

Mechanisms of Dielectric Constant Variations of SrTiO₃ Thin Films

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The dielectric constant variations of SrTiO₃ films, including the bias field dependence, thickness dependence, and grain size dependence have been numerically explained employing a thermodynamic approach.

1. INTRODUCTION

SrTiO₃ is an attractive dielectric for thin film capacitors because of its high dielectric constant [1]. Recent studies have revealed that the dielectric constant of SrTiO₃ thin films varies according to several factors, including the bias field, film thickness, and microstructure [2-4]. However, the mechanisms of these variations have not yet been clarified.

In this study, the thermodynamic approach was employed to explain the dielectric constant behaviors, considering the influences of the dielectric-electrode interfaces and the grain boundaries. To confirm such a theoretical approach, both epitaxially grown and polycrystalline SrTiO₃ thin films with various thicknesses were prepared, and their dielectric constants were measured.

2. THERMODYNAMIC THEORY OF THIN FILM DIELECTRICS

The free energy of a dielectric film, G_f , is assumed to be the sum of the energy of bulk G_b , the energy of the grain boundaries F_g , and the energy of the dielectric-electrode interfaces F_i .

$$G_f = G_b + n F_g / s + F_i / t, \quad (1)$$

where n denotes the dimension of the normal axes of the grain boundaries, s is the grain size, and t is the film thickness.

G_f should be a polynomial of the dielectric polarization P when the dielectric constant has a strong bias field dependence [1,5].

$$G_f = 1/2 c_1 P^2 + 1/4 c_3 P^4 + 1/6 c_5 P^6. \quad (2)$$

Not only G_b but also F_g and F_i could be a polynomial of P , g and that each coefficient c_i should be expressed by the following same form as a function of s and t .

$$c_i = a_i + n g_i / s + b_i / t, \quad (3)$$

$$(i = 1, 3, 5)$$

When the values of a_i , g_i and b_i are given, the dielectric constants can be calculated from G_f by the following equation.

$$\epsilon_r = 1 / \{ \epsilon_0 (\partial^2 G_f / \partial P^2) \} + 1 \quad (4)$$

3. PREPARATION OF SrTiO₃ FILMS

Both epitaxially grown and polycrystalline SrTiO₃ film capacitors with various dielectric thicknesses, 23, 46, 69, and 92 nm, were prepared.

First, epitaxially grown and

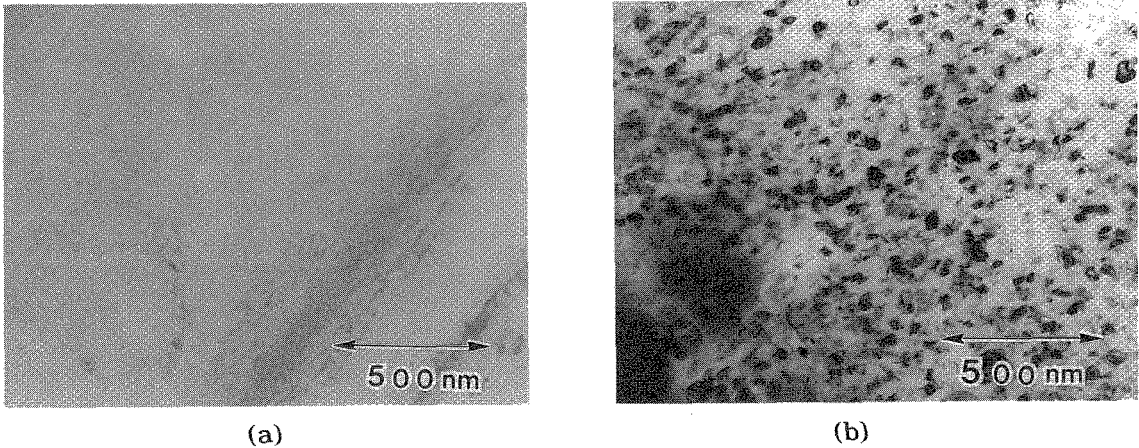


Fig.1 TEM images of SrTiO_3 films with (a) epitaxially grown structure, and (b) polycrystalline structure.

polycrystalline Pt films were prepared as bottom electrodes on $\text{MgO}(100)$ single crystal substrates. The epitaxial Pt films were grown holding the substrates at 400°C , while the polycrystalline films were deposited at room temperature. Both depositions were carried out by rf magnetron sputtering in an Ar atmosphere (0.8 Pa).

Next, both epitaxial and polycrystalline SrTiO_3 films were deposited at the same time on these Pt films. These depositions were also carried out by rf magnetron sputtering at 400°C in Ar/O_2 (=4/1) gas under a pressure of 0.7 Pa. The crystal structure and orientations of the SrTiO_3 films were confirmed by XRD and reflection high energy electron diffraction (RHEED) [4]. No grain boundary was observed in the transmission electron micrograph (TEM) images of the epitaxially grown SrTiO_3 film, as shown in Fig.1(a), while many grain boundaries were observed in the polycrystalline films, as shown in Fig.1(b). The grain size of SrTiO_3 was estimated to be about 50 nm.

Lastly, Ni films were deposited as top electrodes also by rf sputtering in Ar gas (0.8 Pa) at 350°C . The Ni films were chemically etched to form square top electrodes with an area of $0.1 \times 0.1 \text{ mm}$.

4. MEASUREMENT OF THE DIELECTRIC CONSTANT

The dielectric properties were measured at 100 kHz, 0.1 Vrms with an LCR meter (4275A, Yokogawa Hewlett-Packard) at room temperature as a function of the bias field. The bias field was varied from -100 to 100 MV/m.

The dissipation factors exhibited a very small bias field dependence, ranging from 0.01 to 0.02. On the other hand, dielectric constants showed a strong bias field dependence. Figures 2(a) and (b) show the ϵ_r -E characteristic both for the epitaxial and polycrystalline SrTiO_3 films, respectively. The maximum dielectric constants were taken around zero bias field. A stronger bias field application brought about a smaller dielectric constant.

A thinner dielectric film also resulted in a smaller dielectric constant at zero bias field. However, when a strong bias field was applied, the dielectric constants took very close values with each other, indifferent to the film thickness.

Compared within the same thickness, the polycrystalline films exhibited a smaller dielectric constant than the

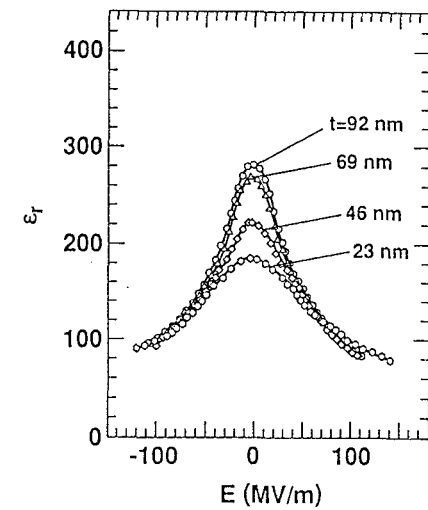
epitaxially grown films. However, when a strong bias field was applied, the difference was also reduced.

The energy function parameters c_i ($i=1, 3, 5$) in Eq.(2) were estimated from the individual ϵ_r -E characteristics by the least squares method. The parameters were plotted as a function of the inverse thickness ($1/t$), as shown in Fig. 4.

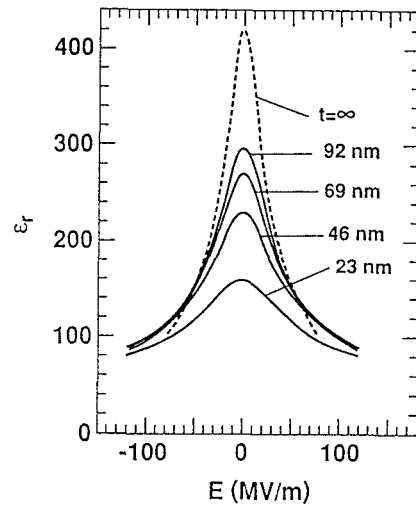
5. NUMERICAL CALCULATIONS

The dielectric constant variations of the SrTiO_3 thin films were calculated from the theoretical equations, Eqs.(1) to (4). Figures 3(a) and 3(b) show the calculated ϵ_r -E characteristic both for the epitaxial and polycrystalline films, respectively.

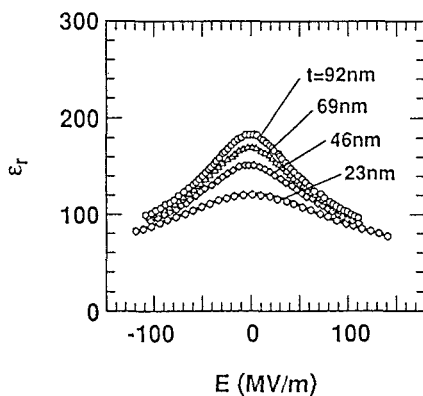
In the calculation for the epitaxially grown films, the influence



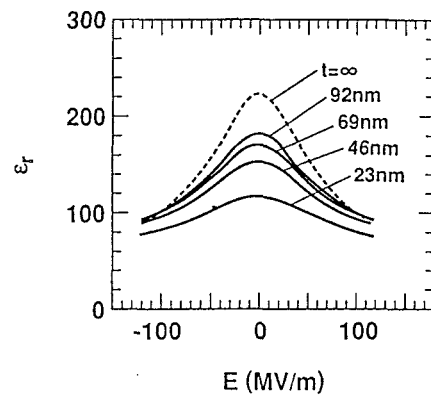
(a)



(a)



(b)



(b)

Fig.2 ϵ_r -E characteristics for SrTiO_3 of (a) epitaxially grown films, and (b) polycrystalline films, at 22 °C.

Fig.3 Theoretical calculation of ϵ_r -E characteristic for (a) epitaxially grown, and (b) polycrystalline films.

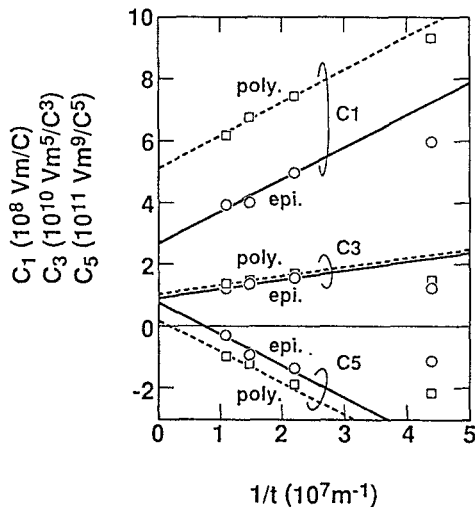


Fig.4 Coefficients c_1 , c_3 , and c_5 as functions of inverse film thickness, measured at 22 °C.

of the grain boundaries was ignored. The unknown parameters a_i and b_i in Eq.(3) were separated and determined as listed in Table I, from the inverse thickness ($1/t$) dependences of c_i (Fig. 4).

As for the polycrystalline films, the dimensional number n in Eq.(3) was assumed to be 2, since the grains were considered to have a columnar structure. The grain size s was assumed to be 50 nm from the TEM image (Fig.1(b)). The unknown parameter g_i was determined as listed in Table I from the difference in c_i between the epitaxial and polycrystalline films.

The agreement between the experimental result and the theoretical calculation demonstrates the validity of the theory and the determined parameters.

6. CONCLUSIONS

A thermodynamic approach was employed to explain the dielectric constant variations in SrTiO_3 thin films. The authors successfully

Table I Thermodynamic coefficients for SrTiO_3 thin films at 22 °C. $n=2$ and $s=50$ nm were assumed.

(a) Bulk coefficients

a_1	a_3	a_5
(10^8 VmC^{-1})	$(10^{10} \text{ Vm}^5 \text{C}^{-3})$	$(10^{11} \text{ Vm}^9 \text{C}^{-5})$
2.7	0.95	0.75

(b) Interface coefficients

b_1	b_3	b_5
$(10 \text{ Vm}^2 \text{C}^{-1})$	$(10^3 \text{ Vm}^6 \text{C}^{-3})$	$(10^4 \text{ Vm}^{10} \text{C}^{-5})$
1.06	0.31	-1.0

(c) Grain boundary coefficients

g_1	g_3	g_5
$(10 \text{ Vm}^2 \text{C}^{-1})$	$(10^3 \text{ Vm}^6 \text{C}^{-3})$	$(10^4 \text{ Vm}^{10} \text{C}^{-5})$
0.60	0	-0.35

distinguished the influence of the grain boundary from the influence of the dielectric-electrode interface, using epitaxially grown and polycrystalline SrTiO_3 films with various thicknesses. The agreement between the theoretical calculations and experimental results indicate that a thinner film or a smaller grain inevitably results in the lowering of dielectric constant. Microscopic studies on the interfaces and grain boundaries are required for further understanding of their size effects.

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