ELSEVIER

Materials Science and Engineering B 136 (2007) 203–206

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Short communication

Improvement in fatigue property for a PZT ferroelectric film device with SRO electrode film prepared by chemical solution deposition

H. Miyazaki [a,*], Y. Miwa [b], H. Suzuki [b]

[a] *Department of Material Science, Faculty of Interdisciplinary Science and Engineering, Shimane University, 1060 Nishikawatsu-cho, Matsue, Shimane 690-8504, Japan*

[b] *Department of Materials Science, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan*

Received 27 June 2006; received in revised form 12 September 2006; accepted 23 September 2006

Abstract

PZT films with (1 0 0) and (1 1 0) orientation were prepared by spin coating using the chemical solution deposition (CSD) method on an SRO/Si or a Pt/Ti/SiO_2/Si substrate. The remnant polarization and the saturation polarization of the PZT/SRO/Si film were 21 and 35 μC/cm^2, and those of the PZT/Pt/Ti/SiO_2/Si film were 20 and 31 μC/cm^2. The remnant polarization of the PZT/SRO/Si film maintained more than 10^8 switching cycles, and the fatigue property was observed for the PZT film fabricated on the Pt/Ti/SiO_2/Si electrode.

Keywords: SRO; PZT; Fatigue property; Chemical solution deposition

1. Introduction

Ferroelectric lead zirconate titanate (PZT) thin film capacitors have been studied with great interest in the last decade because of their potential applicability in piezoelectric sensors, actuators and non-volatile memory devices [1–3]. Platinum presents very attractive properties as bottom electrode material for ferroelectric capacitors due to its high electrical conductivity, good stability in oxidation at high temperatures and a high Schottky barrier height, which gives the leakage currents to low values. However, when using Pt film as a ferroelectric device electrode, the Pt electrode cannot use more than 10^6 switching cycles because of the fatigue [4,5]. To improve the fatigue property of the PZT device, different materials like IrO_2 [6], RuO_2 [7], $LaNiO_3$ [8] and $SrRuO_3$ (SRO) [9–12] have been studied as Pt electrode replacements. On the other hand, improvements of the fatigue for PZT device have investigated by using barrier layer [13,14] or oxygen implantation for Pt electrode [15]. In this study, we focused the improvement of the fatigue by using a metal oxide electrode.

SRO is one of the most promising candidates for a PZT device electrode because of its similar lattice constants (the lattice constants for a $Pb_{0.52}Zr_{0.48}TiO_3$: $a = 4.036$ Å, $b = 4.146$ Å; and the lattice constants for an SRO with a pseudo-cubic symmetry: $a = 3.930$ Å) and a low resistivity of about 2.8×10^{-4} Ωcm. The difference in the lattice constant of PZT and SRO is less than 3%.

In a previous study, we fabricated conductive LNO film or SRO film by the chemical solution deposition (CSD) method, and evaluated the electrical properties and the microstructure for those films [16,17]. We also reported preparation of the PZT films using the same CSD method and investigated the dielectric, ferroelectric and piezoelectric properties for the resultant PZT films [18–20]. In this study, we tried to fabricate an SRO electrode film on a Si substrate and a PZT/SRO/Si ferroelectric film device using only the CSD method. Furthermore, we evaluated the dielectric, ferroelectric, fatigue properties for the PZT/SRO/Si film.

2. Experimental

2.1. Film device preparation

Sr metal and $RuCl_3 \cdot 2H_2O$ were used as the starting materials and 2-methoxyethanol was used as the solvent. A stable 0.1 M SRO precursor solution was prepared using Sr metal and $RuCl_3 \cdot 2H_2O$. An SRO precursor film was deposited on the

* Corresponding author.
E-mail address: miya@riko.shimane-u.ac.jp (H. Miyazaki).

0921-5107/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2006.09.024

Si(1 0 0) substrate by spin coating using 0.1 M SRO solution. The precursor SRO film was dried at 150 °C for 10 min and pre-annealed at 420 °C for 10 min to remove residual organics. Finally, the film was annealed at 700 °C by the RTA method. These processes were repeated 10 times, and then, the precursor film was annealed at 700 °C for 2 h in an electric furnace. The electrical resistivity of a fabricated SRO film showed 1.11×10^{-3} Ωcm. To evaluate a ferroelectric property, sheet resistance of the SRO film as a bottom electrode was adjusted lower than 10 Ω/□.

The PZT film deposition process was reported in previous studies [20], and a PZT film was deposited on the resultant SRO film or Pt/Ti/SiO_2/Si by the previously reported CSD method with the composition of $PbZr_{0.53}Ti_{0.47}O_3$ (morphotropic phase boundary composition). The PZT film thickness was controlled at about 0.7 μm. To evaluate the electrical property of the film, Au top electrodes, 2 mm in diameter, were sputtered onto the films through a metal mask.

2.2. Characterization

Crystal structure of the PZT/SRO or the PZT/Pt/Ti/SiO_2/Si films was characterized by XRD with Rigaku RINT-2200. Resistivity of the SRO film was measured by a four-point probe method. Microstructure of the films was observed by AFM using Seiko-Inst. SPI3800N. The hysteresis loop and the fatigue property were investigated at room temperature by a ferroelectric tester of Radiant Technologies RT-6000S.

3. Results and discussion

Fig. 1a shows the XRD patterns for the PZT/SRO/Si film and SRO/Si film, and Fig. 1b shows the XRD patterns for the PZT/Pt/Ti/SiO_2/Si film and the Pt/Ti/SiO_2/Si film, respectively. Both PZT phases in the films indicated a tetragonal perovskite single phase. The resultant SRO film exhibited the (1 2 1) preferred orientation. Here, the lattice of the resultant SRO film was indexed as an orthorhombic cell with JCPDS 43-0471. The PZT phase in PZT/SRO/Si film showed preferential (1 1 0) orientation. The (1 2 1) plane of the orthorhombic SRO could be regarded as the (1 1 0) plane of the pseudo-cubic SRO (JCPDS 80-1259). The PZT lattice constant and the SRO lattice constant were very close, therefore, it is assumed that the (1 1 0)-oriented PZT film was grown on the pseudo-cubic SRO (1 1 0) plane (which is equivalent with the (1 2 1) plane of the orthorhombic SRO). The PZT phase in the PZT/Pt/Ti/SiO_2/Si film showed a (1 0 0) and (0 0 1) orientation strongly, thus the resultant PZT film on Pt was not greatly affected by the Pt substrate.

Resistivity of the resultant SRO film was 1.11×10^{-3} Ωcm, and the value was very similar to that reported in the previous paper [21]. Therefore, the SRO film could be used as an electrode.

It was demonstrated that the CSD-derived PZT thin film with a preferred orientation was successfully deposited on a preferred oriented SRO or Pt electrode. Microstructure of the film affects the electrical property of that, therefore, the surface

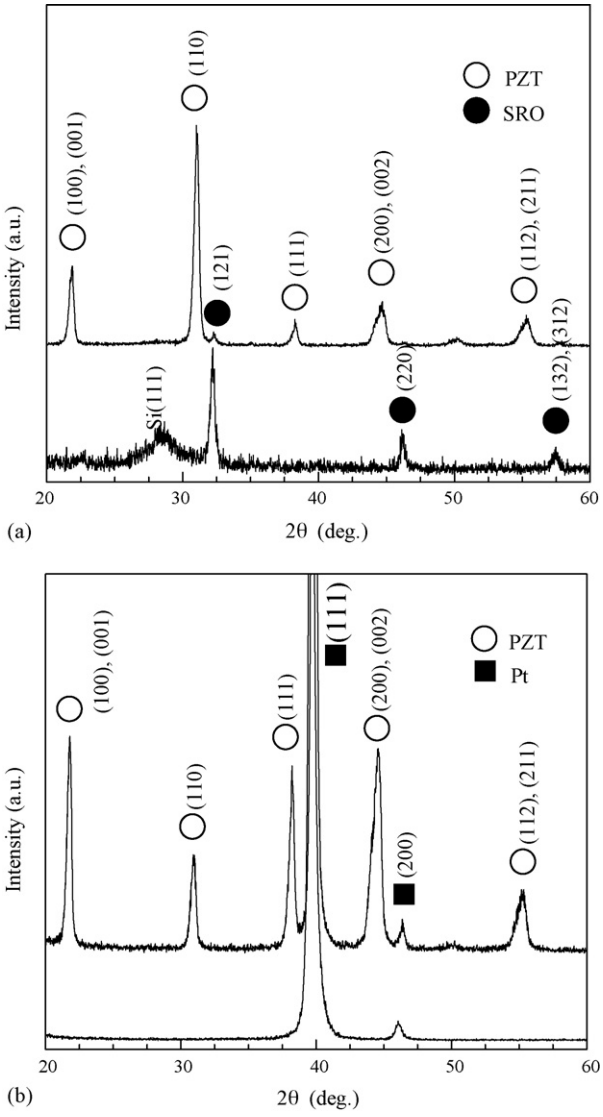

Fig. 1. (a) XRD patterns for a PZT/SRO/Si film (upper) and SRO/Si film (lower). (b) XRD patterns for and a PZT/Pt/Ti/SiO_2/Si film (upper) and a Pt/Ti/SiO_2/Si film (lower).

morphology of the resultant films was observed by AFM. Fig. 2a and b shows the AFM images of the PZT/SRO/Si film and the PZT/Pt/Ti/SiO_2/Si film, respectively. The RMS roughness values of the PZT/SRO/Si film and the PZT/Pt/Ti/SiO_2/Si film were 0.20 nm and 0.25 nm, respectively. It was confirmed that both of the films had a very flat surface. The particle size of the PZT on Pt/Ti/SiO_2/Si was larger than that on SRO/Si. The Pt/Ti/SiO_2/Si substrate film had a very flat surface because it was deposited by sputtering, and homogeneous nucleation occurred on the Pt/Ti/SiO_2/Si substrate film. A lot of the PZT nuclei were generated on the Pt/Ti/SiO_2/Si surface, and the PZT crystals were grown homogeneity on these lots of nuclei. Therefore, the PZT column became narrow on the Pt/Ti/SiO_2/Si substrate film. It is assumed that the particle size on the film surface depended on the column width, and this result agreed with the SEM observation.

A gold top electrode was deposited on the PZT films by sputtering to evaluate the electrical properties of the PZT