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Compositional dependence of the properties of ferroelectric $Pb(Zr_xTi_{1-x})O_3$ thin film capacitors deposited on single-layered $PtRhO_y$ electrode barriers

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Abstract

Single-layered $PtRhO_y$ thin films were investigated as electrode barriers for ferroelectric $Pb(Zr_xTi_{1-x})O_3$ (PZT) ($x = 0.2$–0.8) thin film capacitors. $PtRhO_y$ thin films were deposited directly on n+ Si wafers by means of the reactive sputtering method. $PtRhO_y$/PZT/$PtRhO_y$/n+ Si capacitors showed well-defined *P–E* hysteresis loops. The remanent polarizations, as well as the polarization loss after the switching repetitions, were varied with the ratio of Zr/Ti. Especially, $Pb(Zr_{0.4}Ti_{0.6})O_3$ thin film capacitor showed the superior ferroelectric properties, such as the *P–E* hysteresis characteristics and the polarization fatigue. The typical remanent polarization and the coercive field of this capacitor were 22 $\mu C/cm^2$ and 87 kV/cm, respectively, and the polarization loss was only less than 5% after 10^{11} switching repetitions. From the measurement of the depth profile and the microstructure of this capacitor, it could be convinced that single-layered $PtRhO_y$ films behaved as high quality electrode barriers for PZT thin film capacitors.

Keywords: $PtRhO_y$; Electrode barrier; $Pb(Zr_xTi_{1-x})O_3$; Ferroelectric thin film

1. Introduction

For the realization of high density ferroelectric memories (FRAM) devices, lowering stack height of capacitor in capacitor over bit (COB) structures [1,2] to 400 nm should be accomplished with the decrease in thickness of ferroelectric thin films and electrodes below 100 nm for successful node separation. Moreover, in PZT-based COB structures, the bottom electrode inhibits the diffusion of oxygen towards plug, such as n+ polycrystalline Si (poly-Si) or W, to reduce the contact resistance, as well as to enhance the polarization fatigue resistance. Several electrode-barrier structures have been proposed for the integration of ferroelectric memory devices. Among them, hybrid electrodes, such as Pt/IrO_2 [3] and Ir/IrO_2 [3,4], and Pt/RuO_2 [5] and multilayer electrodes, such as $PtRhO_y/PtRh/PtRhO_y$ [6] and $PtIrO_y/PtIr/PtIrO_y$ [7], resulted in negligible polarization fatigue for PZT based capacitors. However, development of a simple and thin electrode barrier can be necessary from the practical aspect point of view.

In this paper, we show that a $PtRhO_y$ thin layer itself acts as fatigue free electrodes, as well as diffusion/reaction barriers, for PZT capacitors. In addition, we present that the x in $Pb(Zr_xTi_{1-x})O_3$ affects the $PtRhO_y$ electrode-barrier properties.

2. Experimental procedures

The electrode barrier of a $PtRhO_y$ layer was deposited onto n+ Si wafers by means of the reactive rf-sputtering method using a Pt–10 wt.%Rh alloy target (PtRh, purity 99.99%) in Ar + O_2 ambient. The partial pressure of Ar and O_2 were 6.7×10^{-1} Pa and 2.7×10^{-1} Pa, respectively. The deposition rate of $PtRhO_y$ thin films at rf-power of 50 W was about 10 nm/min and the thickness of $PtRhO_y$ was about 120 nm. In order to investigate the effect of the substrate temperature (T_{sub}) on the electrode barrier properties of $PtRhO_y$, the substrates were prepared at various

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T_{sub} ranging from 50 to 650 °C. The sol–gel derived PZT thin films of about 240 nm-thickness, with compositions of $Pb_{1.1}(Zr_xTi_{1-x})O_3$ ($x = 0.2$–0.8), were deposited on these substrates by using a conventional spin-coating method, which was described elsewhere [8]. Post-deposition annealing was performed at a temperature of 625 °C for 1 h in O_2 ambient. 80 nm-thickness $PtRhO_y$ top electrodes of 3×10^{-4} cm^2 area were deposited on the surface of PZT thin films using a shadow mask.

The *P–E* hysteresis loops were measured using a standardized ferroelectric tester (RT66A, Radiant Technologies) and also the polarization fatigue tests were performed using an externally generated square wave with amplitude of ±5 V and a frequency of 1 MHz. The dc electrical current–voltage characteristics of these capacitors were measured using an electrometer/source (Keithley 617). The chemical binding states, as well as the compositional ratio, of $PtRhO_y$ was determined using X-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) spectroscopy was used to determine the crystallinity of $PtRhO_y$ and PZT. Auger electron spectroscopy (AES) was used to investigate the depth profiles of the elements in PZT/$PtRhO_y$/Si films.

3. Results and discussion

Fig. 1(a) and (b) shows the XRD patterns of $PtRhO_y$ deposited on n+ Si (1 0 0) wafers at various T_{sub} and PZT deposited on them ($T_{sub} = 400$ °C). The [1 1 1]-axis orientation was found for $PtRhO_y$ thin films. The intensity of (1 1 1) peaks revealed higher at the substrate temperature of 300–400 °C, while the amorphous halo revealed remarkably, which implies the amorphous and crystalline phase are mixed in the $PtRhO_y$ films deposited at low temperature (<150 °C). As seen in Fig. 1(b), the PZT thin films ($x = 0.2$–0.6) showed the randomly oriented perovskite phase, despite the [1 1 1]-axis orientation of $PtRhO_y$, while any perovskite peaks in the XRD patterns of the Zr-rich PZT thin films ($x \geq 0.7$) were hardly observed.

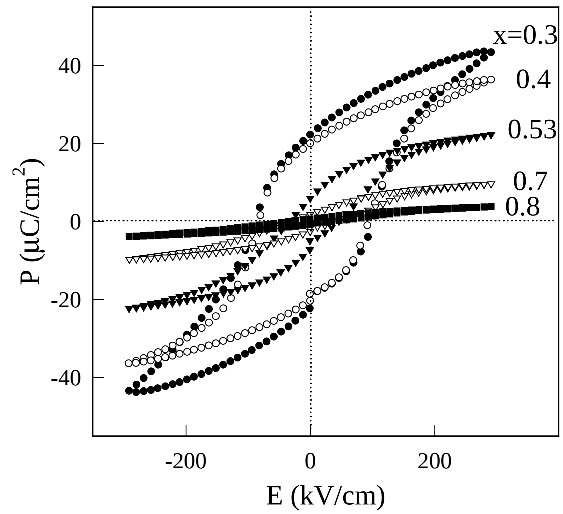

Fig. 2. Typical *P–E* hysteresis loops of $PtRhO_y/Pb(Zr_xTi_{1-x})O_3/PtRhO_y$/n+ Si ($x = 0.3$–$0.7$) thin film capacitors.

Fig. 2 shows the typical *P–E* hysteresis loops of PZT capacitors ($x = 0.3$–0.8), which are well-defined loops. The Ti-rich PZT capacitors ($x \leq 0.3$) did not show the saturated *P–E* loops, whereas the Zr-rich PZT capacitors ($x \geq 0.8$) showed the negligible remanent polarization (P_r). The values of P_r, as well as the values of coercive field (E_c), of these capacitors were likely to decrease with increasing x in $Pb(Zr_xTi_{1-x})O_3$. The polarization fatigue behaviors of these capacitors were shown in Fig. 3. It was found that the values of the polarization loss of all PZT capacitors after 10^{11} switching repetitions were only less than about 25%. In addition, the negligible polarization loss (≤10%) was found for PZT capacitors around $x = 0.5$. Amongst $Pb(Zr_xTi_{1-x})O_3$ thin film capacitors, a capacitor of $x = 0.4$ has the superior polarization fatigue behaviors, which

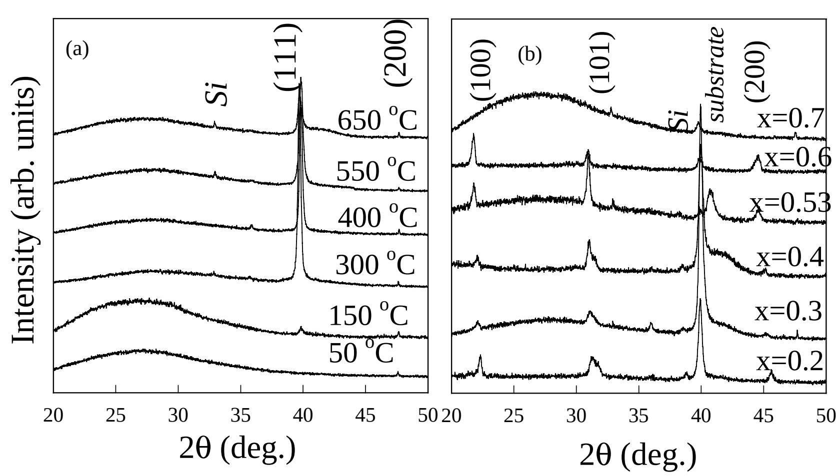

Fig. 1. XRD patterns of (a) $PtRhO_y$ deposited on n+ Si wafers at various substrate temperatures and (b) $Pb(Zr_xTi_y)O_3$ ($x = 0.2$–0.7) thin films deposited on $PtRhO_y$ ($T_{sub} = 400$ °C).

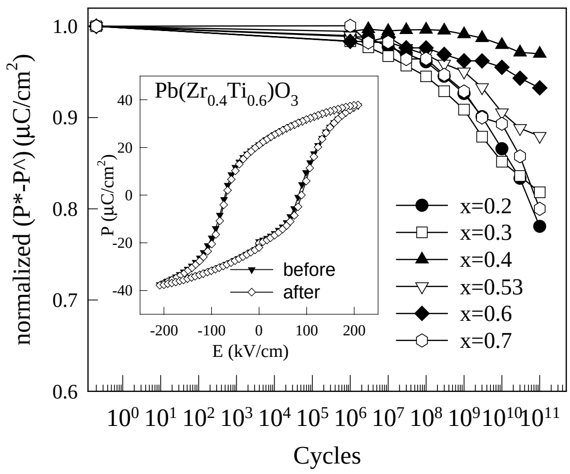

Fig. 3. Polarization fatigue behaviors of $Pb(Zr_xTi_{1-x})O_3$ ($x = 0.2$–0.7) thin film capacitors. The inset shows the *P–E* hysteresis loops of a $Pb(Zr_{0.4}Ti_{0.6})O_3$ thin film capacitor before and after 10^{11} switching repetitions.

shows a lack of polarization loss even after 10^{11} switching repetitions, as shown in the inset of Fig. 3. This capacitor showed the well-saturated *P–E* loops, where P_r and E_c were 22 μC/cm^2 and 87 kV/cm, respectively. These values were nearly constant in various $PtRhO_y$ electrode barriers deposited at various T_{sub} of 300–650 °C, as seen in Fig. 4. Otherwise, only the P_r decreased to 10 μC/cm^2 for $T_{sub} = 150$ °C and no *P–E* hysteresis loop, in addition, was found for a $PtRhO_y$ electrode barrier deposited at T_{sub} of 50 °C. Such decrease of P_r with constant E_c in *P–E* hysteresis loops, as also shown in the inset of Fig. 4, could be easily demonstrated by using a resistor connected in series with a ferroelectric capacitor characterized by P_r and E_c. In the case of $PtRhO_y/Pb(Zr_{0.4}Ti_{0.6})O_3/PtRhO_y$/n+ Si capacitors, by changing the two probe contacts in the electrical measurement from top-to-bottom n+ Si to top-to-bottom

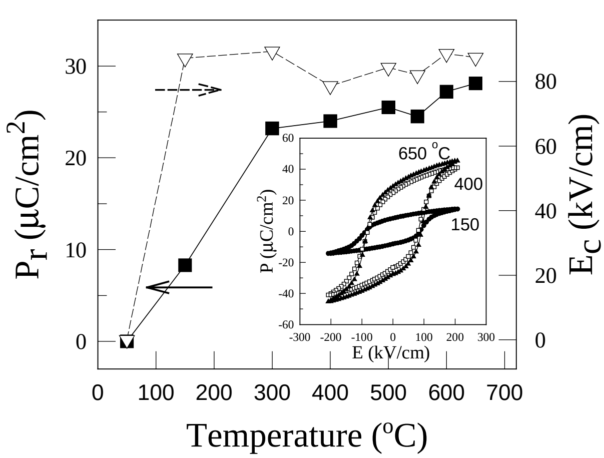

Fig. 4. The variation of P_r and E_c of $Pb(Zr_{0.4}Ti_{0.6})O_3$ thin film capacitors with the substrate temperature of $PtRhO_y$ electrode barriers. The inset shows the typical *P–E* hysteresis loops of $Pb(Zr_{0.4}Ti_{0.6})O_3$ thin film capacitors having three different $PtRhO_y$ electrode barriers deposited at 150, 400, and 650 °C.

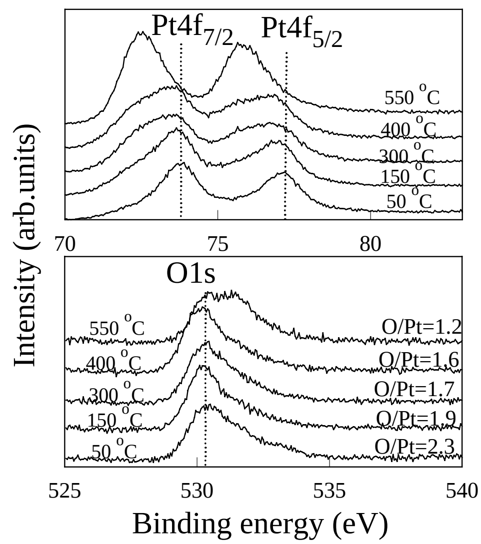

Fig. 5. XPS spectra of Pt 4f and O 1s for $PtRhO_y$ thin films deposited at various T_{sub}.

$PtRhO_y$, it could be easily found that such serial resistance effect arose mainly from the interface states between PZT and bottom $PtRhO_y$, deposited at low substrate temperatures (≤150 °C). We suggest that the existence of such resistive interface states between PZT/$PtRhO_y$ is closely related to the chemical binding states, as well as oxygen content, on the surface of $PtRhO_y$ electrode barrier, as shown in Fig. 5. The XPS spectra of Pt 4f and O 1s, respectively, obtained from $PtRhO_y$ thin films deposited at various T_{sub} were shown in Fig. 5. It can be seen that the XPS peaks for Pt $4f_{7/2}$ are extending over the binding energy range of two binding states, namely PtO_2 and PtO (74.1 and 72.4 eV [9], respectively), in which the binding states of PtO in $PtRhO_y$ increased with increasing T_{sub}, while those of PtO_2 decreased. From the compositional analysis of the XPS spectra, it was found that the atomic ratio of O to Pt (O/Pt) decreased monotonically from 2.3 to 1.5 with increasing the substrate temperature ranging from 50 to 550 °C, whereas the value of Rh/Pt remained constant at about 0.12.

Fig. 6 shows the typical polarization fatigue behaviors of $Pb(Zr_{0.4}Ti_{0.6})O_3$ capacitors having three kinds of $PtRhO_y$ electrode barriers, deposited at T_{sub} of 150, 400, and 650 °C. For all these capacitors, the polarization loss after 10^{11} switching repetitions was less that only 5% and the polarization fatigue behaviors were not dependent on the substrate temperature of $PtRhO_y$ electrode barriers. This result implies that the pure serial resistance effect by the interface states between PZT/$PtRhO_y$ does not affect the polarization loss by the polarization reversal. The leakage current of $PtRhO_y/Pb(Zr_{0.4}Ti_{0.6})O_3/PtRhO_y$/n+ Si capacitor having a $PtRhO_y$ electrode barrier deposited at 400 °C was about 2×10^{-7} A/cm^2 at a field of 200 kV/cm, which is comparable to that of PZT capacitors having multilayer electrode barriers reported earlier [7].

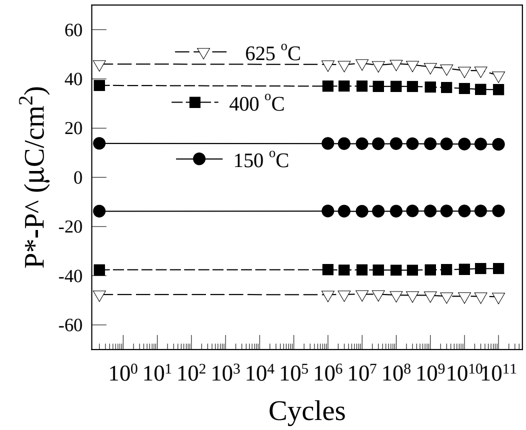

Fig. 6. Polarization fatigue behaviors of $PtRhO_y/Pb(Zr_{0.4}Ti_{0.6})O_3/PtRhO_y$/n+ Si capacitors having three different $PtRhO_y$ electrode barriers deposited at 150, 400, and 650 °C.

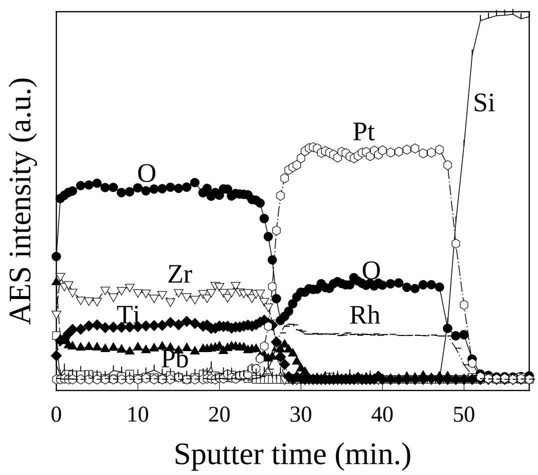

Fig. 7. AES depth profile of a $PtRhO_y/Pb(Zr_{0.4}Ti_{0.6})O_3/PtRhO_y$/n+ Si.

Fig. 7 shows the AES depth profile of $PtRhO_y/Pb(Zr_{0.4}Ti_{0.6})O_3/PtRhO_y$/n+ Si. This AES profile revealed the typical patterns of the polarization fatigue free capacitors [1], which showed the uniform composition profiles in the PZT thin film, especially the uniform oxygen profile up to the $PZT/PtRhO_y$ interface. No diffusion of PZT elements could be also seen in the range of the $PtRhO_y$ thin film, as well as in the Si wafer. This result indicates that high quality ferroelectric properties of $PtRhO_y/Pb(Zr_{0.4}Ti_{0.6})O_3/PtRhO_y$/n+ Si capacitors result basically in the high quality interfacial properties of $PZT/PtRhO_y$, which arises from the high quality electrode barrier properties of a $PtRhO_y$ thin film itself.

4. Conclusion

We have investigated the $PtRhO_y$ thin films as electrode barriers for PZT thin film capacitors, as well as the characteristics of ferroelectric $Pb(Zr_xTi_{1-x})O_3$ ($x = 0.2$–0.8) thin film capacitors prepared on them. The sol–gel derived PZT thin film capacitors deposited on $PtRhO_y$/n+ Si ($PtRhO_y/PZT/PtRhO_y$/n+ Si) showed well-defined *P–E* hysteresis loops, where the remanent polarizations, as well as the polarization loss, were varied with the ratio of Zr/Ti. Especially, $Pb(Zr_{0.4}Ti_{0.6})O_3$ thin film capacitor showed the superior ferroelectric properties with negligible polarization loss after 10^{11} switching repetitions. The values of remanent polarization and coercive field were 22 μC/cm^2 and 87 kV/cm, respectively. Such high quality ferroelectric properties of these capacitors are believed to be due to the high quality interfacial properties of $PZT/PtRhO_y$, which arise from the high quality electrode barrier properties of a $PtRhO_y$ thin film for PZT thin film capacitors. Such simple electrode barriers using $PtRhO_y$ thin films should give great benefits in the development of future high density FRAM processing.

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