



Dielectric Properties of Homoepitaxial SrTiO₃ Thin Films Grown in the Step-Flow Mode

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Abstract. We have deposited SrTiO₃ thin films on Nb-doped SrTiO₃ substrates by pulsed laser deposition at temperatures of up to 1400°C. Reflection high energy electron diffraction was used to monitor the film growth mode at various temperatures and it was shown that growth proceeded in the step-flow mode at above 900°C. Capacitors were formed by evaporating platinum pads on the film surface and gold pads on the substrate. Films grown in the step-flow mode showed consistently higher dielectric constants below 200 K than films grown in the layer-by-layer mode. Films with the highest dielectric constant (ϵ) were obtained using a stoichiometric ablation target at an oxygen pressure of 10^{-6} Torr.

Keywords: SrTiO₃, step-flow, dielectric constant

1. Introduction

The dielectric constant of SrTiO₃ increases rapidly when the material is cooled below 200 K. At about 110 K SrTiO₃ undergoes a structural cubic-to-tetragonal phase transition and at about 10 K enters a quantum paraelectric state, as has been proposed by Müller and Burkard [1]. A temperature independent dielectric constant has been observed in bulk SrTiO₃ in the quantum paraelectric state. In good bulk samples the dielectric constant can be as high as 25,000 in this temperature range [2]. A strong field dependence has also been observed. The dielectric constant can be reduced by up to 80% from the maximum value by applying a bias field of 5 kV/cm [3]. These properties, combined with the excellent

lattice matching with high- T_c cuprate superconductors, make SrTiO₃ an excellent candidate for use as a voltage-tunable element in cryogenic microwave circuits. Such applications, however, require the use of thin films which always show dramatically lower dielectric constants and higher loss figures than the bulk crystals. While acceptable loss figures have been achieved in relatively thick films [4], the maximum value of the dielectric constant has remained below 1400 [5].

We have recently shown that the dielectric constant of homoepitaxial SrTiO₃ films can be improved by growing the films in the step flow-mode [6]. In this work we have studied the influence of the Sr/Ti ratio of the ablation target and oxygen pressure on the dielectric constant of the films.

2. Experiment

The films were grown on single crystal SrTiO₃ substrates with a typical size of 5 mm × 10 mm. Nb-doped substrates (Shinkosha) with a maximum doping level of 0.5 wt % were used for preparing samples for capacitance measurements. Undoped substrates were used for growth mode monitoring by reflection high energy electron diffraction (RHEED). The undoped substrates were etched in NH₄F-HF prior to use and the presence of the step-and-terrace surface structure was verified by atomic force microscopy (AFM) [7]. The 0.5 wt % Nb-doped substrates were polished but not etched. Straight and nearly equidistant step edges required for step-flow growth were obtained in both cases by annealing the substrates in 10⁻⁶ Torr of oxygen at 1000°C for 2 h. Typical terrace width of these substrates was 150 nm.

Step-flow growth of SrTiO₃ requires the use of substrate temperatures above 900°C. This temperature range is not achievable with resistive or radiative lamp heaters if RHEED monitoring is required during film growth [8]. A Nd:YAG laser heater [9] was used in the present work to reach temperatures of up to 1400°C, while still maintaining compatibility with an oxygen environment and RHEED growth monitoring.

The oxygen pressure in the deposition chamber was varied between 10⁻⁶ Torr and 1 atm. The differentially-pumped RHEED system could be used at chamber pressures of up to 10⁻³ Torr. The sample temperature was monitored with an optical pyrometer operating at a wavelength of 2.5 μm. The pyrometer temperature scale was calibrated against the gold melting point to compensate for the unknown emissivity factor of the sample.

The RHEED specular spot intensity was monitored with a CCD camera and recorded with a personal computer. The time dependence of the specular spot intensity was used to determine the film growth mode and to choose the appropriate deposition temperature, deposition laser pulse energy and repetition rate.

A KrF excimer laser was used to ablate the SrTiO₃ targets at a fluence of ≈ 5 J/cm². A single crystal target (Shinkosha) was used to fabricate stoichiometric films. Pressed and sintered powder targets of Sr_{0.95}Ti_{1.05}O₃ and Sr_{1.05}Ti_{0.95}O₃ (Toshiba) were used to study the influence of a slight deviation of the Sr/Ti ratio from the stoichiometric conditions.

After deposition the films were cooled to 400°C and kept in pure oxygen at a pressure of 1 atm for at

least 2 h. Aluminum pads with a diameter of 0.5 mm were ex situ evaporated on the film surface. Better contact was obtained with platinum contact pads of the same size which were in situ evaporated on the film surface at room temperature through a shadow mask before the samples were removed from the deposition chamber. The capacitor structure was completed by evaporating gold either on the back side of the substrate or on a clean part of the substrate which was covered by a sample mounting clamp during deposition. No differences were observed in the measured capacitance values between the two electrode geometries.

Capacitance measurements were performed with a HP4284A precision LCR meter. The sample was mounted on a variable-temperature probe and slowly inserted into a liquid helium storage dewar to measure the temperature dependence of the dielectric constant. Bias dependence was measured by applying a dc bias voltage of up to ± 1 V to the sample, corresponding to a field strength of about 25 kV/cm for a typical film thickness of 400 nm. The film thicknesses were measured with a profilometer after deposition.

3. Step-flow Growth

The growth mode of the SrTiO₃ film was determined by monitoring the time dependence of the RHEED specular spot intensity. It is well-known that the RHEED intensity shows oscillatory behavior during layer-by-layer growth with the oscillation period corresponding to the growth of a single molecular layer [7]. The intensity oscillations are caused by a periodic change of the surface roughness during film growth.

Step-flow growth can not normally be monitored by electron diffraction because the growth proceeds in a steady state and there is no change in surface roughness [10]. During pulsed laser deposition, however, growth proceeds by periodic high supersaturation followed by surface diffusion. The surface roughness therefore increases rapidly immediately after a deposition pulse and recovers gradually. Step-flow growth occurs if the recovery time between deposition laser pulses is long enough for all deposited atoms to diffuse to stable attachment sites at step edges. This condition can be reached by increasing the substrate temperature to a point where small islands which can nucleate during the period of

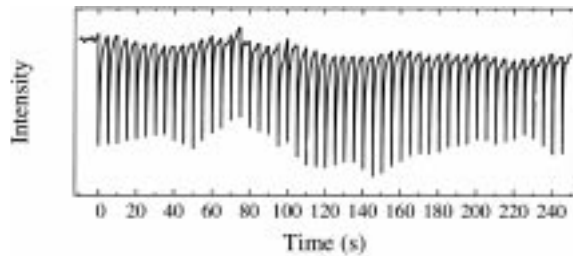


Fig. 1. Time dependence of the RHEED specular spot intensity during step-flow growth.

high supersaturation are not stable on the terraces, and by using low excimer laser repetition rates.

Figure 1 shows the time dependence of the RHEED specular spot intensity during homoepitaxial SrTiO₃ growth at 1200°C. The excimer laser repetition rate was 0.5 Hz. As can be seen in the figure, the RHEED intensity recovered completely after each deposition pulse, indicating that a smooth surface was restored, as would be expected for step-flow growth.

The dielectric constant of the films grown in the step-flow mode was found to be significantly higher than the dielectric constant of films grown in the layer-by-layer mode at temperatures below 800°C.

4. Film Stoichiometry

All films had a thickness of about 380 nm and required 12,000 excimer laser pulses at a 0.5 Hz repetition rate to deposit. Depositions were performed at 1200°C in all cases. The oxygen pressure was maintained at 10^{-6} Torr. After deposition the samples were cooled to 400°C and kept in pure oxygen for at least 2 h. Platinum pads were used as top electrodes on the film surface, gold electrodes were deposited on the Nb-doped substrate.

The results of capacitance measurements are shown in Fig. 2. All measurements were performed without dc bias at a frequency of 200 kHz. The stoichiometric film had the highest dielectric constant, reaching 4000 at 60 K (Fig. 2a). The Ti-rich film (Fig. 2b) had a similar temperature dependence, but slightly lower dielectric constant at all temperatures. The drop of ϵ below 50 K was also larger. The temperature dependence observed in the Sr-rich case (Fig. 2c) was very similar to the films grown at about 700°C in the layer-by-layer mode.

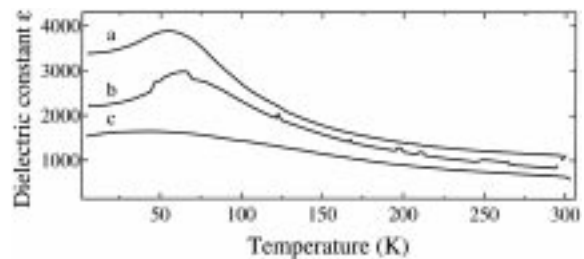


Fig. 2. Temperature dependence of the dielectric constant of (a) a stoichiometric film, (b) Ti-rich film, and (c) Sr-rich film.

It is interesting to note that the ϵ value of the stoichiometric film measured at room temperature was higher than that typically observed in bulk samples. Possible sources of error were carefully checked by repeating the measurements with various electrode configurations and materials, including platinum, aluminum, gold, magnesium, and nickel/chromium. The choice of metals only affected the shape of the CV curve, but not the room temperature ϵ value. Ion milling was used to define the area of the capacitors by etching away the film from around a measurement pad in one sample. This processing did not change the measured capacitance. The only source of uncertainty remains in the capacitor thickness due to the possible presence of conducting dead layers either on the film surface or at the film/substrate interface. We have deposited films with various thicknesses ranging from 80 nm to 500 nm. Films thinner than 100 nm had a very large leakage current, making it impossible to measure the $\epsilon(T)$ dependence. These measurements indicated that any low-capacitance layers present in the films can not alone be responsible for the observed increase of ϵ in films with a thickness of ≈ 400 nm.

5. Oxygen Pressure

The oxygen pressure during growth influences the surface diffusion rate of adatoms and can therefore have a direct effect on the film crystallinity. The density of oxygen vacancies in the film can also depend on the oxygen pressure. The best crystallinity and surface morphology was obtained at an oxygen pressure of 10^{-6} Torr. These films also had the highest dielectric constants. The $\epsilon(T)$ curves of three

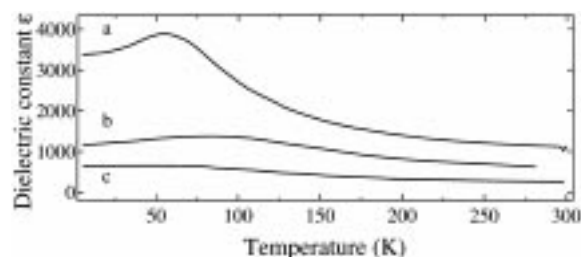


Fig. 3. Dielectric constants of films deposited at (a) 10^{-6} Torr, (b) 10^{-3} Torr, and (c) 100 mTorr of oxygen.

films deposited at 10^{-6} Torr, 10^{-3} Torr, and 100 mTorr are shown in Fig. 3.

The films grown at 10^{-6} Torr (Fig. 3a) had the best surface morphology, with straight unbunched steps and island-free terraces. Indeed, the AFM images of the film surface were nearly indistinguishable from those obtained from the clean substrate surface. Films deposited at 10^{-3} Torr showed step bunching and faceting. Heavily bunched steps and islands appeared on the surface of films deposited at 100 mTorr. The growth mode could not be directly verified by RHEED during the 100 mTorr deposition. In this case a few laser pulses were fired at 10^{-3} Torr to check that full RHEED recovery occurs. Pressure was then increased to 100 mTorr while maintaining the same substrate temperature.

The dielectric constant of the films appeared to correlate directly with the surface morphology. Increase in defects visible on the film surface by AFM was always accompanied by lower ϵ values being observed in capacitance measurements (Figs. 3b,c).

6. Conclusions

We have shown that the dielectric constant of homoepitaxial SrTiO₃ films is very sensitive to the crystallinity of the films. A dramatic increase of the

dielectric constant was observed in high-quality films grown in the step-flow mode. Increase of lattice defects either due to stoichiometry offsets or other deposition parameters, such as increased oxygen pressure, reduced the dielectric constant to values which have typically been observed in SrTiO₃ thin films.

The best film quality and the highest ϵ values were observed in films deposited between 1000°C and 1300°C at 10^{-6} Torr of oxygen. No step bunching or islands were observed on the film surfaces. The highest dielectric constant measured without bias reached 4000.

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References

1. K.A. Müller and H. Burkard, *Phys. Rev. B*, **19**, 3593 (1979).
2. T. Sakudo and H. Unoki, *Phys. Rev. Lett.*, **26**, 851 (1971).
3. E. Sawaguchi, A. Kikuchi, and Y. Kodera, *J. Phys. Soc. Japan*, **17**, 1666 (1962).
4. H.-C. Li, W. Si, A.D. West, and X.X. Xi, *Appl. Phys. Lett.*, **73**, 190 (1998).
5. A.T. Findikoglu, C. Doughty, S.M. Anlage, Q. Li, X.X. Xi, and T. Venkatesan, *Appl. Phys. Lett.*, **63**, 3215 (1993).
6. M. Lippmaa, S. Ohashi, N. Nakagawa, Y. Inaguma, M. Itoh, H. Koinuma, and M. Kawasaki, *to be published*.
7. M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, *Science*, **266**, 1540 (1994).
8. J.C. Clark, J.P. Maria, K.J. Hubbard, and D.G. Schlom, *Rev. Sci. Instrum.*, **68**, 2538 (1997).
9. S. Ohashi, M. Lippmaa, N. Nakagawa, H. Nagasawa, H. Koinuma, and M. Kawasaki, *Rev. Sci. Instrum.*, **70**, 178 (1999).
10. T. Frey, C.C. Chi, C.C. Tsuei, T. Shaw, and F. Bozso, *Phys. Rev. B*, **49**, 3483 (1994).