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Structure and dielectric properties of amorphous SrTiO3 thin films at elevated temperatures

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Thin amorphous films of strontium titanate were prepared by sputtering a $SrTiO_3$ powder target with a neutralized ion beam. Structural observations by X-ray diffraction and transmission electron microscopy revealed that the amorphous films crystallized into cubic $SrTiO_3$ by annealing at a temperature ≥723 K for 1 h. Dielectric properties of the amorphous films were measured as a function of temperature over a frequency range from 10^2 to 10^5 Hz. The results showed that within this frequency range a marked dielectric relaxation occurred below the crystallization temperature. The relaxation process is found to be well described by the Cole-Cole relation.

1. INTRODUCTION

Since strontium titanate ($SrTiO_3$) is a stable paraelectric material having a rather high bulk dielectric permittivity around room temperature, various applications to electronic devices are widely investigated [1-3]. Most of these works are concerned mainly with crystalline films, which were prepared by deposition above crystallization temperature or by post annealing of amorphous films [4-6]. In contrast, rather a few studies are available for the dielectric properties of amorphous film itself [5-8]. It has been found that amorphous films fabricated from ferroelectric materials, e.g. $LiNbO_3$, showed a dielectric anomaly near the crystallization temperature [9]. It seems also interesting to examine the dielectric behavior of amorphous films prepared from paraelectric materials. The aim of this work is to investigate the temperature dependence of the dielectric properties of thin amorphous $SrTiO_3$ films and to discuss the results based on dielectric relaxation.

2. EXPERIMENTAL PROCEDURE

Thin films were prepared by an ion-beam sputtering method. A neutralized argon ion-beam was employed to deposit the films. A target for sputtering was pressed powders of $SrTiO_3$ with commercial purity. Thin films were formed on glass (Corning #7059) and cleaved (001) NaCl substrates at an ambient temperature. The thickness of the films ranged 100 to 300 nm depending on the purpose of experiments. Thin films for electrical measurements were formed on the glass substrates on which platinum strips with 1 mm wide were pre-sputtered.

Structural properties of the films were evaluated by X-ray diffraction (XRD) using Cu Kα radiation, and by transmission electron microscopy (TEM) operating at 200 kV. For XRD and electrical measurements, samples deposited on glass substrates were used, and those for TEM were prepared from the films deposited on NaCl substrates by dissolving NaCl and mounting on platinum grids. Thermal annealing treatments were performed at a temperature below 973 K for 1 h in air. For measuring dielectric properties, 1 mm wide aluminum strips were deposited on the top surface of the films to form a metal (Al) / insulator (a-$SrTiO_3$) / metal (Pt) (MIM) configuration.

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The capacitance, C, and dissipation factor, $\tan\delta$, of the MIM structure were measured as a function of frequency in a temperature range 300-800 K under a flowing argon atmosphere. The real part of permittivity, ε' was obtained from C and the geometry of the metal contacts according to the relation; $\varepsilon' = C\ t\ /\ (S\ \varepsilon_0)$, where ε_0 is the permittivity of vacuum, t the thickness of the dielectric film (~300 nm) and S the area of the metal contact (~1 mm^2). The imaginary part of permittivity, ε'', was estimated by the relation; $\varepsilon'' = \varepsilon' \tan\delta$. The chemical composition of the films was analyzed with the help of an energy dispersive X-ray spectrometer. The results indicated that the atomic ratio of Sr / Ti was close to unity, irrespective of the heat treatments.

3. RESULTS AND DISCUSSION

3. 1. Structural observation

Typical X-ray diffraction patterns from the as-prepared and annealed films are shown in Fig. 1. The pattern for the as-prepared film consists of only a very broad peak. Although the contribution from the glass substrate can not be ignored, a part of diffuse peak around $2\theta = 30°$ is assumed to be due to the amorphous phase of $SrTiO_3$. After annealing at 773K, a sharp diffraction peak came to appear,

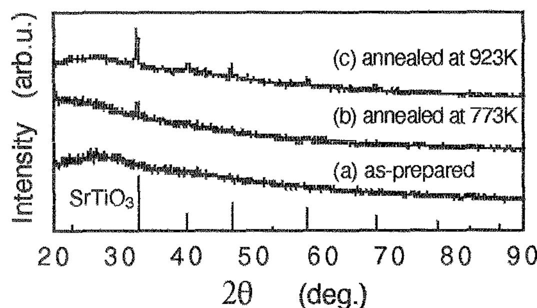

Fig. 1 X-ray (Cu Kα) diffraction patterns for $SrTiO_3$ films; (a) as-prepared, (b) 773 K annealed and (c) 923 K annealed.

indicating the crystallization of the amorphous film. Further annealing at 923 K for 1 h yielded a number of peaks, which can be indexed in terms of the $SrTiO_3$ phase (cubic perovskite, a = 0.3905 nm). Figure 2 shows high resolution electron micrographs and corresponding selected area diffraction patterns for the as-prepared and 723 K annealed samples; both of which exhibited a halo-like diffraction pattern as well as the bright field image characteristic of an amorphous phase. Accordingly, it is concluded that the ion-beam sputtered $SrTiO_3$ films are in an amorphous state below about 773 K, and are crystallized into the cubic $SrTiO_3$ phase with increasing temperature up to about 923 K.

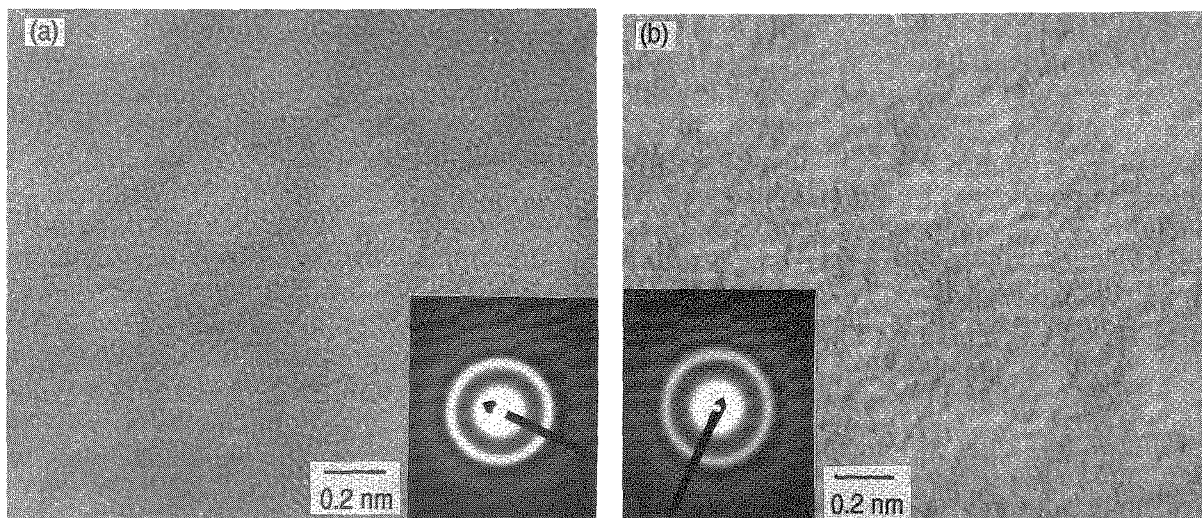

Fig. 2 High resolution electron micrographs and selected area diffraction patterns for thin films of $SrTiO_3$; (a) as-prepared and (b) annealed at 723 K.

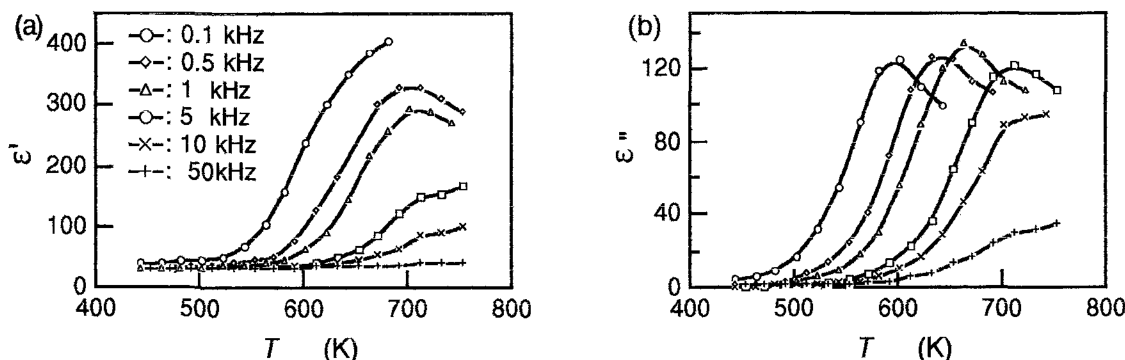

Fig. 3 Temperature dependence of dielectric permittivities of amorphous $SrTiO_3$ films at different frequencies; (a) ε' and (b) ε".

3. 2. Temperature and frequency dependence of dielectric parameters

Temperature dependence of the dielectric parameters for the $SrTiO_3$ amorphous films was measured as a function of frequency; Figure 3 shows the change in the real part (ε') and imaginary part (ε") of dielectric permittivities with temperature and frequency. It is clearly seen that both ε' and ε" increased and attained a peak as the temperature raised. The peak temperature increased with increasing measuring frequency. The frequency dispersion of the dielectric parameters is given in Fig. 4. Decreasing behavior in the plots of ε' and the appearance of maxima in ε" with the increase in frequency suggest the dielectric relaxation occurring in a frequency range between ~10^2 and 10^5 Hz at temperatures higher than about 500 K.

In Fig. 5, ε" was plotted with respect to the corresponding ε' (Cole-Cole plots). These plots can be fitted well to a hemicircle with the angle of about 0.8 π, almost independent of temperature. This indicates that the operating relaxation process was accompanied with some amounts of distribution in the relaxation time. The figure also exhibits two limiting values of the permittivity; the high frequency limit $\varepsilon'_\infty = 30$ and static permittivity $\varepsilon'_s = 390$. The activation energy *(E)* for the dielectric relaxation can be estimated from the frequency dependence on the peak temperatures of the dissipation loss, as shown in Fig. 6. The least square fits of these plots enabled the estimation of the activation energy of about 1.1 eV.

3. 3. Evaluation of dielectric relaxation

It is known that the Debye-type dielectric relaxation can be written by the Cole-Cole relation in the complex form;

$$\varepsilon_{complex} = \varepsilon'_\infty + (\varepsilon'_s - \varepsilon'_\infty) / \{1 + (i\omega\tau)^\beta\}, \quad (1)$$

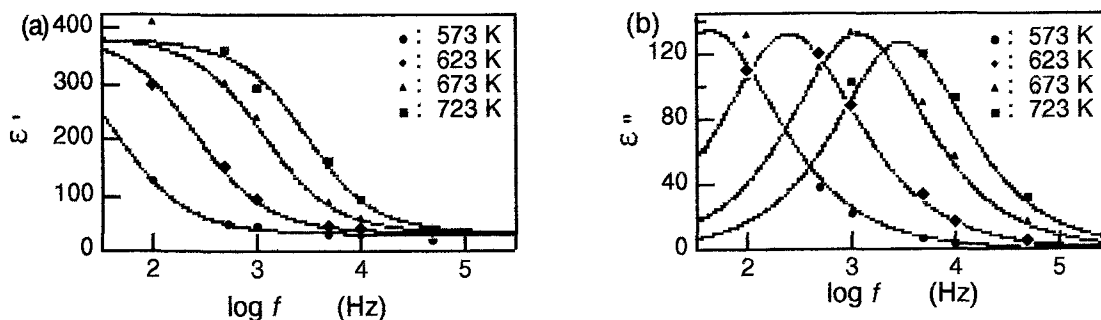

Fig. 4 Frequency dependence of dielectric permittivities for amorphous $SrTiO_3$ films at different temperatures; (a) ε' and (b) ε". Symbols indicate experimental points and solid curves are calculated by using eqs. (2) - (4)..

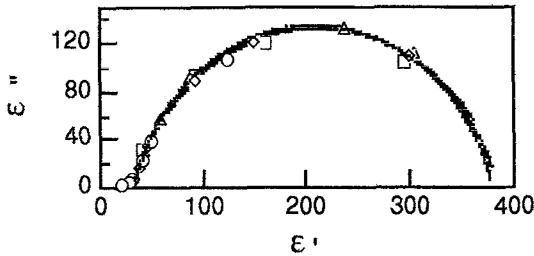

Fig. 5 Cole-Cole plot (ε" vs ε') for a-$SrTiO_3$. Symbols: experimental, solid curve: calculated.

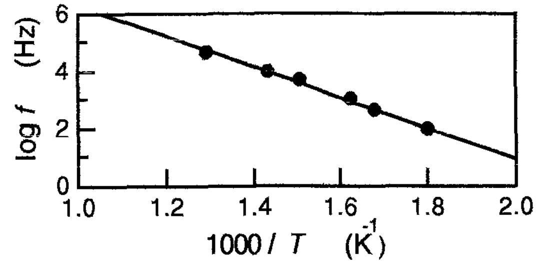

Fig. 6 Arrhenius plot of frequency vs inverse of peak temperature of tanδ.

where ω is the angular frequency (= 2πf), τ the relaxation time, and β a factor relating to the distribution of the relaxation time. Here the the relaxation time is thought to depend on temperature according to the following relation;

$$\tau = \tau_0 \exp(E / kT), \qquad (2)$$

where τ_0 is the relaxation time at the temperature T -> ∞ and k the Boltzman constant. From eq. (1), both the real and imaginary parts of the dielectric permittivities are expressed in terms of the Cole-Cole relations as follows;

$$\varepsilon' = \varepsilon'_\infty + \frac{(\varepsilon'_s - \varepsilon'_\infty)\{1 + (\omega\tau)^\beta \sin(1-\beta)\pi/2\}}{1+2(\omega\tau)^\beta \sin(1-\beta)\pi/2 + (\omega\tau)^{2\beta}}, \qquad (3)$$

$$\varepsilon'' = \frac{(\varepsilon'_s - \varepsilon'_\infty)(\omega\tau)^\beta \cos(1-\beta)\pi/2\}}{1+2(\omega\tau)^\beta \sin(1-\beta)\pi/2 + (\omega\tau)^{2\beta}}. \qquad (4)$$

By applying the relaxation parameters obtained in this work to the equations (2), (3) and (4), the temperature and frequency dispersions of ε' and ε" were calculated; the results are represented by solid curves in Figs. 4, and 5. It is apparent that the calculated curves agreed well with the experimental points below about 700 K. The pre-exponential factor, τ_0 in eq.(2) was estimated to be 8 x 10^{-13} sec, which is characteristic to an ionic process for the relaxation. Accordingly, the dielectric relaxation in the $SrTiO_3$ amorphous film is regarded as being governed by the Cole-Cole type of a dipolar relaxation model. At higher temperatures > 700 K, structural changes towards the crystallization seem to influence the relaxation behavior, resulting in the deviation from the Cole-Cole relations.

4. SUMMARY

Amorphous $SrTiO_3$ films exhibited a remarkable dielectric relaxation in a frequency range from 10^2 to 10^5 Hz at temperatures ≥500 K. The activation energy for the relaxation was estimated to be 1.1 eV with τ_0 = 8 x 10^{-13} sec. Both the temperature and frequency dipersion of dielectric permittivities were well described by the Cole-Cole relation.

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