Dielectric loss and defect mode of SrTiO$_3$ thin films under direct-current bias

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(Received 2 November 2000; accepted for publication 5 March 2001)

The dielectric behavior of SrTiO$_3$ thin films prepared by the pulsed-laser deposition technique on SrTiO$_3$ single-crystal substrates is studied under dc electric field. A high dielectric constant maximum $\varepsilon_{\text{max}}$ ($\sim$2280) and a low-loss tan $\delta$ ($\sim$0.001) are obtained. Compared with the observation in SrTiO$_3$ single crystals, an additional dielectric loss peak with frequency dispersion is observed around 150 K (at 1 kHz). With increasing dc bias, the peak is suppressed and finally disappears at $\sim$350 kV/cm; however, the temperature at which the peak occurs is independent of electric field. The possible physical mechanism of the peak is briefly discussed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1367299]

Currently, one of the most studied dielectric materials for tunable microwave devices 1,2 is the perovskite SrTiO$_3$. 3–6 The incipient ferroelectric SrTiO$_3$ shows a high nonlinear electric field effect at low temperatures and a reasonably low dielectric loss tan $\delta$ ($\sim$10$^{-4}$). 3,4 However, it is also found that when SrTiO$_3$ is made as a thin film, the dielectric loss is increased by more than an order of magnitude (tan $\delta$ $\sim$10$^{-2}$). 5–7 The understanding of the physical nature of the dielectric loss in SrTiO$_3$, especially under high dc electric field is highly desirable. However, studies of the dielectric loss under high dc electric field for SrTiO$_3$ single crystals and thin films are scarce. 8

Recently, with the progress in the preparation process of thin films, especially, by pulsed-laser deposition, high-quality thin films have been prepared with high $\varepsilon_{\text{max}}$ ($\sim$2000) and low-loss tan $\delta$ ($\sim$10$^{-5}$). 9 This indicates that thin films have become very promising candidates for practical applications. However, it is reported that for these thin films, some additional dielectric loss peaks appear around 70 and 150 K. 9,10 Obviously, understanding of this additional loss peak is important.

In this letter, we report on the dielectric behavior of SrTiO$_3$ thin films deposited on SrTiO$_3$ single-crystal substrates by pulsed-laser deposition. Under high dc electric fields up to 350 kV/cm, it is found that a noticeable dielectric loss peak with frequency dispersion is present around 150 K (at 1 kHz). The peak is suppressed and finally disappeared with increasing dc bias, but the temperature at which the dielectric loss peak occurs does not change. This implies that the dielectric loss peak is a “defect mode” (or “impurity mode”), which might relate to the soft mode behavior of the host lattice of SrTiO$_3$.

SrTiO$_3$ thin-film samples with a thickness of 1 $\mu$m were prepared by the pulsed-laser deposition technique on SrTiO$_3$ single-crystal substrates. The samples adopt a parallel-plate capacitor structure, i.e., Au/SrTiO$_3$ thin-film/SrRuO$_3$/SrTiO$_3$ single-crystal substrate. First, a thin layer SrRuO$_3$ layer was deposited on the SrTiO$_3$ single-crystal substrate as a bottom electrode, then the SrTiO$_3$ thin film was deposited on the SrRuO$_3$ layer, and finally, a layer of gold was deposited on the SrTiO$_3$ thin film as a top electrode.

The complex dielectric permittivity was measured using an HP 4284A LCR meter with an ac field of 100 mV/µm. The temperature dependence of the dielectric properties was measured in a cryostat system (ADP202 Cryostat) in the temperature range 12–300 K, and under a vacuum of better than 10$^{-4}$ Torr. The dc voltage was applied to the sample and a blocking circuit was adopted to separate the high dc voltage from the LCR meter.

The typical dielectric behavior for the SrTiO$_3$ thin-film samples is shown in Fig. 1(a). It can be seen that $\varepsilon$ increases continuously with decreasing temperature, attaining the

![Figure 1](image)

*FIG. 1. (a) Temperature dependence of $\varepsilon$ and tan $\delta$ for the SrTiO$_3$ thin-film sample at 0.1, 1, and 10 kHz (tan $\delta$ peaks: from left to right; $\varepsilon$: the data overlap each other). The inset shows the temperature dependence of the relaxation rate (circles: experimental data; solid line: the Arrhenius law). (b) Fit to the Barrett relation (circles: experimental data; solid curve: the Barrett relation).*
value 2280 at 12 K. As shown in Fig. 1(b), the \( \varepsilon \) could be fitted well to the Barrett relation \(^1\)

\[
\varepsilon = C[(T/2)\coth(T/2T_0) - T_0],
\]

with \( T_1 = 128 \text{ K}, T_0 = 26.4 \text{ K}, \) and \( C = 8.5 \times 10^4 \text{ K}. \) Compared with the parameters obtained in SrTiO\(_3\) ceramics \( (T_1 = 84 \text{ K}, T_0 = 25.1 \text{ K}, \) and \( C = 8 \times 10^3 \text{ K}) \), \(^1\) and single crystal \( (T_1 = 84 \text{ K}, T_0 = 35.5 \text{ K}, \) and \( C = 8 \times 10^4 \text{ K}) \), \(^1\) these values are reasonable. For dielectric loss tan \( \delta \), as \( T < 50 \text{ K} \), the tan \( \delta \) increases quickly, corresponding to the increase in \( \varepsilon \). This is also similar to the behavior observed in SrTiO\(_3\) ceramics or single crystals.

Compared with the observation in SrTiO\(_3\) single crystals, an additional dielectric loss peak with frequency dispersion is observed around 150 K (at 1 kHz) for the thin film, hereafter denoted as mode I. A similar peak has been also observed in other samples. The relaxation rate for the polarization derived from the temperature dependence of the imaginary part of the permittivity for the sample is plotted in the inset of Fig. 1(a). The data were fitted to the Arrhenius law

\[
\nu = \nu_0 \exp\left[\frac{U}{k_B T}\right],
\]

where \( \nu_0 \) is the attempt frequency, \( U \) is the activation energy for relaxation, and \( T \) is the temperature. The fit parameters are \( U = 0.25 \text{ eV} \) and \( \nu_0 = 1 \times 10^{11} \text{ Hz} \).

By applying dc electric fields, the dielectric behavior is greatly modulated. Figure 2 shows the temperature dependence of the dielectric behavior in the electric-field range of 10–80 kV/cm at frequencies of 0.1, 1, and 10 kHz. It can be seen that a broad dielectric constant peak, denoted as peak A, is induced; this is similar to the peak that has been widely reported in the earlier literature in SrTiO\(_3\) single crystals. \(^8\),\(^1\)\(^4\)–\(^1\)\(^6\) Peak A induced by the electric field in the \( \varepsilon \) vs. \( T \) curve indicates the occurrence of an “electric-field-induced peak,” which was assigned to a “ferroelectric peak” by some authors. \(^1\)\(^4\)–\(^1\)\(^6\) On the other hand, for mode I around 150 K, although the intensity decreases with the increasing electric field, the relaxation rate follows the Arrhenius law with almost same activation energy \( U \) and attempt frequency \( \nu_0 \), and the temperature of mode I remains almost the same.

In order to explore further the nature of the dielectric behavior under dc electric fields, the dc electric field was extended to 350 kV/cm. As shown in the inset of Fig. 3, with increasing electric field, the intensity of mode I (tan \( \delta \) peaks) continually decreased, and finally disappears at \( \sim 350 \text{ kV/cm} \). However the temperature \( (T_m) \) at which the tan \( \delta \) peak occurs is independent of the electric field. This is different from any “ordered phase” or “induced ferroelectric peak,” whose temperature increases with increasing electric field, \(^8\),\(^1\)\(^4\)–\(^1\)\(^6\) but is similar to the so-called “defect mode” (or “impurity mode”) observed in SrTiO\(_3\) doped with Bi. \(^1\)\(^2\) This indicates that mode I is due to some defect/impurity effects, rather than an intrinsic mechanism (lattice vibration).

It is well known that SrTiO\(_3\) is a typical soft mode incipient ferroelectric. \(^1\) In SrTiO\(_3\) samples, even for high-quality SrTiO\(_3\) single crystals, low concentration unavoidable defects/impurities (for example, oxygen vacancies), and/or strain due to the mismatch between the film and the substrate may be present, hence, some dielectric anomalies, especially in the \( \varepsilon '' \) part, can be observed. This has been confirmed in many studies. \(^1\)\(^2\),\(^1\)\(^7\)–\(^1\)\(^9\) In the present work, for the SrTiO\(_3\) thin film, the concentration of defect/impurity and strain is expected to be higher than that of single crystals. We suggest that mode I is similar to the defect mode (or impurity mode) observed in single-crystal SrTiO\(_3\) (Ref. 8) and Bi: SrTiO\(_3\), \(^1\)\(^7\) and could be attributed to reorientation and/or hopping of the dipoles formed by the defect/impurity interacting with the soft modes of the lattice of SrTiO\(_3\).

For the reorientation of the dipoles, the polarization strength can be qualitatively described by the Debye–Langevin model. \(^1\)\(^0\) Adopting the modified Debye–Langevin model, the polarization step can be written as

\[
\Delta \varepsilon = nq^2 \delta^2 / k_B T,
\]
where \( n \) is the concentration of the dipoles, \( q \) is the number of electrons, and \( \delta \) is the effective dipole moment taking into account of the coupling effect between the dipole and the lattice. As mentioned above, the relaxation rate versus temperature follows the Arrhenius law, and the \( T_m \) is independent of the electric field, i.e., the infinite frequency \( \nu_0 \) and the potential barrier remain the same with increasing dc electric field; however, the intensity of the peak is greatly suppressed with increasing electric field. This implies that application of the dc bias has no influence on the frequency of the reorientation of the dipoles and the potential barrier. However, the local environment of the dipole is modulated, in other words, the coupling between the dipoles (formed by defects and/or impurities) and the lattice vibration—soft mode is modified by the application of the dc electric field, i.e., the effective dipole moment \( \delta \) in Eq. (3) is modulated. In fact, from the previous work of Fleury and Worlock,\(^{16} \) we know that the soft modes of SrTiO\(_3\) can be “harden” by increasing dc bias. In the present work, with increasing dc bias, the system also becomes more and more “stiff,” and the effective dipole moment \( \delta \) decreases, which leads to the decrease in the intensity of the polarization step. Obviously, this phenomenon is expected to be observed in the so-called “soft-mode materials,” in which the system is soft, the matrix has high polarizability, and the polarization effect of the defects and/or impurities can be greatly amplified, and their polarization gives the high permittivity. Indeed, two phonon-assisted impurity dielectric modes were observed in Bi:SrTiO\(_3\),\(^{12} \) whose activation energies of the dielectric relaxation are exactly the same as those of the phonons observed. In Li-doped KTaO\(_3\),\(^{21} \) a dielectric relaxation peak was also observed with activation energies of the dielectric relaxation of 0.22 eV. At this moment, a detailed physical picture is not clear, and further studies need to be conducted.

The dielectric behavior of SrTiO\(_3\) thin films deposited on SrTiO\(_3\) single-crystal substrates is reported in this letter. Compared to results of the SrTiO\(_3\) single crystals, an additional dielectric loss peak with frequency dispersion is observed around 150 K (at 1 kHz). This peak is suppressed and finally disappears with increasing dc bias, however, the temperature at which the loss peak occurs is independent of the electric field. This peak is attributed to the defect mode or impurity mode, which comes from the coupling effect between the dipoles of the defects/impurities and the soft mode of the host lattice of SrTiO\(_3\). This work was supported by a grant from DARPA under Contract No. DABT63-98-1-002. The authors would like to thank Dr. X. X. Xi for his helpful discussion.

\(^{1} \) O. G. Vendik, Ferroelectrics \textbf{12}, 85 (1976).