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Deposition and XPS Study of Pb, Zr, and Ti Films

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Abstract

Lead zirconate titanate (PZT) is significant material in electrical and optical devices for their ferroelectric, piezoelectric and dielectric properties. In this research, PZT films were fabricated by reactive RF co-sputtering method using Pb, Zr, and Ti targets. From XPS study, lead, zirconium, and titanium are successfully deposited on Si(100) substrate. Thickness of PZT films was measured with a surface profiler and the thickness was decreased as the oxygen gas ratio increased in the sputter gas.

Key words: XPS, Lead Zirconate Titanate, Sputter, Ferroelectric

1. Introduction

In these days, many researches are focused on the ferroelectric materials used for memory devices. Specially, ferroelectric materials are widely used for non-volatile memory (NVM). The NVMs have not only the merit of read only memory (ROM) which is the input information is stored without power but also the merit of random access memory (RAM) which has the flexibility of input and output of information[1-4]. These features are good for apply to mobile devices. Lead zirconate titanate (PZT) film is one of ferroelectric materials. The PZT thin films have many advantages with several limitations such as internal diffusion and imprint effect[5-8].

The typical methods to fabricate PZT films are atomic epitaxial deposition, sol-gel method, chemical vapor deposition, and sputtering method. There are several kinds of methods sputtering including direct current (DC) sputtering and radio frequency (RF) sputtering. DC sputtering uses direct current and its structure is simple. However, it needs high pressure and this method is easy to heat up the substrate. So the kinds of metals are limited to apply this method. The targets for RF sputtering could be metals, metal oxides, insulators, and dielectric materials. Specially, the plasma could be maintained in low pressure. In this research, PZT films are deposited on Si(100) substrate using reactive RF co-sputtering method and the chemical environments of the PZT films are studied by X-ray photoelectron spectroscopy (XPS).

2. Experimental Section

Fig. 1 depicts the schematic diagram of RF co-sputtering system used in this research. We used three metal targets (Pb, Zr, Ti) for fabrication of PZT films.

The substrates, Si(100), can be heated up to desired temperature and the different powers can be employed to each target. And the flow rates of sputter gas (Ar) and reactive gas (O_2) are controlled with independent mass flow controllers (MFC).

The Si(100) substrate was heated during deposition and the temperature was maintained at 573K. The substrate was cleaned with diluted acetone before introduction in the sputtering chamber. The substrate holder was rotated at 12 rpm to be PZT thin films deposited evenly. And lead, zirconium, and titanium were used as targets for reactive RF co-sputtering, and the sputter gas was mixture of high purity Ar and O_2 gas with different mixing ratio. The total sputter gas flow rate was fixed at 20 sccm and the O_2 gas flow rate was varied. The base pressure of reactive RF co-sputtering chamber was

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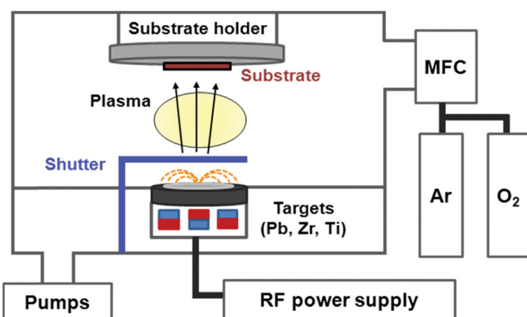

Fig. 1. Schematic diagram of RF co-sputtering system.

maintained at 1.89~6.60×10^{-7} Torr and the working pressure was maintained at 43.1~45.7×10^{-3} Torr and 44.1~49.8×10^{-3} Torr for pre-sputtering and sputtering, respectively. The RF co-sputtering chamber was evacuated by a roughing pump (RP) and a turbo molecular pump (TMP). The RF powers were differently applied on lead, zirconium, and titanium targets during sputtering with 30, 200, and 250 W, respectively. The pre-sputtering was conducted for 10 min to stabilize the plasma and to clean up the target. Then sputtering was performed for 10 min to grow PZT thin films.

To investigate the chemical environment of the obtained PZT films, X-ray photoelectron spectroscopy (XPS, ESCALab MKII, VG, UK) with Mg Kα X-ray source (1253.6 eV) was used. The XPS analysis was performed in ultrahigh vacuum (UHV) chamber and the base pressure of UHV chamber was maintained below 3.0×10^{-10} Torr by a RP, a TMP, a Ti-sublimation pump, and two ion pumps. The XPS spectra were obtained with a concentric hemispherical analyzer (CHA) in constant analyzer energy (CAE) mode. XPS survey and high resolution narrow spectra were obtained after 4 and 9 scans to increase signal to noise ratio. In order to measure the thickness of the deposited PZT films on the substrate, surface profiler (Alpha-Step 500, Tencor, USA) was used and the edge of substrate were masked with Kapton tape before deposition.

3. Results and Discussion

3.1. Optimization

In order to fabricate PZT films, optimization of the RF powers for each targets were crucial. The mixing ratio of the sputter gas was 18:2 of Ar to O_2 for Pb, Zr, and Ti oxide thin films.

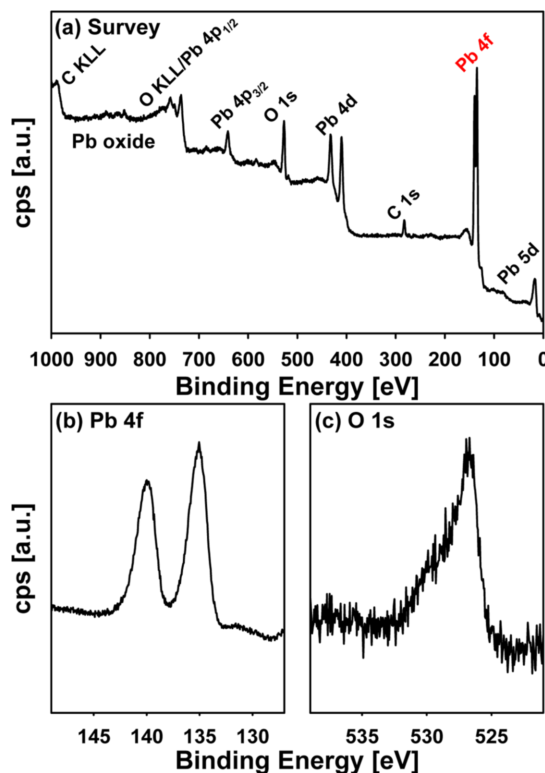

Fig. 2. XPS survey spectra of Pb oxide film in (a) and high resolution XPS spectra of Pb 4f and O 1s in (b) and (c), respectively.

Lead oxide thin films were obtained at various RF powers. Among those, the optimized RF power was 30 W and the XPS spectra of Pb oxide thin films are shown in Fig. 2. Several XPS peaks were observed including C KLL and O KLL Auger peaks shown in Fig. 2(a). The doublet peak centered at 135.5 eV of binding energy is assigned to Pb 4f peaks which are the main XPS peak of Pb. XPS peaks of Pb 5d, Pb 4d, and Pb $4p_{3/2}$ were observed as well centered at about 20, 410, and 640 eV, respectively. The contaminant, carbon, was detected centered at the binding energy of around 285 eV. The source of contamination of the Pb oxide films was either residual carbon in the co-sputtering chamber or CO_2 gas in air.

For detailed chemical information, high resolution XPS spectra was taken in the binding energy range of Pb 4f and O 1s region shown in Fig. 2(b) and (c), respectively. Doublet peaks centered at 135 and 140 eV of Pb $4f_{7/2}$ and Pb $4f_{5/2}$, respectively, were observed. The O 1s peak centered at around 528 eV was detected.

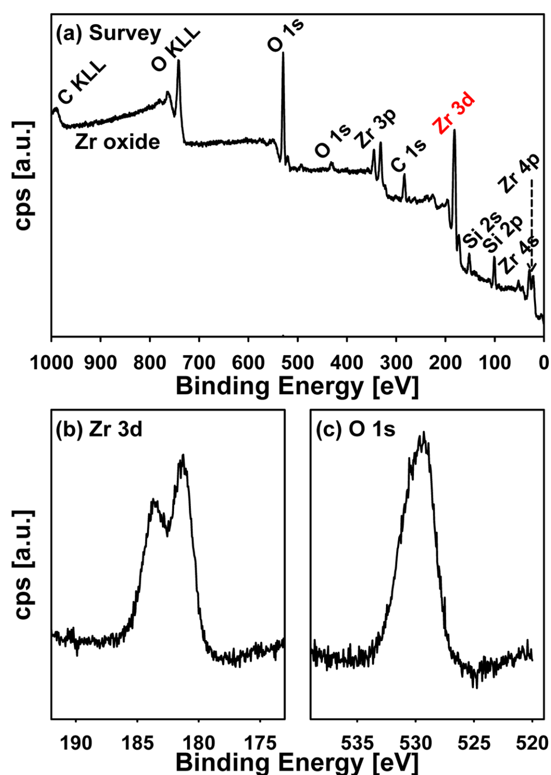

Fig. 3. XPS survey spectra of Zr oxide film in (a) and high resolution XPS spectra of Zr 3d and O 1s in (b) and (c), respectively.

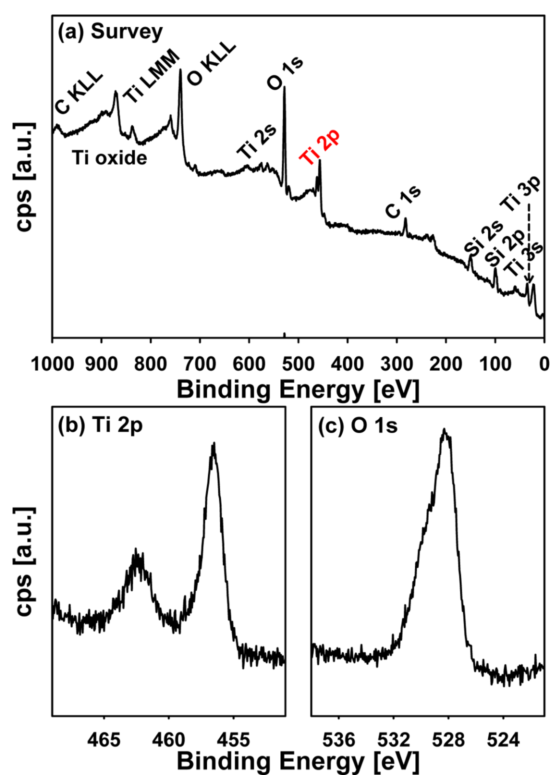

Fig. 4. XPS survey spectra of Ti oxide film in (a) and high resolution XPS spectra of Ti 2p and O 1s in (b) and (c), respectively.

These XPS results confirmed that Pb oxide films were successfully deposited on Si(100) substrate with 30 W of RF power.

Zirconium oxide thin films were obtained at the optimized RF power, 200 W, and the XPS spectra of Zr oxide thin films are shown in Fig. 3. In Fig. 3(a), the characteristic Zr XPS peaks were observed at the binding energies of Zr 3d (183 eV), Zr 3p (345 eV for $3p_{1/2}$ and 331 eV for $3p_{3/2}$) and Zr 4p and 4s as well. Because the thickness of the Zr oxide film was thin, the Si 2p and Si 2s peaks were detected at 102 and 153 eV, respectively. The high resolution XPS spectra of Zr 3d and O 1s are shown in Fig. 3(b) and (c), respectively. Zr oxide films were successfully deposited with 200 W of RF power that is confirmed by XPS results.

Titanium oxide thin films were deposited on Si(100) at 250 W of the optimized RF power and the XPS spectra of Ti oxide thin films are shown in Fig. 4. The characteristic Si peaks were detected due to the thin thickness of the Ti oxide thin films. In the survey XPS spectra of Ti oxide thin films shown in Fig. 4(a), Ti 2p (458 eV), Ti 3p (37 eV), and Ti 2s (62 eV) were detected. The O 1s XPS peak centered at 530 eV was evolved as well. From the XPS results, Ti oxide thin films were successfully deposited at 250 W of RF power.

3.2. Deposition of PZT Films

Through the optimization process for RF power for each sputter targets, 30, 200, and 250 W of RF power were set for Pb, Zr, and Ti targets, respectively. The PZT films were deposited on Si(100) substrate with different oxygen ratio in the sputter gas. The notation PZT-X used hereafter means that the PZT thin film was obtained at X sccm of O_2 gas flow rate while the total sputter gas flow rate was fixed at 20 sccm. The thickness of the obtained PZT thin films were measured with a surface profiler and shown in Fig. 5. Even though the sputtering time was kept constant at 10 min, the thickness of the PZT films was dramatically decreased when

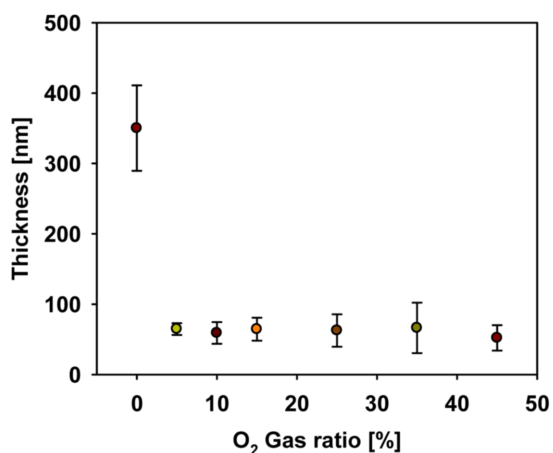

Fig. 5. Thickness of PZT films obtained at various O_2 gas ratios.

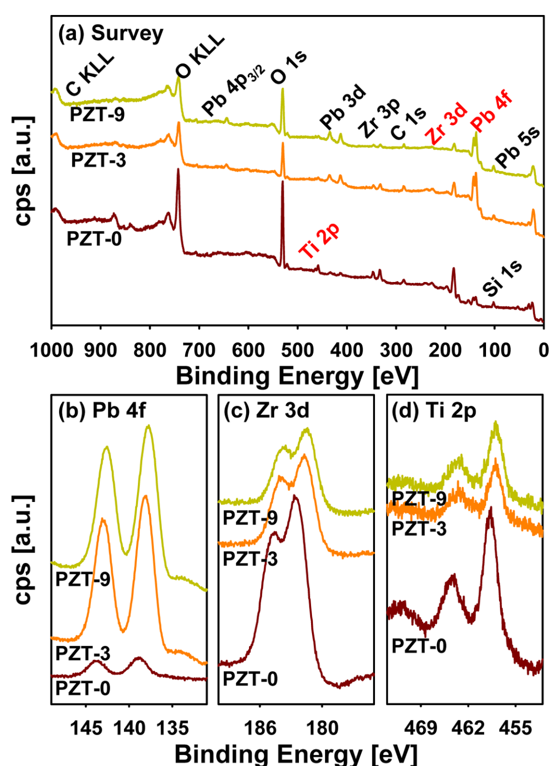

Fig. 6. Representative XPS spectra of PZT films obtained at different oxygen ratio.

oxygen gas was introduced in the sputter gas. After oxygen gas was fed into the co-sputter chamber, the thickness of the PZT films were relatively constant as about 60 nm.

The representative XPS spectra of PZT films obtained with different oxygen flow rates are shown in Fig. 6. From the XPS survey spectra of PZT films, Pb 4f, Zr 3d, and Ti 2p peaks were observed. This implies that the PZT thin films were successfully deposited on Si(100) substrate. From the XPS results, it is interesting to note that the peak intensity of Pb was increased while the peak intensities of Zr and Ti were decreased as oxygen gas ratio increased in the sputter gas. When the reactive gas ratio was increased in the sputter gas, sputter yield was decreased in general[9]. Zr and Ti followed the general propensity but Ph showed opposite result. This phenomenon could be explained that the volatile properties of Pb. Metallic Pb is more volatile than Pb oxide[10]. The more oxygen gas in the sputter gas was, the more lead oxide formed. In this regard, the peak intensity of Pb increased because less volatile Pb oxide formed as the ratio of oxygen in the sputter gas increased.

4. Conclusions

In this research, we fabricate PZT thin films successfully at various oxygen gas ratios in the sputter gas applying RF co-sputtering method. The thickness of the PZT films decreased from 350 nm without oxygen to 65 nm with oxygen in the sputter gas.

Acknowledgements

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