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# Deposition of $PbTiO_3$ film by the spray–ICP technique

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$PbTiO_3$ thin films were prepared on various substrates by spraying an ultrasonically atomized aqueous solution of $Pb(NO_3)_2+TiO(NO_3)_2$ into an inductively coupled plasma (ICP) under atmospheric pressure. Single-phase $PbTiO_3$ with perovskite structure was obtained at 500–650 °C. The perovskite obtained below 600 °C showed less tetragonality due to the effect of grain size. The $PbTiO_3$ films crystallized with preferred (1 1 1) and (0 0 1) orientations on sapphire (0 0 1) and MgO (1 0 0), respectively. Based on the analysis of ICP emission spectra, it is suggested that a reoxidation of titanium preceded that of lead in the plasma, and also that OH in the plasma played an important role in the deposition of $PbTiO_3$.

## 1. Introduction

Thin $PbTiO_3$ films, which are useful materials as ferroelectrics [1, 2], have attracted much attention for microelectronic applications. Thin $PbTiO_3$ films have been prepared by various methods: r.f. sputtering [3, 4] has been widely used so far. However, the precise control of the film composition is difficult because of difference in the sputtering yield of each element. Chemical vapour deposition (CVD) [5, 6] and the sol–gel method [7] require expensive organometallic compounds as the source material. In addition, the CVD method requires a reduced atmosphere and the sol–gel process is relatively complicated. Other techniques [8, 9] also have similar demerits to those mentioned above.

The spray pyrolysis technique assisted by an inductively coupled plasma (spray–ICP technique) has been recognized as an useful method for synthesis of oxides. The processing is performed by spraying atomized source solutions of metal salts into an ICP. This method has many advantages; it is free from contamination from the electrode, it has a fast deposition rate owing to the ultra-high temperature reaction, and has easy composition control by using aqueous source solutions.Ultrafine powders [10–12], such as MgO [13], $ZrO_2$ [14] and $ZrO_2$–$SiO_2$ [15], have been prepared by this method. The process of oxidation in a plasma has been estimated from the point of mobility of ultrafine powder in solutions by Kagawa *et al.* [16]. Recently, dense films of $ZrO_2$ [17] and chromium compounds [18] were deposited on various substrates. $PbTiO_3$ film has not been yet synthesized by the spray–ICP technique because of the difficulty of preparing a stable mixed solution of lead and titanium salt.

This study was concerned with the direct preparation of $PbTiO_3$ film on various substrates from a mixed solution of $Pb(NO_3)_2$ and $TiO(NO_3)_2$ by the spray–ICP technique under atmospheric pressure. A stable mixed solution of $Pb(NO_3)_2$ and $TiO(NO_3)_2$ was obtained by dissolving $H_4TiO_4$ in nitric acid solution [19]. In addition, the deposition process in plasma was deduced based on the plasma emission analysis in the ultraviolet–visible region and on the composition analysis of the films.

## 2. Experimental procedure

Mother solutions were prepared by mixing the aqueous solutions of $Pb(NO_3)_2$ and $TiO(NO_3)_2$. The total concentration of metals was 0.25 M (Pb/Ti = 1). $TiO(NO_3)_2$ solution was prepared as follows: titanium hydroxide was precipitated by hydrolysing titanium chloride at pH 2 controlled with ammonium solution, washed with water, and dissolved with nitric acid solution.

The resultant $TiO(NO_3)_2$ solution was stored at about 7 °C to prohibit the formation of sparingly soluble precipitate of $H_2TiO_3$. The mother solution was ultrasonically atomized in the argon carrier gas and was introduced through a nozzle with 2 mm diameter into the centre of the ICP. A schematic diagram of our apparatus is shown in Fig. 1. Typical conditions of the spray-ICP technique in this study are shown in Table 1. The ICP torch was formed in two coaxial quartz tubes (inner diameter, 44 mm) cooled by water. The Ar–ICP was generated with a three-turn work coil (inner diameter, 68 mm) and an r.f. oscillator, and was stabilized with a sheath gas. This technique was similar to that originally reported

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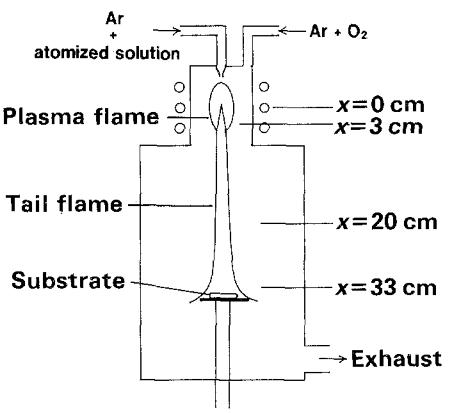

*Figure 1* Schematic diagram of the spray–ICP system. $x$ is the distance from the centre of the work coil. Plasma emission was measured at $x = 3$, 20 and 33 cm.

TABLE I Typical spray–ICP conditions for deposition of $PbTiO_3$

| | |
|---|---|
| R.f. frequency | 4 MHz |
| R.f. power | 6–7 kW |
| Pressure | 760 torr |
| Plasma gas (Ar) | 15 SLM |
| Sheath gas (Ar) | 10 SLM |
| ($O_2$) | 0–4 SLM |
| Carrier gas (Ar) | 2 SLM |
| Position of substrate from centre of work coil | 35 cm |
| Feeding rate of mother solution | 20 ml h$^{-1}$ |

by Kagawa *et al.* [17]. Sintered high-purity alumina, Si(1 0 0), sapphire (0 0 1) and MgO (1 0 0) plates (10–20 mm wide by 0.5 mm thick) were used as substrates. The substrate was heated to 300–700 °C by the ICP flame. The substrate temperature was measured by a thermocouple located just behind the substrate.

Plasma emission in the ultraviolet–visible region was measured through two pinholes (1 mm diameter) by using an optical spectrometer (MS-60, Koken-Kogyo). When a thermal equilibrium in the plasma is assumed, the atomic temperature, $T$, can be estimated from the slope of the plots of $\ln(I_{mn}/A_{mn}v_{mn}g_m)$ versus $E_m$ [20], where $I_{mn}$ is radiation intensity from an excitation level m to a subordinate level n, $A_{mn}$ is the transition probability for $m \rightarrow n$, $v_{mn}$ is the frequency of the spectrum for $m \rightarrow n$, $g_m$ is the statistical weight for the m level and $E_m$ is the energy of the m level [21]. When only $H_2O$ was introduced into plasma, the emission intensities of atomic argon (420.07, 425.94, 451.10 and 549.59 nm) were used for the calculation, and when the mixed solution of $Pb(NO_3)_2$ and $TiO(NO_3)_2$ was introduced into the plasma the emission intensities of atomic titanium (308.80, 323.45 and 336.12 nm) were used.

The films were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray microprobe analysis (XMPA). The film compositions were determined by an ICP spectroscopic analysis after the film was dissolved in concentrated nitric acid.

## 3. Results and discussion

### 3.1. $PbTiO_3$ films deposited without the addition of oxygen to the sheath gas

Fig. 2 shows the composition of films deposited on substrates of sintered alumina and sapphire (0 0 1) without the addition of oxygen to the sheath gas. When the substrate temperature was below 400 °C, the deposits were identified as a mixed phase of pyrochlore and perovskite. The film looked like aggregates of ultrafine powders. The film formed above 500 °C was the single phase of rutile, and lead could not be detected. The rutile films were dark-blue in colour and semiconductive. The same results were obtained on the sapphire (0 0 1) substrate. The film composition mainly depended on the substrate temperature. These results suggest that the amount of oxygen from the $H_2O$ and the nitric ions in the mother solution was insufficient for the reoxidation of lead and titanium in the plasma. Therefore, the introduction of oxygen into the plasma was necessary for the deposition of the perovskite films with stoichiometric composition.

### 3.2. $PbTiO_3$ films deposited with the addition of oxygen to the sheath gas

Figs 3 and 4 show the effect of substrate temperature on microstructures and compositions of films deposited on the sintered alumina with the addition of oxygen into the sheath gas ($O_2 = 2$ SLM). The deposition rate was about 100 nm min$^{-1}$ at 650 °C. While the feed rate of oxygen was in the range of 0.5–4 SLM, the natures of the films did not change. The nature of the films obtained below 400 °C were analogous to those without the addition of oxygen. The perovskite single phase was obtained at 500–650 °C and the film consisted of a relatively dense texture of perovskite particles. The atomic ratio Pb/Pb + Ti of the films was nearly 0.5 below 650 °C. Above 700 °C, only a columnar rutile grew, and lead could not be detected by both XMPA and ICP analyses.

Fig. 5 shows lattice constants and grain size of the films as a function of substrate temperature. On lowering the substrate temperature, the grain size of $PbTiO_3$ became small and the $a$-axis extended while the $c$-axis shrank. The perovskite phase of $PbTiO_3$ was, therefore, considered to have less tetragonality as the substrate temperature decreased, owing to the effect of grain size [22]. The critical grain size of tetragonal $PbTiO_3$ was estimated from this result to

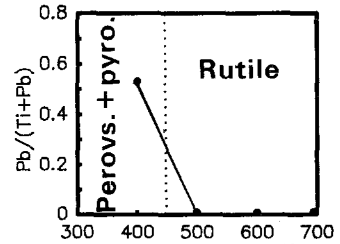

*Figure 2* The effect of substrate temperature on the composition of films prepared on sintered alumina without oxygen added to the sheath gas.

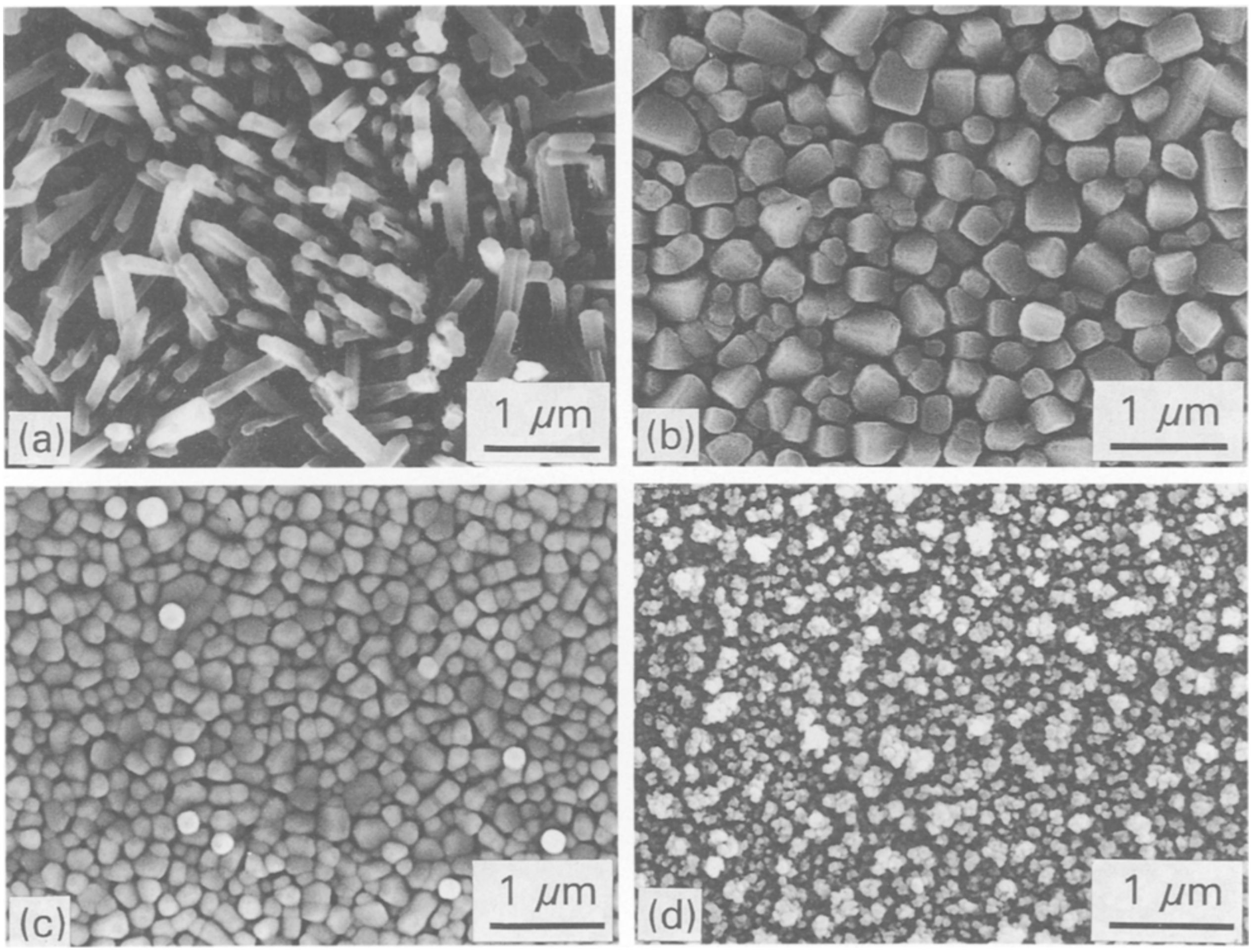

*Figure 3* SEM images of the film surface deposited on sintered alumina at (a) 700 °C, (b) 650 °C, (c) 600 °C and (d) 300 °C with oxygen added to the sheath gas.

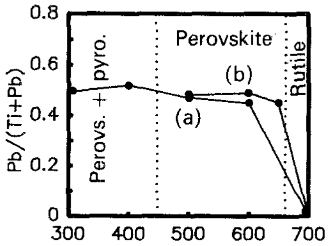

*Figure 4* The effect of substrate temperature on the composition of films prepared on (a) sintered alumina and (b) sapphire (0 0 1) with oxygen added to the sheath gas.

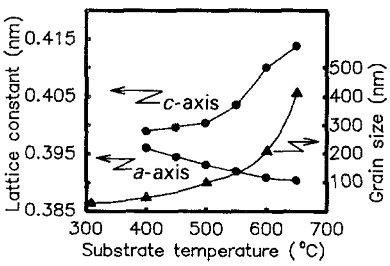

*Figure 5* The effect of substrate temperature on the lattice constant and grain size of $PbTiO_3$ deposited on sintered alumina.

be about 30 nm, which almost agreed with the value obtained by Uchino *et al.* [22]. Fig. 6 shows XRD patterns of films deposited at 650 °C on sintered alumina, Si (1 0 0), sapphire (0 0 1) and MgO (1 0 0). The films deposited at 650 °C were transparent and slightly whitish in colour. The $PbTiO_3$ films crystallized with preferred (1 1 1) orientation on sapphire (0 0 1) and (0 0 1) orientation on MgO (1 0 0). The lattice parameters of the film on MgO shifted slightly towards a

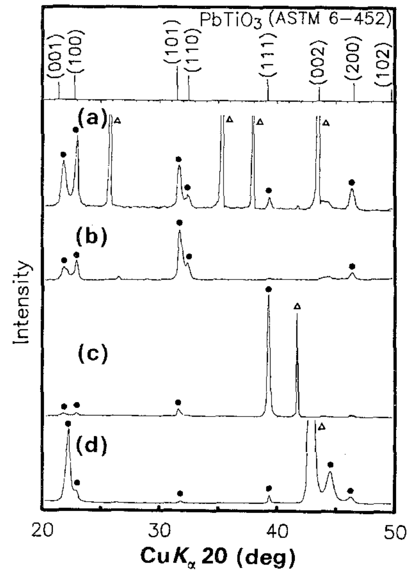

*Figure 6* XRD patterns of films deposited at 650 °C on (a) sintered alumina, (b) Si (1 0 0), (c) sapphire (0 0 1) and (d) MgO (1 0 0). (●) Perovskite, (△) substrate.

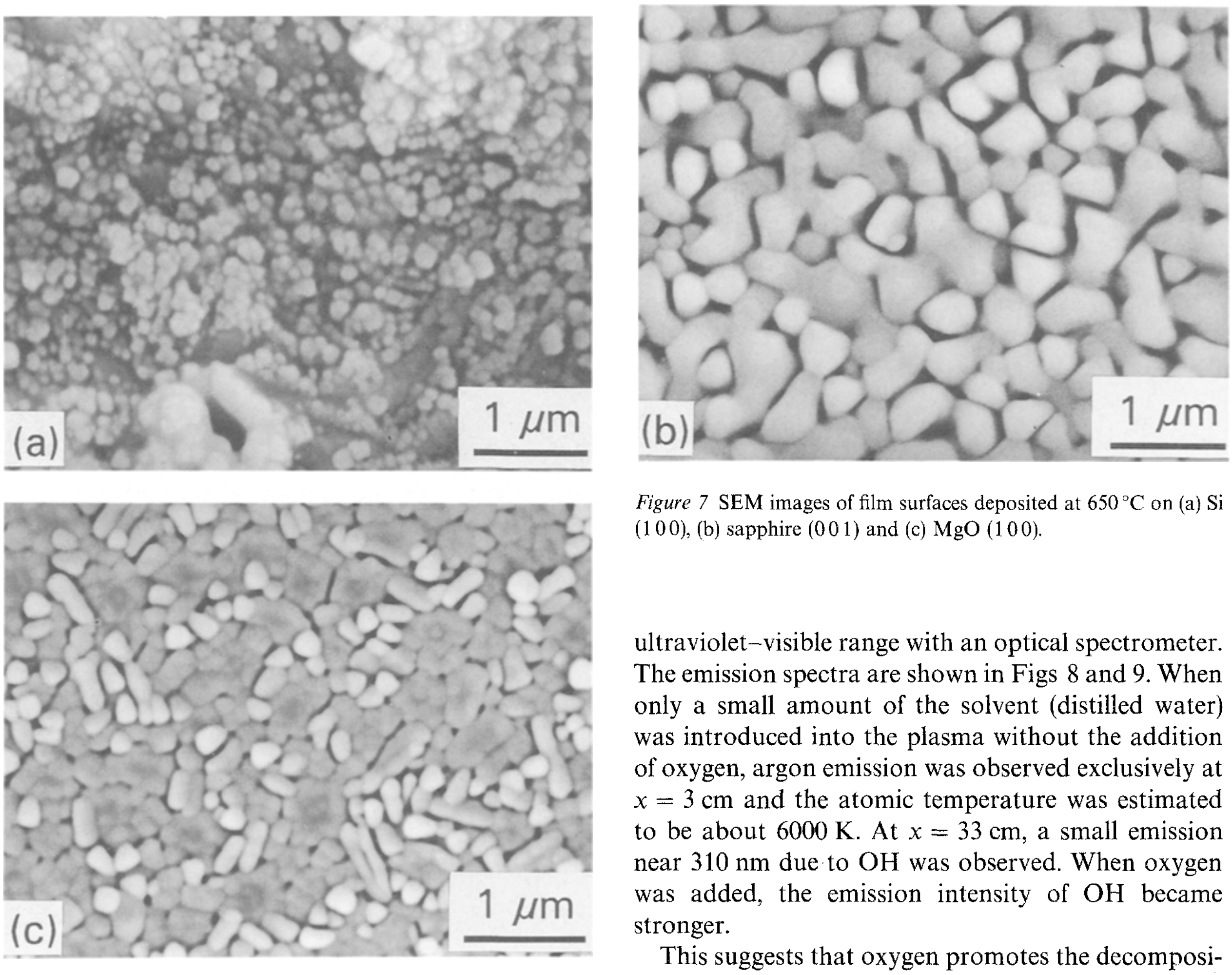

*Figure 7* SEM images of film surfaces deposited at 650 °C on (a) Si (1 0 0), (b) sapphire (0 0 1) and (c) MgO (1 0 0).

lower tetragonality. The $PbTiO_3$ films deposited on silicon were not oriented as well as on sintered alumina substrate. The $PbTiO_3$ films having their polarization axis parallel to $\langle 0 0 1 \rangle$ are very useful for the various applications. The degree of *c*-axis orientation, $\alpha = \sum I(0 0 1)/\sum I(h k l)$, of the film deposited at 650 °C on MgO was 0.8–0.9, where $I(0 0 1)$ and $I(h k l)$ are the XRD intensities of (0 0 1) and $(h k l)$ reflections. This value was as large as that obtained by the sputtering method [23].

SEM images of the surface of $PbTiO_3$ films deposited on Si (1 0 0), sapphire (0 0 1) and MgO (1 0 0) at 650 °C are compared in Fig. 7. A significant dependence of the microstructure of the films on the substrate was observed. Coagulation of ultrafine particles and a glass-like phase were observed in the film on silicon probably due to a reaction between $PbTiO_3$ and silicon. On sapphire, the particles and their coagulation had triangular planes parallel to the substrate suggesting the (1 1 1) orientation. The grains were smaller and packed denser on MgO than on sapphire, although a clear indication of the (0 0 1) orientation was not recognized.

### 3.3. Species in the plasma

As mentioned above, even a small addition of oxygen into the plasma influenced the products. Therefore, in order to estimate the deposition process of $PbTiO_3$, a plasma emission analysis was carried out in the ultraviolet–visible range with an optical spectrometer. The emission spectra are shown in Figs 8 and 9. When only a small amount of the solvent (distilled water) was introduced into the plasma without the addition of oxygen, argon emission was observed exclusively at $x = 3$ cm and the atomic temperature was estimated to be about 6000 K. At $x = 33$ cm, a small emission near 310 nm due to OH was observed. When oxygen was added, the emission intensity of OH became stronger.

This suggests that oxygen promotes the decomposition of $H_2O$ into OH. When a mixed solution of $Pb(NO_3)_2 + TiO(NO_3)_2$ was introduced into the plasma, strong emission peaks ascribed to titanium and lead were observed at $x = 3$ cm instead of those of argon, and the atomic temperature of titanium was relatively low (4500 K) compared with the argon temperature in the above case. However, at $x = 20$ cm, the titanium emission became weaker than that of lead. The OH peaks were weaker than that on atomizing

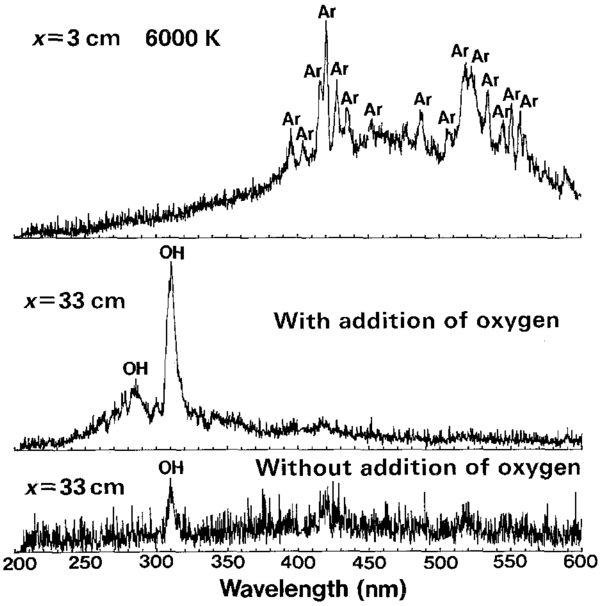

*Figure 8* Emission spectra of the ICP flame when only distilled water was sprayed. $x$ is the distance from the centre of the work coil.

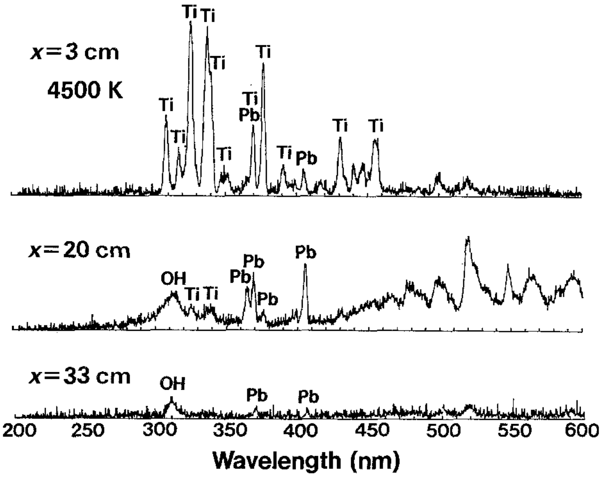

*Figure 9* Emission spectra of the ICP flame when a mixed solution of $Pb(NO_3)_2$ and $TiO(NO_3)_2$ was sprayed. Oxygen was added to the sheath gas (2 SLM). $x$ is the distance from the centre of the work coil.

only water. At $x = 33$ cm, weak irradiations of lead and OH were detected. This observation indicates that the reaction between titanium, lead and the species containing oxygen does not occur instantaneously, but the reactions of titanium with OH, O or $O_2$ precedes those of lead.

From the results mentioned above, the deposition process of $PbTiO_3$ could be deduced to consist of the following stages. (1) In the ICP flame produced near the work coil ($x = 3$ cm), the solvent ($H_2O$) evaporated momentarily, and the metal salts were decomposed to atoms by the ultra-high temperature [24]. (2) In the tail flame in the reaction chamber, the metal atoms reacted with OH or $O_2$, and consequently formed precursors of $PbTiO_3$. In this stage, the reaction of titanium precedes that of lead, possibly because the standard free energy of formation of $TiO_2$ is greater than that of PbO [25]. In the preparation of ultrafine powder of $SnO_2$–$Al_2O_3$ system, Kagawa *et al.* [16] suggested from measurements of mobility of the powder that $Al_2O_3$ nucleated earlier than $SnO_2$. On the other hand, the metals react with OH, O or $O_2$ to form the oxide as follows

$$\begin{aligned} \mathrm{Ti[g]} + \mathrm{4OH[g]} &= \mathrm{TiO_2[g]} + \mathrm{2H_2O[g]} \\ K_p &= 2.82\times10^{39} \qquad (1) \end{aligned}$$

$$\begin{aligned} \mathrm{Ti[g]} + \mathrm{O_2[g]} &= \mathrm{TiO_2[g]} \\ K_p &= 1.86\times10^{22} \qquad (2) \end{aligned}$$

$$\begin{aligned} \mathrm{Ti[g]} + \mathrm{2O[g]} &= \mathrm{TiO_2[g]} \\ K_p &= 1.06\times10^{29} \qquad (3) \end{aligned}$$

$$\begin{aligned} \mathrm{Pb[g]} + \mathrm{2OH[g]} &= \mathrm{PbO[g]} + \mathrm{H_2O[g]} \\ K_p &= 3.62\times10^{12} \qquad (4) \end{aligned}$$

$$\begin{aligned} \mathrm{Pb[g]} + \mathrm{1/2O_2[g]} &= \mathrm{PbO[g]} \\ K_p &= 9.26\times10^{2} \qquad (5) \end{aligned}$$

$$\begin{aligned} \mathrm{Pb[g]} + \mathrm{O[g]} &= \mathrm{PbO[g]} \\ K_p &= 2.22\times10^{6} \qquad (6) \end{aligned}$$

where $K_p$ is the equilibrium constant at 1300 K [25]. The equilibrium constant for oxidation with OH (Reactions 1 and 4) is somewhat greater than that with $O_2$ (Reactions 2 and 5) or with O (Reactions 3 and 6). It was, therefore, believed that in the early stage of the reaction in plasma, ultrafine precursors were generated in the form of oxides of titanium and/or lead, which were produced mainly by the reaction with OH. (3) Crystallization and crystal growth of $PbTiO_3$ proceeded on the substrate at a proper temperature (500–650 °C). However, lead evaporated in the form of PbO at the substrate temperature above 700 °C. Without the addition of oxygen, as shown above, the films formed above 500 °C consisted of only a rutile phase, and lead could not be detected. The evaporation of lead was, therefore, considered to be accelerated by the lack of OH and oxygen. We believed that the active OH, which was increased by the addition of oxygen, also contributed to the depression of the evaporation of lead compound and the stable deposition of $PbTiO_3$.

## 4. Conclusion

$PbTiO_3$ thin films were prepared on various substrates by spraying an ultrasonically atomized mixed solution of $Pb(NO_3)_2 + TiO(NO_3)_2$ into an inductively coupled plasma (ICP) under atmospheric pressure. The perovskite single phase was obtained at 500–650 °C. The films were relatively dense. It should be noted that a dense $PbTiO_3$ film was obtained directly from aqueous solution at relatively low temperature under atmospheric pressure. These results were attributed to the gas-phase reaction activated to an extremely high degree by the assistance of the ultra-high temperature ICP. $PbTiO_3$ obtained below 600 °C showed lower tetragonality owing to the effect of grain size. The orientation of the film depended strongly on the crystal structure of the substrate, i.e. $PbTiO_3$ crystallized with preferred (1 1 1) and (0 0 1) orientations on sapphire (0 0 1) and MgO (1 0 0), respectively. The composition of the films was influenced mainly by the substrate temperature and the addition of oxygen.

Based on the analysis of emission spectra, reoxidation of titanium was considered to occur at an earlier stage in the plasma than that of lead, and it was also believed that OH played an important role in the reoxidation of metal atoms. Without the addition of oxygen, no single-phase $PbTiO_3$ was obtained, because insufficient amounts of OH and $O_2$ existed in the plasma. It was suggested that OH accelerated the reoxidation of metal atoms and depressed the evaporation of lead compound.

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## References

1. G. SHIRANE, R. PEPINSKY and B. C. FRAZER, *Acta. Crystallogr.* **9** (1956) 131.
2. V. G. BHIDE, M. S. HEGDE and K. G. DESHMUKH, *J. Am. Ceram. Soc.* **51** (1968) 565.

3. M. OKUYAMA, Y. MATSUI, H. NAKANO, T. NAKAGAWA and Y. HAMAKAWA, *Jpn J. Appl. Phys.* **18** (1979) 1633.
4. H. MAIWA, N. ICHINOSE and K. OKAZAKI, *ibid.* **31** (1992) 3029.
5. T. NAKAGAWA, J. KAWAGUCHI, M. OKUYAMA and Y. HAMAKAWA, *ibid.* **21** (1982) L655.
6. A. ANDO, T. KATAYAMA, M. SHIMIZU and T. SHIOSAKI, *ibid.* **31** (1992) 3001.
7. S. L. SWARTZ, S. J. BRIGHT, P. J. MELLING and T. R. SHROUT, *Ferroelectrics* **108** (1990) 71.
8. H. TABATA, O. MURATA, T. KAWAI, S. KAWAI and M. OKUYAMA, *Jpn J. Appl. Phys.* **31** (1992) 2968.
9. S. HYAMIZU, A. YAHASHI and Y. SHIBATA, *ibid.* **31** (1992) 2975.
10. T. ONO, M. KAGAWA, Y. SYONO, M. IKEBE and Y. MUTO, *Plasma Chem. Plasma Proc.* **7** (1987) 201.
11. J. P. POLLINGER and G. L. MESSING, *Advan. Ceram.* **21** (1987) 217.
12. Y. C. LAU, P. KONG and E. PFENDER, in Proceedings of ISPC- 8, Tokyo, Japan, August, 1987, p. 2381.
13. M. KAGAWA, M. KIKUCHI, R. OHNO and T. NAGAE, *J. Am. Ceram. Soc.* **64** (1981) C7.
14. M. KAGAWA, M. KIKUCHI, Y. SYONO and T. NAGAE, *ibid.* **66** (1983) 751.
15. T. ONO, M. KAGAWA and Y. SYONO, *J. Mater. Sci.* **20** (1985) 2483.
16. M. KAGAWA, Y. IMAMURA, S. USUI and Y. SYONO, *J. Mater. Sci. Lett.* **3** (1984) 699.
17. M. KAGAWA, H. KOMATSU, Y. SYONO and A. YAMADA, *Adv. Ceram.* **24** (1988) 951.
18. M. SUZUKI, M. KAGAWA, Y. SYONO and T. HIRAI, *J. Crystal Growth* **99** (1990) 611.
19. H. YAMAMURA, S. KURAMOTO, H. HANEDA, A. WATANABE and S. SIRASAKI, *Yogyo-Kyokai-shi* **94** (1986) 470 (in Japanese).
20. H. R. GRIEM, "Plasma Spectroscopy" (McGraw-Hill, New York, 1964) p. 269.
21. W. L. WIESE, M. W. SMITH and B. M. GLENNON, "Atomic Transition Probabilities, (US Government Printing Office, Washington, DC, 1966) NSRDS-NBS4.
22. K. UCHINO, E. SADANAGA and T. HIROSE, *J. Am. Ceram. Soc.* **72** (1989) 1555.
23. K. IIJIMA, Y. TOMITA, R. TAKAYAMA and I. UEDA, *J. Appl. Phys.* **60** (1986) 361.
24. M. KAGAWA, F. HONDA, H. ONODERA and T. NAGAE, *Mater. Res. Bull.* **18** (1983) 1081.
25. D. D. WAGMAN, W. H. EVANS, V. B. PARKER, R. H. SCHUMM, I. HALOW, S. M. BAILEY, K. L. CHURNEY and R. L. NUTTALL, "NBS Tables of Chemical Thermodynamic Properties", The Japan Society of Calorimetry and Thermal Analysis, Thermodynamic Data Base MALT2, Kagaku Gijutsusha, Tokyo, Japan (1992).

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