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# Self-patterning Technique of Photosensitive $La_{0.5}Sr_{0.5}CoO_3$ Electrode on Ferroelectric $Sr_{0.9}Bi_{2.1}Ta_2O_9$ Thin Films

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**ABSTRACT**

$La_{0.5}Sr_{0.5}CoO_3$ (LSCO) electrodes were prepared on ferroelectric $Sr_{0.9}Bi_{2.1}Ta_2O_9$ (SBT) thin films by spin coating method using photosensitive sol-gel solution. Self-patterning technique of photosensitive sol-gel solution has advantages such as simple manufacturing process compared to photoresist/dry etching process. Lanthanum(III) 2-methoxyethoxide, Strontium diethoxide, Cobalt(II)2-methoxyethoxide were used as starting materials for LSCO electrode. UV irradiation on LSCO thin films lead to decrease solubility by M-O-M bond formation and the solubility difference allows us to obtain self-patterning. There was little composition change of the LSCO thin films between before leaching and after leaching in 2-methoxyethanol. The lowest resistivity of LSCO thin films deposited on $SiO_2$/Si substrate was $1.1\times10^{-2}$ Ωcm when the thin film was annealed at 740°C. The values of Pr/Ps and 2Pr of LSCO/SBT/Pt capacitor on the applied voltage of 5 V were 0.51, 8.89 μC/cm², respectively.

***Key words : Self-patterning, Photosensitve, SBT, LSCO, Sol-gel solution***

## 1. Introduction

Micro patterning of thin films is one of the main issues in the manufacturing of ferroelectric micro devices. The most widely applied techniques for fine patterning of the ferroelectric films are ion milling/reactive ion etching. However, such processes tend to degrade the capacitor performance. Metal alkoxides chelated with β-diketonate ligands show absorption bands in the UV region. N. Tohge et al. reported that the UV irradiation on the gel films dissociates the chelate rings and simultaneously decreases the solubility of these gel films by M-O-M bond formation in organic solvent such as alcohol and the solubility difference allows us to obtain a fine pattern successfully.[1)]

In general, precious metals such as Pt and Au have been used as electrode materials for ferroelectric devices. However, in such devices, some ferroelectric thin films undergo mechanical stress causing device failure.[2)] Conductive perovskite oxides such as $SrRuO_3$, $La_{0.5}Sr_{0.5}CoO_3$, $LaNiO_3$, and $La_{0.7}Sr_{0.3}MnO_3$ have attracted much attention for their excellent potential as an electrode for ferroelectric thin films because of improving the fatigue of ferroelectric thin film memory.[3)] Among these oxides, the $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) has been extensively studied due to its desirable metallic properties and the (pseudo-) cubic perovskite structure. It have been known that LSCO exhibit the improvement of reliability characteristics such as fatigue which has been a critical issue in ferroelectric memory technology.[4-7)]

Ferroelectric Random Access Memory (FRAM) has considerable potential as a new memory because of its properties for ideal memory such as random access, high-density integration, fast read and write operation, long endurance, excellent retention and non-volatility with unlimited practical usage.[8,9)] Especially, $Sr_{0.9}Bi_{2.1}Ta_2O_9$ (SBT), a kind of ferroelectric material, is suitable material for high integration because of its excellent fatigue resistance, low leakage current and insensitivity to film thickness.[10)]

In this study, self-patterning technique of LSCO oxide as a top electrode on ferroelectric SBT thin films was attempted by using sol-gel method.

## 2. Experimental Method

For photosensitive LSCO solution, Lanthanum (III)2-methoxyethoxide[$La(OCH_2CH_2OCH_3)_3$], Strontium diethoxide[$Sr(OC_2H_5)_2$], Cobalt(II)2-methoxyethoxide[$Co(OCH_2CH_2OCH_3)_2$] were used as starting materials and were chelated by Ethylacetoacetate (EAcAc), a kind of β-diketonate ligands. 2-methoxyethanol was used as a solvent. After chelating each metal alkoxide, they were combined and stirred. $HNO_3$ was added as catalyst for fast hydrolysis. For ferroelectric SBT solution, $Sr(OC_2H_5)_2$, $Ta(OC_2H_5)_5$, and $Bi(TMHD)_3$ were chosen as starting materials. $Sr(OC_2H_5)_2$,

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$Ta(OC_2H_5)_5$ were also chelated by Ethylacetoacetate (EAcAc). $Pt/TiO_2/SiO_2/Si$ with 2000 Å of Pt and 400 Å of $TiO_2$ was used as a substrate. The substrates coated by 0.1 M SBT solution for 30 sec at 2500 rpm on $Pt/TiO_2/SiO_2/Si$ were baked at about 400°C for 5 min and annealed at 780°C in oxygen ambient for 1 h. These films were also coated by 0.1 M photosensitive LSCO solution and irradiated by UV light (220 - 320 nm) with mercury lamp (Oriel Model 68811, 400 W). After being leached by 2-methoxyethanol for 10 seconds, the thin films were baked at 400°C for 5 min. To observe the P-E properties according to the annealing temperature change of LSCO as a top electrode, the thin films were post annealed at 660, 700, 740, 780°C for 1 h, respectively. Fig.1 shows schematic diagram for synthesis of photosensitive LSCO solution and total procedure.

In order to observe composition change of LSCO thin films between before leaching and after leaching, EPMA (JEOL, JXA-8900A) was used. The baking temperature of LSCO thin films was measured from TG-DSC (Setaram TGA 92 16-18). The crystalline phases annealed at various temperatures were identified by an X-ray diffractometer (MAC Science. Co., Ltd., M03XHF[22]). Both micro-structure and patterning figure were observed by SEM photographs (JEOL, JSM-6700F). The resistivity was investigated by four point probe method (Changnam Tech, CMT-SR1000) The electrical properties such as polarization-electrical field (P-E) characteristics were performed by RT66A (Radient Technologies, Inc.)

## 3. Results and Discussion

To understand the composition change between before leaching and after leaching, EPMA results of LSCO thin films baked at 400°C are shown in Table 1. Photosensitive

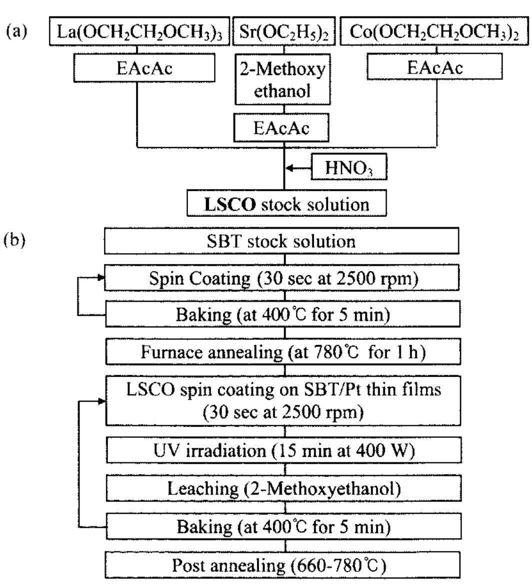


**Fig. 1.** (a) Schematic diagram for synthesis of photosensitive LSCO solution and (b) the total procedure of self-patterned $LSCO/SBT/Pt/TiO_2$ thin films.

**Table 1.** EPMA Results of LSCO Thin Films Baked at 400°C

| Element | Cation ratio (before leaching) | Cation ratio (after leaching) |
|---|---|---|
| | Compositions (rel. to $O_3$) | |
| La | 0.52 | 0.50 |
| Sr | 0.56 | 0.55 |
| Co | 1.02 | 0.99 |

LSCO stock solution with La/Sr/Co = 0.5/0.5/1 molarity was used. These data are average values after measuring La,Sr and Co composition three times, respectively. At this survey, the error range of EPMA measurement was ±0.1 molarity. There was little difference in La/Sr/Co molarity between before leaching and after leaching as shown in Table 1. These results show that leaching process don't affect the composition of self patterned LSCO thin film and also suggest that LSCO thin film with accurate chemical composition can be patterned.

In order to decide baking temperature for decomposing organic material from LSCO gel powder, TG-DSC curves were analyzied. From Fig. 2, LSCO gel powder exhibited

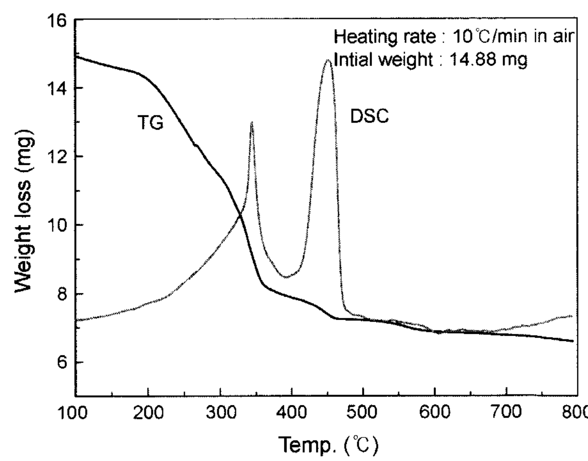


**Fig. 2.** TG-DSC curves of LSCO gel powder.

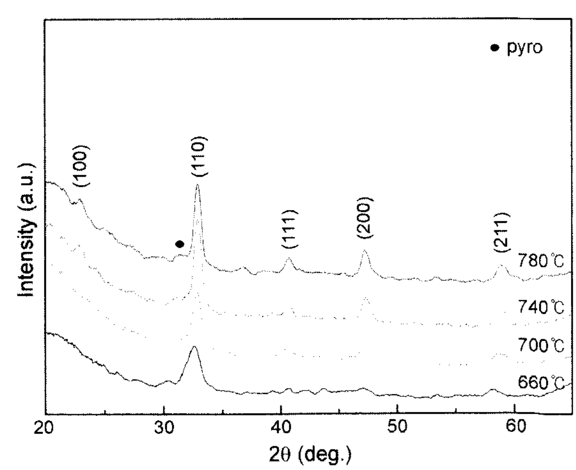


**Fig. 3.** XRD patterns of LSCO thin films annealed at 660, 700, 740, and 780°C for 1 h.

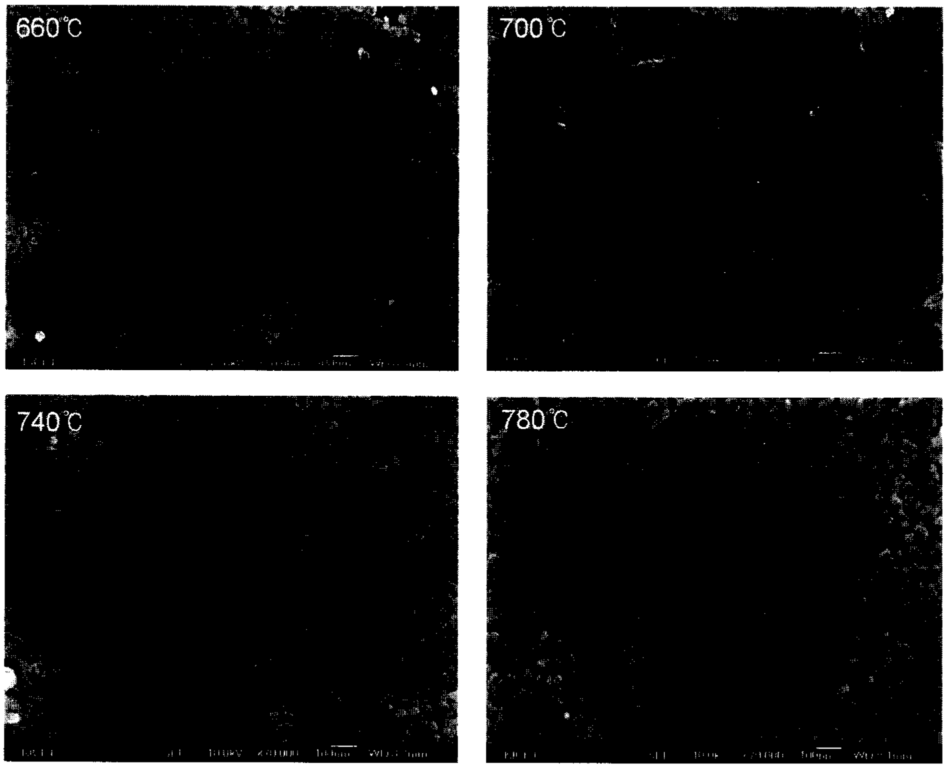


**Fig. 4.** SEM micrographs of LSCO thin films annealed at 660, 700, 740, and 780°C for 1 h.

exothermic peaks around 350 and 450°C, respectively. These peaks mean decomposition and phase transformation. Therefore LSCO thin films were baked at 400°C and post annealed at 660~780°C for crystallization with perovskite structure.

X-ray diffraction patterns of the LSCO thin films were showed in Fig. 3. As furnace annealing temperature was increased to 740°C, the intensity of (110) peak increased. It means that the perovskite phase was dominant and the crystallinity of LSCO thin films increased. However, the intensity of (110) peak decreased as furnace annealing temperature was increased from 740°C to 780°C.

SEM micrographs of LSCO films annealed at various temperatures were showed in Fig. 4. In case of LSCO thin films annealed at 660°C, 50–60 nm size grains existed in matrix. As the temperature increased, grains started to grow. There were 80–100 nm size grains such as rod with increasing temperature to 780°C. However, pore was also increased. Consequently, resistivity increased and P-E property decreased at 780°C.

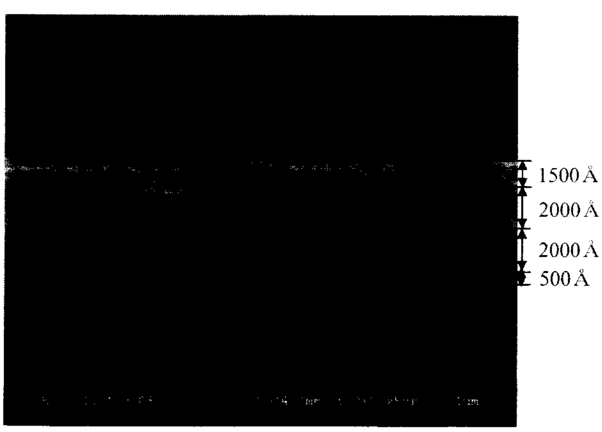


**Fig. 5.** The cross-section of $LSCO/SBT/Pt/TiO_2/SiO_2/Si$ thin films.

Fig. 5 shows the cross-section of LSCO thin films on $SBT/Pt/TiO_2/SiO_2/Si$ substrate. The thicknesses of both SBT and LSCO thin films were approximately 2000 Å and 1500 Å, respectively. These thin films were multi-coated by sol-gel method. AFM images and roughness of LSCO thin films were shown in Fig. 6 and Table 2, respectively. Roughness increased as annealing temperature was increased.

The SEM micrographs of self-patterned LSCO thin films on $SBT/Pt/TiO_2/SiO_2/Si$ substrate were showed in Fig. 7. These LSCO thin films were leached in 2-methoxyethanol for 10 sec after being illuminated by UV through photomask without photoresist. The finest pattern in this figure was approximately 3 μm. It is expected that finer pattern can be obtained if collimated UV light is used.

The resistivity was measured by four-point probe method.

**Table 2.** Roughness of LSCO Thin Films Annealed at Various Temperatures for 1 h.

| | Furnace annealing temperature (°C) | | | |
|---|---|---|---|---|
| | 660 | 700 | 740 | 780 |
| RMS roughness (Å) | 77.8 | 84.3 | 92.5 | 107 |
| Average roughness (Å) | 54.5 | 61.4 | 75.6 | 85.2 |

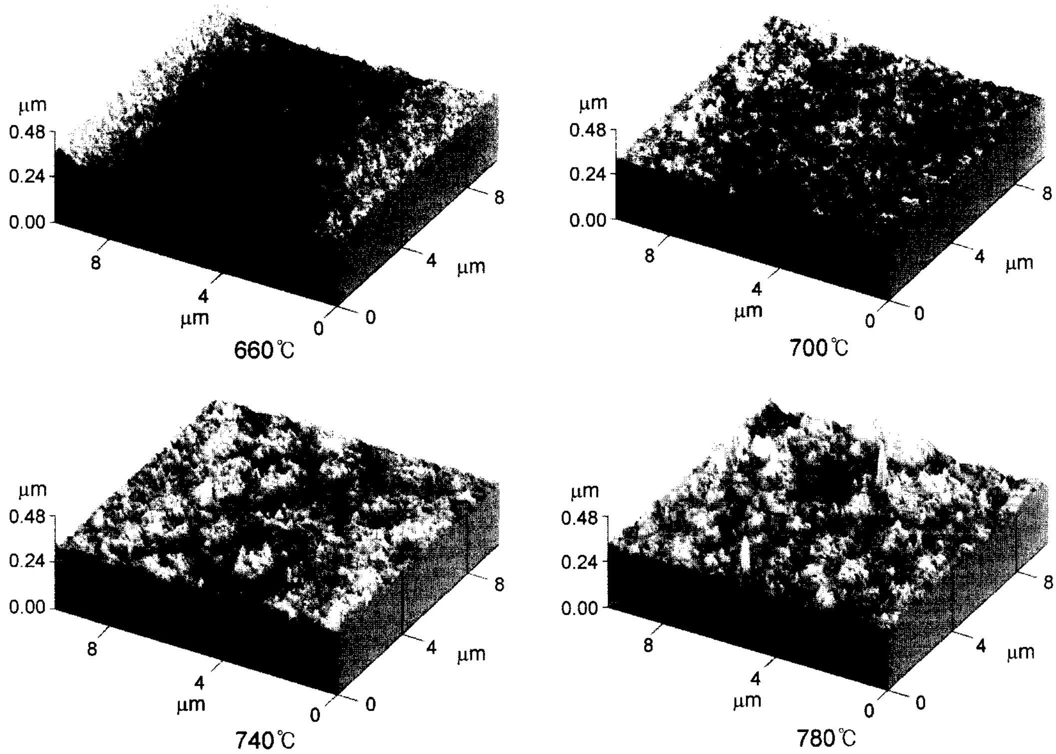


**Fig. 6.** AFM images of LSCO thin films annealed at 660, 700, 740, and 780°C for 1 h.

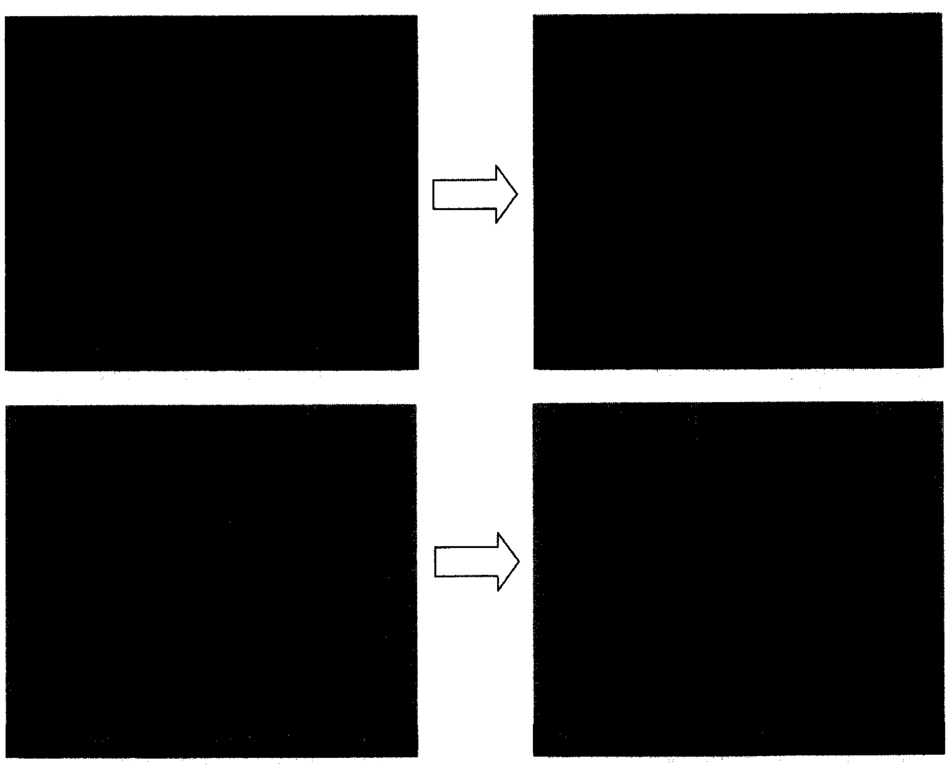

**Fig. 7.** SEM micrographs of self patterned LSCO thin films on $SBT/Pt/TiO_2/SiO_2/Si$ substrates.

Fig. 8 shows a plot of resistivity as a function of furnace annealing temperature for LSCO thin films deposited on $SiO_2/Si$ substrate. The resistivity decreased as the annealing temperature increased from 680°C to 740°C. The lowest resistivity was $1.1\times10^{-2}$ Ωcm when LSCO thin films was annealed at 740°C. However, resistivity increased as annealing temperature increased to 780°C. Because pores and roughness increased at 780°C as shown in Figs. 4 and 6.

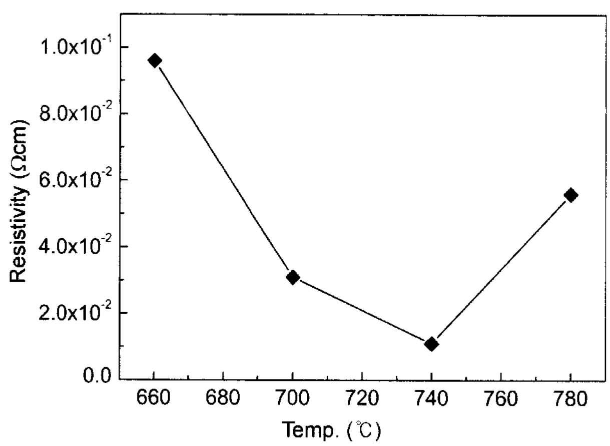


**Fig. 8.** Resistivities of LSCO thin films as a function of furnace annealing temperature.

Hysteresis loops of LSCO/SBT/Pt thin films annealed at various temperatures were shown in Fig. 9. The values of Pr/Ps and 2Pr of LSCO/SBT /Pt capacitor on the applied voltage of 5 V were 0.51, 8.89 $\mu C/cm^2$, respectively. These capacitors had less 2Pr values and squareness than Pt/SBT/Pt capacitors. Because, in general, Pt electrode had higher electrical property than LSCO oxide electrode and leakage current of LSCO electrode increased . In case of Pt/SBT/Pt capacitors, 2Pr values increased as annealing temperature increased from 660°C to 780°C.[11] However, LSCO/SBT/Pt capacitor had the highest 2Pr value when it was annealed at 740°C. Because LSCO electrode had the lowest resistivity at 740°C and had higher resistivity at 780°C. Although LSCO/SBT/Pt capacitor had low 2Pr value, it shows the possibility of self-patterning technique of LSCO electrode as a top electrode.

## 4. Conclusion

Ferroelectric SBT and photosensitive LSCO electrodes were prepared by spin coating method using sol-sel solution. A minimum 3 μm size LSCO patterns were successfully formed by self-patterning technique. The lowest resistivity of LSCO thin films deposited on $SiO_2$/Si substrate was $1.1 \times 10^{-2}$ cm when thin film was annealed at 740°C. The values of Pr/Ps and 2Pr of LSCO/SBT/Pt capacitor on the applied voltage of 5 V were 0.51, 8.89 $\mu C/cm^2$, respectively. These results suggest that self-patterning technique of the LSCO thin films as a top electrode on ferroelectric SBT materials could be used.


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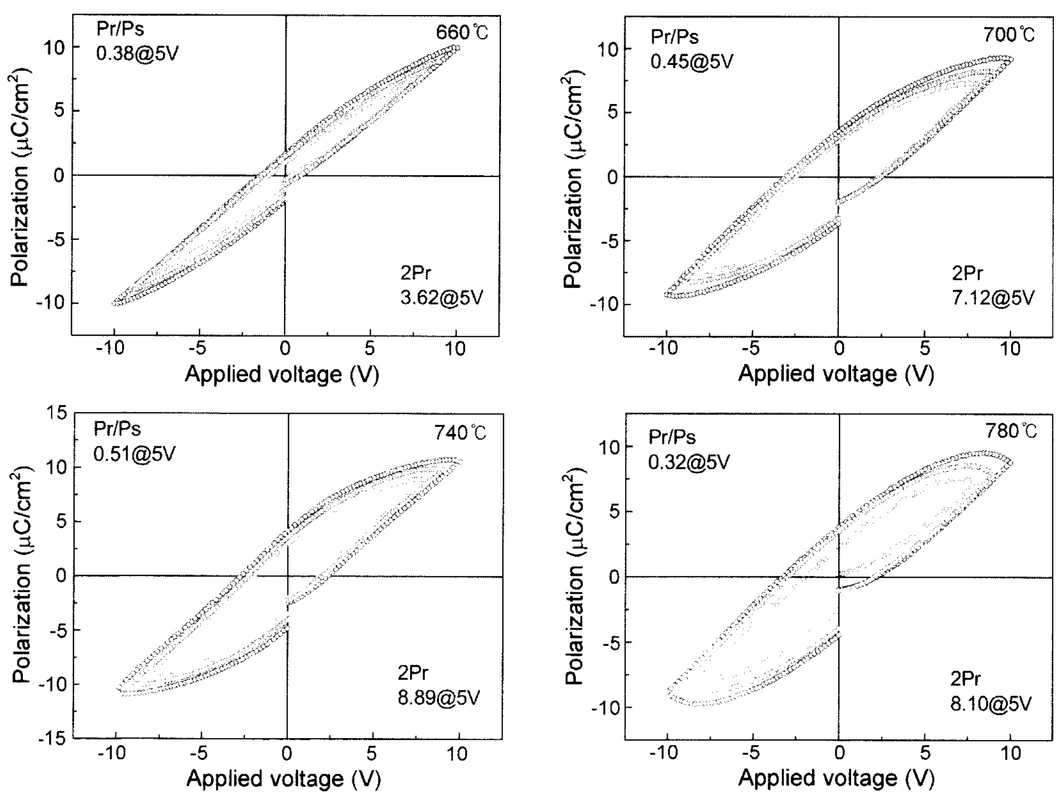


**Fig. 9.** Hysteresis loops of LSCO/SBT/Pt thin films annealed at 660, 700, 740, and 780°C for 1 h.

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