

Low Temperature Crystallization of (Pb,Ba)TiO₃ Ferroelectric Thin Films by MOCVD Method and Hydrothermal Treatment at 240°C

Takuji Naoyama, Minoru Noda, Masanori Okuyama, Hironori Fujisawa*, Masaru Shimizu*
Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan
Fax: +81-6-6850-6341, e-mail: nao429@semi.ee.es.osaka-u.ac.jp, okuyama@ee.es.osaka-u.ac.jp
* University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2201, Japan

(Pb,Ba)TiO₃ films showing perovskite structure were successfully crystallized by hydrothermal treatment at low temperature of 240°C. PbTiO₃ precursor films of 120 nm thickness were prepared on Pt/TiO_x/SiO₂/Si substrate by metal organic chemical vapor deposition method at 330°C and transformed into crystalline (Pb,Ba)TiO₃ thin films by hydrothermal treatment in Ba(OH)₂ - Pb(OH)₂ alkaline solutions. When the PbTiO₃ precursor film does not contain the crystallites, the treated thin film has a random orientation. However, a small amount of crystallites in the PbTiO₃ precursor film might affect the crystallization of (Pb,Ba)TiO₃ thin films although crystallite states are not observed by x-ray diffraction. Moreover, when the PbTiO₃ precursor film is pre-crystallized, showing a small amount of (100) orientation, the treated (Pb,Ba)TiO₃ thin film has (100) main orientation. According to AFM observation, the pre-crystallized PbTiO₃ precursor film has small grains that act as seed nuclei during hydrothermal treatment. The (Pb,Ba)TiO₃ thin film treated at 240°C for 3 h in 0.2 M Ba(OH)₂ - 0.1 M Pb(OH)₂ solution has a hysteresis loop with good shape, and the polarization at zero electric field of the treated thin film is 8 μC/cm².

Key words: hydrothermal, MOCVD, (Pb,Ba)TiO₃, low-temperature

1. INTRODUCTION

Ferroelectric random access memory (FeRAM) is nonvolatile and can be operated at high-speed with low power. Therefore, FeRAM has the potential to become a key device in the next generation's information age. Conventionally, ferroelectric thin film is prepared in the front process of FeRAM ULSI because the preparation temperature is higher than melting temperature of the Al wiring or decomposition temperatures of low-k dielectric layer, and so exclusive manufacture line is required. Therefore, it is desired that ferroelectric thin film is prepared at low temperature which enable that the preparation can be carried out in the end process and the process cost is reduced very much.

Ferroelectric films are deposited by various deposition methods, such as sol-gel, metal organic deposition, metal organic chemical vapor deposition (MOCVD) and pulsed laser deposition method and are crystallized at high temperature of 600°C or higher. [1,2,3] Another crystallization method is the hydrothermal synthesis method, which enables the preparation of crystalline perovskite thin films in alkaline aqueous solutions at very low temperature in the range of 100-240°C. [4] PbTiO₃ thin film prepared by a conventional hydrothermal synthesis method in KOH solution has excellent ferroelectric characteristics. [5] But this conventional hydrothermal synthesis method cannot be applied to the ULSI process because

it uses KOH alkaline solution. Additionally, it uses the precipitation of crystals from a solution and thus needs long time (more than 10 hours) for deposition. In order to solve these problems, we have tried to deposit the film by sol-gel and hydrothermal treatment processes and succeeded in preparing them for only 3 hours. The gel films produced by the sol-gel method are transformed into crystalline thin films through hydrothermal treatment in alkaline aqueous solutions except for KOH. [6] Recently, it has been shown that (Pb,Ba)TiO₃ thin films prepared by this technique have good P-E hysteresis loop and polarization at zero electric field is $P_{(E=0)}$ of about 21.5 μC/cm². And good fatigue endurance up to 10⁹ cycles is obtained. [7] It is expected that the MOCVD method will become the main preparation method of ferroelectric thin film in the future rather than the chemical solution deposition. Therefore, we believe that a combination of the MOCVD method and hydrothermal treatment is a very important technique for the ULSI process.

In this study, PbTiO₃ precursor films were deposited by the MOCVD method on Pt/TiO_x/SiO₂/Si substrate and were transformed into crystalline (Pb,Ba)TiO₃ thin films by hydrothermal treatment using Ba(OH)₂ - Pb(OH)₂ solutions. The treated (Pb,Ba)TiO₃ thin films were characterized on structural and electrical properties.

2. EXPERIMENTAL

PbTiO₃ precursor films were deposited on Pt/TiO_x/SiO₂/Si substrate by MOCVD method and transformed into crystalline (Pb,Ba)TiO₃ thin films by hydrothermal treatment in Ba(OH)₂ - Pb(OH)₂ alkaline mixture aqueous solutions. Figure 1 shows the autoclave system used for hydrothermal treatment of (Pb,Ba)TiO₃ films. The preparation conditions of MOCVD PbTiO₃ precursor films and (Pb,Ba)TiO₃ thin films treated hydrothermally are listed in Tables I and II, respectively. Al electrodes were deposited on the treated (Pb,Ba)TiO₃ thin films. The crystalline structures were investigated by x-ray diffraction (XRD; Rigaku, RINT2000). The morphologies of the PbTiO₃ precursor film and treated (Pb,Ba)TiO₃ thin films were observed by atomic force microscopy (AFM). The Chemical bonding states of PbTiO₃ precursor films were characterized by x-ray photoelectron spectroscopy (XPS; Shimadzu, AXIS HSi). A gold thin film, 5-10 nm thick, was deposited on the PbTiO₃ precursor film by sputtering at room temperature to avoid building-up charges and to use its peak as a reference peak in XPS investigations. Polarization–electric field (P-E) hysteresis loops were evaluated using a ferroelectric test system with virtual ground circuitry (Toyo-technica, FCE-1).

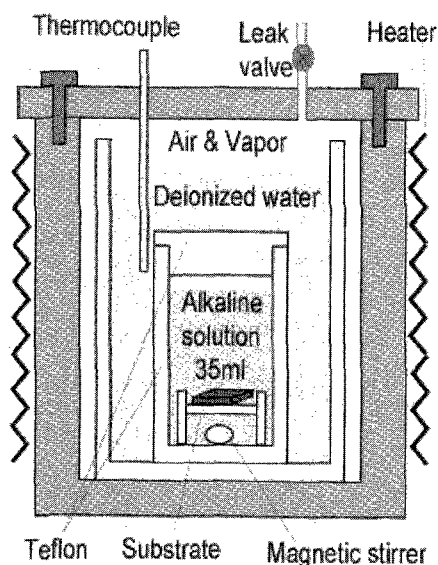


Fig. 1. Autoclave system used for hydrothermal treatment of (Pb,Ba)TiO₃ films.

Table I. Preparation conditions of MOCVD PbTiO₃ precursor films.

Substrate	Pt/TiO _x /SiO ₂ /Si
Preparation temperature	330°C
Film thickness	120nm ^a , 140nm ^b
Composition ratio of Pb/Ti by XRF	45/55 ^a , 52/48 ^b

a) non-crystallized and b) pre-crystallized PbTiO₃ precursor films

Table II. Hydrothermal treatment conditions of (Pb,Ba)TiO₃ thin films.

Solution temperature/ Holding time	240°C/ 3h
Ba(OH) ₂ - Pb(OH) ₂ concentration	0.2 M - 0.1 M (pH > 12)
Solution volume	35ml
Timing of pressure leak	below 100°C
Rinse	boiling deionized water
Drying	200°C/ 10 min in air

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of the MOCVD PbTiO₃ precursor films and the (Pb,Ba)TiO₃ thin films treated hydrothermally under the condition of 240°C/ 3h/ Ba(OH)₂ 0.2 M - Pb(OH)₂ 0.1 M. There are two kinds of PbTiO₃ precursor films. One is non-crystallized film and is Ti-rich, and the other is the pre-crystallized film and is Pb-rich. When the PbTiO₃ precursor film is not crystallized, the treated thin film shows random orientation. However, when the PbTiO₃ precursor film is pre-crystallized, showing a small (100) orientation, the treated (Pb,Ba)TiO₃ thin film has (100) main orientation. The Ba(OH)₂ and the Pb(OH)₂ concentrations are fixed to be 0.2 M and 0.1 M, respectively. [7] The MOCVD precursor film is more difficult to be crystallized by hydrothermal treatment than the sol-gel film. It is assumed that the MOCVD precursor film density is higher than the sol-gel film density, making more difficult for the solutions used in hydrothermal treatment to penetrate into a MOCVD precursor film than into a sol-gel precursor film.

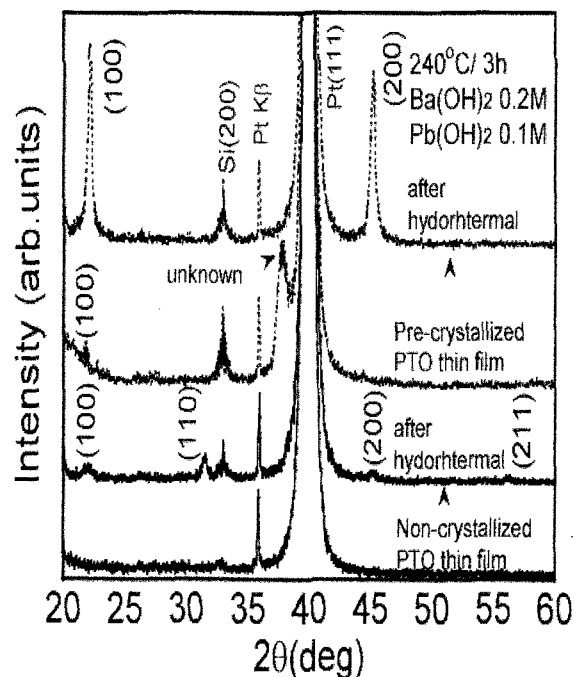


Fig. 2. XRD patterns of the PbTiO₃ precursor films and the (Pb,Ba)TiO₃ thin films prepared hydrothermally under the condition of 240°C/ 3h/ Ba(OH)₂ 0.2 M - Pb(OH)₂ 0.1 M.

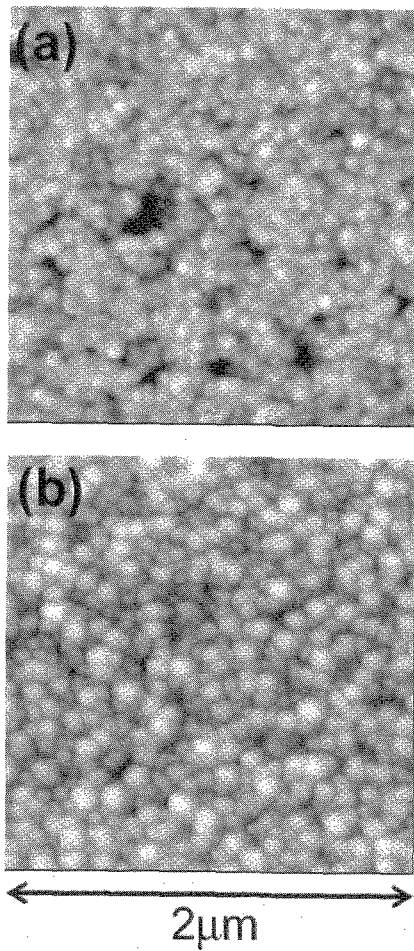


Fig. 3. Surface morphology of (a) the PbTiO_3 pre-crystallized precursor film and (b) the $(\text{Pb,Ba})\text{TiO}_3$ thin film treated hydrothermally.

Figures 3 and 4 show the surface morphology of the PbTiO_3 precursor films with different crystallization states and the $(\text{Pb,Ba})\text{TiO}_3$ thin films treated hydrothermally. The pre-crystallized PbTiO_3 precursor film has small grains of about 30-60 nm in size as shown in Fig. 3(a), and the RMS roughness (σ_{RMS}) is 5.6 nm and the height between maximum and minimum (Z_{max}) was 54.8 nm. The grains of treated thin film grow two times in size than the grains in PbTiO_3 precursor film before hydrothermal treatment. The σ_{RMS} and Z_{max} of treated $(\text{Pb,Ba})\text{TiO}_3$ thin film is 10.7 nm and 78.8 nm, respectively. In contrast, non-crystallized PbTiO_3 precursor film does not grow clear grains, having σ_{RMS} of 2.2 nm and Z_{max} of 21.7 nm as shown in Fig. 4(a). After hydrothermal treatment, the growths of grains with various shapes are observed in various shapes and size varies from 50-100 nm, σ_{RMS} 6.4 nm and Z_{max} 55.6 nm. As for uniformity of shape and grain, the $(\text{Pb,Ba})\text{TiO}_3$ thin film of Fig. 3(b) is better than the one of Fig. 4(b). It is thought that reactivity in hydrothermal treatment is larger in the pre-crystallized precursor films than the non-crystallized those because the surface

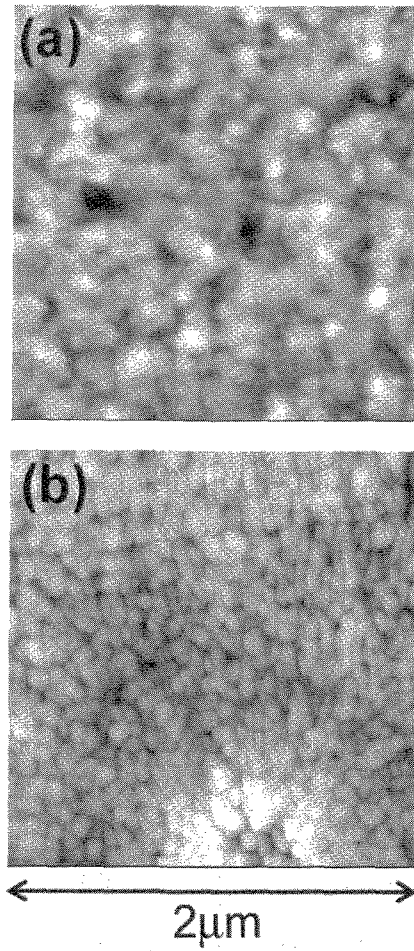


Fig. 4. Surface morphology of (a) the PbTiO_3 non-crystallized precursor film and (b) the $(\text{Pb,Ba})\text{TiO}_3$ thin film treated hydrothermally.

Table III. AFM data of pre-crystallized PbTiO_3 precursor films and treated $(\text{Pb,Ba})\text{TiO}_3$ thin films.

	pre-crystallized PTO film	PBT thin film
grain size (nm)	30-60	80-110
σ_{RMS} (nm)	5.6	10.7
Z_{max} (nm)	54.8	78.8
uniform shape and grain		better

Table III. AFM data of non-crystallized PbTiO_3 precursor films and treated $(\text{Pb,Ba})\text{TiO}_3$ thin films.

	non-crystallized PTO film	PBT thin films
grain size (nm)	---	50-100
σ_{RMS} (nm)	2.2	5.6
Z_{max} (nm)	21.7	55.6
uniform shape and grain		bad

area of precursor film contacted with alkaline solution increase when RMS roughness is large.

According to the XRD patterns and AFM observation, the pre-crystallized grains are considered to work as seed nuclei.

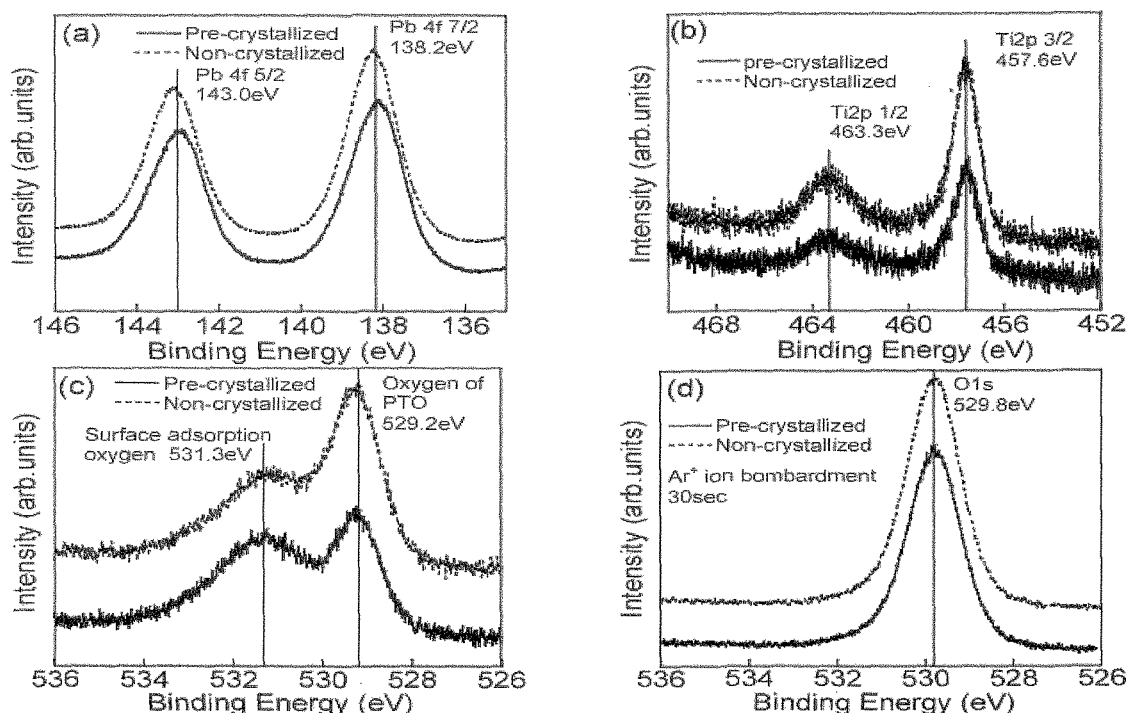


Fig. 5. XPS spectra of (a) Pb4f, (b) Ti2p, (c) O1s and (d) O1s after Ar⁺ ion bombardment in the PbTiO₃ precursor films with different crystallization states.

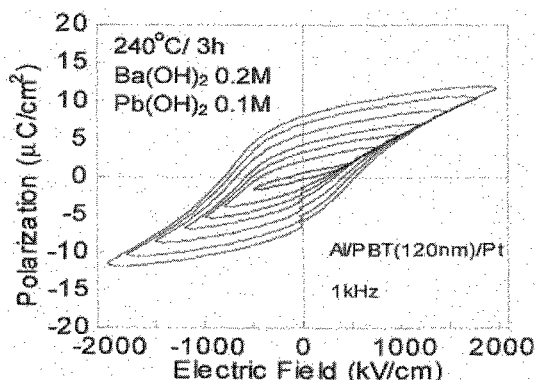


Fig. 6. P-E hysteresis loops of the (Pb,Ba)TiO₃ thin film treated hydrothermally at 240°C for 3 h in 0.2 M Ba(OH)₂ - 0.1 M Pb(OH)₂ solution.

Figure 5 shows the XPS spectra of (a) Pb4f, (b) Ti2p, (c) O1s and (d) O1s after Ar⁺ ion bombardment in the PbTiO₃ precursor films with differential crystallization states. The Pb-O and Ti-O bondings are not changed as no peak shift have been seen on the Pb4f, Ti2p and O1s spectra shown in Figs. 5(a), 5(b) and 5(c). The peaks of the O1s spectra around 531.3 eV can be presumed to be surface-adsorbed oxygen because that peak disappeared after etching the surface for 30 sec by Ar⁺ ions as shown in Fig. 5(d).

Figure 6 shows the P-E hysteresis loops of the (Pb,Ba)TiO₃ thin film obtained from pre-crystallized PbTiO₃ films treated hydrothermally at 240°C for 3 h in 0.2 M Ba(OH)₂ - 0.1 M Pb(OH)₂ solution. The P-E hysteresis loops were measured at ± 20 V at 1 kHz. The treated thin film has P_(E=0) of 8 μC/cm².

4. CONCLUSIONS

(Pb,Ba)TiO₃ thin films were successfully prepared by MOCVD method at 330°C and hydrothermal treatment at 240°C for 3 h in 0.2 M Ba(OH)₂ - 0.1 M Pb(OH)₂ solutions. We consider that this technique can enable the low temperature preparation of the ferroelectric thin film and adjust to the ULSI process.

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