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Engineering of the frequency dependence of the ferroelectric properties of thin film Pt/$Ba_{0.5}Sr_{0.5}TiO_3$/Pt structures

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ABSTRACT

Engineering of a frequency dependent permittivity can be of interest for various sensor application. In this work a strong modification of the frequency dependence of the ferroelectric properties is achieved via a controlled diffusion of the metal electrode (Pt) into the ferroelectric layer ((Ba,Sr)TiO_3). For this purpose a series of $Ba_{0.5}Sr_{0.5}TiO_3$ layers is deposited onto Pt coated sapphire at various temperatures range from 660 °C to 760 °C. Using an additional Pt top electrode, the electronic properties of the resulting capacitors are investigated via frequency dependent cryoelectronic measurements. The structure and stoichiometry of the layers are analyzed via X-ray and Rutherford backscattering spectrometry, respectively. The analysis of the permittivity and loss tangent shows a strong frequency dependence of the permittivity in a small region of the deposition temperatures (680–710 °C), i.e. the permittivity changes from $\varepsilon_{eff} \simeq 600$ at low frequency to $\varepsilon_{eff} \simeq 20$ at high frequency. This behavior is caused by a partial diffusion of Pt into the ferroelectric layer and can be explained by the Maxwell–Wagner model.

1. Introduction

Recently, high-*k* dielectric and ferroelectric perovskite-type titanates, such as (Ba,Sr)TiO_3 (BSTO) and Pb(Zr,Ti)O_3, have been studied extensively due to possible application in voltage-tunable capacitors, integrated passive devices, and nonvolatile memories [1–3] and [4]. With regards to practical implementation thin film applications are of special interest that consist of a parallel plate arrangement, i.e. an electrode/ferroelectric/electrode multilayer structure. In these arrangement high electric fields and thus high polarization can easily be achieved [5,6]. However, on the one hand the growth of a perovskite onto a typically metallic electrode usually requires elevated temperatures. Which leads to improved structural properties of the oxides. On the other hand, degradation of the electrode is expected to set in at the interface to the oxide at elevated temperature. Therefore the optimization of the deposition parameters and especially the temperature is crucial for the performance of the ferroelectric layers in these multilayers.

In this study, we report on a detailed work on the dependence of the structural, stoichiometric, and electronic properties of Pt/BSTO/Pt capacitive structures on the deposition temperature. The temperature dependent diffusion of Pt atoms into the BSTO layer is analyzed in details and a Maxwell–Wagner like behavior is obtained. We demonstrate that a strongly frequency-dependent permittivity can be achieved and engineered using the diffusion of Pt into the BSTO layer.

2. Sample preparation and experimental techniques

Pt/$Ba_{0.5}Sr_{0.5}TiO_3$/Pt multilayer are deposited via RF-magnetron sputtering technology on r-cut Al_2O_3 (sapphire) substrates. The Pt layers are deposited at an elevated substrate temperature (heater temperature of 180 °C), a discharge power of 100 W on a 2″ target, and Ar process gas at a pressure of 0.27 mbar, resulting in a deposition rate of 0.36 nm/s. The thickness of the first Pt layer is typically 100 nm. Subsequently $Ba_{0.5}Sr_{0.5}TiO_3$ (BSTO) is deposited on the Pt layer using a mixture of $Ar/O_2 \simeq 1/1$ as sputtering gas, a gas pressure of 4.2×10^{-2} mbar and a RF power of 120 W resulting in a deposition rate of 0.06 nm/s. Various deposition temperatures in the range of 660–760 °C (heater temperatures) are chosen [7]. After deposition the BSTO/Pt film is cooled down to room temperature in pure O_2 at a rate of 5 °C/min. Finally the second Pt electrode is locally deposited on the BSTO layer using a shadow mask with a circular aperture with a diameter of 2 mm.

The analysis of the film surface via SEM shows a granular structure. Up to a thickness of ~100 nm gaps between the grains appear that lead to shorts between the upper and lower Pt electrodes, whereas samples with BSTO film thicknesses of 300 nm and thicker are completely covered with the ferroelectric layer.

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3. Experimental results and discussion

Fig. 1(a) shows typical XRD diffraction patterns (Cu $K\alpha$) for Bragg–Brentano geometry obtained for three samples that are deposited at different heater temperature. Different phases are visible in the plot, the amount of these phases strongly depend on the substrate temperature. Samples deposited at a lower heater temperature (700 °C) have large amounts of (101) oriented SrO_2 and BaO_2 and comparably small amounts of BSTO ((111) and (211)), whereas for the sample grown at higher heater temperature the amount of SrO_2 and BaO_2 decreases and the BSTO phases increase strongly. Definitely a further increase of the heater temperature beyond 760 °C would improve the BSTO content and epitaxy, however in this case the ferroelectric properties decrease strongly as demonstrated among others via conductivity measurements in the following.

The conductivity is investigated for the samples without shorts, i.e. samples with BSTO thickness of 600 nm. Fig. 2 demonstrates that the room temperature conductivity increases linearly with the substrate temperature, i.e. with increasing deposition temperature the ferroelectric (i.e. isolating) BSTO layer becomes more and more conducting and finally is not dielectric anymore. This is a first indication, that conducting material (Pt) might diffuse into the BSTO layer and lead to conductance. This will be discussed in detail below in context of Fig. 5.

The most important measurements are the frequency dependent measurements of the permittivity and loss tangent of the Pt/BSTO/Pt samples.

Fig. 3 shows typical examples of the frequency dependence of our samples with BSTO layer that are deposited at different substrate temperature. The permittivity ε_{eff} is evaluated from capacitance values using the standard equation for a parallel plate capacitor

$$C = \varepsilon_{eff}\varepsilon_o \frac{A}{d}, \quad (1)$$

where C is the measured capacitance of the sample, ε_0 is the vacuum permittivity, and d and A represent the thickness of the BSTO layer and the area of the upper Pt electrode, respectively.

Different behaviors can be distinguished:

(1) For low deposition temperatures (i.e. $T_H < 680$ °C) an extremely small permittivity is recorded for the complete temperature range. For instance for $T_H = 660$ °C the effective permittivity is smaller than 10 for the complete frequency region. This is understandable since the sample consist of several low-k phases (e.g. SrO_2 and BaO_2) and only a small amount of BSTO (see also XRD data in Fig. 1).

(2) For high deposition temperatures ($T_H \geq 720$ °C) the BSTO film is conducting ($\sigma > 9$ mS/m, see Fig. 2) with a conductivity comparable to that of doped Si. For these samples no capacitance can be measured. Therefore no data are displayed in Fig. 3 for samples grown at this temperature regime.

(3) Only in the intermediate regime (i.e. 680 °C $< T_H <$ 720 °C) high permittivity is observed. However the permittivity ε_{eff} is strongly frequency dependent (see Fig. 3). At low frequency it

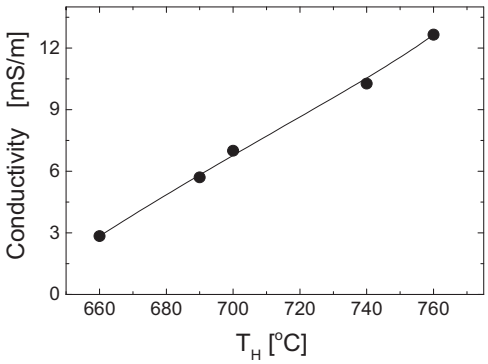

Fig. 2. Conductance as function of the heater temperature for the samples with a 600 nm thick BSTO layer measured at room temperature.

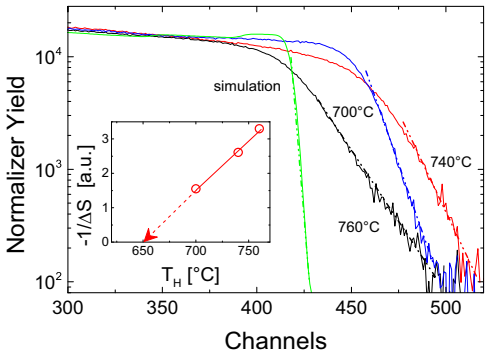

Fig. 5. Semilogarithmic plot of a small part of the RBS spectra of samples with BSTO layer deposited at different heater temperatures. The part represents the regime of the Pt bottom electrode and the onset of the BSTO layer and therefore characterizes the diffusion of Pt into the BSTO layer. The dashed lines indicate the slopes that result from the Arrhenius behavior, Eq. (4). The resulting dependence of the change of the slopes is shown in the inset as function of the heater temperature. The expected linearity indicates an onset of the diffusion of Pt into BSTO at about 650 °C heater temperature.

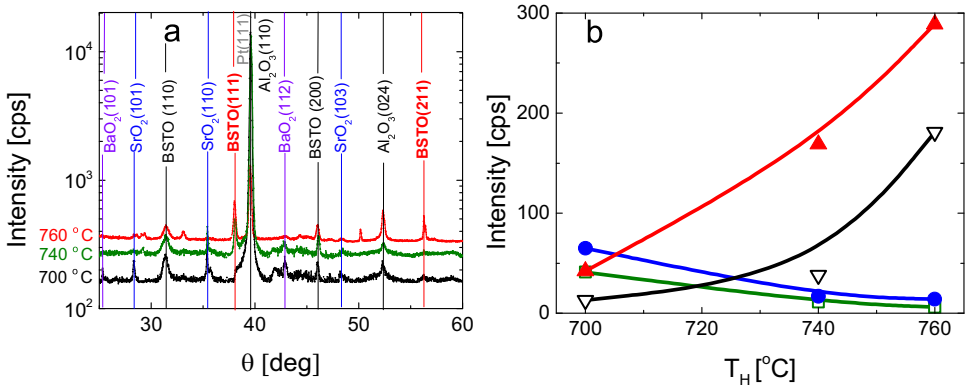

Fig. 1. (a) Bragg–Brentano X-ray diffraction pattern for BSTO films on Pt/Al_2O_3 deposited at different heater temperatures. The thickness of the BSTO layer is 600 nm, for better visibility the curves are shifted with respect to each other and the different lines indicate the position of different BaO, SrO and BSTO phases, respectively. (b) XRD intensities for different phases (background intensity is subtracted) as function of heater temperature, BSTO (111) (solid triangles), BSTO (211) (open triangles), SrO_2 (101) (solid circles), and BaO_2 (101) (open squares).