

## Interface diffusion and chemical reaction of PZT layer/Si(111) sample during the annealing treatment in air

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The interface diffusion and chemical reaction between a PZT ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ) layer and a Si(111) substrate during the annealing treatment in air have been studied by using XPS (X-Ray Photoelectron Spectroscopy) and AES (Auger Electron Spectroscopy). The results indicate that the Ti element in the PZT precursor reacted with residual carbon and silicon, diffused from the Si substrate, to form  $\text{TiC}_x$ ,  $\text{TiSi}_x$  species in the PZT layer during the thermal treatment. A great interface diffusion and chemical reaction took place on the interface of PZT/Si also. The silicon atoms diffused from silicon substrate onto the surface of PZT layer. The oxygen atoms, which came from air, diffused into silicon substrate also and reacted with Si atoms to form a  $\text{SiO}_2$  interlayer between the PZT layer and the Si(111) substrate. The thickness of  $\text{SiO}_2$  interlayer was proportional to the square root of treatment time. The formation of the  $\text{SiO}_2$  interlayer was governed by the diffusion of oxygen in the PZT layer at low annealing temperature, and governed by the diffusion of oxygen in  $\text{SiO}_2$  interlayer at high annealing temperature. The apparent activation energy of the interface oxidation reaction was about 39.1 kJ/mol.

**Keywords** PZT, silicon, interface diffusion, interface reaction, AES, XPS

### Introduction

In recent years, tremendous attention has been paid to the use of PZT ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ) films for non-volatile memory applications, gate insulators, storage capacitors in high-density dynamic random access memories

(DRAMS) and for surface acoustic wave devices, pyroelectric type sensors and supersonic wave probes.<sup>1-4</sup> The ferroelectric properties of PZT film not only depend on the perovskite structure but also depend on the interface states between PZT layer and substrate.<sup>5,6</sup> The electric performances and perovskite structure of PZT film can be decreased greatly by the interface diffusion and chemical reaction.<sup>7</sup> A buffer layer inserted between the PZT layer and the Si substrate can improve the dielectric and ferroelectric properties dramatically.<sup>8,9</sup> These phenomena were concerned in interface diffusion and chemical reaction between the PZT layer and the silicon substrate. Because the annealing temperature must be higher than 450°C from PZT precursor to form perovskite phase<sup>10</sup> and it is difficult to analyze the buried interface, it is not very clear about the interface reaction and interface states between the PZT layer and the Si substrate during the thermal treatment. Thus, this work attempts to elucidate the mechanism of the interface diffusion and chemical reaction of PZT/Si(111) film sample during the thermal treatment in air.

The interface diffusion and chemical reaction between a PZT layer and a silicon substrate have been studied. The results indicated that Si atoms, diffused from the substrate, not only reacted with oxygen, came from air, to form a  $\text{SiO}_2$  interlayer, but also diffused onto the surface of PZT layer. The element Ti reacted with

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residual organic carbon and silicon atoms diffused from the substrate to form  $\text{TiSi}_x$  species and  $\text{TiC}_x$  species in the PZT layer, respectively. The Pb, Zr and Ti elements also diffused into the  $\text{SiO}_2$  interlayer during thermal treatment. The formation of the  $\text{SiO}_2$  interlayer was governed by the diffusion step of oxygen from air and silicon from the substrate. The activation energy of the interface oxidation was about 39.1 kJ/mol.

## Experimental

First,  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  was added into  $\text{CH}_3\text{-OC}_2\text{H}_4\text{OH}$  to make a solution. The solution was refluxed at 120°C for 10 h, then it was mixed with the solution of  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  and  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  at 80°C for 1 h. After hydrolyzed in part, the precursor of PZT was formed.<sup>11</sup>

P-type Si(111) wafers with 2.4  $\Omega$  cm resistance were cleaned by HF solution and used as substrates. A  $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  (PZT) precursor film was deposited on the substrate using a sol-gel method.<sup>11</sup> The film was coated by using spin-coating method conducted at 500 rpm for 8 s followed by 4000 rpm for 15 s. The thickness of the PZT layer was about 80 nm. After the film was dried, it was calcined in an air furnace. First, the temperature was raised to 400°C at 2°C/min and maintained at 400°C for 30 min to promote the decomposition of organic compounds. Then, the temperature was raised to pre-set temperatures at 2°C/min and maintained in a definite hours to form perovskite phase. At last, the film was cooled naturally.

The XPS spectra were measured in a PHI 5300 ESCA system. During XPS analysis, a Mg  $K_\alpha$  X-ray beam was used, and the power was set at 250 W. A hemispherical analyzer with a position sensitive detector at a pass energy of 37.75 eV was used. The base vacuum of chamber was maintained at  $2.6 \times 10^{-7}$  Pa during XPS analysis. For depth profile analysis, the energy and the current of Ar ion beam were set at 3.0 keV and 20  $\mu\text{A}$ , respectively. The beam was focused to a spot of  $8 \times 8$  mm, and the sputtering rate was about 2.0 nm/min for a thermal oxidized  $\text{SiO}_2$  thin film.

The AES spectra were measured in a PHI 610 SAM system. A coaxial electron gun with a single pass cylindrical mirror analyzer (CMA) was used. The energy resolution of the CMA was set at 0.3% to obtain a good energy resolution. For AES analysis, the electron beam energy and the beam current were 3.0 keV and 0.5  $\mu\text{A}$ ,

respectively. The electron beam was incident at an angle of 60° with respect to the specimen surface. In order to obtain the line shape of AES, the AES spectra were taken in an integrate mode. The linear background subtraction was adopted to get high signal/background ratios. The kinetic energy of AES peak was used to identify the chemical states of element. During the depth profile analysis, the energy and beam current of Ar ion beam were 3.0 keV and 6  $\mu\text{A}$ , respectively. The beam was focused to a spot of  $1 \times 1$  mm, and the sputtering rate was about 40.0 nm/min for a thermal oxidized  $\text{SiO}_2$  thin film.

## Results and discussion

### Interface reaction of PZT layer with silicon substrate

The depth profile spectrum of PZT/Si(111) precursor film is shown in Fig. 1, which showed that the distributions of Pb, Zr and Ti in PZT precursor layer were homogenous with depth. The thickness of PZT precursor layer was about 80 nm, and the width of the interface between the PZT precursor layer and the Si substrate was very narrow (about 10 nm), implying that the interface diffusion and reaction in the PZT precursor layer/Si sample were very slight during the deposition of precursor layer. In addition, the qualitative analysis of AES indicated that there were a few residual organic carbon species in the precursor layer. The XPS studies indicated that the elements of Pb, Zr and Ti existed as  $\text{Pb}(\text{OH})_2$ ,  $\text{Zr}(\text{OH})_4$  and  $\text{Ti}(\text{OH})_4$  in the precursor layer.

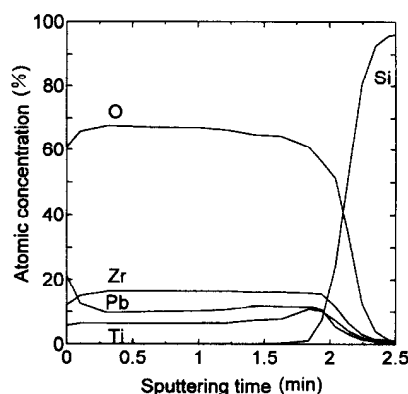


Fig. 1 AES depth profile of PZT/Si precursor sample.

The depth profile spectrum of the PZT film/Si(111) sample treated at 800°C for 1 h is shown in Fig. 2. The sample consists of a PZT layer, a silicon oxide layer and a Si substrate. From quantitative analysis of the AES depth profile, it can be reasoned that the silicon oxide layer consisted of SiO<sub>2</sub> species. A great interface diffusion and chemical reaction took place between PZT layer and Si substrate after annealed at 800°C for 1 h in air. The silicon atoms diffused from silicon substrate into the surface of sample. Oxygen diffused from air into silicon substrate and reacted with silicon to form SiO<sub>2</sub> species.<sup>12</sup> The interface diffusion and oxidation resulted in the formation of a SiO<sub>2</sub> interlayer between the PZT layer and Si substrate. The interface diffusion and reaction resulted in the heterogeneous distributions of Pb, Ti and Zr elements in the PZT layer also.

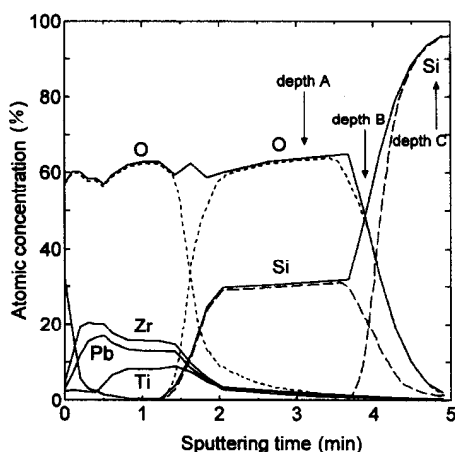


Fig. 2 AES depth profile of PZT/Si film sample treated at 800°C for 1 h in air.

The Auger line shapes of Si LVV (LMM) at various depths of PZT layer/Si sample annealed at 800°C 1 h are shown in Fig. 3. The kinetic energy of Si LVV on the surface was 72.5 eV, which can be attributed to SiO<sub>2</sub> species.<sup>13</sup> The Si LVV spectra in the PZT layer and SiO<sub>2</sub> layer consisted of two peaks. The kinetic energies were 72.5 and 88.5 eV, which can be attributed to SiO<sub>2</sub> and pure silicon species, respectively.<sup>13</sup> This result indicated that silicon atoms, which diffused from substrate, were oxidized into SiO<sub>2</sub> species on the interface. But, silicon was not oxidized completely as SiO<sub>2</sub>, and partial silicon still existed as free silicon in the interlayer.

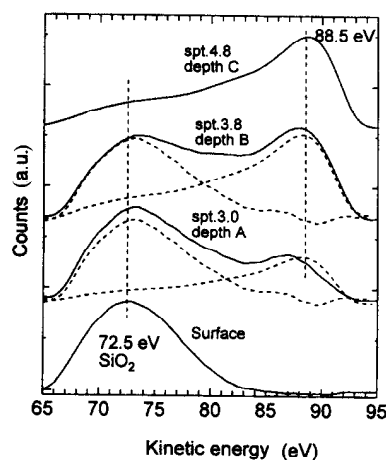
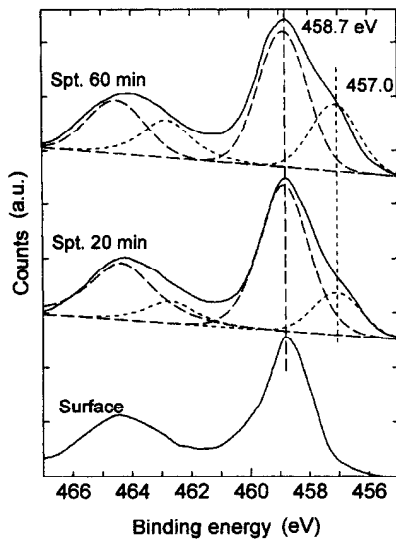


Fig. 3 Si LVV spectra in various depth of PZT/Si film sample treated at 800°C for 1 h in air.

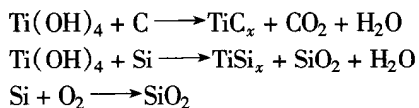
The chemical states of elements in the PZT layer were studied by using XPS. The Ti 2*p* spectra in various depths of the PZT layer are shown in Fig. 4. The binding energy of Ti 2*p*<sub>3/2</sub> on the surface of the PZT layer is 458.7 eV and can be attributed to PZT species. With the increase of depth, a shoulder peak appeared at the low binding energy side and increased with increase of sputtering time. After curve fitting, the binding energy of this shoulder peak was 457.0 eV, and can be attributed to TiC<sub>x</sub> or TiSi<sub>x</sub> species.<sup>14</sup> This shoulder peak did not appear in PZT/Pt film sample after sputtered by Ar ion beam, indicating that this shoulder peak did not produce by sputtering reduction of Ar ion. It resulted from the existence of TiC<sub>x</sub> and TiSi<sub>x</sub> species in the PZT layer.

Based on the C 1*s* and Si 2*p* spectra in different depth of PZT/Si sample obtained in this Laboratory, the C 1*s* spectrum consisted of two peaks at 285.0 and 280.8 eV on the surface of PZT layer, which can be attributed to residual carbon and metal carbide.<sup>14</sup> The peak at lower binding energy of 280.8 eV increased with increase of sputtering time, indicating that metal carbide formed in the PZT layer. In addition, the Si 2*p* spectra in the PZT layer also consisted of two peaks with binding energies of 103.2 eV and 98.8 eV, respectively. These two peaks can be attributed to SiO<sub>2</sub> and TiSi<sub>x</sub> species.<sup>14</sup> The latter was very weak (about 2%), indicating that most silicon atoms existed as SiO<sub>2</sub> species and only a few silicon atoms formed TiSi<sub>x</sub> species during annealing in air.



**Fig. 4** Ti 2p spectra in various depth of PZT/Si film sample treated at 800°C for 1 h in air.

The above results suggested that the interface diffusion and chemical reaction of PZT/Si (111) precursor sample took place during the thermal treatment. A few silicon atoms diffused from substrate into PZT layer to form SiO<sub>2</sub> and TiSi<sub>x</sub> species. The oxidation of Si on the interface resulted in the formation of a SiO<sub>2</sub> interlayer, which has a low dielectric constant. The formations of TiC<sub>x</sub> and TiSi<sub>x</sub> species were formed at a sparsely oxygen environment in the PZT layer. This sparsely oxygen environment was caused by the oxidation of silicon, which exhausted most oxygen. The formation and existence of TiC<sub>x</sub> and TiSi<sub>x</sub> in the PZT layer can influence the ferroelectric properties and the crystallization of PZT perovskite phase. XRD indicated that there is nearly no any characteristic diffraction peaks of PZT phase in the PZT/Si(111) sample after being treated in 800°C for 1 h, but the perovskite structure was formed for PZT/Pt/Si sample. The dielectric constant of PZT film/Si(111) sample is 13, which was much lower than that in PZT/Pt/Si sample (620) due to the formation of a SiO<sub>2</sub> layer (10) on interface. These solid reactions in the PZT/Si(111) precursor film during thermal treatment can be described as follows:



#### *Effects of annealing temperature on interface oxidation*

The interface diffusion and reaction were mainly governed by thermal treatment temperature. Here, the PZT layer/Si(111) samples treated at 500°C, 550°C, 600°C, 650°C, 700°C and 800°C for 1 h in air were studied by using AES depth profile and Auger line shape analysis. The AES depth profile spectra showed that all PZT/Si samples consisted of three layers although the treatment temperature was greatly different. The AES depth profile spectrum of PZT/Si film sample treated at 500°C for 1 h is shown in Fig. 5. The concentration of oxygen decreased with depth in the PZT layer and increased in the SiO<sub>2</sub> interlayer, implying that the diffusion process of oxygen in the PZT layer was a slow step and the diffusion of oxygen in SiO<sub>2</sub> was a fast step. Thus the concentration of oxygen in the SiO<sub>2</sub> layer was proportional to the concentration of silicon. Fig. 5 showed that the diffusion of silicon from the substrate into the PZT layer was at a decrease distribution, implying that the diffusion of silicon was a slow process also. Otherwise, a very thin interlayer could be seen between the SiO<sub>2</sub> layer and Si substrate. The line shape spectra of Si LVV on the interlayer are shown in Fig. 6. It showed that the peak energies of Si LVV on the interface of SiO<sub>2</sub> and Si substrate were 72.5, 81.2 and 88.5 eV, respectively, which were corresponded to SiO<sub>2</sub>, SiO and Si species, respectively. The SiO species was formed by the oxidation of Si in a sparsely oxygen environment. When the treatment temperature reached 600°C, oxygen in the PZT and SiO<sub>2</sub> layer distributed more homogeneously and so did silicon in the SiO<sub>2</sub> layer. The SiO interface layer between SiO<sub>2</sub> layer and Si substrate disappeared, implying that the diffusion of oxygen in the PZT and SiO<sub>2</sub> layer was fast enough to provide oxygen in SiO<sub>2</sub>/Si interface to form SiO<sub>2</sub> species. With the increase of annealing temperature, the loss of lattice oxygen in the PZT layer took place. The concentration of oxygen in the PZT layer decreased from 65% to 50% when the treatment temperature increased from 500°C to 800°C, meaning that PZT layer lost the lattice oxygen at high treatment temperature. The loss of lattice oxygen can influence the formation of the perovskite phase in the PZT layer also. At low treatment temperature, a sparsely oxygen environment can be formed in SiO<sub>2</sub>/Si interface due to low diffusion speed of oxygen in the PZT layer. At high treatment temperature, the diffusion of oxygen was fast e-

nough to provide oxygen.

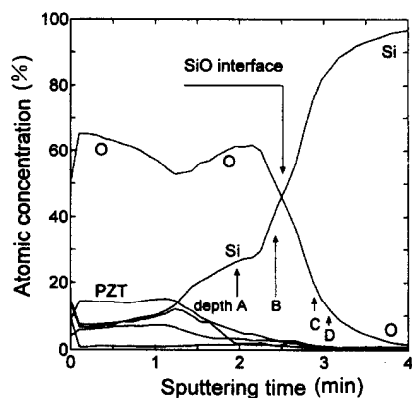


Fig. 5 AES depth profile of PZT/Si film sample treated at 500°C for 1 h in air.

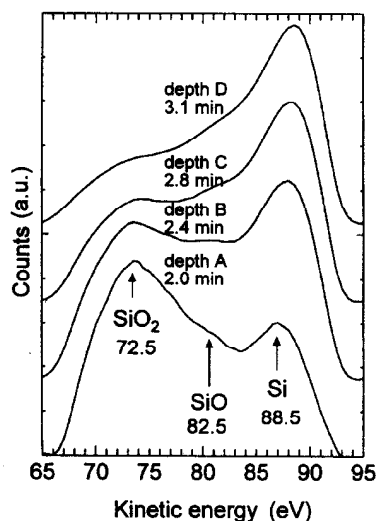


Fig. 6 Si LVV spectra in various depth of PZT/Si film sample treated at 500°C for 1 h in air.

in the PZT layer was mainly governed by treatment temperature, but not by treatment time. When treatment time was over 2 h, a transition layer that can be considered as a SiO compound according to quantitative measurement appeared between the SiO<sub>2</sub> layer and the Si substrate. The line shape of Si LVV also indicated that the composition of the transition layer was SiO species. With the increase of annealing time, the defect in the PZT layer decreased, and the thickness of SiO<sub>2</sub> interlayer increased. The diffusion resistance of oxygen in the PZT and SiO<sub>2</sub> interlayer increased with annealing time, which made the diffusion of oxygen across the PZT and SiO<sub>2</sub> layer much slower. Thus, it can not provide enough oxygen onto the interface and form a sparsely oxygen environment on the interface between the SiO<sub>2</sub> layer and the Si(111) substrate. This environment resulted in the formation of SiO species on the interface.

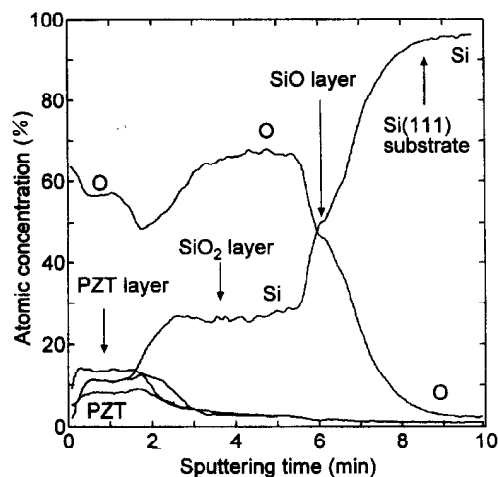


Fig. 7 AES depth profile of PZT/Si film sample treated at 800°C for 7 h in air.

#### Effects of treatment time on the interface oxidation

The PZT/Si(111) samples were treated in air at 800°C from 0.5 to 7 h. The AES depth profile spectrum of PZT/Si sample treated at 800°C for 7 h is shown in Fig. 7, which indicated that the diffusions of Si and PZT were intensified, and the thickness of SiO<sub>2</sub> interlayer increased also. The concentration of oxygen in the PZT layer was independent of annealing time and maintained at 55%, implying that the loss of lattice oxygen

#### Kinetics of interface oxidation

The kinetics of interface oxidation in PZT/Si sample has been studied here. The relationship of the thickness of SiO<sub>2</sub> interlayer with reaction time is shown in Fig. 8a. The thickness of SiO<sub>2</sub> interlayer was proportional to the square root of reaction time. This relationship can be described as  $d = 0.79 \times t^{1/2} - 0.5$  by fitting the experimental data.<sup>15,16</sup> Here,  $d$  was the thickness of SiO<sub>2</sub> interlayer and  $t$  was the thermal treatment time.

Based on references,<sup>15,16</sup> when the thickness-time relationship is in parabola, the formation of interlayer was controlled by the diffusion rate. Otherwise, the formation of interlayer was controlled by the chemical reaction when the thickness-time relationship was in linear. Thus, it can be concluded from the equation that the formation of SiO<sub>2</sub> interlayer was governed by the diffusion of oxygen in the SiO<sub>2</sub> layer at 800°C in air. The effect of treatment temperature on the thickness of SiO<sub>2</sub> layer is shown in Fig. 8b. Considering the theory of thermodynamics, the formation rate of SiO<sub>2</sub> interlayer was a function of temperature. The logarithm of apparent reaction

rate constant  $\ln K$ , which was equal to  $\ln d^2$ , was proportional to the reciprocal of reaction temperature.<sup>15,16</sup> From the slope of this line, the apparent activation energy of this interface oxidation can be calculated using Arrhenius equation, and the result was 39.1 kJ/mol, which is less than the activation energy of the diffusion for O<sub>2</sub> in SiO<sub>2</sub> (115.8 kJ/mol).<sup>17</sup> Because the SiO<sub>2</sub> interlayer was very thin and many defects existed in SiO<sub>2</sub> interlayer, which made the diffusion of oxygen much easy. Otherwise, the bulk crystal of SiO<sub>2</sub> has a good structure, thus it is very difficult for oxygen to diffuse across it.

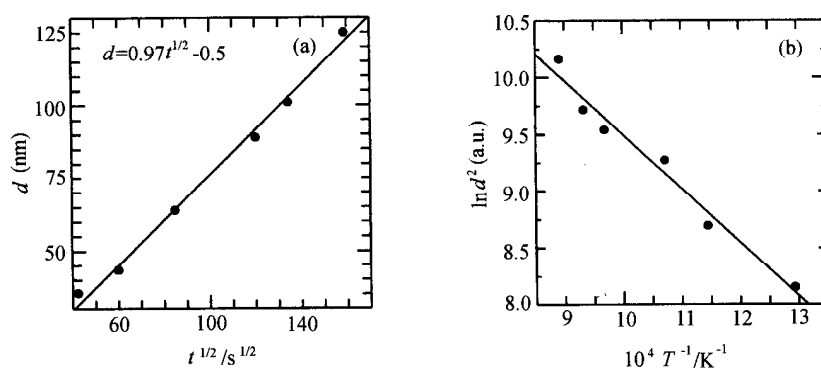


Fig. 8 Influence of annealing time and temperature on the thickness of SiO<sub>2</sub> interlayer.

## Conclusion

1. The interface diffusion and chemical reaction took place during the thermal treatment. Oxygen diffused into silicon substrate and silicon also diffused onto the surface of sample. Oxygen reacted with silicon on the interface to form a SiO<sub>2</sub> interlayer also. The Ti element reacted with residual organic carbon and silicon diffused from substrate to form TiC<sub>x</sub> and TiSi<sub>x</sub> species in PZT layer.

2. The formation of SiO<sub>2</sub> interlayer was mainly governed by the diffusion process of oxygen in the PZT layer and the diffusion of silicon in the SiO<sub>2</sub> layer at low treatment temperature, while it was mainly governed by the diffusion of oxygen in the SiO<sub>2</sub> interlayer at high treatment temperature. The appearance activation energy of interface oxidation was 39.1 kJ/mol.

3. The concentration of oxygen in PZT layer decreased from 65% to 50% with the temperature increasing from 500 to 800°C, in contrast, the concentration of oxygen in the PZT layer was independent of the annealing time.

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