XPS Studies of PZT Films Deposited by Metallic Lead and Ceramic PZT Dual Target Co-Sputtering

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Abstract. The dependence of the chemical states of the constituent elements of a PZT thin film prepared by RF magnetron co-sputtering using ceramic PZT and metallic Pb dual target materials on the Ar^+ etching time was studied using XPS. The metallic Pb, lead oxide and Pb in PZT led to the different binding energies of the Pb lines. The intensity of binding energy of metallic Pb relative to that of bulk Pb increased with the depth of the film. The peak position and the line shape of the O_{1s} electron was associated with the different binding energies of oxygen, which interacts with Pb and Ti and Zr atoms to form the metal oxides, and the softening of the O_{1s} bonds by the bonding interaction in Ti—O, Zr—O and Pb—O. The broad $Ti_{2p3/2}$ line in the PZT film could has been associated with the various charge state of Ti and no spectral changes of Ti_{2p} and Zr_{3d} were observed as the Ar^+ ion sputtering time was increased.

Keywords: XPS, PZT, binding energy, RF sputtering, thin film

Introduction

Ferroelectric thin film materials, including lead-zirconate-titanate ($Pb(Zr_x,Ti_{1-x})O_3$, PZT), exhibit high dielectric constants, pyroelectricity and electro-optical and large spontaneous polarization characteristics. They can therefore be used in transducers, surface acoustic wave (SAW) devices, piezoelectric sensors, electro-optical modulators/switches, non-volatile random-access memories (NVRAMs), ferroelectric random-access memories (FRAMs), dynamic random-access memories (DRAMs) and ferroelectric field-effect transistors (FeFETs) [1–8], among other devices.

Several reports have involved an X-ray photoelectron spectroscopy (XPS) surface composition analysis of PZT thin films prepared by laser ablation [9–12], reactive evaporation [13], MOCVD [14, 15], sol-gel [16–21], helicon wave plasma [22] and DC magnetron sputtering [23–25]. There is no XPS report about the PZT thin films prepared by RF magnetron co-sputtering using ceramic PZT and metallic Pb dual target materials. In this investigation, the chemical states of each element throughout the thickness of PZT films prepared by RF magnetron co-sputtering using ceramic PZT and metallic Pb dual target materials, were studied by XPS.

Experimental

In this study, PZT thin films were deposited on $Pt/Ti/SiO_2/Si$ substrate using a dual-target system, whose target materials, metallic lead (99.99%) and ceramic PZT ($PbZr_{0.54}Ti_{0.46}O_3$), were powered by RF magnetron. The substrates were Si(100) wafers with 150 nm-thick layers of thermally grown silicon dioxide, over which a 50 nm-thick titanium was deposited as an intermediate film and a 150 nm-thick platinum film was deposited as the bottom electrode. Table 1 presents typical deposition conditions of the PZT films.

The XPS study was performed using a VG Scientific ESCALAB 250 system with 150 W of monochromatic Al K_α X-ray radiation (1486.8 eV) in a six-channel hemispherical analyzer. The XPS characterization was conducted inside an ultrahigh vacuum chamber with a base pressure of 2×10^{-10} Torr. Narrow scans of Pb_{4f}, Zr_{3d}, Ti_{2p}, and O_{1s} were acquired with a 20 eV pass energy with 100 ms of dwell time, to provide good

Table 1. Experimental conditions for deposition of the PZT film.

Target RF power	PZT:80 W, Pb:25 W
Target diameter	75 mm
Sputtering gas	Ar
Base pressure	1.2×10^{-3} Pa
Working pressure	0.15 Pa
Deposition time	0.75 h
Substrate temperature	580°C
Substrate material	Pt(150 nm)/Ti(50 nm)/SiO$_2$(150 nm)/Si

PZT target composition: PbZr$_{0.54}$Ti$_{0.46}$O$_3$.

Table 2. Experimental conditions for XPS analysis.

Spot size of monochromatic X-ray (μm)	500
Analysis area of photoelectron (μm)	500
Waiting time for signal collection (ms)	100
Take-off angle of photoelectron	54.7°
Narrow scan range (eV)	
Pb$_{4f}$	132–146
Zr$_{3d}$	180–188
Ti$_{2p}$	452–468
O$_{1s}$	528–534

insight into the form of the chemical bonds. The position of the peak shifted from its expected position, so the position of the peak in the spectrum was calibrated using to C$_{1s}$ at 284.6 eV. Depth profiling was performed using Ar$^+$ ion bombardment under ion gun conditions of 3 kV and 1 μA. One minute of sputtering time corresponded to approximately a 0.2 nm depth of film. Table 2 describes the analytical conditions adopted.

Results and Discussion

High-resolution spectra of the Pb$_{4f}$, Zr$_{3d}$, Ti$_{2p}$ and O$_{1s}$ photoelectron lines for the PZT thin film were obtained as a function of Ar$^+$ ion sputtering time, as shown in Fig. 1. Pb$_{4f7/2}$ exhibited dual peaks at 136.7 and 138 eV, as shown in Fig. 1(a). The peak at a binding energy of 136.7 eV was associated with the metallic Pb. The broadened binding energy of Pb$_{4f7/2}$ around 138 eV was primarily attributable to the Pb in PZT(137.8 eV) and Pb oxide(138.8 eV) [15]. The Pb$_{4f7/2}$ dual peaks were consistent with the binding energies of 136.3 and 138.1 eV reported for PZT films prepared by the sol-gel process [18]. The intensity of the binding energy of the Pb lines increases at surface layer, and then remains almost constant. This results could be attributable to the increase in the amount of

Pb in the surface layer, by the diffusion of Pb from the interior of the thin film towards the surface [26]. The appearance of metallic Pb can be attributable to the reduction of the Pb^{2+} ion to metallic Pb^0 [15] and be sputtered from the Pb target during deposition. As the sputtering time increased, the intensity of the metallic Pb peak relative to that of bulk Pb increased with the depth of the film.

In contrast, Fig. 1(b) shows the broadened binding energy of the O$_{1s}$ line around 530.8 eV consistent with to values reported for the PZT thin film [14, 15, 18, 27]. Pb(Zr,Ti)O$_3$ in its paraelectric phase has a simple cubic structure with a Pb cation in large eight-fold coordinated sites and Zr or Ti cations in octahedrally coordinated sites, while oxygen occupies the central sites of the face. The broad O$_{1s}$ lines in the PZT film could have been associated with the length of the oxygen bond which was a function of the hybridization density of different states of oxygen, due to its interaction with Pb and Ti and Zr, forming lead oxide, titanium oxide and zirconium oxide, respectively. Therefore, the position of the peak and the line shape that corresponded to the O$_{1s}$ electron was primarily attributable to the different binding energies of oxygen in various oxides states. In the case of the PZT thin film, the softening of bonds was caused by the bonding interaction in Ti—O, Zr—O, and Pb—O, and so the O$_{1s}$ binding energy of PZT was around 531.2 eV [14, 15, 18, 27]. The hybridization state and the electronic density of the cation and anion were directly related to the state of polarization [10, 28]. In the ferroelectric phase, the hybridization between Ti and O was weak, and resulted in a shortening of the Ti—O bond, increasing d–p overlap and the generation of ferroelectric characteristics.

The binding energy of the elements in the bulk film are 459 eV for the Ti$_{2p3/2}$ line, and 183.5 eV for the Zr$_{3d5/2}$ line, as shown in Fig. 1(c) and (d). These values were consistent with that reported for the PZT films [18, 29]. The broad Ti$_{2p3/2}$ line in the PZT film could has been associated with the various charge state of Ti [15]. In general, the high charge state has a high binding energy. The higher binding energy of Ti$_{2p3/2}$ corresponds to Ti^{4+} coordinated with O^{2-} and lower that of Ti$_{2p3/2}$ corresponds to a chemically reduced state such as Ti^{3+} or Ti^{2+}. In the PZT system, both Ti^{4+} and Ti^{3+} bond with the same neighbor environment of oxygen atoms. No spectral changes of Ti$_{2p}$ and Zr$_{3d}$ were observed as the Ar$^+$ ion sputtering time was increased.

Fig. 1. XPS narrow scan spectra of (a) Pb$_{4f}$, (b) O$_{1s}$, (c) Ti$_{2p}$ and (d) Zr$_{3d}$, at various Ar$^+$ ion sputtering time.

Conclusion

The dependence of the chemical states of the constituent elements of the PZT thin film prepared by RF magnetron co-sputtering using ceramic PZT and metallic Pb dual target materials, on the Ar$^+$ etching time, was investigated using XPS. The different binding energies of the Pb lines correspond to metallic Pb, Pb oxide, and Pb in PZT. The high intensity of the binding energy of the Pb lines at the surface layer was attributable to the diffusion of Pb from the interior of the film toward to the surface of the film, and the intensity of metallic Pb, relative to bulk Pb, increased with the depth below the surface of the film. The peak position and the shape of the line that corresponded to the O$_{1s}$ electron was related to the different binding energies of oxygen in its various oxides states. The broad O$_{1s}$ lines resulted from the interaction of oxygen with Pb and Ti and Zr atoms, the softening of O$_{1s}$ bonds resulted from the bonding interactions in Ti—O, Zr—O and Pb—O. The broad Ti$_{2p3/2}$ line in the PZT film could has been associated with the various charge state of Ti and no spectral changes of Ti$_{2p}$ and Zr$_{3d}$ were observed as the Ar$^+$ ion sputtering time was increased.

Acknowledgment

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