J Mater Sci (2007) 42:389–392
DOI 10.1007/s10853-006-1088-2

LETTER

Effect of oxygen vacancies on nonlinear dielectric properties of $SrTiO_3$ thin films

X. Z. Liu · B. W. Tao · Y. R. Li

Received: 3 June 2005 / Accepted: 2 October 2006 / Published online: 6 December 2006
© Springer Science+Business Media, LLC 2006

Ferroelectrics (FE) are a class of nonlinear dielectrics which exhibit an electric field dependent dielectric constant. High temperature superconductors (HTSC) offer lower microwave surface resistance than conventional materials. There have been significant interest and effort in combining the low microwave losses of HTSC with the voltage control of FE dielectric constant ε_r to implement high quality voltage tunable microwave devices, such as phase shifters, filters, delay lines, and tunable oscillators [1–4]. In such devices, it is desirable to have a large capacitance change ratio [tunability = $(C_{max}–C_{min})/C_{max}$] under a certain electric field range accompanied by a small dielectric loss. $SrTiO_3$ (STO) thin films which posses a transition peak located at 60–70 K is one of the most interesting FE materials due to its high nonlinearity and reasonably low dielectric loss.

A main focus on research for effective utilization of STO thin films is the development of materials with simultaneously optimized permittivity (absolute magnitude as well as its electric field dependence.) and low dielectric loss (tanδ). However, the tunability and dielectric loss in STO thin films have not been comparable to that of bulk materials. Comparing with STO single crystal, most STO thin films showed low dielectric constant, low tunability and large dielectric loss. Many reasons have been suggested to the degradation in dielectric properties of STO thin films. The tetragonal distortion (ratio of in-plane and surface normal lattice parameters, $D = a/c$), the dead layer near interface, and the local polar regions near charged defects like oxygen vacancies are expected to degrade the dielectric properties of STO thin films [5–7].

Several researchers have investigated the effect of oxygen vacancies on dielectric properties of hetero-epitaxially grown STO thin films [8, 9]. It is worthwhile to note that the study of oxygen vacancies on dielectric properties of hetero-epitaxial STO thin films is complicated because of the additional effect of film stress due to film-substrate crystal lattice mismatch and difference in thermal expansion coefficients. There have been no systematic studies on the influence of oxygen vacancies on dielectric properties of STO thin films. In this study, STO thin films were homo-epitaxially grown on Nb doped STO (Nb:STO) substrate. No additional stress is caused by lattice constant mismatch and thermal expansion coefficient differences between films and substrate in the homo-epitaxial STO thin films. The effect of oxygen vacancies on dielectric properties of STO thin films are presented.

STO thin films were deposited on Nb:STO substrates by pulsed laser deposition (PLD). KrF excimer laser radiation (Lamda Physik Compex 201) with repetition rate of 5 Hz was focused on a rotating target set in the chamber through a quartz window. The incident angle of laser beam to the target surface was fixed to be 45°. The output laser pulse energy was kept as 150 mJ which yielded a growth rate of 0.02 nm per pulse. The laser energy density was about 2 J/cm^2.

X. Z. Liu · B. W. Tao (✉) · Y. R. Li
The National Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science & Technology of China, Jianshe Road, Chengdu 610054, China
e-mail: bwtao@uestc.edu.cn

X. Z. Liu
e-mail: xzliu@uestc.edu.cn

The film thickness was kept to be 500 nm. A piece of STO single crystal was adopted for target to suppress droplet creation during PLD process. Substrates were placed parallel to the target surface with a target-substrate distance of 50 mm. Pure oxygen, which was introduced into the chamber through a needle valve, was used as reactive agent during deposition. The pressure during deposition was varied from 1 Pa to 20 Pa. The substrate was heated to 740 °C by radiation from a Pt resistive heater aided with an embedded thermocouple. After deposition the samples were cooled inside the chamber to room temperature keeping the oxygen pressure constant.

For low frequency dielectric property measurements, parallel capacitors were made by evaporating Au films onto the STO thin films through shadow masks as the top electrode. The Nb:STO substrate was used as the bottom electrode. The area of top electrode was 0.2 mm^2. Capacitance and dielectric dissipation of the capacitors were measured using a LCR meter with a signal level of 0.1 Vrms. The leakage current were measured using a digital multimeter. In the measurements of *C–V* and *I–V* characteristics, bias was applied to the Au top electrode, and the Nb:STO substrate was connected to a ground terminal. Atomic force microscopy (AFM) was employed to characterize the surface morphology of STO thin films.

Although the oxygen ambient is used to prevent the formation of oxygen vacancies in the deposited film, it has been shown that oxide films grown using PLD are still oxygen deficient. The concentration of oxygen vacancies is closely related to oxygen partial pressure during deposition. The dielectric properties of STO thin films deposited at different oxygen partial pressures are shown in Fig. 1. For STO thin films grown at 10 Pa oxygen pressure, when the biased DC electric field was 200 kV/cm, the dielectric constant percent tunning was 47%, and the maximum dielectric loss tangent was 1.2%. However for STO thin films deposited at 2 Pa oxygen pressure, even with an applied DC electric field of 100 kV/cm, the dielectric constant percent tunning was 53%, and the maximum dielectric loss tangent was 0.55%. It has been suggested that STO thin films deposited at low oxygen pressure have higher oxygen vacancy concentration than those deposited at high oxygen pressure. Oxygen vacancies affect the nearest neighbor distance by reducing the Coulomb attractive force between cation and anion atoms, resulting in an increased lattice parameter and increased dielectric tunability.

It was expected that higher dielectric percent tunning could be displayed with higher DC electric field. However, when the bias electric field applied on STO

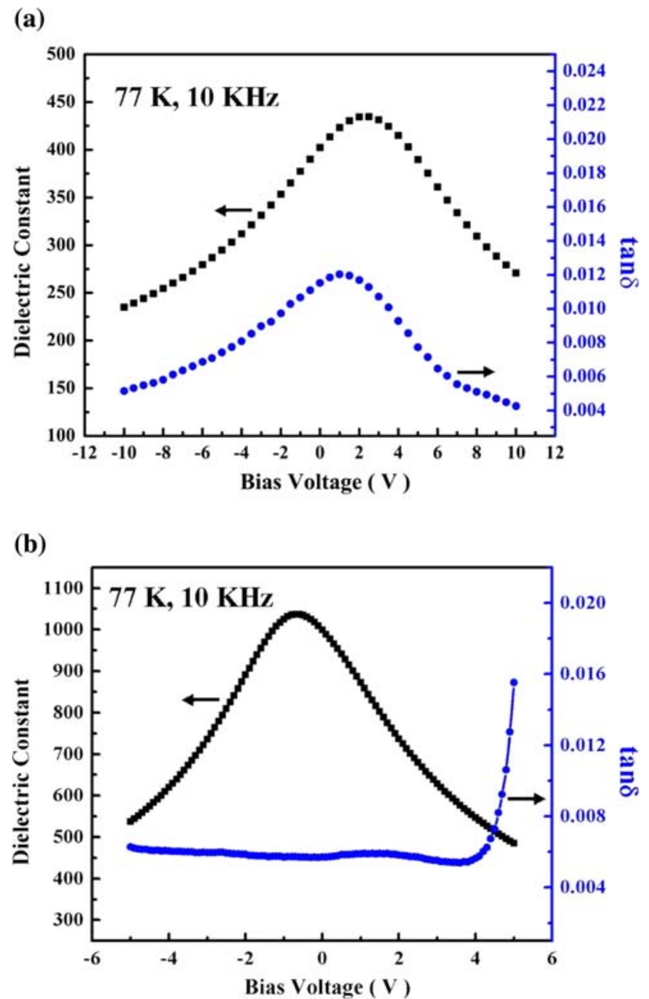

Fig. 1 Dielectric properties of $SrTiO_3$ (STO) thin films deposited at different oxygen partial pressures. (**a**) 10 Pa, (**b**) 2 Pa

thin films deposited at low oxygen pressure was higher than 100 kV/cm, the dielectric dissipation drastically increased as shown in Fig. 1b because of rapid increase of leakage current. The leakage current density of STO thin films grown at different oxygen partial pressure are shown in Fig. 2. When the biased electric field is lower than 60 kV/cm, the leakage current density of STO thin films deposited at 2 Pa oxygen pressure is one order lower than that of STO thin films deposited at 10 Pa oxygen pressure. However, the STO thin films deposited at 10 Pa oxygen pressure can withstand much larger electric field. Even the electric field is as high as 200 kV/cm, the leakage current still keeps at a low value as shown in Fig. 2a. While for STO thin films deposited at 2 Pa oxygen pressure, when the electric field is higher than 60 kV/cm, the leakage current density increased rapidly. Under the electric field of 100 kV/cm, the leakage current density of STO thin films deposited at 2 Pa oxygen pressure is one order

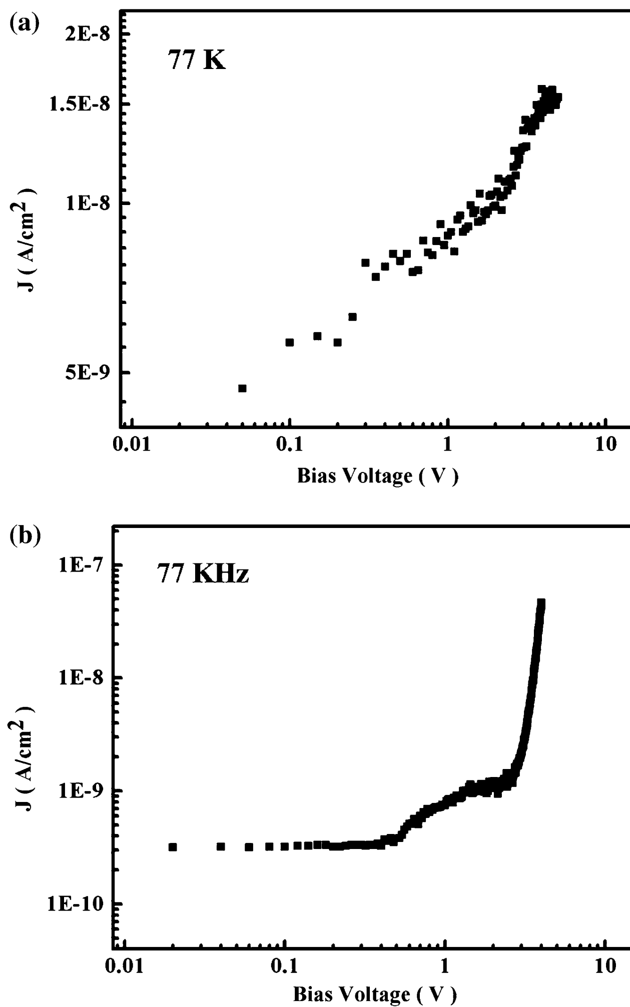

Fig. 2 Leakage of $SrTiO_3$ (STO) thin films grown at different oxygen pressure. (**a**) 10 Pa, (**b**) 2 Pa

larger than that of STO thin films deposited at 10 Pa oxygen pressure. The enhanced leakage current density increase energy dissipation. So if the dielectric loss tangent kept low enough, the STO thin films deposited at low oxygen pressure can not withstand large electric field to get higher dielectric percent tunning.

The leakage current of STO thin films deposited at low oxygen pressure is controlled by positive charge trapping within the films. Oxygen vacancies acts as electron traps. For STO thin films with high oxygen vacancy concentration, electrons injected from electrode are most likely trapped by oxygen vacancies under low electric field. Low leakage current density was displayed before the electron traps saturate. Under high electric field the leakage current density increased rapidly because of high de-trapping current of the trapped charges. The leakage current of STO thin films deposited at high oxygen pressure is controlled by enhanced ionic polarization with large grains. The effect of oxygen pressure on surface morphology of STO thin films is shown in Fig. 3. The STO thin films grown at low oxygen pressure are characterized by dense structure with fine grains as shown in Fig. 3b. However the STO thin films deposited at high oxygen pressure showed large size pellicular grains as shown in Fig. 3a. STO thin films with large size grains have short conduction paths along grain boundaries, which cause an increase in the leakage current density even under low bias electric field. The low concentration of oxygen vacancies, better crystallization, and low de-trapping current of the trapped electrons are suggested to low leakage

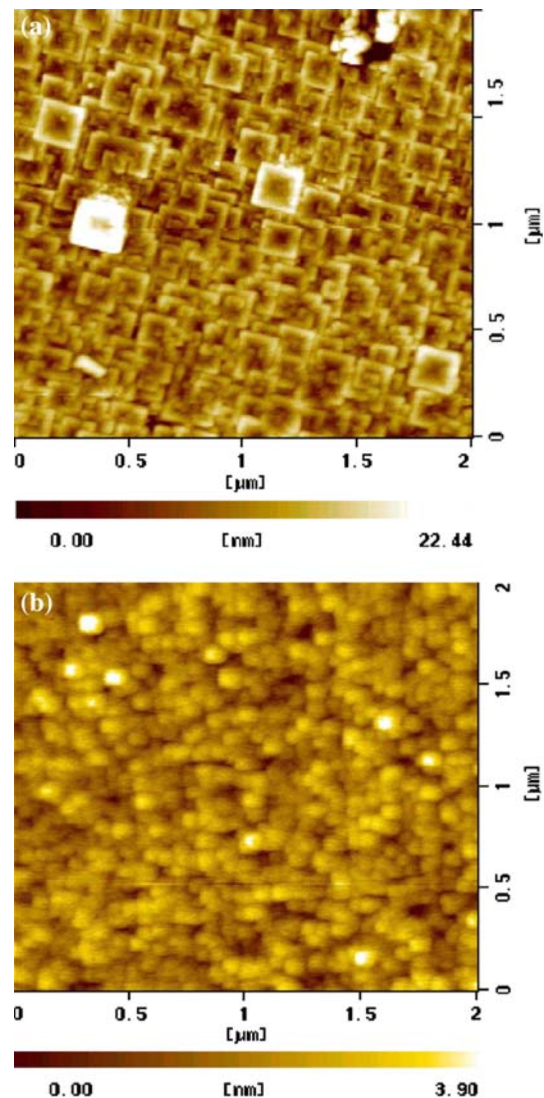

Fig. 3 Effect of oxygen pressure on atomic force microscopy (AFM) morphology of $SrTiO_3$ (STO) thin films. (**a**) 10 Pa, (**b**) 2 Pa

current under high electric field for STO thin films grown at high oxygen pressure.

In summary, the STO thin films were homo-epitaxially grown on Nb doped STO substrate to exclude the additional effect of film stress due to film-substrate lattice mismatch and difference in thermal expansion coefficients. The effect of oxygen vacancies on dielectric properties of homo-epitaxially grown STO thin films was studied. STO thin films with low oxygen vacancy concentration displayed low zero-bias permittivity, low dielectric tunability, and high dielectric dissipation. While the STO thin films with high concentration of oxygen vacancies exhibited reduced dielectric loss and high dielectric tunabilty. But It cannot withstand large electric field because of rapid increase of leakage current density under high electric field.

References

1. Hermann AM, Price JC, Scott JF, Yandrofski RM, Naziripour A, Galt D, Duan HM, Paranthaman M, Tello R, Cuchario J, Ahrenkiel RK (1993) Bull Am Phys Soc 38:689
2. Naziripour A, Outzourhit A, Trefny JU, Zhang Z-H, Barnes F, Cleckler J, Hermann AM (1994) Physica C 233:387
3. Hermann AM, Yandrofski RM, Scott JF, Naziripour A, Galt D, Price JC, Cuchario J, Ahrenkiel RK (1994) J Supercond 7:463
4. Chakalov RA, Ivanov ZG, Biokov YuA, Larsson P, Carlsson E, Gevorgian S, Claeson T (1998) Physica C 308:279
5. Gim Y, Hudson T, Fan Y, Kwon C, Findikoglu AT, Gibbons BJ, Park BH, Jia QX (2000) Appl Phys Lett 77:1200
6. Canedy CL, Li H, Alpay SP, Salamanca-Riba L, Roytburd AL, Ramesh R (2000) Appl Phys Lett 77:1695
7. Chang W, Horwitz JS, Carter AC, Pond JM, Kirchoefer SW, Gilmore CM, Chrisey DB (1999) Appl Phys Lett 74:1033
8. Tarsa EJ, Hachfield EA, Quinlan FT, Park JS, Eddy M (1996) Appl Phys Lett 68:490
9. Lee ST, Fujimura N, Ito T (1995) Jpn J Appl Phys Part 1 34:5168