Controlling the Crystal Orientations of Lead Titanate Thin Films

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Controlling the Crystal Orientations of Lead Titanate Thin Films

Toshio Ogawa, Atsuo Senda and Tohru Kasanami

Murata Manufacturing Co., Ltd., Nagaokakyo-shi, Kyoto 617

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Various substrates were investigated for use in crystal-oriented $PbTiO_3$ thin films deposited by rf magnetron sputtering. In fabricating ferroelectric thin films with controlled crystal orientations, a close relationship was found between the thermal expansion coefficients of the films and substrates. Where the thermal expansion coefficient of the substrate was larger than that of the film, as in the case of a single-crystal MgO substrate, horizontal compressive mechanical stress along the plane of the film led to a *c*-axis-oriented film. Conversely, where the thermal expansion coefficient of the substrate was smaller than that of the film, as in the case of a quartz glass substrate, tensile stress in the film gave rise to an *a*-axis-oriented film. The Curie point of the film material determined the amount of mechanical stress present during cooling. Based on the above, new substrates of glass ceramics for use in *c*-axis-oriented films were developed.

KEYWORDS: crystal orientation, *c*-axis-oriented film, *a*-axis oriented film, glass ceramics, $PbTiO_3$ thin film, rf magnetron sputtering

§1. Introduction

It is necessary to align the crystal orientations of ferroelectric thin films in the direction of spontaneous polarization for films with high remanent polarizations because the substrates on which the films are deposited restrict the amount that thin films can be transformed. In the case of ferroelectric nonvolatile memory capacitors,[1,2] it is believed that orienting crystals in the direction of spontaneous polarization prevents deterioration of the film characteristics with repeated polarization reversal cycles since the volume of the films change less with each reversal in polarization. Various substrates with different thermal expansion coefficients were investigated in an effort to control the crystal orientation of ferroelectric thin films. This paper describes the characteristics of new substrates used to fabricate *c*-axis-oriented $PbTiO_3$ films, as well as the relationships between thin film compositions, the kinds of substrates, and the crystal orientation of the films.

§2. Experimental Procedure

Two types of targets were employed. These were $PbTiO_3$ ceramics modified with La_2O_3, the tetragonality c/a and Curie point of which were 1.048, 430°C and 1.032, 320°C, respectively. Both had more than 98% relative densities. The substrates, sapphire (r & c), quartz glass, single-crystal MgO(100), and glass ceramics, were placed on a holder under a heater. The substrate temperature and oxygen concentration in argon were set to 600°C and 10%, respectively. A representative experiment included the use of a film with a thickness of 1.5 μm, a total gas pressure of 1.0×10^{-2} Torr, and an rf power of 2.5 W/cm^2.*

The structure of the films was examined by X-ray diffraction (CuKα) and reflection high energy electron diffraction (RHEED) and their composition by fluorescence X-ray analysis and electron probe microanalysis (EPMA).

*T. Ogawa, A. Senda and T. Kasanami: Extended Abstracts of the 50th Autumn Meeting of the Japan Society of Applied Physics, Fukuoka, September, 29p-ZC-4, 1989.

§3. Results and Discussion

3.1 *$PbTiO_3$ phase preparation*

A perovskite phase could be produced by sputtering at a substrate temperature (T_s) of between 600°C and 700°C in the cases of both ceramic targets with different Curie points.[3] The film compositions of the perovskite phases were the same as those of the targets. Figure 1 shows the dependence of the $PbTiO_3$ phase on both the oxygen concentration in argon and the sputtering gas pressure at a T_s of 600°C. The region of the perovskite phase in which yellow transparent films were produced was determined by the oxygen concentration of the sputtering gas and the gas pressure, independent of the kind of substrate. A film with a composition of $c/a=1.032$ (Fig. 1(a)), furthermore, was prepared at a lower sputtering gas pressure than that used in fabricating one with a composition of $c/a=1.048$ (Fig. 1(b)). We believe that the $PbTiO_3$ phase ($c/a=1.032$) was formed at a lower gas pressure due to the suppression of PbO vaporization from the film. This suppression was caused by greater substitution of La for Pb at the A (Pb) sites of the perovskite lattices.

3.2 *Crystal orientation control by substrates*

$PbTiO_3$ thin films on an r-plane sapphire substrate preferred orientations in the (111) and (101)/(110) directions. The sputtering gas pressure strongly affected the crystal orientation of the films on sapphire substrates, as shown in Fig. 2. The same tendency of the crystal orientation was also observed in the case of films deposited on *c*-plane sapphire. Films with *c*-axis orientations were formed on the substrates of single-crystal MgO, independent of sputtering conditions (Fig. 3). In the case of quartz glass substrates, *a*-axis-oriented films were similarly fabricated by sputtering a ceramic target with a composition of $c/a=1.032$ over a wide range of sputtering gas pressure. However, as shown in Fig. 4, films built up on quartz glass substrates by sputtering another ceramic

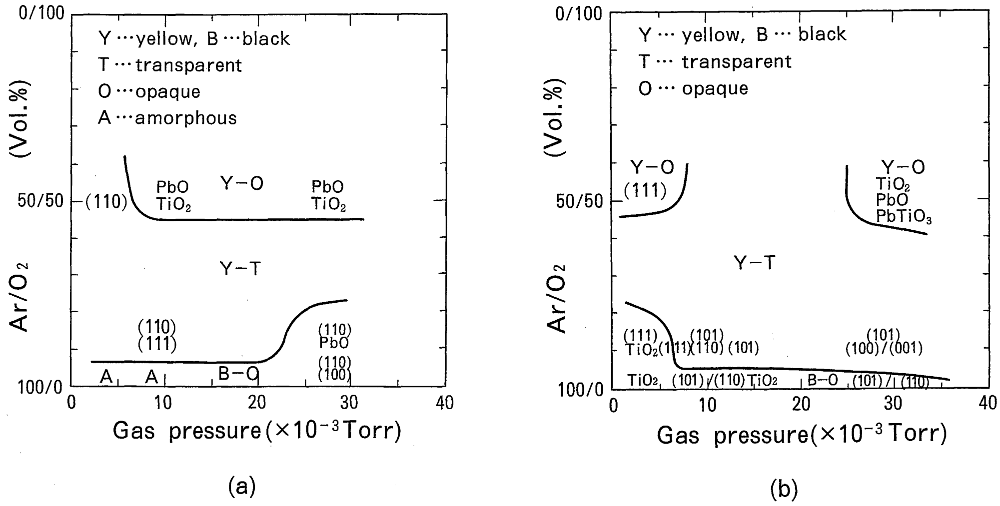

Fig. 1. The effect of the sputtering gas pressure and gas ratio of Ar/O_2 on $PbTiO_3$ phases with compositions of $c/a=1.032$ (a) and $c/a=1.048$ (b) deposited on r-plane sapphire at a T_s of 600°C.

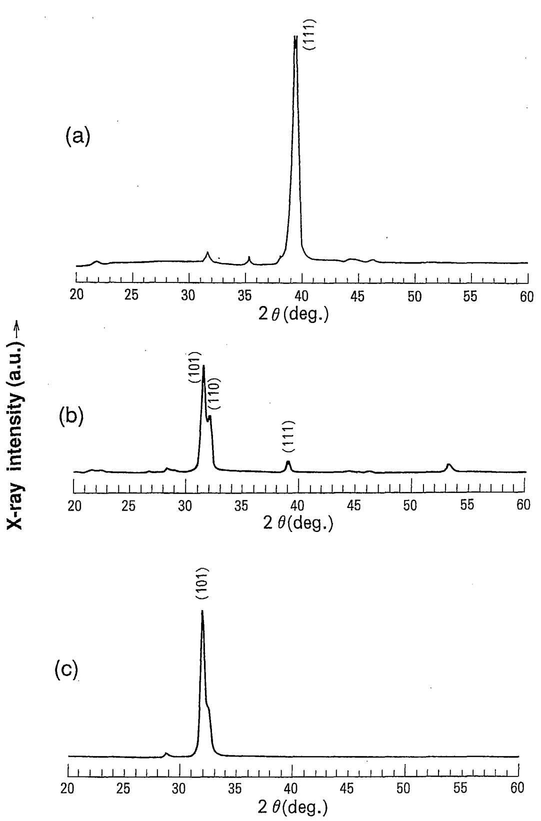

Fig. 2. X-ray diffraction patterns of $PbTiO_3$ ($c/a=1.048$) films on r-plane sapphire. The sputtering conditions were T_s, 600°C; rf power, 200 W; $Ar/O_2=90/10$ Vol.%; sputtering gas pressure, (a) 8.8×10^{-3} Torr, (b) 9.2×10^{-3} Torr, (c) 1.3×10^{-2} Torr.

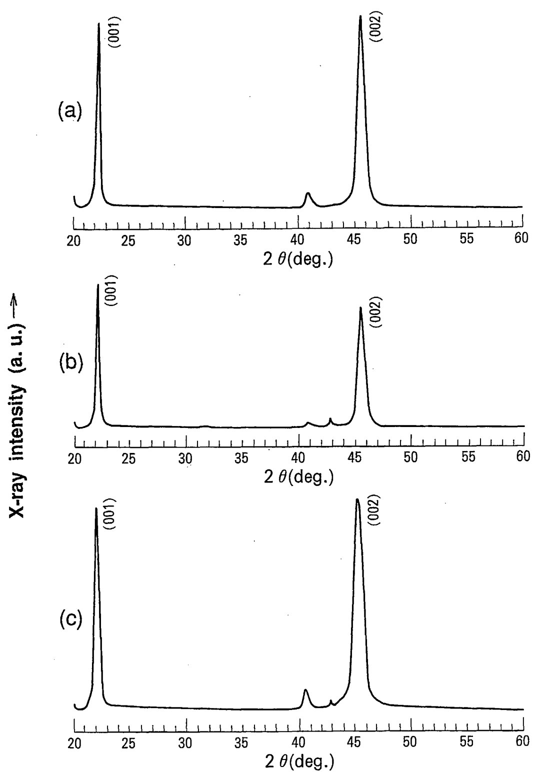

Fig. 3. The crystal orientation of c-axis-oriented $PbTiO_3$ ($c/a=1.032$) films on single-crystal MgO. The sputtering conditions were T_s, 600°C; rf power, 200 W; (a) $Ar/O_2=50/50$ Vol.%, (b) and (c), $Ar/O_2=90/10$ Vol.%; sputtering gas pressure, (a) and (b), 4.0×10^{-3} Torr, (c) 9.0×10^{-3} Torr.

target of $c/a=1.048$ had crystal orientations which varied with small variations in the sputtering gas pressure. The effect of substrates on the crystal orientation of films can be explained by the mechanical stress on the films, which was caused by the difference in the thermal expansion coefficients between the films and substrates. Figure 5 shows the thermal expansion characteristics of the substrates and $PbTiO_3$ ceramics. The films deposited on single-crystal MgO suffered horizontal compressive stress along the plane of the film while being cooled from a T_s of 600°C to room temperature. Tensile stress, however, acted on the films fabricated on quartz glass substrates. It was thought that these mechanical stresses transformed the crystallized films into c-axis- and a-axis-oriented films at the Curie point, as illustrated in Fig. 6.

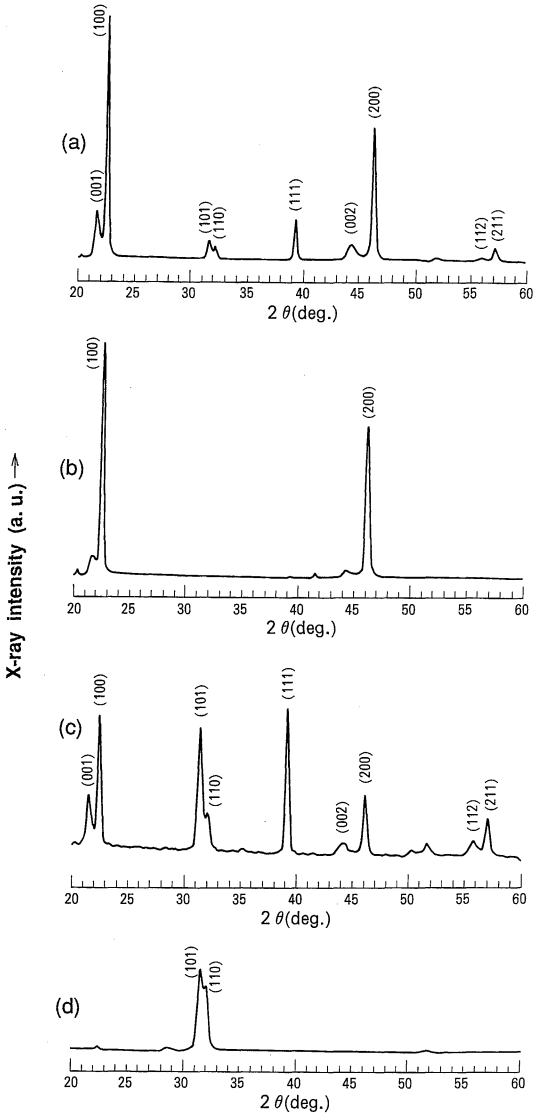

Fig. 4. X-ray diffraction patterns of $PbTiO_3$ ($c/a=1.048$) films on quartz glass. The sputtering conditions were T_s, 600°C; rf power, 200 W; $Ar/O_2=90/10$ Vol.%; sputtering gas pressure, (a) 8.8×10^{-3} Torr, (b) 9.2×10^{-3} Torr, (c) 1.3×10^{-2} Torr, (d) 3.0×10^{-2} Torr.

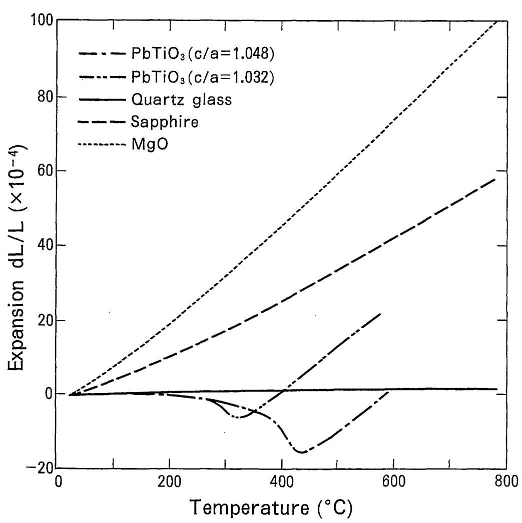

Fig. 5. Thermal expansion characteristics of various substrates and $PbTiO_3$ ceramics.

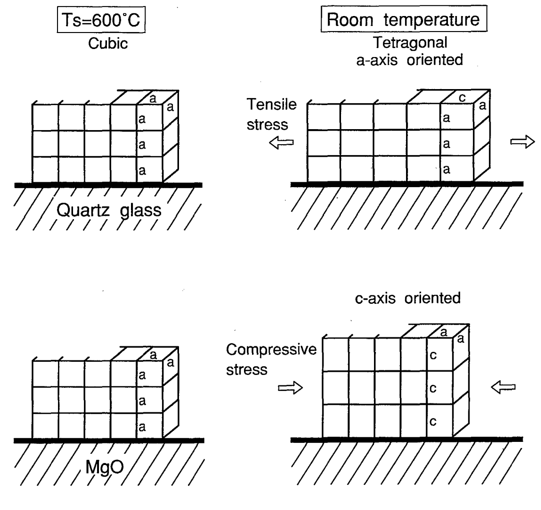

Fig. 6. Model of the effect of mechanical stresses on crystal orientation during cooling through a film's Curie point.

The effect of film composition on crystal orientation of the films was also investigated. For quartz glass substrates, We believe that the tensile stress on the film fabricated from a ceramic with a composition of $c/a=1.032$ was larger than that on the film produced from a ceramic of $c/a=1.048$ because the Curie point of the former film material was 110°C lower than that of the latter. As mentioned previously, *a*-axis-oriented films ($c/a=1.038$) were produced over a wide range of sputtering conditions, in particular, sputtering gas pressure, on quartz glass substrates. In the case where $c/a=1.048$, *a*-axis-oriented films were fabricated at only one particular sputtering gas pressure (refer to Fig. 4(b)).

The RHEED patterns of $PbTiO_3$ film surfaces with *c*-axis, *a*-axis, and (111)-direction orientations are shown in Fig. 7. Epitaxial films were fabricated on single-crystal MgO, and nearly epitaxial films on sapphire (r & c). In the case of a film surface on quartz glass, however, a ring pattern was observed. It was believed that in preparing

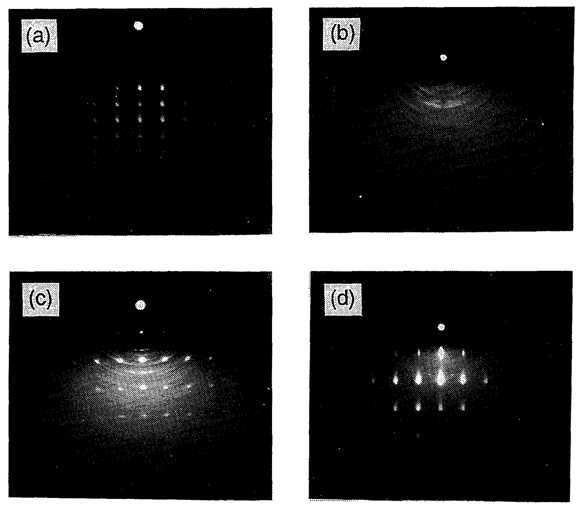

Fig. 7. RHEED patterns of crystal-oriented $PbTiO_3$ film surfaces: *c*-axis-oriented film on single-crystal MgO (a), *a*-axis-oriented film on quartz glass (b), (111)-direction-oriented film on r-plane sapphire (c), (111)-direction-oriented film on *c*-plane sapphire (d).

ferroelectric thin films both the crystallinity of substrates and the difference in the thermal expansion coefficients between the films and substrates had significant impact on the quality of the films.

3.3 *Glass ceramic substrates for c-axis-oriented films*[4)]

The crystal orientation of $PbTiO_3$ films must be aligned in the *c*-axis direction for the films to possess high remanent polarizations. To date, the substrates typically used to fabricate *c*-axis-oriented films were single-crystal MgO, which has a large thermal expansion coefficient of $140\times10^{-7}/°C$. In an effort to find lower-priced alternatives to single-crystal MgO, we investigated new substrates with large thermal expansion coefficients similiar to that of single-crystal MgO to allow *c*-axis crystal orientations. In this pursuit, glass ceramics composed mainly of α-quartz or cristobalite were used as substrates for *c*-axis-oriented films. Figure 8 shows the thermal expansion characteristics of the glass ceramics. When $PbTiO_3$ films were deposited on these glass ceramic substrates, the films were strongly oriented in the *c*-axis direction, as shown in Fig. 9.

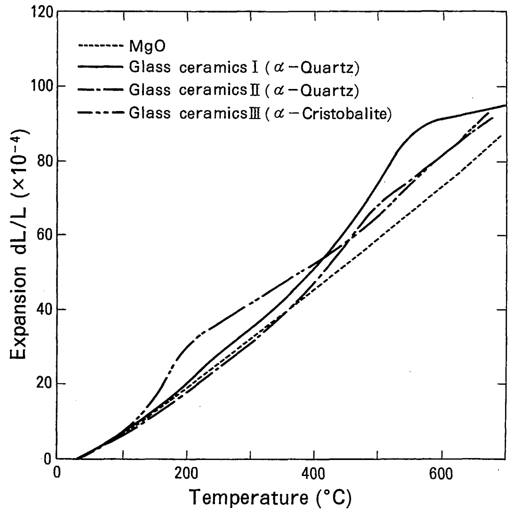

Fig. 8. Thermal expansion characteristics of glass ceramic substrates.

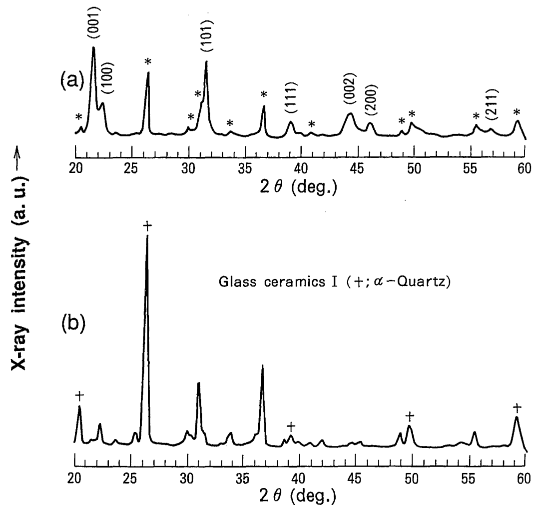

Fig. 9. X-ray diffraction patterns of $PbTiO_3$ ($c/a=1.048$) film on glass ceramics I (a), and the substrate (b). Diffraction lines from the substrate are shown with *'s.

§4. Conclusions

Utilizing mechanical stresses generated by the difference in thermal expansion coefficients between the substrates and films was found to be very useful in controlling the crystal orientations of $PbTiO_3$ thin films. The amount of stress, moreover, was controlled by changing the Curie points of the $PbTiO_3$ film materials. We investigated substrates which added compressive stresses to ferroelectric films, and in so doing, developed glass ceramic substrates for use in *c*-axis-oriented films as substitutes for single-crystal MgO.

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