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Electrode interface controlled electrical properties in epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$ films grown on Si substrates with $SrTiO_3$ buffer layer

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ABSTRACT

Electrical properties of ferroelectric capacitors based on $PbZr_{0.52}Ti_{0.48}O_3$ thin films grown by pulsed laser deposition on silicon substrate with $SrTiO_3$ buffer layer grown by molecular beam epitaxy were studied. A $SrRuO_3$ layer was deposited as bottom electrode also by pulse laser deposition and Pt, Ir, Ru, $SrRuO_3$ were used as top contacts. Electrical characterization comprised hysteresis and capacitance–voltage measurements in the temperature range from 150 K to 400 K. It was found that the macroscopic electrical properties are affected by the electrode interface, by the choice of the top electrode. However, even for metals with very different work functions (e.g. Pt and $SrRuO_3$) the properties of the top and bottom electrode interfaces remain fairly symmetric suggesting a strong influence from the bound polarization charges located near the interface.

1. Introduction

Lead titanate–zirconate Pb(Zr,Ti)O_3, known as (PZT), is a material with various applications, from non-volatile memories, to pyroelectric detectors and electro-optic switches [1]. Its properties can be modified by the Zr/Ti ratio. The phase diagram is quite rich, with a morphotropic phase boundary at a Zr/Ti ratio of 52/48. At higher Ti content the PZT is ferroelectric with tetragonal structures. At higher Zr content the PZT is ferroelectric with rhombohedral structure, while at very high content of Zr is antiferroelectric with orthorhombic structure. At the morphotropic phase boundary the presence of a monoclinic PZT was also reported [2–4]. The compositions at or near the morphotropic phase boundary are often preferred for various applications due to their enhanced properties such as higher dielectric constant and piezoelectric coefficient [5–7].

In recent years great efforts were dedicated to the integration of the PZT films into the semiconductor technology, especially on Si. Growing PZT films directly on Si wafers was not successful in the past due to parasitic phases (silicates) occurring at the interface [8,9]. Buffer layers were then used, but this can have negative impact on the polarization value due to the incomplete compensation of the depolarization field [10,11]. On the other hand, the technological progress in terms of deposition techniques allows nowadays growing high quality epitaxial PZT layers on single crystal substrates like $SrTiO_3$ (STO). However, further integration of the PZT layers with Si technology would require the growth of the PZT layers with epitaxial quality directly on the Si wafers. The easiest way is to deposit a STO buffer layer on Si [12–14]. This was achieved by using molecular beam epitaxy (MBE) [15,16]. It was already proven that the STO layer deposited by this method is of epitaxial quality and can be used as template for growing good quality ferroelectric films on Si wafers [17,18]. Capacitor-like structures can be obtained in this way on Si substrates. Their properties can be further optimized by the right choice of the electrode materials. It was already demonstrated that electrode interfaces can greatly affect the macroscopic electrical properties of ferroelectric tetragonal PZT [19,20] epitaxially grown on single crystal STO substrates. The effect of the electrode interfaces on the properties of PZT capacitors deposited on STO buffered Si substrate and with composition near the morphotropic phase boundary was less studied.

In this work PZT films with Zr/Ti ratio of 52/48 were grown by pulsed laser deposition (PLD) on a bottom $SrRuO_3$ (SRO) electrode grown by the same technique on a STO/SiO_2/Si substrate. The STO buffer layer was grown by MBE [15,16]. Several metals were then used as top electrodes of the capacitor-like structures: Pt, Ir, Ru, and SRO. It was found that the electrical properties are affected by the metal used as top contact, with the best results obtained in the case of top SRO electrodes.

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2. Experimental methods

2.1. Sample preparation

Due to the fact that MBE allow ultra-high vacuum and a very low deposition rate it is possible to grow good quality STO buffer layer on Si (001). The growth details of STO can be found in [15,16]. SRO bottom electrode and PZT ferroelectric layer were deposited by pulsed laser deposition (PLD) using a KrF pulsed excimer laser with a wavelength of 248 nm. Ceramic targets with 99% purity were used for the deposition of the PZT and SRO films. The target was rotated during deposition, with a constant speed of 25 rot/min, in order to avoid crater formation. The distance from target to substrate was about 6 cm. The chamber was pumped down to 10^{-4} Pa. For SRO growth the substrate was heated to 700 °C in 55 min. The ablation process was carried out at a laser fluence of 2 J/cm^2 and a repetition rate of 5 Hz, for 1500 pulses, in an oxygen atmosphere of 13.3 Pa. For PZT growth the substrate was cooled down from 700 °C to 575 °C at a rate of 10 °C/min. The ablation process was carried out at a laser fluence of 2 J/cm^2 and a repetition rate of 5 Hz, for 10 000 pulses, in an oxygen atmosphere of 20 Pa. After deposition the film was annealed for 1 h in 10^5 Pa O_2 pressure, and then cooled down at room temperature. The capacitor structures used for electrical measurements were defined by the deposition of a 100×100 μm^2 area for the top electrodes using a shadow mask. Different metals were used as top contacts: SRO, Pt, Ir and Ru. SRO was deposited by PLD at room temperature, while Pt, Ir and Ru were deposited by radio-frequency (RF) sputtering. Both deposition methods are based on the generation of a plasma plume, containing the elements that will form the thin film on the substrate. The plasma properties are different, considering that the plasma is generated by different methods [21,22]. It was found that PLD is more suited for deposition of films with complex structures from ceramic (absorbing) targets, while RF-sputtering is more suited for metallization [23]. This is the reason why SRO was deposited by PLD and the metals by RF sputtering. Being different materials one cannot asses if the deposition method has influence on the properties of the interface between electrode and the PZT film. For this purpose, the same material should be deposited by different techniques but this was not considered in the present study and can be subject for future work.

One has to mention that SRO is a ferromagnetic oxide with metallic behavior, being considered as a "bad metal" [24–27]. Therefore, just for the simplicity of the discussion we will refer to SRO as to a metal. The SRO/PZT/metal capacitors which are subject of the present study will be also referred as metal–ferroelectric–metal (MFM) [28].

2.2. Measurements methods

The surface morphology and the local ferroelectric behavior were analyzed by atomic force microscopy (AFM) and piezoelectric force microscopy (PFM) using a MFP-3D-SA model microscope from Asylum Research. The crystal structure and epitaxial relationships were investigated by high resolution X-ray diffraction (HR-XRD) using a Bruker D8 Advance diffractometer in parallel beam setting. The measurements were performed in coplanar geometry with horizontal sample stage, using monochromatized Cu–Kα1 radiation (Kα = 1.5406 Å). The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HR-TEM) investigations have been performed on a JEM ARM 200F analytical microscope operated at 200 kV with a C_S corrector for the probe mode. The cross-section sample for TEM investigations has been prepared by mechanical thinning followed by Ar^+ ion milling on a Gatan PIPS machine at 4 kV acceleration voltage and 6° beam incidence angle.

The hysteresis measurements were performed by using a TF2000 ferritester, while the capacitance–voltage (C–V) characteristic were recorded using a HP 4194A Impedance/Gain Analyzer. The current–voltage (I–V) characteristics were raised by using a Keithley 6517 electrometer with an incorporated dc voltage source. The temperature measurements were performed by introducing the samples into a Lake Shore cryoprober model CPX-VF with CuBe needles. The data acquisition was automatic, special software being developed for each type of measurements.

3. Results

3.1. Structural characterization

The X-ray diffraction diagrams of the films deposited on STO-buffered Si (001) substrate reveal only the (00 l) (l = 1, 2, 3) peaks of PZT, SRO and STO, showing that the films have highly c axis oriented pseudocubic structures (see Fig. 1(a)). The layer fringes which appear around the SRO and STO peaks (Fig. 1(a)) indicate that the interfaces which delimitate these layers (or at least one of them) are very smooth and parallel, a specific feature for epitaxial thin films. The rocking curve of PZT obtained for the (001) planes is sharp, with a full width at half maximum of 0.4° (Fig. 1(b)), proving the very good alignment of this layer with the substrate. In view of determining the epitaxial relationship between the (001) silicon plane and (001) STO, azimuth-scans were performed on tilted crystal planes of the Si substrate (Si (113) has been used) and of the pseudocubic PZT layer (PZT (103) has been used). The PZT layer has been used for this purpose instead of the much thinner buffer layers due to its much higher intensity, and taking into account the well-known cube-on-cube type epitaxy of PZT on SRO and on STO. The φ-scans are presented in Fig. 1(c), and indicate the following in-plane orientation: PZT [100]//SRO [100]//STO [100]//Si [110]. The epitaxial growth is favored by the relationship between lattice parameters: $a_{STO} \approx a_{Si}/\sqrt{2}$ (a_{STO} = 3.905 Å, a_{Si} = 5.4307 Å – lattice parameters corresponding to the relaxed crystalline lattices). Summarizing the XRD analysis showed without any doubt that the growth of the films is epitaxial.

A detailed structural characterization was performed by TEM and HRTEM analysis. The higher magnification TEM image in Fig. 2(a) reveals the presence of an amorphous layer beneath the STO film, which corresponds to the native SiO_2 layer. The selected area electron diffraction pattern in the inset of Fig. 2(a) reveals the crystallization status of the as-deposited layers and the orientation relationship with respect to the Si substrate. The diffraction spots have been marked with corresponding Miller indices and subscripts indicating the Si substrate (the strongest spots) or the as-deposited layers. The electron diffraction (ED) pattern reveals the ordered single-crystal-like growth of the STO, SRO and PZT layers. It is interesting to observe that, despite the presence of the amorphous SiO_2 layer, there is a clear orientation relationship between the crystallographic planes in the STO layer and the Si substrate. In the ED image one can notice that all the diffraction spots appear like doublets, revealing the epitaxial relationship between the STO, SRO and PZT layers as well as the lattice mismatch between the PZT and STO/SRO lattices. The HR-TEM image at the STO–Si interface (Fig. 32(b)) confirms the single crystal growth of the STO thin layer and the well-defined orientation relationship $(001)_{STO} \parallel (001)_{Si}$ and $(010)_{STO} \parallel (110)_{Si}$ with respect to the Si(001) substrate, despite the presence of the 4 nm thick amorphous SiO_2 layer.

The local ferroelectric properties were investigated using PFM. The bottom SRO electrode was grounded during PFM measurement. Fig. 3(a) shows the microscopic ferroelectric properties as well as the surface topography. The surface topography revealed a smooth layer with roughness less than 1 nm, specific to an epitaxial PZT film [29]. The out of plane PFM phase image gives information on the polarization orientation. This can be changed by applying a dc bias to the tip during the scan. Here an external DC bias of −20 V was applied to a 10×10 μm^2 area followed by +20 V applied to a 4×4 μm^2 area. The change in contrast between the two regions evidence the presence of switchable polarization in the PZT film as shown in Fig. 4(b).