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Dielectric properties of amorphous $BaTiO_3$ films deposited by RF magnetron sputtering

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Abstract

In the present paper, dielectric properties of a-$BaTiO_3$ films have been investigated as a function of frequency (10^{-1} to 10^5 Hz) and temperature (25–350 °C) using the dielectric spectroscopy technique. Relaxation and ac-conductivity processes were analyzed in order to study charge transport in the bulk and at the electrode-film interfaces. It seems that the oxygen vacancies play an essential role in both processes.

Keywords: $BaTiO_3$ films; Dielectric properties

1. Introduction

In the recent years, there has been extensive research into thin films of perovskite materials in view of their applicability as integrated capacitors in electronics. Barium titanate ($BaTiO_3$) constitutes a very promising material for these applications. This is motivated by its ability to show high dielectric constant, low loss factor, low leakage current and high breakdown field. To get the highest dielectric constants (>100), which are obtained for the crystalline phase, it is necessary to deposit the films at high temperatures (>500 °C). This constitute a serious problem for processes, which require low temperatures (plastic substrates, for instance). To circumvent this problem, herein we studied the properties of amorphous $BaTiO_3$ that can be easily deposited at room temperature by the RF magnetron sputtering technique.

On the other hand, the lifetime of titanate materials under operating conditions is limited by their resistance degradation[1] which is closely related to the motion of ionic defects (oxygen vacancies). Therefore, ionic transport is an important parameter to study in these materials in order to understand their failure mechanisms.[2] Up to now, ionic transport and resistance degradation were mainly studied by dc transport measurements. Additional information can be gained from ac dielectric measurements. So, the present work aims to study the dielectric properties of a-$BaTiO_3$ films and to distinguish between bulk conductivity and charge transport at the electrode-bulk interfaces.

2. Experimental procedure

In this study, metal-insulator-metal (MIM) capacitors with a Cu/a-$BaTiO_3$/Cu structure were employed. Glass was used as the starting substrate. A bi-layer of chromium (100 nm) and copper (450 nm) was firstly evaporated. Then, $BaTiO_3$ (160 nm thick) films were deposited by RF magnetron sputtering at low temperature (the substrates were water-cooled) under an atmosphere of pure argon gas (10^{-2} mbars). As a result, the elaborated films are amorphous. Top Cu-electrodes were deposited by thermal evaporation through a shadow mask to constitute planar MIM capacitors of 1.77 mm^2 area. Dielectric measurements (dielectric constant, loss factor and ac conductivity) were acquired in the frequency domain (10^{-1}–10^5 Hz) at temperature ranging from 25 to 350 °C using a Novocontrol impedance analyzer. Temperature was controlled by a Linkam hot-stage. During measurements, samples were enclosed in a dark shielded cell filled with dry nitrogen. Micro-structural properties were studied using X-ray diffraction analysis (XRD, Fe Kα radiation) and chemical composition of the films was determined using X-ray photoelectron spectroscopy (XPS, Mg Kα radiation).

3. Results and discussion

XRD analysis, performed at grazing incidence,[3] confirms that barium titanate films are in an amorphous state. We could not

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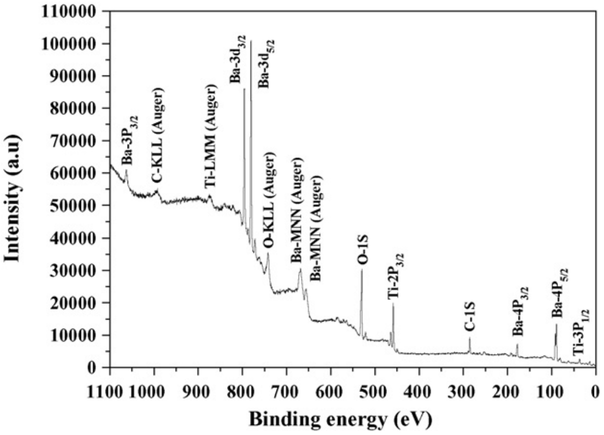

Fig. 1. XPS spectrum of a 0.16 μm–thick barium titanate film.

detect any oxidation layer, such as copper oxides, at the film-electrode interfaces. Fig. 1 displays the XPS spectrum of the material. Traces amount of carbon are detected around 284.5 eV (C 1s) which probably come from residual hydrocarbon species adsorbed at the surface.[4] The O (1s) transition is detected at 529.5 eV and is assigned to oxygen in the $BaTiO_3$ lattice. This is in a good agreement with previous reports.[5] From the XPS data, we can extract the molar ratio of the different chemical species. We found that barium titanate films elaborated under an inerte atmosphere (pure argon gas) are slightly nonstoichiometric with some oxygen deficiency ($BaTiO_{3-\delta}$).

In Fig. 2, the dielectric constant ε' (Fig. 2(a)) and the loss factor $\tan\delta$ (Fig. 2(b)) are plotted as a function of frequency (10^{-1} to 10^5 Hz) and temperature (25–350 °C). At low temperatures, ε' is about 16 and remains constant in the entire frequency range. A noticeable feature in the dielectric behavior is that the low frequency value of ε' starts to rise with temperature to display a strong dispersion phenomenon. Simultaneously, in the $\tan\delta$ measurements we observe a marked loss peak (dielectric relaxation) that shifts to higher frequencies with temperature. Fig. 3 displays the evolution of ac-conductivity as a function of frequency. At temperatures lower than 100 °C, the ac conductivity varies as a power law with frequency. This is a typical behavior of an ac-conduction dominated by a short range hopping process with a distribution of energy barriers. At high temperatures ($T > 125$ °C), the conductivity shows a first plateau which can be ascribed to the bulk conduction. We note that at higher temperatures, bulk conductivity in titanates materials is predominately ionic according to the motion of the oxygen vacancies. In addition, at even higher temperatures ($T > 250$ °C), the ac conductivity exhibits what could appear as a second plateau (see Fig. 3). It is thought that this behavior is related to the electrode-film interface.[6,7] Generally speaking, in case of a metal-insulator contact characterized by a total charge transfer ("ohmic" contact), charge carriers are regularly evacuated at the interface (complete discharge of the oxygen vacancies). Then, only the bulk conductivity is measured and σ_{ac} displays one plateau at low frequencies. On the contrary, when there is no charge transfer at electrodes (inhibition of the discharge of the oxygen vacancies), charge carriers pile up at the electrode giving rise to a space charge that creates an electric field that opposes the applied field. In that case the conductivity falls off to zero. The intermediate and more general case corresponds to a partial charge transfer at the electrode-film interfaces ("leaky" electrodes). In that case an electrode space charge is maintained (reduction of the electric field in the bulk) but transfer of charges at electrodes is now allowed. This leads to the appearance of a second plateau at low frequencies. The overall ac conductivity can be described by the following empirical law[8]: $\sigma_{ac}(\omega) = \sigma_i(T) + k_1(T)\omega^{\alpha 1} + \sigma_b(T) + k_2(T)\omega^{\alpha 2}$, where T is the absolute temperature, ω the angular frequency, k_1 and k_2 are

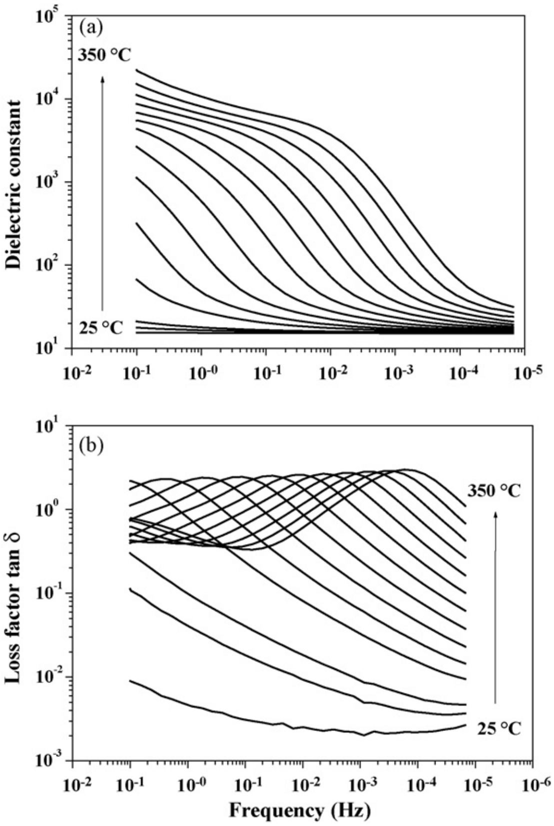

Fig. 2. Frequency dependence of dielectric constant (a) and loss factor (b) from 25 to 350 °C (25 °C step).

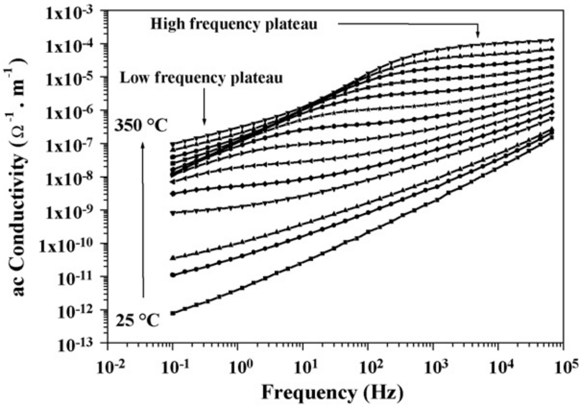

Fig. 3. Frequency dependence of the ac conductivity from 25 to 350 °C (25 °C step).

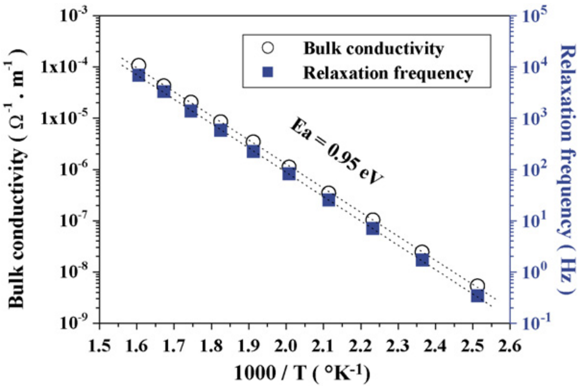

Fig. 4. Temperature dependence of the bulk conductivity and the relaxation frequency (Arrhenius diagram).

two constant, σ_b and σ_i correspond to the bulk and interfacial conductivities, respectively. The exponent α1 is close to 1 when temperature varies from 225 to 350 °C whereas the exponent α2 is found to vary between 0.9 and 0.5 when temperature increases from 25 to 225 °C.

As already noted in Fig. 2(b), the frequency position of the relaxation peak (f_{relax}) shifts to higher frequencies as the temperature increases according to an Arrhenius law. Activation energy of the relaxation process is extracted from the Arrhenius plot and is found to be around 0.95 eV (see Fig. 4). We can compare this behavior with the temperature variation of the bulk conductivity (extracted from the high-frequency plateau in Fig. 3). This is shown in Fig. 4 where it appears that the bulk conductivity and the relaxation peak have the same activation energy. This shows that the conduction and the relaxation processes have the same origin. The value of the activation energy (0.95 eV) well agrees with those (0.9–1.1 eV) determined for ionic motion of oxygen vacancies in titanate materials.[6,9–11] Therefore, we expect the motion of the oxygen vacancies within the sample as the main cause of both processes. This is consistent with the XPS data that show an oxygen deficiency. Observed phenomena are also in a good agreement with those reported in crystalline $BaTiO_3$[12] where it was inferred that both conduction and relaxation have the same origin (hopping of oxygen vacancies).

In an attempt to reduce the density of oxygen vacancies, so as to decrease the ac-conductivity of films, we added oxygen in the sputtering gas during the deposition phase. Fig. 5 displays (at 300 °C) the frequency dependence of the ac conductivity for films grown under three different atmospheres: 100% Ar, 90% Ar + 10% O_2 and 80% Ar + 20% O_2. An interesting feature shown in the ac conductivity measurements is that the bulk conductivity (appearing as a plateau between 1 Hz and 1 kHz in the ac characteristics) is closely dependent on the oxygen rate in the deposition gas (Fig. 5). The bulk conductivity decreases by about one decade, from 1.24×10^{-6} to $2.95 \times 10^{-7}\ \Omega^{-1}\,\mathrm{m}^{-1}$, when the oxygen rate increases from 0 to 20%.

Through this dielectric study, we were able to separately observe the effect of different parts of the sample as, in our case the bulk and the electrode-film interface, on the charge transport phenomena.

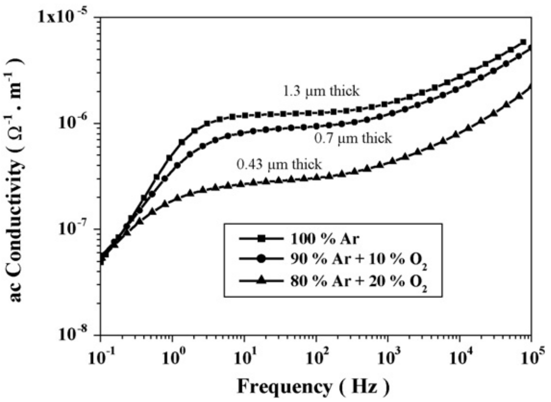

Fig. 5. Frequency dependence of the ac-conductivity at 300 °C for films grown under different atmospheres.

4. Conclusion

In summary, dielectric properties of sputtered a-$BaTiO_3$ films were studied as a function of frequency and temperature. The effect of charge transport in the bulk and in the electrode-film interfaces were clearly separated. The bulk-conduction process is thermally activated with an activation energy close to 0.95 eV. Such activation energy is related to the motion of oxygen vacancies within the film.

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