# Hydrogen Annealing effect on the dielectric properties of $(Pb_{0.72}La_{0.28})Ti_{0.93}O_3$ thin film

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**Abstract**

Dielectric thin films of $(Pb_{0.72}La_{0.28})Ti_{0.93}O_3$ were deposited on $Pt(111)/Ti/SiO_2/Si$ substrates in situ by pulsed laser deposition(PLD) and annealed with different gases which are forming gas and oxygen gas, respectively. The diffusion of hydrogen into the ferroelectric film was caused by annealing process and resulted in the destruction of polarization. The dielectric properties of forming gas annealed PLT thin films, which are dielectric constant, ferroelectric characteristic, and leakage current characteristics, were degraded

**Key Words** : PLT, Hydrogen annealing

## 1. Introduction

Lanthanum doped lead titanate(PLT) thin film can be applied to both the dynamic random access memories and nonvolatile ferroelectric random access memories because it allows a wide range of dielectric and ferroelectric properties[1]. The PLT at a La concentration of 28 moles paraelectric at room temperature and behaves like a normal dielectric because $T_C$ is -25℃.

One serious problem which is occurred during the product processing is severe degradation of their dielectric properties caused by annealing in the hydrogen-containing atmosphere. The degradation in electrical properties has been investigated, and it has been suggested that the catalytic activity of Pt plays a role in the degradation of PZT/Pt structures[2].

We have investigated the effect of forming gas annealing treatment on the PLT thin films.

## 2. Experimental

We used a pulsed laser deposition method (third-harmonic 355 nm Quantel Brilliant Q-switched Nd:YAG laser) to grow the films[3].

The pulse repetition time was 5 Hz, the laser energy density 3.0 J/cm$^2$ and the laser power 0.7 W.

$(Pb_{0.72}La_{0.28})Ti_{0.93}O_3$ films with a thickness of 600 nm were deposited at substrate temperature 600℃ with 200 mTorr of oxygen pressure by a two-step deposition process. Two-step process to grow PLT films was adopted and verified to be useful to enlarge the grain size of the film and to reduce the leakage current characteristics[4].

The deposited PLT thin film was annealed in the forming gas (5% $H_2$+95% $N_2$) at 400℃ for 30 minutes. Top gold electrode is deposited by thermal evaporation. We compare the results for the thin films without forming gas annealing treatment

## 3. Results and Discussion

Figure 1 shows the leakage current characteristics of annealing treated films in $O_2$ and forming gas ambient. The forming gas annealed PLT film shows at least one-order higher leakage current density than that of the oxygen gas annealed PLT film till 400 kV/cm of applied electric field as expected. The higher leakage current density of forming gas annealed PLT film is because of the hydrogen in the atmosphere and the smaller grain size[4].

The dielectric constant of the forming gas annealed film is lower than that of the oxygen gas annealed film. At 1 kHz, the relative dielectric constants are about 850 and 1350 for the films annealed in forming gas and oxygen gas, respectively.

Figure 2 plots the polarization - field hysteresis loops of forming gas and oxygen gas annealed films. The ferroelectric property of the film annealed with forming gas is degraded comparing to that of the film annealed with oxygen gas. It is expected that it is because the reacted oxygen with the hydrogen contained in the forming gas prevent the polarization of Ti in PLT perovskite structure[5].

X-ray diffraction (XRD) patterns of PLT thin films are shown in Fig. 3. Oxygen-deficient $Ti_6O_{11}$ (or $Ti_6O_{12}^{-6}$) is clearly observed as shown in Fig. 3(b). This observation makes us follow out that electrical degradation of the film could be mainly due to the catalytic reaction between Pt and hydrogen, which is expected to result in the Pb loss and formation of $Ti_6O_{11}$[6].

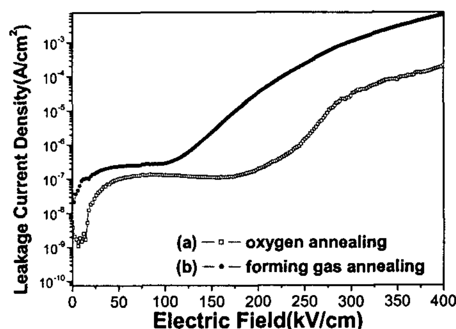


**Fig. 1.** Leakage current density of PLT thin film (a) annealed in oxygen ambient and (b) annealed in forming gas ambient.

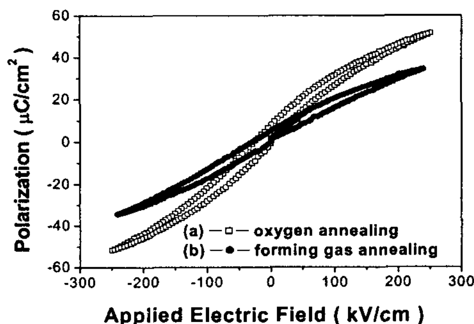


**Fig. 2.** Hysterisis loops of (a) oxygen annealed and (b) forming gas annealed PLT films.

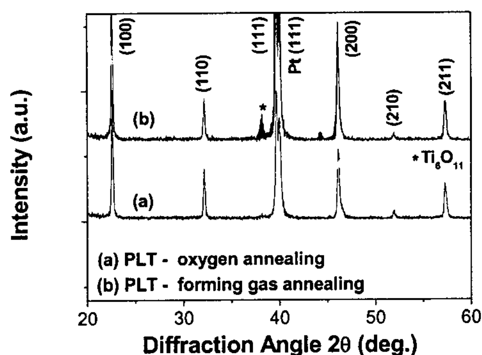


Fig. 3. XRD patterns of the PLT thin films (a) after oxygen annealing and (b) forming gas annealing.

## 4. Conclusion

To investigate the effects of hydrogen annealing on the $(Pb_{0.72}La_{0.28})Ti_{0.93}O_3$ film, we have deposited PLT thin film and annealed with the forming gas which was containing 5% $H_2$ and 95% $N_2$. The forming gas annealed film shows higher leakage current density and degradation of the ferroelectric property as well. The hydrogen gas contained in the forming gas affects on the electrical degradation by reacting with Pt electrode and ferroelectric degradation by coupled with oxygen impeding the movement of Ti atom in the perovskite structure.

## Acknowledgement

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