Ferroelectric characteristics of $Au/PbTiO_3/YBa_2Cu_3O_{7-\delta}$ and $Au/PbZr_{0.52}Ti_{0.48}O_3/YBa_2Cu_3O_{7-\delta}$ capacitors in a radiation environment

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Ferroelectric characteristics of Au/$PbTiO_3$/$YBa_2Cu_3O_{7-\delta}$ and Au/$PbZr_{0.52}Ti_{0.48}O_3$/$YBa_2Cu_3O_{7-\delta}$ capacitors in a radiation environment

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Abstract. $PbTiO_3/YBa_2Cu_3O_{7-\delta}$ (PTO/YBCO) and $PbZr_{0.52}Ti_{0.48}O_3/YBa_2Cu_3O_{7-\delta}$ (PZT/YBCO) structures were fabricated on $SrTiO_3$ and $LaAlO_3$ substrates by the pulsed excimer laser deposition (PLD) method, respectively. In order to investigate total dose radiation effects on the Au/PTO/YBCO and Au/PZT/YBCO ferroelectric (FE) capacitors, the capacitance–voltage (C–V) and the retained polarization properties of the capacitor were measured before and after γ-ray irradiation. The results showed that, with the increment of the γ dose, the retained polarization ΔP and the dielectric constant ε of the FE capacitors decreased; but the absolute value of the negative and positive coercive fields of the PZT capacitor increased while that of the PTO capacitor decreased. The results have been interpreted by radiation-induced positive charges and the defect trap model.

1. Introduction

$PbTiO_3$ and $PbZr_xTi_{1-x}O_3$ are important FE materials for the storage element of high speed nonvolatile memory. They also have much potential to be used in commercial, space and military fields. In recent years, the tolerances of PZT capacitors to radiation have been studied widely [1, 2], and the results showed that the PZT capacitors had less sensitivity to neutron and pulsed radiation [3]. In regard to their tolerance to total dose radiation, many authors gave various results [1–6]. R A Moore reported that the ΔP of a PZT capacitor which had been irradiated at a dose of 5×10^3 Gy (SiO_2) was about 30% lower than that pre-irradiation [5]. J R Schwank reported that, with increment of irradiation dose, four kinds of PZT capacitor showed different retained polarization [6], and the degradation of ΔP for the PZT capacitor sample coded SNL1 was the least in all of the samples while that of sample coded Krysalls was the most. At the dose of 10^5 Gy (Si), the degradation of ΔP for the former sample was about 20% while that of the latter sample was near 100%. In those studies, Pt metal was used as electrodes of the PZT capacitors. Up to now, few reports have been seen on the radiation effects of a PTO or PZT capacitor with a YBCO bottom electrode.

YBCO has a similar perovskite crystal structure and a small lattice mismatch with PTO or PZT making it an attractive electrode for a PTO and PZT ferroelectric capacitors. The FE capacitors which have the superconductor–ferroelectric structure could overcome fatigue

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effects during read or write operation for the FE memory [7]. Recently, the superconductor–ferroelectric heterostructures have become of great interest to prepare superconductor field effect transistors [8, 9]. In this paper, the PTO, PZT and YBCO thin films have been made by the PLD technique, and the electric characteristics of the Au/PTO/YBCO and Au/PZT/YBCO ferroelectric capacitors after γ-ray irradiation have been investigated. The results show that, with the increment of total dose, the retained polarization ΔP and the dielectric constant ε decreased obviously. In addition, the changes of the positive and negative coercive field were related to the kind of FE material during irradiation.

2. Experiment

The PTO/YBCO thin films were grown on ⟨001⟩ $SrTiO_3$ wafers while the PZT/YBCO structures were grown on ⟨001⟩ $LaAlO_3$ wafers by the PLD method. A YAG:Nd laser with 355 nm wavelength, 4 J cm^{-2} fluence, 100 mJ pulsed energy and 10 Hz repeat rate were employed. During growth of YBCO, PTO and PZT layers, the substrate temperatures were from 570 to 760 °C. The thickness of the PTO or PZT layer was about 0.6 μm. The YBCO layer was used as a bottom electrode with a thickness of 200 nm. The top Au electrodes of the FE capacitors were fabricated by the thermal evaporation method. Each top electrode thickness and area were about 100 nm and 6.8×10^{-5} cm^2, respectively. The ΔP property of the FE capacitors was measured by using the Sawyer–Tower circuit, and the sense capacitance in the circuit was 10 nF. During the measurement of ΔP, a ± 4 V square wave was used as the input signal at a frequency of 1 MHz. The C–V property of the FE capacitors was obtained by using a 1 MHz HP4280 C–V meter.

The FE capacitors were stressed with a bias of 0 V during ^{60}Co γ-ray irradiation. The total dose range was 0–2×10^5 Gy (Si), and the dose rate was 6.7 Gy (Si) s^{-1}. The ΔP and the C–V properties were measured before and after irradiation.

3. Results and discussion

3.1. Change of the retained polarization during irradiation

In order to investigate the electric property of PTO or PZT ferroelectric capacitors in a nonvolatile memory, the ΔP was measured with a pulsed polarization method [5], that is, a series of square wave pulses was used to simulate write and read operation across the FE capacitor in a Sawyer–Tower circuit [5]. When a binary ‘0’ state was written and read for an FE capacitor, two separated positive pulses were applied on the top electrode of the capacitor: one was used to simulate the write operation and the other was used to simulate the read operation. When a ‘1’ state was written and read, the capacitor was written with a negative pulse first, then was read with a positive pulse. The reads of the ‘1’ state and the ‘0’ state were called switch read and nonswitch read, respectively. The retained polarization ΔP could be obtained from the difference of the read voltage between the ‘1’ and the ‘0’ state, and could be stated as [5]:

$$\Delta P = \frac{(V_{S1} - V_{S0})C_S}{A_{FE} \times 1000}$$

where ΔP was given in μC cm^{-2}. The switch read V_{S1} and the nonswitch read V_{S0} measured in mV were the sense capacitor voltage when the ‘1’ and ‘0’ state were read, respectively. C_S was the sense capacitance and was given in μF. A_{FE} was the area of the FE capacitor and was given in cm^2.

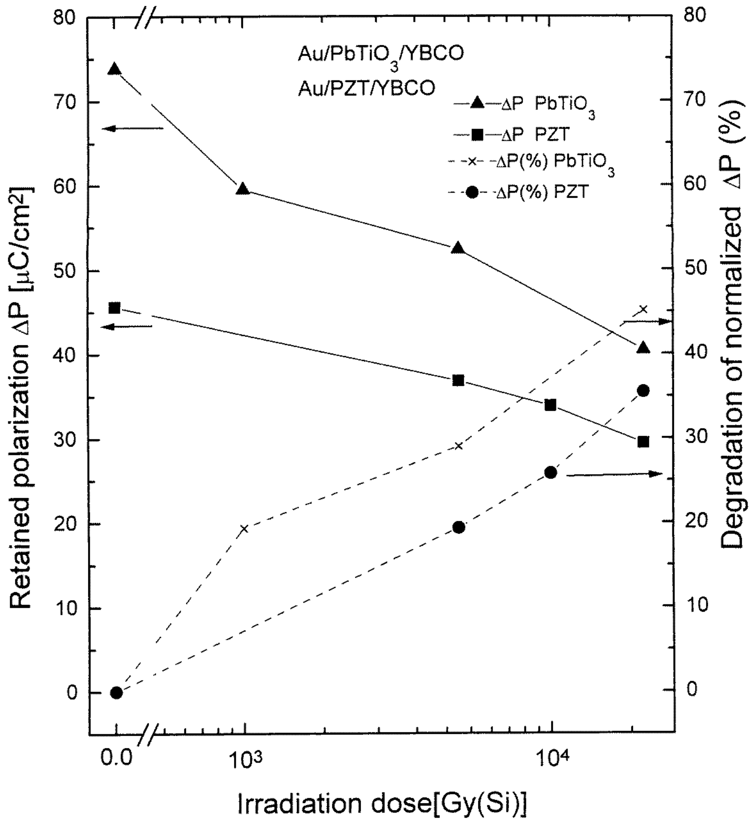

Figure 1. Retained polarization ΔP of the PTO and PZT capacitors versus γ-irradiation dose. They were measured by read and write operation for binary '0' and '1' states of the PTO or PZT capacitor in a Sawyer–Tower circuit.

ΔP of the Au/PTO/YBCO and Au/PZT/YBCO ferroelectric capacitors have been measured before and after irradiation and are shown in figure 1. The maximum dose is 2×10^4 Gy (Si). With the increment of the dose, the ΔP shows obvious degradation. After irradiation with the dose of 2×10^4 Gy (Si), the ΔP of the PTO and PZT capacitors are 45% and 35% lower than their original values, respectively. At a dose of 5×10^3 Gy (Si), the degradation of the ΔP of the PTO capacitors is 29% lower than its original value; the result is the same as that of R A Moore [5]. But that of the PZT capacitor is 19% and is lower than that of R A Moore.

Figure 1 also shows that the degradation rate of the ΔP varied at different dose range: in the range of 0–1×10^3 Gy (Si), the rates of PTO and PZT capacitors are 19% and 8% respectively. But in the wide range of 10^3–2×10^4 Gy (Si), the rates are 26% and 27% respectively. So at low dose the degradation of the ΔP of the PTO capacitor is more than that of the PZT capacitor. It may be considered there are many neutral defects at the PTO and PZT layer. A large amount of electron–hole pairs would be generated throughout FE layers during irradiation, and the holes can be trapped by defects in the layer: this process can be called ionizing of the defects [10, 12]. Most of the trapped charges accumulate at grain boundaries and electrodes and could screen spontaneous polarization in the FE layers and result in the degradation of the ΔP [12]. In addition, there is a distribution for the defect energy level: at low dose the shallow level defects have more probability of capturing holes than the deep level defects; at high dose the shallow level defects are saturated and only the deep level defects could capture holes. It could be considered that there are more shallow level defects in a PTO layer than in a PZT layer, therefore, at low dose, the degradation of ΔP of the PTO capacitor is more than that of the PZT capacitor.

In addition, according to results for the ΔP of PZT memories, which was shown in [12], after the PZT memories were irradiated at 5×10^4 Gy (Si), the ΔP are degraded for 5 V bias and short-circuited bias. Because the experimental conditions in [12] are different from ours, the results which are shown in the reference are different from ours which are shown in figure 1.

3.2. C–V characteristics during irradiation

C–V curves of FE capacitors were measured before and after irradiation, and the dielectric constant ε and coercive field E_c could be obtained from the C–V curves: the input voltage across the FE capacitor swept from the negative to the positive first, and the dielectric constant ε_+ was obtained at the positive coercive field E_{c+}; then the sweep voltage returned from the positive to the negative, and the dielectric constant ε_- was obtained at the negative coercive field E_{c-}. In fact, when the ε_+ and the ε_- were obtained the spontaneous polarization was reversing.

The changes of the ε and the E_c after irradiation are shown in figures 2 and 3, respectively. Figure 2 shows that the degradation of the dielectric constant, $\Delta\varepsilon = [\varepsilon(x) - \varepsilon(0)]/\varepsilon(0)$, decreased gradually with the increment of irradiation dose. $\varepsilon(0)$ and $\varepsilon(x)$ are the dielectric constants before and after irradiation respectively. As the dose was 2×10^5 Gy (Si), for the PTO capacitor, $\Delta\varepsilon_-$ and $\Delta\varepsilon_+$ were 16% and 18.7%, respectively; for the PZT capacitor, $\Delta\varepsilon_-$ and $\Delta\varepsilon_+$ were 13.3% and 18.1%, respectively. So the $\Delta\varepsilon$ of the PTO capacitor were similar to that of the PZT capacitor after irradiation with a dose of 2×10^5 Gy (Si). But, at the dose of 10^3 Gy (Si), the $\Delta\varepsilon_-$ and $\Delta\varepsilon_+$ of the PTO were 11.3% and 12.5% respectively while those of PZT were 0.6% and 1.2% respectively. So, at low dose, the change of $\Delta\varepsilon$ of the PTO capacitor is more than that of the PZT capacitor. The explanation of this fact is similar to that of the retained polarization ΔP. In general, figures 1 and 2 show that the degradation of dielectric constant was similar to that of the ΔP, and the facts could be interpreted with radiation theory about FE materials.

According to the radiation theory [6, 10, 12], the change of the ferroelectric property during irradiation is attributed to the capture of charges. PTO and PZT ferroelectric layers could be considered as an insulator, in particular as purely dielectric materials in their bulk domains where strong spontaneous polarization exists. At grain boundaries the polarization tends to produce strong local internal electric field and cause a strong bending of the energy band and induce the ionization of trap states [3]. In addition, in the FE layers there are some defects such as oxygen or lead vacancies; most of the defects exist at the interface of the domains and at the interface of FE/YBCO or Au/FE. These defects can trap movable charges. During total dose irradiation, large numbers of electron–hole pairs would be generated in the FE layers; when the FE capacitors are stressed with an external bias of 0 V, the electron–hole pairs would be separated by the strong local internal electric field at grain boundaries. Because the mass of a hole is larger than that of an electron, the electrons are swept out of the FE layer quickly by the field while the holes move slowly and could be trapped by the defects. So, most of the trapped positive charges would be distributed at the surface of domains or the interface of FE/YBCO and Au/FE and forming positive charges. The larger the total dose, the more positive charges the defects could capture.

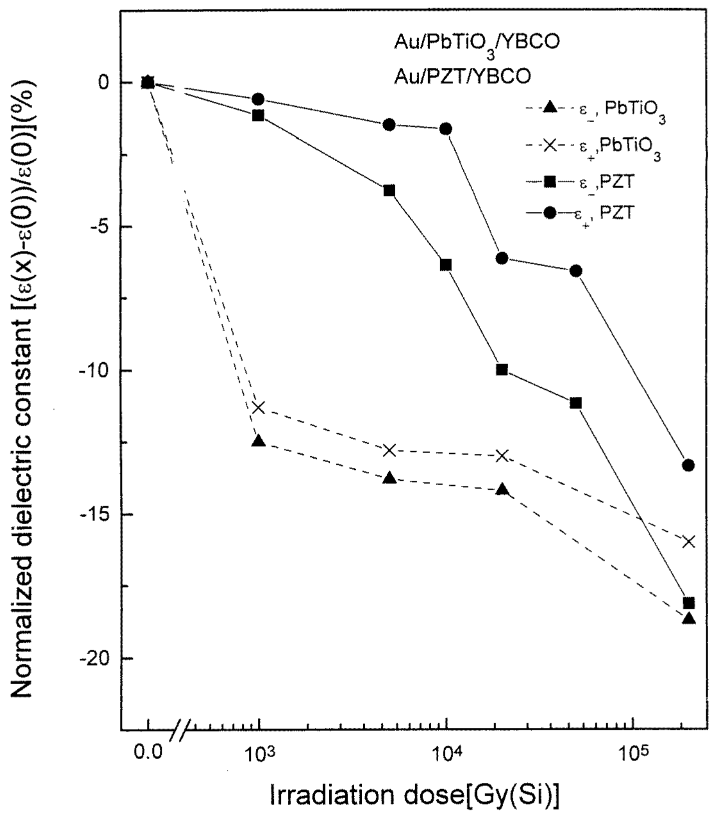

Figure 2. The degradation of relative dielectric constants ε of the PTO and PZT capacitors versus irradiation dose. $\varepsilon(0)$: before irradiation; $\varepsilon(x)$: after irradiation. ε_- and ε_+ were obtained at negative and positive coercive field, respectively.

The trapped charges can screen the depolarization fields [11], so ΔP and ε should decrease during irradiation.

In addition, in our FE capacitors, the top electrode is made of Au and the top interface of the capacitor is Au/FE; the bottom electrode is made of YBCO and the bottom interface of the capacitor is the FE/YBCO. YBCO is an oxygen deficient perovskite structure; its lattice constants are 0.382 and 0.389 nm along the a-axis and the b-axis, respectively; the average lattice constant in the (a, b)-plane is 0.385 nm. In the (a, b)-plane, the lattice constants of the Au, PTO and PZT crystal layers are 0.408, 0.390 and 0.404 nm, respectively. The lattice mismatches of the top and bottom interface of the PTO capacitor are 4.6% and 1.3% respectively while those of the PZT are 1% and 4.7% respectively. Therefore, the lattice mismatch at the top interface of the PTO capacitor is almost the same as that of the bottom interface of the PZT capacitor; and the lattice mismatch at the bottom interface of the PTO capacitor is similar to that of the top interface of the PZT capacitor. The total effects of the lattice mismatch of the PTO capacitor are the same as those of the PZT capacitor. This why the degradation of ΔP and the ε of the PTO capacitor are similar to those of the PZT capacitor after high dose irradiation.

Figure 3 shows that, as the FE capacitors were stressed with a bias of 0 V during irradiation, with the increment of irradiation dose, for the PTO capacitor, the negative

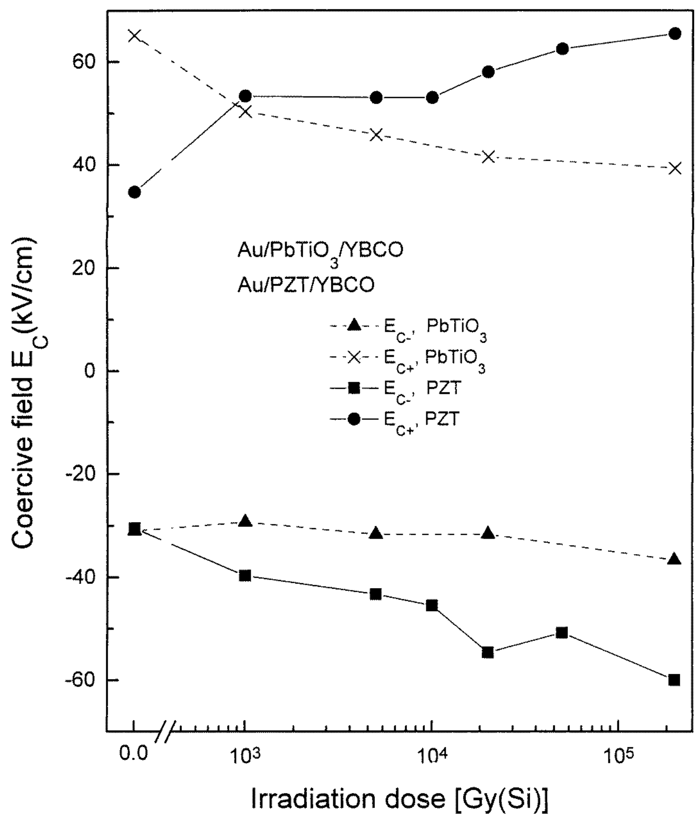

Figure 3. The coercive field of the PTO and PZT capacitors versus the irradiation dose. E_{c-} and E_{c+} were negative and positive coercive field, respectively.

coercive field E_{c-} and positive coercive field E_{c+} drifted towards the negative voltage direction; for the PZT capacitor, the absolute value of the E_{c-} and E_{c+} increased obviously. How to explain the appearance of the PTO capacitor is unknown. But the result of the PZT capacitor could be interpreted with radiation theory of FE materials [6, 10, 12].

According to the radiation theory, during irradiation the change of the coercive field E_c is due to the accumulation of the trapped positive charges in the PZT ferroelectric layer, especially at the Au/PZT and PZT/YBCO interfaces. As an external bias which is applied on the Au top electrode reverses the direction of spontaneous polarization, it would not only overcome the effect of internal polarized field, but also overcome the effect of the trapped charges at the interfaces. Therefore, higher external bias was needed to apply across the FE capacitor to reverse the polarization than pre-irradiation. This results in the increment of coercive field. With the increment of irradiation dose, the number of trapped charges increased, and the coercive field increased.

4. Conclusion

In summary, for the PTO and PZT ferroelectric capacitors, our analysis shows that, with the increment of the total dose, the dielectric constant ε and the retained polarization ΔP

decreased obviously. The absolute value of the E_{c-} and E_{c+} of the PZT capacitor increased while the E_{c-} and E_{c+} of the PTO capacitor drifted towards the negative direction. Most of the facts could be explained with a defect theory: there are many defects in the FE layer and at the Au/FE interface and the FE/YBCO interface, and these defects can capture the radiation-induced positive charges during irradiation and result in degradation of the ferroelectric characteristics of the FE capacitor.

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