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Chemical solution deposition of multiferroic $La_{0.7}Sr_{0.3}MnO_3$, $BaTiO_3$ thin films prepared by ink plotting

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ABSTRACT

Ferroelectric $BaTiO_3$ (BTO) as well as ferromagnetic $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films were prepared by chemical solution deposition (CSD). Based on these, a multiferroic architecture stack of $La_{0.7}Sr_{0.3}MnO_3/BaTiO_3$ layers was developed. Aqueous, environment friendly precursor solutions were formulated for both materials. These are used for ink plotting on $SrTiO_3$ (1 0 0) substrates. Films were subjected to a subsequent thermal treatment at the corresponding crystallization temperature. The structural as well as the magnetic and electric properties are presented. The Curie temperature of the ferromagnetic LSMO layer with a film thickness of only 60 nm was determined to 360 K. The magnetization curve indicates a hysteresis loop with a saturation magnetization above 400 emu/cm^3. The ferroelectric character of the BTO films was demonstrated by polarization curves.

1. Introduction

Multiferroic systems consist of a ferroelectric and a ferromagnetic layer, where the layers are essentially elastically coupled. This allows to control the electric polarization of the ferroelectric layer by a magnetic field or to alter the magnetization of the ferromagnetic layer by an electric field. The coupling of magnetic and ferroelectric orders in a material is known as the "magneto-electric effect" [1]. $BaTiO_3$ is a very intensively studied ferroelectric crystal [2–4], with a lattice constant of the tetragonal BTO crystal structure, $a_{BTO} = 3.99$ Å. $La_{0.7}Sr_{0.3}MnO_3$ is a ferromagnetic material with a lattice constant of $a = 3.87$ Å, which is very close to the value of $BaTiO_3$ leading to tensile strain in LSMO films. LSMO offers the advantage that its lattice parameter can be finely tuned by the polarization of the ferroelectric BTO crystal [5,6]. Consequently, the magnetic properties of the LSMO film can be influenced by the polarization of the BTO crystals.

Chemical solution deposition (CSD), in particular ink plotting, is a promising process for a low-cost large-scale fabrication of complicated coatings and high end decorated patterns [7,8]. Studies reported in this article concentrate on a sol–gel ink plotting which is a new approach for manufacturing multiferroic layer structures. Aqueous, environment friendly precursor solutions of $BaTiO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ were developed for the preparation of multiferroic architectures on $SrTiO_3$ substrates obtained from a complete CSD route. Complexing agents were used to stabilise the metal salts at high concentration during gelation of the films, according to methods described before other materials [9–11].

2. Experimental

Solutions of Mn, La and Sr acetates were prepared independently in water being stabilised by glycine (Sr and La) and EDTA (Mn). Stoichiometric amounts of the solved salts were mixed and accurately stirred in order to obtain a solution of 0.05 M referred to Mn. The solution was adjusted with mQ water and ethanol to achieve a proportion of 90/10 of both solvents. TREG in a 5% and hexadecyltrimethylammonium bromide in 0.5 g/l was added to the previously prepared 0.05 M (Mn) solution. The measured properties of the $La_{0.7}Sr_{0.3}MnO_3$ precursor solution are reported in Table 1.

An aqueous $BaTiO_3$ precursor solution was prepared using titanium propoxide (TIP) (Fluka, ≥97.0%) as Ti^{4+} source and barium acetate ($Ba(OAc)_2$) (Sigma–Aldrich, ≥99.0%) as Ba^{2+} source. Citric acid (CA) (Acros Organics, 99.5%), triethanolamine (TEA) (Acros Organics, 99+%), ethanolamine (EA) (Sigma–Aldrich, ≥99.0%), ethyleneglycol (EG) (Sigma–Aldrich, ≥99.5%) and ethanol (EtOH) (Absolute, Panreac) are added for stabilisation. All materials were used without further purification. First, a Ti-precursor solution was prepared by adding TEA to TIP in a molar ratio of 2:1 and H_2O in a 60:1 molar ratio to Ti^{4+}, to obtain a final Ti^{4+} concentration of 0.57 M. The final pH of the solution was 8. A Ba^{2+}-precursor solution was prepared by dissolving $Ba(OAc)_2$ in H_2O (in 1:112 molar ratio). EG and CA are added as complexing agents in a 4:4:1 molar ratio to Ba^{2+}. Afterwards, the pH of the solution was increased to 8.5 by adding EA. The final Ba^{2+} concentration was set to be 0.33 M. To obtain a stable $BaTiO_3$ solution, stoichiometric amounts of both precursors are mixed to obtain a final concentration of 0.21 M. Optimization of concentration, ratios of stabilising agents and pH was performed based on theoretical calculations of distribution diagrams using the EQUIL-Hyperquad program [12,13].

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Table 1
Properties of the LSMO solution.

Density	1.0155 g/cm^3
Viscosity	1.3 mPa s
Contact angle (LAO)	52.33°
Surface tension	29.19 mN/m
Colour	Uncolored, transparent

The viscosity of the solution was determined using a Brookfield DVE viscometer and the surface tension and wettability on several substrates was studied by the pendant drop method using an optical tensiometer (Kruss DSA 30).

Deposition of LSMO and BTO inks was carried out on $SrTiO_3$ (1 0 0) substrates by ink plotting using a “Sonoplot GIX Microplotter”. The Sonoplot ink plotter is capable of applying picoliters of fluid continuously creating features onto a surface. Ink is loaded by capillary forces into a hollow glass needle, which is attached to a piezoelectric element. At the resonant frequency of the loaded dispenser the fluid is sprayed out of a 10 or 30 μm diameter opening at the end of the needle. First, LSMO as well as BTO single layers were plotted separately on STO substrates. In a next step BTO layers were coated on top of a LSMO film. The wet films were dried and annealed in a tube furnace from “Ströhlein Instruments”. LSMO films were pyrolized at temperatures between 250 °C and 500 °C in air and crystallized at 900 °C for 5 h in oxygen atmosphere [14]. BTO films were pyrolized and crystallized at 500 °C and 700 °C in air [15]. Crack formation in BTO layers can be avoided by using a slow heating rate of 60 K/h. The desirable thickness of BTO layers was obtained through multiple coating and annealing processes. The phase structure of $BaTiO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ thin films was characterized by X-ray diffraction. Topography and film thickness were studied by atomic force microscopy AFM DI 3100. SQUID (Superconducting Quantum Interference Design) measurements were used to investigate the magnetic properties of LSMO layers. In order to perform the electric characterization of the BTO films, a capacitor stack of a LSMO layer/triple layer BTO/liquid silver contact was fabricated. Polarization measurements were performed at room temperature at 1000 Hz.

3. Results and discussion

3.1. *Aqueous $BaTiO_3$ precursor solutions*

We have prepared different aqueous $BaTiO_3$ precursor solutions by using triethanolamine (TEA), citric acid (CA) and ethyleneglycol (EG) as complexing agents to inhibit the hydrolysis of the Ti-alkoxide and Ba-acetate by the presence of water. Heating of a small volume of the solution poured into a petri-dish to 60 °C for 2 h leads to stable and transparent gels. The density of the solution, i.e. 1.184 g/cm^3, was determined by standard pycnometry. We find a surface tension value (γ) of 41.59 ± 0.25 mN/m as determined by the pendant drop method using the Young–Laplace approach. The viscosity of the solution was 10.9 cP.

3.2. *Structure characterization of single LSMO and BTO layers*

The surface morphology of the LSMO films was investigated by AFM, as shown in Fig. 1 [16]. The average grain size is up to 120 nm, as seen in the corresponding line scan. The value of the root mean square Rms was measured to be about 40 nm. The surface structure is essential for ink plotting of BTO layers on top of the LSMO film. The LSMO layer thickness lies in the range of 60–100 nm. The X-ray

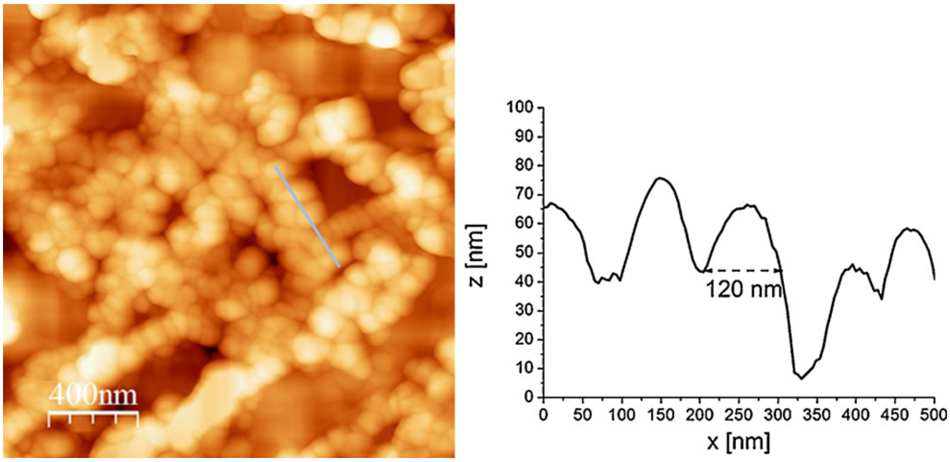

Fig. 1. AFM measurements of crystallized LSMO film on a STO substrate with the corresponding line scan.

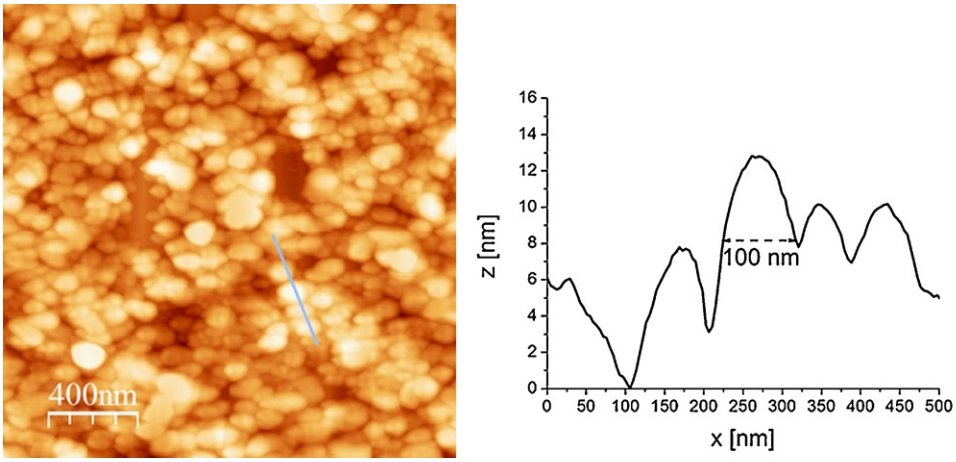

Fig. 2. AFM measurements of crystallized BTO film with the corresponding line scan on a STO substrate prepared by ink plotting.

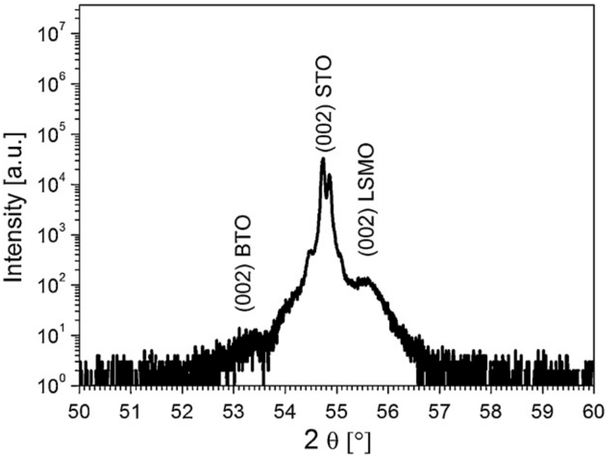

Fig. 3. Typical θ–2θ X-ray diffraction pattern for a $La_{0.7}Sr_{0.3}MnO_3/BaTiO_3$ film architecture grown by chemical solution deposition on $SrTiO_3$ substrate.

diffraction spectrum obtained for a LSMO thin film deposited on a (1 0 0) STO oriented substrate reveals a $La_{0.7}Sr_{0.3}MnO_3$ film composition with a perovskite-type structure, presenting a (0 0 1) preferred growth direction, see Fig. 3.

An AFM image of the surface of a crystallized BTO film on a STO substrate is shown in Fig. 2. The surface structure indicates a very smooth surface. The value of the root mean square Rms is about 5 nm. Corresponding to the line scan shown in Fig. 2 the average grain size is up to 100 nm. The BTO layer thickness was measured to be about 15 nm. The films were found to be crack-free, revealing the basis for a perfect isolating film character which is one of the most important requirements for multiferroic films.

3.3. Magnetic characterization of a LSMO layer

The temperature dependence of the magnetization of a single LSMO layer on STO was measured by SQUID in the temperature range from 5 to 350 K. To determine the ferromagnetic ordering temperature T_C the magnetization curve was obtained by initially cooling the sample and then measuring its magnetic moment m with increasing temperature under an applied external magnetic field of $\mu_0 H = 0.3$ T. The measurement of the Curie temperature T_C is shown in Fig. 4a. The value of T_C has been derived by extrapolating the linear part of m^2 (T) to $m = 0$, resulting in $T_C = 360$ K. This value is insignificantly lower than the reported value for bulk LSMO ($T_C = 370$ K) [17,18] which can be explained by the finite thickness of the film [19,20]. By comparing the measured T_C value with those of references on LSMO films, we conclude that the accurate $La_{0.7}Sr_{0.3}MnO_3$ phase was obtained. The field dependent measurement of the magnetic moment m was performed at a temperature of 10 K and is reported in Fig. 4b. The magnetic moment of the LSMO layer saturates at an external field of $\mu_0 H = 0.2$ T. The saturation magnetization is about 280 emu/cm^3 for a 60 nm thick LSMO layer. Taking into consideration the LSMO surface roughness, the saturated magnetization at 10 K is modified to a value above 400 emu/cm^3 which is in the range of the respective bulk LSMO phase [17]. All magnetic measurements have been adjusted according to the diamagnetic part of the signal originating from the STO substrate.

3.4. Electrical characterization

To realize crack-free, fully isolating ferroelectric films extremely thin BTO layers were prepared by ink plotting using a capillary of only 10 μm opening. Furthermore, a very slow heating rate of 60 K/h was realized during pyrolysis of the BTO films. The combination of the use of thin films and slow heating rates induces a careful oxidation reaction of the solvents. This leads to dense and crack-free BTO films with a film thickness of only 15–20 nm. To increase the film thickness the coating – annealing process was repeated several times.

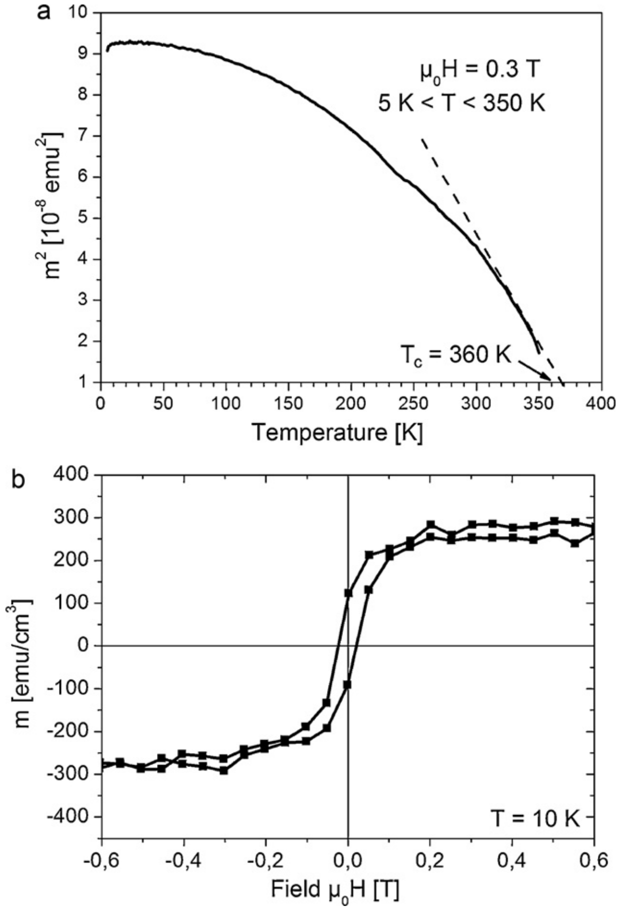

Fig. 4. (a) Temperature dependence of the magnetic moment m of the LSMO phase. (b) Field dependence of the magnetic moment m of the LSMO phase.

Electrical characterization of ferroelectric BTO films requires an electric conducting substrate. Therefore, a hetero-structure was fabricated with LSMO acting as a ferromagnetic ground layer and simultaneously as an electric contact to the bottom electrode followed by the ferroelectric BTO layer on top. A liquid silver contact was deposited on top of the BTO layer, acting as the second electric contact. The size of the silver paint contact is estimated to be 0.1–0.2 mm^2. The schematic of such a multiferroic device is shown in Fig. 5. Polarization measurements were carried out at a heterostructure stack of LSMO/triple layer BTO/silver. The polarization

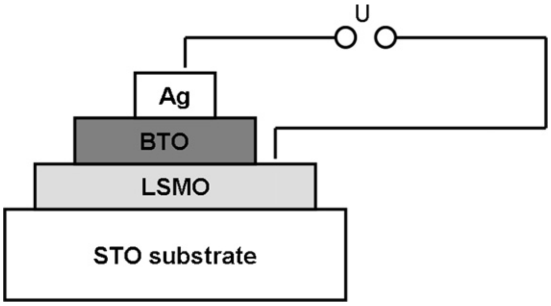

Fig. 5. Schematic of the multiferroic system setup.

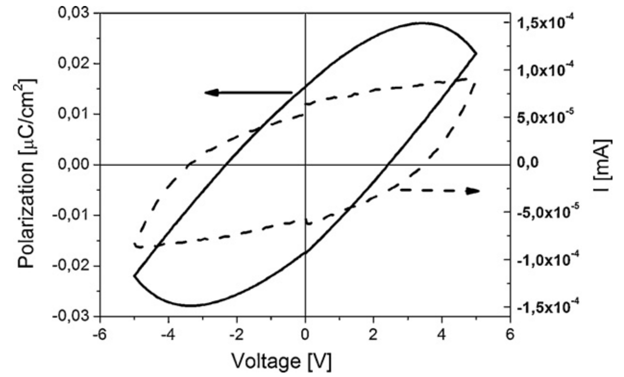

Fig. 6. Hysteresis loop of polarization measurements of a $BaTiO_3$ triple layer at room temperature with corresponding current (*I*–*V*) loop.

and corresponding displacement of the ions was recorded as a function of the applied voltage. When an electric field is applied along the BTO film a dipole alignment parallel to the electric field can be measured. Dipole alignment and corresponding elongation of the BTO crystal structure is reflected in hysteresis loops of polarization measurements [21]. The polarization hysteresis loop of a triple layer of BTO is shown in Fig. 6. The remanent polarization (P_r) at room temperature is 0.015 $\mu C/cm^2$ and a saturation polarization of 0.025 $\mu C/cm^2$ was obtained for a 5 V maximum applied voltage. These values clearly demonstrate the ferroelectric functionality of the BTO thin film. We obtained good reproducibility of these values of polarization when changing the measured multiferroic architecture. Nevertheless, a decrease of the saturation polarization is observed in the hysteresis loop. The decrease is due to a slight remaining leakage current originating mostly from the relatively large silver contact area. The relative low polarization value is caused by the leakage current, because the applied field was not high enough for saturating the complete contact area of the sample. Furthermore, the leakage currents are likely attributed to a small BTO film thickness as reported in [22]. Yet, the switching processes still are detected.

4. Conclusions

In this study we demonstrated the preparation of a multiferroic device by complete chemical solution deposition route using environment friendly water based precursor solutions of LSMO and BTO. Requirements for the fabrication of such architecture are a very flat and homogeneous $La_{0.7}Sr_{0.3}MnO_3$ film as well as a crack free and non-porous $BaTiO_3$ layer on top. The magnetic properties of the LSMO layer reveal a Curie temperature T_C of 360 K and a saturation magnetization above 400 emu/cm^3 for a 60 nm film thickness. Polarization measurements were carried out to demonstrate the switching processes of the BTO film when applying an electric field.

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