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2001 J. Phys.: Condens. Matter 13 5261

(http://iopscience.iop.org/0953-8984/13/22/319)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 5261–5268 www.iop.org/Journals/cm PII: S0953-8984(01)23408-0

# Effect of oxygen content on the dielectric and ferroelectric properties of laser-deposited $BaTiO_3$ thin films

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Received 5 December 2000, in final form 4 January 2001

**Abstract**

$BaTiO_3$ thin films were epitaxially grown on $SrTiO_3$ (001) and $LaNiO_3/SrTiO_3$ substrates by pulsed laser deposition under different oxygen pressures. The oxygen content in the $BaTiO_3$ films was determined using modified Rutherford backscattering. The structural characteristics of the films were analysed by x-ray diffraction $\theta/2\theta$ scan, $\varphi$ scan, and symmetric and asymmetric $\omega$ scans. The dielectric and ferroelectric properties of the films were measured by an impedance analyser and by a Sawyer–Tower circuit, respectively. It was found that the atomic ratio of O/Ba and Ti/Ba in the $BaTiO_3$ films increases with oxygen pressure. The films fabricated in the intermediate oxygen pressure range of 2 to 10 Pa show the *c*-axis oriented tetragonal structure with a stoichiometry close to the ideal value. These films exhibit a relatively large dielectric constant, small dielectric loss and good ferroelectricity with a symmetric hysteresis loop. For growth at low oxygen pressure i.e. 0.1 Pa, the film with tetragonal *c*-axis orientation shows significant degradation in its dielectric properties. For a higher deposition oxygen pressure of 20 Pa, the film has tetragonal *a*-axis orientation and shows no ferroelectricity but has the largest dielectric constant.

## 1. Introduction

Barium titanate ($BaTiO_3$) is one of the most important ferroelectric materials, and has attracted much attention for its remarkable properties such as high dielectric constant, good ferroelectric properties, and large electro-optic and non-linear optic coefficients [1–5]. $BaTiO_3$ thin films have many potential device applications as ferroelectric random access memories, electro-optic switches, optical modulators and waveguides. Over the years, epitaxial $BaTiO_3$ thin films have been prepared by a variety of methods, such as magnetron sputtering [6], metallorganic chemical vapour deposition [7], molecular beam epitaxy [8] and pulsed laser deposition

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0953-8984/01/225261+08$30.00  

(PLD) [9,10]. In these methods, oxide thin films were produced under ambient oxygen gas. The oxygen content contained in these films is a critical factor, which influences their structure and properties, so the measurement of this oxygen content is very important.

Recently we measured the atomic composition and electron structure of $BaTiO_3$ thin film using x-ray photoelectron spectrometry [11], which, however, has low sensitivity in detecting the lighter elements such as hydrogen and oxygen. The quantitative elemental analysis of oxide thin films has been addressed using mainly nuclear techniques [12], such as Rutherford backscattering spectrometry (RBS), elastic recoil detection analysis and nuclear reaction analysis.

In this paper, a modified RBS technique with higher incident ion beam energy [13] was employed to determine quantitatively the atomic composition of $BaTiO_3$ thin films grown by PLD under different ambient oxygen gas pressures. The combined effect of the oxygen content and crystalline structure on the dielectric and ferroelectric properties of these films was investigated.

## 2. Experiment

Epitaxial $BaTiO_3$ thin films were grown on $SrTiO_3$ (001) substrates by pulsed laser deposition. An XeCl excimer laser beam (308 nm, 28 ns, 4 Hz) operating at 2 J cm$^{-2}$ was focused to a spot of 1 × 3 mm on the surface of a rotating $BaTiO_3$ single-crystal target. The $SrTiO_3$ substrate was placed on a single silicon heater. The distance between the substrate and the target was 35 mm. The $BaTiO_3$ thin films were fabricated at a substrate temperature of 700 °C under different oxygen gas pressures of 0.1, 2, 7 and 20 Pa, corresponding to sample numbers 1, 2, 3 and 4, respectively. After deposition, the thin films were annealed at 450 °C in ambient oxygen of 1 atm for 20 min, then the films were slowly cooled to room temperature. The thickness of the films was about 450 nm.

The modified RBS measurements, used to determine the atomic composition in the $BaTiO_3$ thin films, were performed using a 5.85 MeV $^4$He beam which gave an accuracy of ±5% for measuring the oxygen content and a sensitivity 10 times that of a 2 MeV $^4$He beam formerly used [13]. The lattice parameters, crystalline phase, crystallographic orientation and epitaxial characterization of the films were determined by x-ray diffraction (XRD) $\theta/2\theta$ scan, $\varphi$ scan and symmetric and asymmetric $\omega$ scans (rocking curves). The dielectric and ferroelectric measurements of the films were performed by an impedance analyser (HP 4274A) and by a Sawyer–Tower circuit, respectively.

## 3. Results and discussion

The dependence of the $BaTiO_3$ thin film composition on oxygen pressure during the film growth process was investigated through the RBS analysis. Figure 1 shows the atomic ratio of O/Ba as a function of oxygen pressure for samples 1, 2, 3 and 4. The results indicate that the atomic ratio of O/Ba increases from sample 1 to sample 4, indicating that the oxygen content increases with increasing oxygen pressure during film growth. The atomic ratio of Ti/Ba for samples 1, 2, 3 and 4 is presented in figure 2. It can be seen that the Ti/Ba cation ratio also increases with increasing oxygen pressure, i.e., the Ti content in $BaTiO_3$ thin films can be adjusted by the deposition oxygen pressure. The film composition dependence on the deposition gas pressure was also observed for $SrTiO_3$ thin film, and the pressure dependence of the cation ratio can be explained by different factors of backscattering for different cations by the background gas [14]. For sample 1, the ratios of Ti/Ba are close to 1 while the oxygen content is lower than the ideal value, indicating that the $BaTiO_3$ thin films grown under lower oxygen pressures are deficient of oxygen. The stoichiometry of samples 2 and 3 is very close to the ideal value. The ratios of Ti/Ba and O/Ba of sample 4 are greater than 1 and 3, respectively. According to the experimental curves in figures 1 and 2, it can be seen that the $BaTiO_3$ thin films fabricated under oxygen pressures from 2 to 10 Pa have a stoichiometry close to the ideal value.

The XRD $\theta/2\theta$ patterns of samples 1, 2, 3 and 4 are very similar, the major difference being a shift in peak positions to higher angles with increase of oxygen content from sample

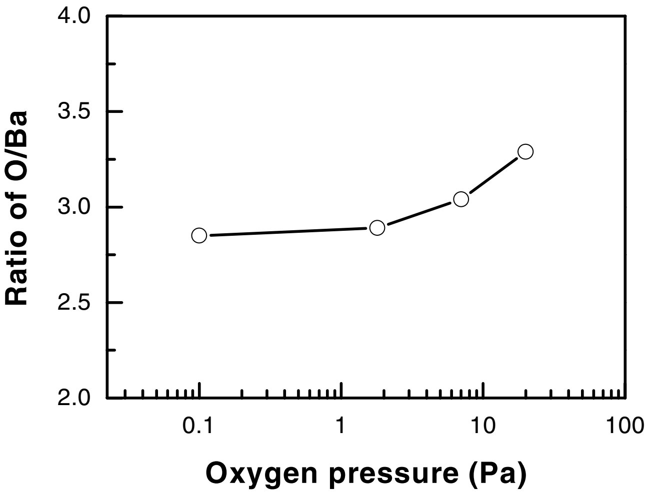


**Figure 1.** Dependency of the O/Ba atomic ratio in the $BaTiO_3$ thin films on deposition oxygen pressure. The oxygen pressure is 0.1, 2, 7 and 20 Pa, respectively.

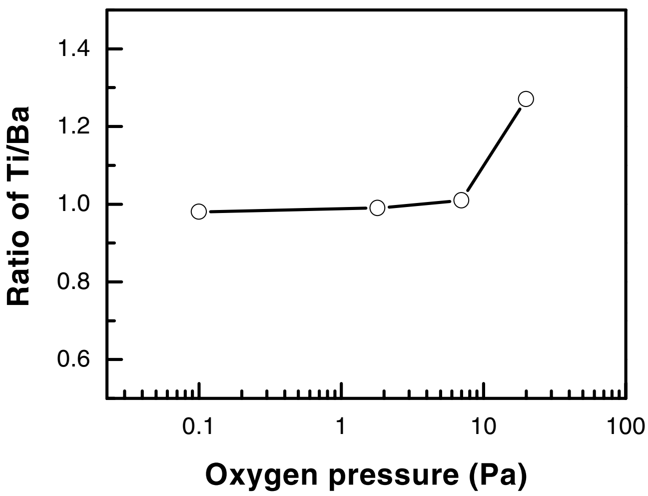


**Figure 2.** Dependency of the Ti/Ba atomic ratio in the $BaTiO_3$ thin films on deposition oxygen pressure. The oxygen pressure is 0.1, 2, 7 and 20 Pa, respectively.

1 to sample 4. Figure 3 shows the XRD $\theta/2\theta$ scan patterns from the films as a function of deposition oxygen pressure. Only the XRD peaks of ($h$00) or (00$l$) reflection can be observed, indicating that our PLD $BaTiO_3$ films exhibit a preferred orientation with single phase. The lattice parameters are found to be sensitive to oxygen pressures. The out-of-plane lattice constant for the $BaTiO_3$ films as a function of oxygen pressure is plotted in figure 4, and has values of 0.4148, 0.4096, 0.4016 and 0.4006 nm, corresponding to deposition oxygen pressures of 0.1, 2, 7 and 20 Pa, respectively. From XRD $\{303\}$ asymmetric $\omega$ scans, the ratios of the out-of-plane lattice constant to the in-plane lattice constant were determined to be 1.043, 1.025, 1.001 and 0.994 for samples 1, 2, 3 and 4, respectively. Therefore, the films grown under lower oxygen pressures exhibit the $c$-axis oriented tetragonal phase, corresponding to samples 1 to 3. Their lattice constants are : $c = 0.4148$, $a = b = 0.3974$ nm for sample 1; $c = 0.4096$, $a = b = 0.3996$ nm for sample 2; $c = 0.4016$, $a = b = 0.4012$ nm for sample 3. It is evident that the $c$-axis lattice constant of the films is found to be lengthened at low pressures. Similar results were also observed in $SrTiO_3$ films [14] and $YBa_2Cu_3O_7$films [15], and it has been suggested that this is caused by the oxygen deficiency in the films. On the other hand, sample 4 has an $a$-axis oriented tetragonal phase, i.e. the $c$-axis lies on the in-plane and the lattice constants are: $c = 0.4030$, $a = b = 0.4006$ nm.

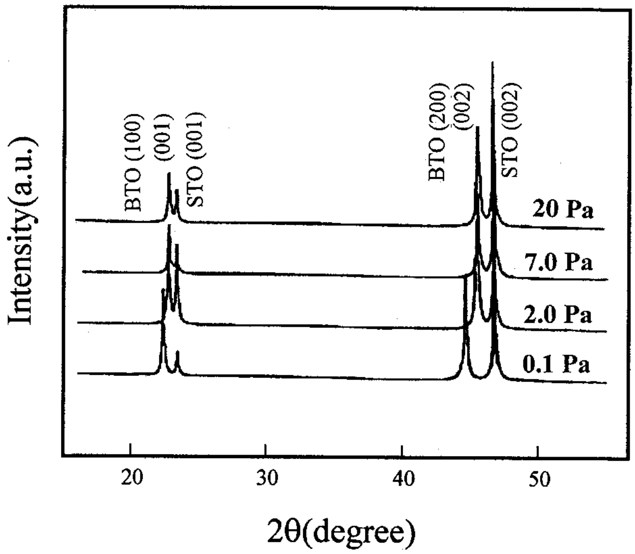


**Figure 3.** XRD $\theta/2\theta$ patterns for $BaTiO_3$ thin films deposited on $SrTiO_3$ (001) substrate by PLD under different oxygen gas pressures.

The full width half maxaximum (FWHM) values of the XRD symmetric $\omega$ scan from the (002) peaks for samples 1, 2 and 3 are 0.27°, 0.25° and 0.37°, respectively. For sample 4, the corresponding FWHM is 0.24°. The results suggest that the $BaTiO_3$ films grown on $SrTiO_3$ substrates exhibit a narrow rocking curve in a broad oxygen pressure range from 0.1 to 20 Pa, which indicates that the films have a very high degree of crystallinity along the out-of-plane direction. The in-plane epitaxial orientation was evaluated by $\varphi$ scan. The $\varphi$ scan patterns obtained from samples 1, 2, 3 and 4 show that the peaks of the films were located at the same position as that of the substrates and appeared every 90°. No in-plane misorientations were observed. The characteristic fourfold symmetry demonstrating in-plane alignment of the films and narrow FWHM are indicative of high quality epitaxial films. Details of various XRD

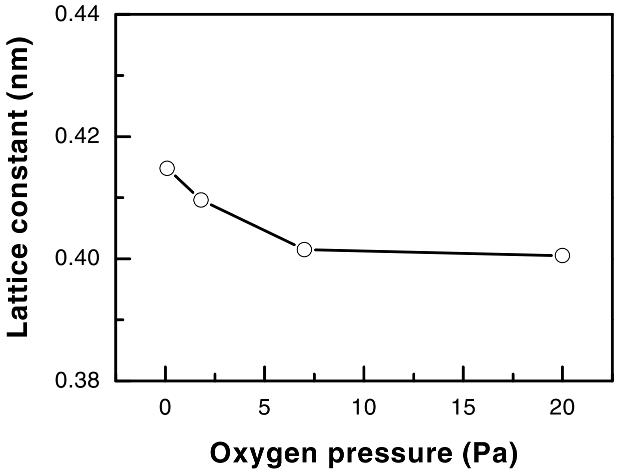


**Figure 4.** Variation in the out-of-plane lattice constant of $BaTiO_3$ thin films as a function of deposition oxygen pressure.

measurements are described in our prior work [9].

To investigate the dielectric and ferroelectric properties we fabricated $BaTiO_3$ thin films (450 nm thickness) on $LaNiO_3/SrTiO_3$ substrates at a temperature of 700 °C in oxygen pressures of 0.1, 2, 7, 10 and 20 Pa, respectively. The corresponding samples were numbers 5, 6, 7, 8 and 9, respectively. A thin metallic $LaNiO_3$ lafyer (300 nm thickness) was used as the bottom electrode with a resistivity $\rho$ of $\sim 2 \times 10^{-4}$ Ω-cm at room temperature [16]. The Au top electrode was thermally evaporated and patterned to an area of $2.5 \times 10^{-3}$ cm$^2$ for the capacitors.

We measured the dielectric constant and dielectric loss for samples 5 to 9 by using an HP-4274A impedance analyser at room temperature at a frequency of 1 kHz. The results are shown in table 1. It can be seen that the $BaTiO_3$ thin films grown under 2–10 Pa have a relatively small dielectric loss of 0.04 and a larger dielectric constant between 600–700. Thus, the $BaTiO_3$ thin films fabricated under this oxygen pressure range have good dielectric properties due to high epitaxial quality. The $BaTiO_3$ thin film grown at 0.1 Pa has a relatively small dielectric constant and large dielectric loss due to the large leak current from the oxygen deficiency. For the $BaTiO_3$ thin film fabricated at 20 Pa, since it is $a$-axis oriented as derived from the XRD analysis above, its dielectric constant of 3500 is much larger than that of $c$-axis oriented $BaTiO_3$ thin films [17].

The polarization ($P$–$E$) hysteresis loop measurement was performed at room temperature at a frequency of 100 Hz. The data for spontaneous polarization $P_s$, remnant polarization $P_r$ and coercive field $F_c$ from samples 5 to 9 are presented in table 2, and the $P$–$E$ loops for samples 5, 7, 8 and 9 are plotted in figures 5(a) to 5(d), respectively. It can be seen that for the samples deposited at an oxygen pressure lower than 10 Pa, both the spontaneous polarization and the coercive field increase as the oxygen pressure decreases. On the other hand, no ferroelectricity was observed for $BaTiO_3$ film grown at 20 Pa, as shown in figure 5(d).

It is known that the lattice dipole along the $c$-axis for a tetragonal perovskite structure is the origin of the ferroelectric properties associated with $BaTiO_3$. For the $a$-axis oriented $BaTiO_3$ thin film, the polarization vector is parallel to the film surface for $a1$ and $a2$ domains [18] and is along one of the four possible orientations in the film plane. Thus, the $a$-axis

**Table 1.** Dielectric constant and loss for the $BaTiO_3$ thin films grown on $LaNiO_3/SrTiO_3$ substrates under different oxygen pressures.

| Sample number | $P_{O_2}^{a}$ (Pa) | $\varepsilon^{b}$ | $\tan\delta^{c}$ |
|---|---|---|---|
| 5 | 0.1 | 560 | 0.141 |
| 6 | 2 | 600 | 0.040 |
| 7 | 7 | 620 | 0.034 |
| 8 | 10 | 680 | 0.042 |
| 9 | 20 | 3500 | 0.052 |

[a] $P_{O_2}$: oxygen pressure.
[b] $\varepsilon$: dielectric constant.
c $\tan\delta$: dielectric loss.

**Table 2.** Table 2. Spontaneous polarization, remnant polarization and coercive field of the $BaTiO_3$ thin films grown on $LaNiO_3/SrTiO_3$ substrates under different oxygen pressures.

| Sample number | $P_{O_2}^{a}$ (Pa) | $P_s^{b}$ ($\mu$C cm$^{-2}$) | $P_r^{c}$ ($\mu$C cm$^{-2}$) | $F_c^{d}$ (kV cm$^{-1}$) |
|---|---|---|---|---|
| 5 | 0.1 | 3.0 | 1.0 | 33 |
| 6 | 2 | 2.4 | 1.2 | 30 |
| 7 | 7 | 2.0 | 1.0 | 25 |
| 8 | 10 | 1.2 | 0.6 | 20 |
| 9 | 20 | 0 | 0 | 0 |

[a] $P_{O_2}$: oxygen pressure.
[b] $P_s$: spontaneous polarization.
[c] $P_r$: remnant polarization.
[d] $F_c$: coercive field.

oriented $BaTiO_3$ film cannot show ferroelectric hysteresis, as observed in sample 9, due to this 'randomly' oriented polarization [19]. Obviously, only $c$-axis oriented $BaTiO_3$ thin films exhibit ferroelectricity, which is consistent with the measurements for samples 5 to 8.

The influence of deposition oxygen pressure on the dielectric and ferroelectric properties of the $BaTiO_3$ thin films is the combined effect of the oxygen content and the crystalline structure. For the $c$-axis oriented films, when the deposition oxygen pressure decreases, the out-of-plane lattice constant is elongated which enhances the tetragonality $(c/a)$ arising from the oxygen deficiency [9, 14, 20]. Because the ferroelectric dipole originates from ionic displacement in the $c$-axis direction, large spontaneous polarization is obtained in the epitaxial films with the elongated $c$-axis. However, there is an optimum oxygen pressure range. Significant improvements in both dielectric and ferroelectric properties of the films are obtained in the intermediate oxygen pressure range of 2 to 10 Pa. On the other hand, for the film deposited at low oxygen pressure, increase of oxygen deficiency results in more oxygen defects in the film, which then exhibits small dielectric constant and large dielectric loss, and the $P$–$E$ hysteresis loop becomes asymmetric due to the significant oxygen vacancies [21]. For the growth at higher oxygen pressure, for example at 20 Pa, from the $P$–$E$ measurements no ferroelectricity is found, which is in agreement with the analysis of crystalline phase and orientation of the $BaTiO_3$ film with an $a$-axis oriented tetragonal structure.

## 4. Conclusion

We have determined the oxygen content of $BaTiO_3$ thin films grown by PLD under different oxygen gas pressures and have found that the influence of oxygen pressure on the dielectric and ferroelectric properties of the films is the combined effect of the oxygen content and

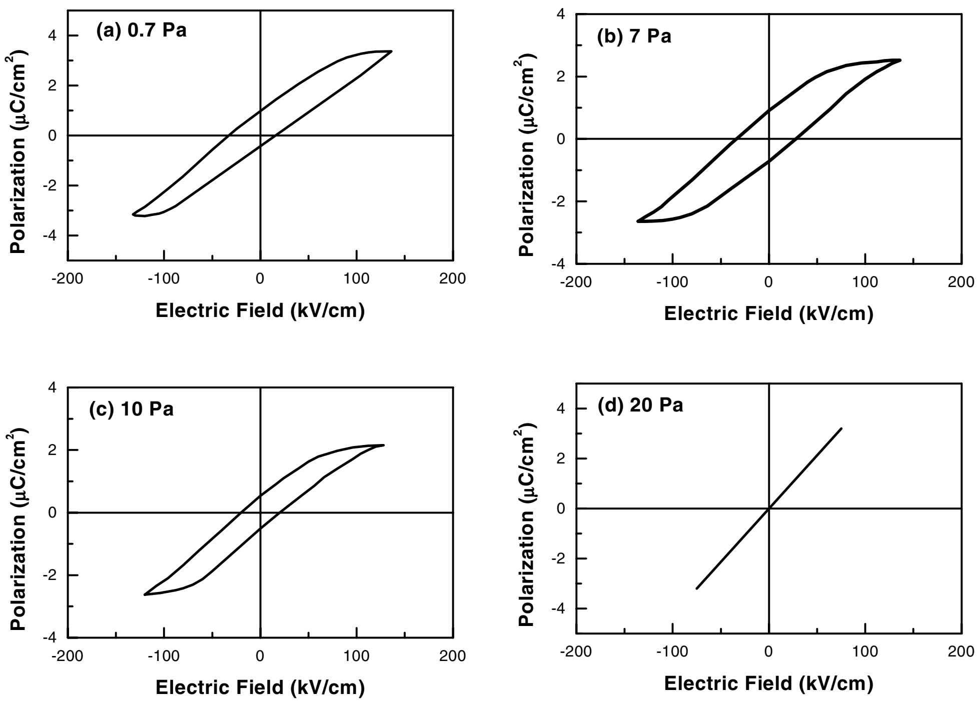


**Figure 5.** *P–E* hysteresis loops for $BaTiO_3$ thin films deposited on $LaNiO_3/SrTiO_3$ substrates at different oxygen pressures of (a) 0.1 Pa, (b) 2 Pa, (c) 7 Pa and (d) 20 Pa.

the crystalline structure. The corresponding optimum pressures have been found. The films fabricated in an intermediate oxygen pressure range of 2 to 10 Pa show the *c*-axis oriented tetragonal structure and a stoichiometry close to the ideal value. In this case, the films exhibit a large dielectric constant, small dielectric loss and good ferroelectricity with a symmetric hysteresis loop. For growth at low oxygen pressure, the film also shows a *c*-axis oriented tetragonal structure, but significant degradation of the dielectric properties is observed. For higher oxygen pressure, the film has a tetragonal *a*-axis orientation, shows no ferroelectricity and has the largest dielectric constant. Our results suggest that the dielectric properties and the ferroelectricity of $BaTiO_3$ films can be tuned by varying the oxygen content.

## Acknowledgments

This work was supported by a grant of the State Key Program of China and Grant No 59832050 of the National Natural Science Foundation of China.

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