Improved SrTiO₃ thin films using oxygen relaxation technique

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(Received 1 August 2005; accepted 18 October 2005; published online 21 November 2005)

The oxygen relaxation technique for thin-film growth is explored. In this technique, films are deposited as nanoscale multilayered structures. After the deposition of each layer, the deposition process is stopped, the sample is cooled down slowly *in situ* in an oxygen-rich atmosphere to a temperature of 250 °C, then it is heated up to the set deposition temperature for growth of the next layer. The results show that by using the oxygen relaxation technique, it is possible to improve the electrical properties and the microstructure of SrTiO₃ films keeping the surface smooth and free from pinholes and pores. The oxygen relaxation technique is more efficient for smaller film thickness repetition. © 2005 American Institute of Physics. [DOI: 10.1063/1.2136432]

Strontium titanate (SrTiO₃, STO) thin films have been extensively studied for application in tunable microwave components. The most commonly investigated devices are varactors, phase-shifters, tunable filters, etc., where the STO films are used as a single layer or are included in multilayer structures.^{1,2} The STO films' undesirably high dielectric loss at microwave frequencies, however, limits their wide practical utilization. It is believed that one reason for the high microwave loss level is the oxygen deficiency in the STO films, and a postdeposition high-temperature annealing in oxygen reach atmosphere is required.³ Very often, however, after such an annealing, pores and/or cracks appear on the film surface.⁴ This is unacceptable because of the possibility of a short circuit between the layers (in multilayered structures).

In this letter, the oxygen relaxation technique for growing STO films with improved electrical properties is explored to investigate the dependence of the STO film quality on the oxygen relaxation treatment.

A set of STO films was on-axis deposited on 5 × 5 mm² (001) LaAlO₃ (LAO) substrates by laser ablation from a stoichiometric SrTiO₃ target. The film thickness of all samples was 400 nm, although they were made without (Sample 1), with one (Sample 2), with three (Sample 3), with five (Sample 4), and seven (Sample 5) intermediate oxygen relaxations, i.e., the films were deposited as nanoscale multilayered structure with one (1 × 400 nm), two (2 × 200 nm), four (4 × 100 nm), six (6 × 65 nm), or eight (8 × 50 nm) layers. After deposition of every layer, the deposition process was stopped, the sample cooled down slowly (20 °C/min) in an oxygen-rich (0.9 atm) atmosphere to a temperature of 250 °C, then heated up to the deposition temperature for growth of the next layer.

For examination of electrical properties, the deposited STO films were covered by (250 nm) YBa₂Cu₃O_{7-x}(YBCO)/(500 nm)Au bilayer. The YBCO layer was *in situ* laser ablated, while the Au one was *ex situ* electron-beam evaporated. The deposition conditions for the STO, YBCO, and Au films can be found elsewhere.⁵ The test structures (planar capacitors) for electrical measurements were patterned by photolithography and Ar-ion milling.

The sample structure was investigated by x-ray diffraction (XRD) performed on a Philips X'Pert PW3098/20 diffractometer with Cu K α radiation. A Veeco scanning probe microscope (SPM) in tapping mode was used for investigation of the STO film surface.

Electrical measurements of the planar capacitors were made at a radio frequency (rf) of 2 MHz and at high frequency (MW) of 6 GHz, at both 300 K and 77 K. To examine the capacitors' tunability $n = C(0V)/C(V_{\max})$, a dc voltage up to 40 V was applied. Measurements at 77 K were performed by immersing the capacitor in liquid nitrogen. The rf measurements were performed using a HP 4285A LCR meter attached to a microwave probe station. Before measurement, a calibration using an open and short circuit was performed. For MW measurements, the substrate was cut and the chip capacitors were placed into a gap in the middle of the half-wavelength microstrip resonator. The measurement and parameter evaluation procedures are described in Ref. 6.

The XRD patterns measured for all YBCO/STO/LAO structures showed only (00 l) reflections of YBCO and STO. A typical XRD pattern is presented in Fig. 1. After a broadening analysis of the obtained XRD patterns, the strain value for all samples were estimated as $|c_f - c_{\text{bulk}}|/c_{\text{bulk}}$, where c_f is the film lattice parameter along the film thickness, and c_{bulk} is the lattice parameter for a bulk STO sample. The strain gradient was estimated as $\Delta c/c_f$, where the Δc is the deviation of the STO lattice parameter the along the film thickness

FIG. 1. Typical XRD pattern of the YBCO/STO/LAO multilayered structure.

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TABLE I. Measurement results.

Sample		Crystal cell parameters			Cryo temperature (77 K)						Room temperature (300 K)			
No.	Number of oxygen Relax.	c_f (Å)	Strain $\frac{ c_f - c_{\text{bulk}} }{c_{\text{bulk}}}$	Strain grad. Δ_c/c_f	Capacitance $C(0)$ (pF)		Q factor		Tuning $C(0 V)/C(V_{\text{max}})$		Capacitance $C(0)$ (pF)		Q factor	
					rf	MW	rf	MW	rf	MW	rf	MW	rf	MW
1	w/o	3.916	0.0028	0.0012	0.32	0.29	140	91	1.45	1.59	0.19	0.19	210	106
2	1	3.916	0.0028	0.0009	0.34	0.30	150	112	1.69	1.28	0.20	0.23	263	113
3	3	3.916	0.0027	0.0009	0.37	0.27	370	124	1.58	1.36	0.21	0.13	250	114
4	5	0.916	0.0026	0.0006	0.45	0.39	500	138	1.60	1.56	0.21	0.22	400	115
5	7	3.915	0.0026	0.0002	0.43	0.38	700	146	1.73	1.80	0.23	0.23	500	117

FIG. 2. SPM images of the STO film surface measured for: (a) Sample No. 1 (without oxygen relaxation); scale in z direction is 50 nm/div. and (b) Sample No. 5 (with seven oxygen relaxations); scale in z direction is 25 nm/div.

from the average STO thin-film lattice parameter. More about XRD measurements can be found elsewhere.^{7,8} A measurements summary is presented in Table I. One can see that increasing the number of oxygen relaxation reduces the strain gradient, while the strain value ($|c_f - c_{\text{bulk}}|/c_{\text{bulk}}$) is more or less constant. It is difficult to provide a strong explanation of the observed phenomenon but one can speculate that, after oxygen relaxation procedures, the STO film does not undergo additional recrystallization, which takes place during the conventional annealing, but becomes a homoepitaxial multilayered structure. The fact that the strain value remains the same after different numbers of oxygen relax-

FIG. 3. Typical C - V and $\tan \delta$ -voltage characteristics measured at (a) 77 K, 2 MHz, and (b) 77 K, 6 GHz.

ations supports the idea that there is no additional recrystallization of the film.

The change in the strain gradient can be explained as follows: Initially, we deal with a strained STO film in which the lattice parameter changes along the thickness. The oxygen relaxation makes the sample consisting of similar homoepitaxial layers, in which, the strain gradient (dispersion of the lattice parameter) is smaller. Another interesting fact is that oxygen relaxation at every 50 nm reduces the strain gradient inside a 400 nm STO film 83%, while one at 65 nm reduces the strain by 50%, showing that the oxygen relaxation technique is more efficient for smaller film thickness repetition.

In Fig. 2 are shown typical surface images obtain by SPM for Sample Nos. 1 and 5. As one can see, the surface is very smooth and free from pinholes and pores, which usually take place after a postdeposition high-temperature annealing. This is important especially for multilayer-based device fabrication.

Results of the rf/MW measurements are also summarized in Table I. Presented there are the capacitance (C), the tuning (n), and the Q factor ($Q \approx 1/\tan \delta$) of the capacitors measured at 2 MHz and 6 GHz and at 77 K and 300 K. The improvement of the electrical properties of the films deposited using the proposed technique is clearly seen at low frequencies, where the Q increases approximately five fold. At high frequencies, the improvement is within the measurement error, which does not exceed 5–10%. The increase in capacitance observed at rf and MW may be attributed to the samples layered structure. (The layered sample with planar capacitor design can be considered as one that consists of few capacitors connected in parallel.)⁹

Figures 3(a) and 3(b) show typical capacitance-voltage (C - V) and $\tan \delta$ - V dependences, measured at 77 K at 2 MHz and 6 GHz, respectively. The weak hysteresis loop that takes place, especially at low frequencies, is attributed to the redistribution of the space charge in the under-electrode area or/and strain-induced ferroelectric domains in the STO

films.¹⁰ As expected, no tuning was detected at room temperature.

In conclusion, the investigation shows that by using the oxygen relaxation technique, it is possible to improve the structural and the electrical properties of the STO films keeping the surface smooth and free from pinholes and pores. The capacitance of the structure increases proportionally to the number of the oxygen relaxations. The same trend is observed at rfs, where the capacitors' Q factor increases about five times, while at microwave frequency the improvement is within the measurement error. Oxygen relaxation repeated at every 50 nm reduces the strain gradient of a 400 nm STO film 83%. Increasing the repetition layer thickness reduces the efficiency of the oxygen relaxation technique.

The authors acknowledge Professor Zdravko Ivanov, Professor Spartak Gevorgian, and Dr. Erik Carlsson from Chalmers University of Technology, Sweden, where part of the experiments were performed. This work was partly supported by the Engineering and Physical Sciences Research Council (EPSRC), UK.

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