Electrical and magnetic properties of polycrystalline Mn-doped BaTiO3 thin films grown on Pt/sapphire substrates by pulsed laser deposition

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Abstract. 5 at.% Mn-doped and undoped, 200 nm thick $BaTiO_3$ thin films have been grown under different oxygen partial pressures by pulsed laser deposition on Pt/sapphire substrates. X-ray diffraction (XRD) measurements reveal the same polycrystalline single-phase perovskite structure for all the thin films despite the different oxygen partial pressure, while their preferred orientation strongly depends on the oxygen partial pressure. The 5 at. % Mn-doping decreases the dielectric loss of the Mn-doped $BaTiO_3$ thin films, however, their relative permittivity is also decreased. Ferroelectricity has been probed on the Mn-doped and undoped $BaTiO_3$ thin films grown under relatively high oxygen partial pressure. A ferromagnetic coupling of the Mn dopant ions has been probed at room tempetature on the Mn-doped $BaTiO_3$ thin films prepared under low oxygen partial pressure and is understood in terms of the bound magnetic polaron model.

Introduction

Much work has been carried out in the field of perovskite oxides due to their relatively simple structure and widespread applications including for example sensors, transducers, and memories. Among the perovskite oxides, $BaTiO_3$ is one of the most intensively studied compounds since more than 60 years [1-5]. $BaTiO_3$, as a typical ABO3 perovskite oxide whose structure can be described as a set of BO_6 octahedrals arranged in a cubic pattern, with the Ba^{2+} ions located in the spaces between the octahedrals and the Ti^{4+} ions occupying the center of the octahedrals [6]. In order to improve the properties of $BaTiO_3$ and to realize multi-functionality, various dopants have been introduced into bulk or thin film $BaTiO_3$ to substitute the Ba^{2+} or Ti^{4+} ions. Wu *et al.* [7] experimentally demonstrated that a proper concentration of Mn dopants in $BaTiO_3$ ceramics can significantly increase its dielectric constant and decrease the dielectric loss, which was accounted for by the reaction: $Mn^{4+} + 2Ti^{3+} \rightarrow Mn^{2+} + 2Ti^{4+}$. Cole *et al.* [8] fabricated a 5 mol % Mg-doped $Ba_{1-x}Sr_xTiO_3$ multilayer structure and showed that Mg-doping reduces the dielectric loss of $Ba_{1-x}Sr_xTiO_3$ to 0.008 and yields a smoother surface compared to undoped $Ba_{1-x}Sr_xTiO_3$. Lin *et al.* [9] prepared epitaxial Co-doped $BaTiO_3$ thin films on Nb-doped $SrTiO_3$ substrates by pulsed laser deposition and observed a ferromagnetic (FM) behavior at room temperature. The largest saturated magnetization of 187 emu/cm^3 was obtained for a Co-doped $BaTiO_3$ thin film thickness of 7 nm. However, polycrystalline, high concentration Mn-doped $BaTiO_3$ thin films grown on low-cost Pt/sapphire substrates and their electrical and magnetic properties were rarely to be reported so far. Furthermore, there is no risk of ferromagnetic precipitate formation in Mn-doped $BaTiO_3$.

Experiment

Here we report on the structural, magnetic and ferroelectric properties of undoped $BaTiO_3$ (BTO) and 5 at.% Mn-doped $BaTiO_3$ (BTMO) thin films which have been prepared by pulsed laser deposition on Pt/c-sapphire substrates. High purity $BaTiO_3$ (4N) powder and a mixture of high purity $BaTiO_3$ (4N) and MnO_2 (5N) powder have been pressed and finally sintered at 1300 ℃ for 12 hours to obtain the undoped and Mn-doped $BaTiO_3$ ceramic target, respectively. The 100 nm thick Pt bottom electrodes has been sputtered on c-sapphire substrates outside the PLD chamber. The BTMO films were grown by pulsed laser deposition using a KrF excimer laser (λ=248 nm)

with a fixed repetition rate of 2 Hz and a deposition temperature of 650 ℃. To investigate the dependence of the electric and magnetic properties of the BTO and BTMO thin films on the ambient gas partial pressure, 0.01 and 0.1 mbar oxygen partial pressures were used. Ca. 100 nm and 200 nm thick films have been prepared using 1000 and 2000 laser pulses, respectively. After deposition, the films were *in-situ* post-annealed for 30 minutes at 650° C and subsequently cooled down to room-temperature with a cooling rate of 5 k/min under a constant oxygen partial pressure of 200 mbar. The crystal structure of the films has been analyzed by means of x-ray diffraction (XRD) using a D8 diffractometer with the CuKα radiation. The magnetic properties of the films have been probed by a superconducting quantum interference device magnetometer (Quantum Design MPMS). For electrical property measurements circular Au top electrodes with a diameter of 0.5 mm were deposited by magnetron sputtering on top of the as-prepared BTO and BTMO thin films using a metal shadow mask to form a parallel-plate capacitor with BTO or BTMO as the dielectric medium. The dielectric properties of the thin films have been analyzed by an impedance analyzer (Agilent 4294A) in the frequency range from 100 Hz to 100 kHz under a driving voltage of 50 mV, the polarization-electric field loops of the films were observed using a Sawyer-Tower circuit [10] at 10 kHz.

Results and Discussion

Fig. 1 shows the XRD θ-2θ patterns of the 200 nm thick BTMO and BTO films grown on Pt/c-sapphire substrates. Only diffraction peaks corresponding to the perovskite structure have been observed, indicating that the prepared thin films have a single perovskite phase. The BTO thin film is preferential (111)-oriented (Fig. 1(a)), the BTMO thin film deposited at 0.1 mbar oxygen pressure reveals a random orientation (Fig. 1(b)), while the BTMO thin film deposited at 0.01 mbar oxygen pressure was highly (001)-oriented (Fig. 1(c)). Although the BTMO films contain 5 at % Mn, only perovskite phases were detected in the BTMO thin films [Fig. 1 (b)(c)], revealing a full substitution of the Ti^{4+} ions (radius 0.068 nm) by Mn^{4+} ions (0.067 nm), i.e. no Mn clusters have been formed.
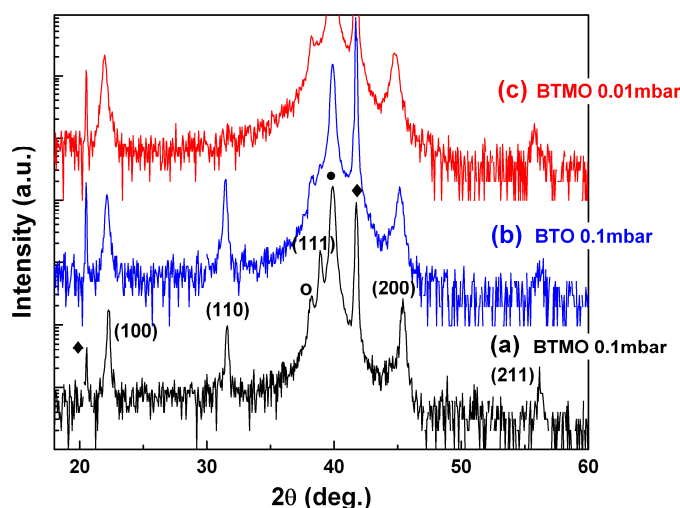

Fig. 1. XRD patterns of (a) BTMO and (b) BTO thin films prepared at 0.1 mbar oxygen pressure, and of a (c) BTMO thin film prepared at 0.01 mbar oxygen pressure on Pt/sapphire substrates. XRD peaks are labeled by the symbols o, ●, and ◆ represent Au, Pt, and c-sapphire reflexes, respectively.

Fig. 2 shows the frequency dependence of the relative permittivity (ε_r) and the dielectric loss (tanδ) at room temperature of the 200 nm thick BTMO and BTO thin films prepared at 0.1 mbar oxygen pressure at 650°C. The tanδ of the BTO film exhibits a noticeable increase with decreasing frequency from 1 kHz to 100 Hz. On the other hand, it can be observed that the tanδ of BTMO thin

film showed no obvious change in the frequency range from 100 Hz to 100 kHz, in addition, the BTMO thin film displayed lower tanδ than the BTO thin film in this frequency range. Chu *et al.* [11] have reported that Mn-doping can reduce the tanδ of BTMO thin films, however, the maximum concentration of Mn in their investigation was 1 at.%. Here we show that the tanδ of BTMO thin films can be further decreased by increasing the Mn concentration. The ε_r of the BTMO and BTO thin film is rather constant over the entire investigated frequency range, revealing a small built-in voltage at the front and bottom electrode. Therefore, the probed ferroelectricity of these thin films is an intrinsic property [12,13]. The ε_r of the BTMO thin films is smaller than that of the BTO thin films, indicating that excessive high concentration of Mn- doping decreases the ε_r of BTMO thin films, that is consistent with the results of BTO ceramics reported by Wu *et al.* [7]. By using a measurement frequency of 10 kHz, the ε_r and tanδ of the BTMO and BTO thin films were respectively found to be 657, 1.6 % and 857, 2.5 %.
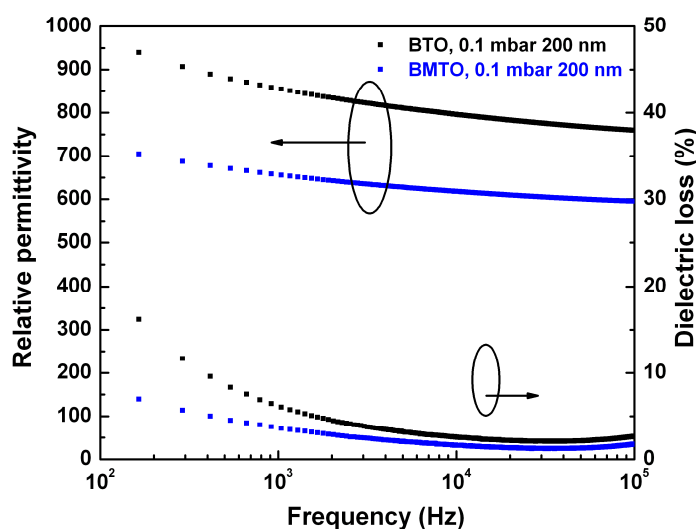

Fig. 2. Frequency dependence of the relative permittivity (ε_r) and dielectric loss (tanδ).

The P-E loops of the BTMO and BTO thin films grown at 0.1 mbar oxygen pressure measured by sawyer-tower circuit at 10 kHz are shown in Fig.3(a). The P-E loops indicate a typical ferroelectric (FE) behavior of both the BTMO and BTO thin films. The remnant polarization Pr and coercive electric field Ec are 2Pr = 6.0 μC/cm^2 and 2Ec = 70 kV/cm for the 200 nm thick BTMO film and 2Pr = 9.6 μC/cm^2 and 2Ec = 86 kV/cm for the 200 nm thick BTO film. The 2Pr value of the BTMO thin film is larger than that of other reported pure polycrystalline BTO thin films grown on different substrates [14-16], indicating a good crystallization quality of the obtained BTMO thin film. For the 100 nm thick BTMO thin film an even larger remnant polarization of 2Pr = 10.2 μC/cm^2 has been observed. This value is comparable to the that of the reported epitaxial (001)-oriented 1 at.% Mn-doped BTO thin film [17], while the coercive electric field was also increased (Fig.3(b)). The increased 2Pr of the 100 nm thick BTMO thin film is due to the larger electric field applied on the thin films with a smaller thickness, such that more ferroelectric domains can be reversed under higher electric field. It should be noticed that even under a high electric field of 800 kV/cm, the BTMO thin films were not broken down and a saturated P-E loop can still be observed, probably arising from the presence of few defects in the 100 nm thick BTMO films. However, for the 200 nm thick BTMO film grown at 0.01 mbar oxygen pressure no saturated P-E loop can be observed (not shown), which is probably due to the large leakage current resulting from oxygen vacancies.
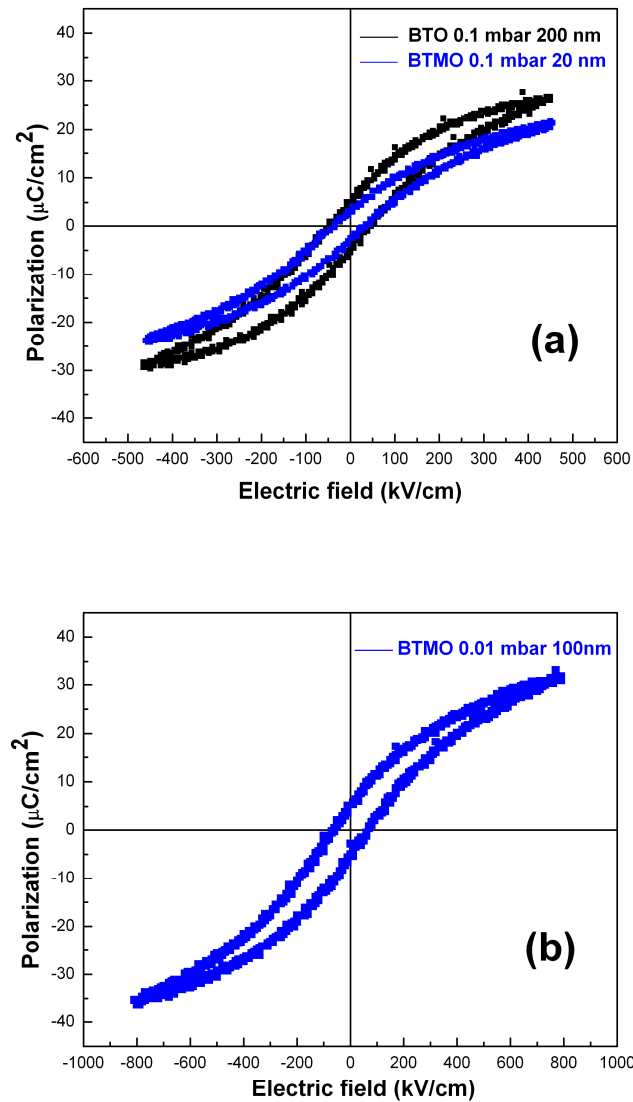
Fig. 3. Polarization-electric field hysteresis loops of (a) the BTMO (200nm) and BTO (200 nm) thin films and of the (b) BTMO (100 nm) thin film grown at 0.1 mbar oxygen pressure.

The magnetization-field (M-H) hysteresis loop is shown in Fig.4 for the BTMO thin film deposited at 0.01 mbar oxygen pressure and reveals a ferromagnetic (FM) coupling of the Mn dopant ions, whereas the BTMO thin film grown at 0.1mbar oxygen pressure is not ferromagnetic. As seen from the XRD pattern in Figure 1(c), no XRD peak corresponding to a non-perovskite structure can be observed, excluding the Mn segregation as the origin of the observed FM behavior of the BTMO thin film grown in low oxygen pressure. One of the possible reasons of the FM behavior in BTMO thin films can be explained by a bound magnetic polaron model (BMP) which has been proposed by Coey *et al.* [18]. In this model, a coupling effect between electrons bound to oxygen vacancies and Mn^{4+} dopant ions is regarded as the origin of ferromagnetism in Mn-doped BTO thin films. By the BMP model, we can also understand the reason why only the BTMO thin film grown in low oxygen pressure (0.01 mbar) shows FM behavior, however, the BTMO thin film prepared in high oxygen pressure (0.1 mbar) is non-ferromagnetic, that is because the former has more oxygen vacancies inside due to the low deposition pressure, giving rise to an enhancement of the exchange interaction between the d spins in the Mn^{4+} and the electrons bound to oxygen vacancies. This can also be proved by P-E loop measurements. The BTMO film grown at low oxygen pressure reveals a large leakage current so that no typical P-E curve can be observed. This is ascribed to the large amount of

oxygen vacancies, while P-E loops can be probed on the BTMO thin film prepared at high oxygen pressure as shown in Fig. 3. Note that for the BTMO thin film grown at low oxygen pressure, the magnetic moment is a superposition of the paramagnetic magnetization from isolated Mn^{4+} outside the BMPs and ferromagnetic magnetization from Mn^{4+} inside the BMPs. The paramagnetic component disappears at 150 k, while the ferromagnetism component is nearly temperature independent.
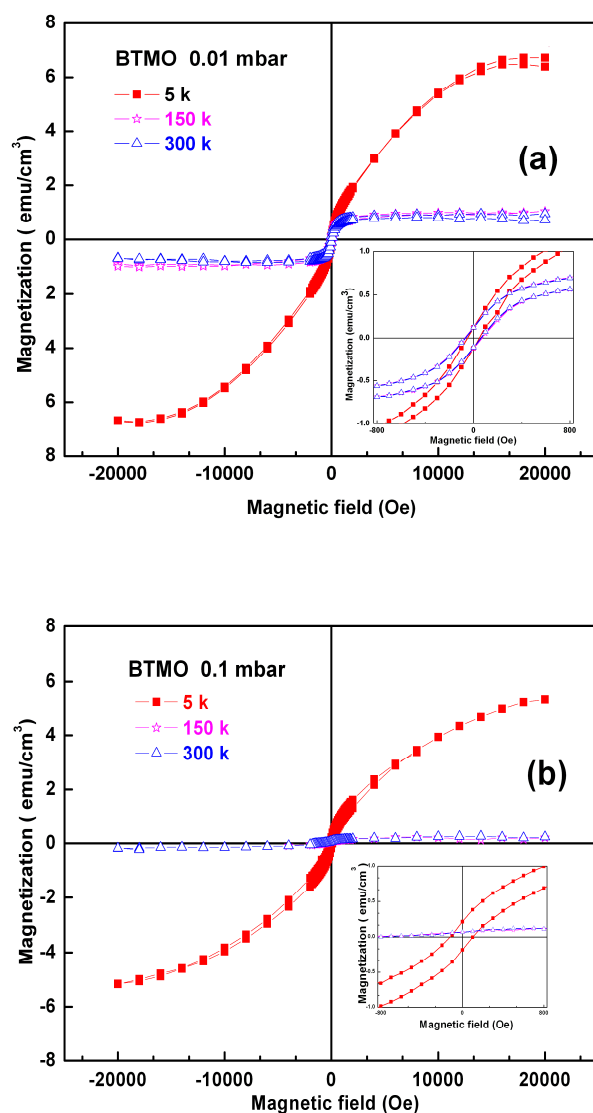

Fig. 4. Magnetization-field hysteresis loop of the BTMO thin films at different oxygen pressure. The inset shows a zoom in low magnetic fields manifesting a hysteresis of the loops. For the BTMO 0.1 mbar, only half loop was measured at 150 and 300 k (Fig. 4(b)).

Summary

In conclusion, 5 at.% Mn-doped $BaTiO_3$ and pure $BaTiO_3$ thin films were prepared on Pt/sapphire substrates at different oxygen pressures by pulsed laser deposition. The films grown at 0.1 mbar oxygen pressure show saturated P-E curves, indicating a typical ferroelectricity. However, the Mn-doped $BaTiO_3$ films grown at 0.01 mbar oxygen pressure reveal no P-E curve probably due to oxygen vacancies causing large leakage currents. The Mn-doped $BaTiO_3$ thin film prepared at low oxygen pressure reveals ferromagnetic coupling at room temperature, which can be explained by a bound magnetic polaron model. Those bound electrons are necessary for mediating the parallel alignment of Mn^{4+} dopant ions but decrease in the same time the breaktrough voltage of the BTMO

capacitors. The result indicates the possibility to introduce ferromagnetism into ferroelectric polycrystalline BTMO thin films on low-cost Pt/sapphire substrates, however, further investigations are necessary to realize the coexistence of ferromagnetism and ferroelectricity in polycrystalline BTMO thin films.

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