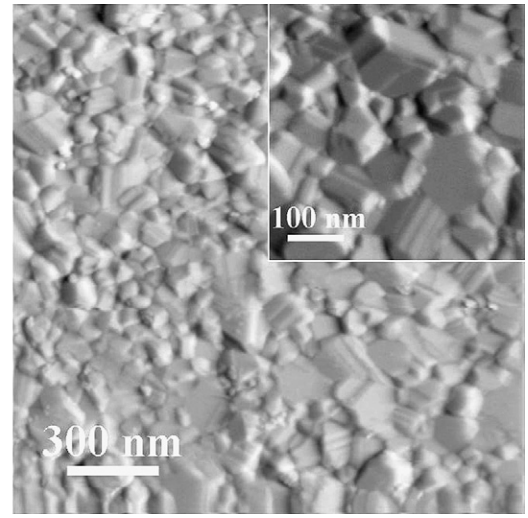

Fig. 2. AFM images of the PNZT film after annealing at 650 °C and before the reduction experiment.

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 (λ(CuKα) = 0.154 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 (1 0 0) (1 1 0) and (1 1 1) 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 (1 1 1) 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 (1 0 0) and (1 1 1) were used to calculate the lattice parameters a (3.99 ± 0.06 Å) and c (4.0 ± 0.5 Å). 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 nm × 1500 nm area was 6.7 nm, while 6.6 nm in a 500 nm × 500 nm, showing a very homogeneous surface with well-faceted grains, some of them exceeding 100 nm × 100 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

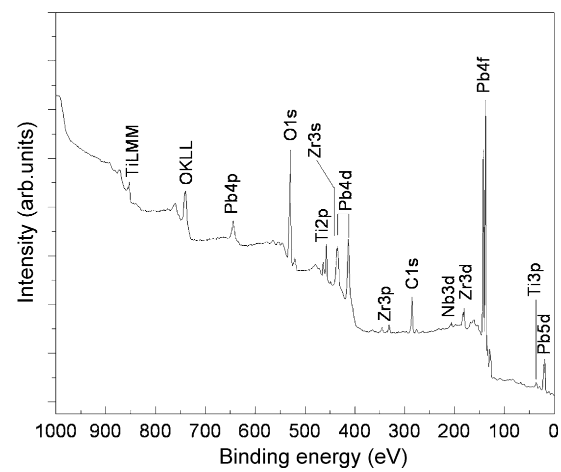

Fig. 3. XPS spectrum of the PNZT film after the annealing at 650 °C and before the reduction experiment.

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

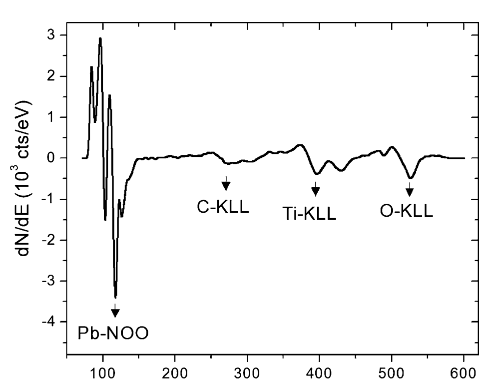

Fig. 4. Auger spectrum of the PNZT film after annealing at 650 °C and before the reduction experiment.