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Properties of ferroelectric $Pb(Zr,Ti)O_3$ thin films on ZnO/Al_2O_3 (0001) epilayers

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Abstract

Thin films of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) were deposited by pulsed laser deposition on ZnO/Al_2O_3 (0001) layers grown by molecular beam epitaxy, and $Pt/SiO_2/Si$ substrates. The ZnO epilayers serve as a crystalline oxide template for PZT deposition, and a conducting material that may be used for electrodes in thin film ferroelectric capacitors. The PZT thin films (thickness ~300 nm) deposited on the ZnO epilayers were determined to be crystalline with preferential (110) orientation based on X-ray diffraction measurements. In comparison, PZT thin films deposited on $Pt/SiO_2/Si$ possess a random crystalline orientation with reduced crystalline quality. Capacitors fabricated from the PZT thin films deposited on ZnO/Al_2O_3 demonstrate ferroelectric hysteresis behavior with a remenant polarization of 15 $\mu C/cm^2$ and coercive field of 55 kV/cm. The crystalline properties and ferroelectric behavior of the PZT suggest that ZnO/Al_2O_3 may provide a desirable platform for future ferroelectric devices.

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Keywords: Pulsed laser deposition; Ferroelectric properties; Zinc Oxide; Lead zirconate titanate

1. Introduction

Ferroelectric oxide materials are of immense interest for future electronic, optoelectronic, and multi-functional devices, where a switchable polarization, strong electro-optic properties, tunable dielectric constant, pyroelectric and piezoelectric properties may be exploited. Ferroelectric oxides in the perovskite structure, such as $BaTiO_3$ and $Pb(Zr,Ti)O_3$ (PZT), are sought in particular due to the large magnitude of the functional properties that they exhibit. The properties of ferroelectric thin films are highly dependent on the crystalline quality and orientation, which are primarily determined by the substrate material and deposition technique. For many device applications, substrates that are compatible with both ferroelectric thin films and semiconductor devices are sought, where potential direct integration of ferroelectrics with semiconductors is envisioned in the future. One promising substrate material for ferroelectric integration is sapphire, which is durable, low cost, and has a low index of refraction and dielectric constant desirable for integrated optical and high frequency device applications. Sapphire has also demonstrated success as a substrate material for wide bandgap semiconductor devices based on GaN materials. Previously, PZT on sapphire has been demonstrated with promising results using GaN [1,2], LSCO [3,4], and $SrTiO_3$ [5] buffer layers. ZnO is emerging as an important wide bandgap semiconductor material for devices operating in the ultraviolet, as discussed in the review article by Look [6]. ZnO may be grown epitaxially on sapphire, and has intrinsic compatibility with ferroelectric oxides as a semiconducting oxide. ZnO has also recently been used as a buffer layer for PZT ferroelectric capacitors on Pt/Si [7]. In this work, PZT thin film deposition on ZnO/Al_2O_3 epilayers and resulting material properties are studied for potential usage in future device applications.

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2. Experimental details

Pulsed laser deposition (PLD) is a research tool but its result can be easily scaled up by using RF sputtering or molecular beam epitaxy. Compared with the sol–gel technique, PLD can grow highly oriented films and has a higher deposition rate. $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films were deposited by PLD on $Pt/SiO_2/Si$ and ZnO/Al_2O_3 structures simultaneously. The $Pt/SiO_2/Si$ substrates used were obtained from Radiant Technologies. The ZnO/Al_2O_3 structures were grown by molecular beam epitaxy using a Zn effusion cell and an oxygen plasma source. ZnO was grown on epi-ready *c*-plane Al_2O_3 (0001) substrates using a low temperature buffer layer process described by Tampo et al. [8]. The ZnO material was determined to grow epitaxially based on in situ reflection high energy electron diffraction and post-growth X-ray diffraction measurements. The ZnO layer thickness was determined to be approximately 300 nm based on optical reflectance. The ZnO epilayer exhibited n-type conducting behavior with carrier concentration and electron mobility of approximately 5×10^{17} cm^{-3} and 50 cm^2/V s. The PZT thin films were deposited by pulsed laser deposition using an excimer laser (λ=248 nm, 25 ns pulse width, 5 Hz, ~2 J/cm^2) at a substrate temperature of 550 °C and oxygen partial pressure of 2 mTorr. After deposition, the sample was annealed at 700 °C for 10 min in an oxygen environment. The thickness of the PZT layer was determined to be approximately 300 nm from optical reflectance measurements. Scanning electron microscope images of the $PZT/ZnO/Al_2O_3$ thin film, as shown in Fig. 1, indicate a densely packed grain structure similar to previous reports of PZT on sapphire [5]. A relatively high particulate density is apparent, a problem often encountered with the pulsed laser deposition process. Particulate density may be reduced through modification of deposition conditions or through usage of a different deposition technique, where the primary purpose of this study is the evaluation of $PZT/ZnO/Al_2O_3$ as a potential future device platform rather than achieving optimal thin film properties.

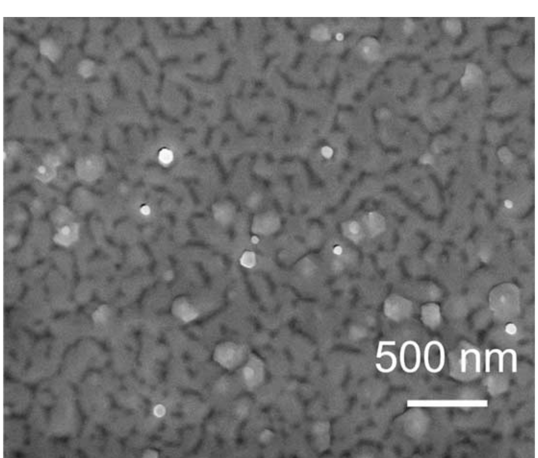

Fig. 1. Scanning electron microscope image of PZT deposited on ZnO/Al_2O_3 (0001).

3. Results and discussion

X-ray diffraction (XRD) measurements (θ–2θ scan) of the PZT thin films deposited on $Pt/SiO_2/Si$ and ZnO/Al_2O_3 structures indicate dramatic differences in crystalline properties. Weak diffraction peaks originating from the PZT and Pt are observed for the $PZT/Pt/SiO_2/Si$ sample (Fig. 2(a)). Diffraction peaks corresponding to PZT (110) and (210) are distinguishable, along with several peaks near the noise level of the diffraction measurement. The lack of strong X-ray diffraction peaks imply poor crystallinity for the PZT thin film that may be due to deposition conditions or degradation of the material during the high temperature anneal following deposition. The $PZT/ZnO/Al_2O_3$ deposited and annealed during the same run shows dramatic improvement XRD characteristics, as indicated in Fig. 2(b). Strong diffraction peaks are observed for the ZnO epilayer and Al_2O_3 substrate, along with a singular strong peak corresponding to (110) PZT. It should be noted that the XRD scan in in Fig. 2(b) is shown on a logarithmic scale to illustrate relative intensities and to reveal any potential weak diffraction peaks. The XRD results indicate a perovskite PZT thin film with preferred (110) orientation and no apparent presence of the undesirable pyrochlore phase. The preferential (110) orientation may be explained by the hexagonal arrangement of oxygen atoms for the (110) face of the perovskite crystal structure corresponding to the hexagonal structure of the ZnO (0001) face. Studies of the epitaxial relationships of PZT/ZnO thin films are needed for further development of these materials for device applications and will be reported separately.

Capacitor structures were fabricated for the PZT samples by depositing Ti/Au (10/20 nm) electrodes with a diameter of 500 μm using a shadow mask. Current–voltage characteristics of the capacitors show high leakage for the $PZT/Pt/SiO_2/Si$ sample, with current flow $>10^{-5}$ A for applied bias of several volts. The leaky behavior may be attributed to Pt spiking in the PZT arising from the high temperature anneal and causing a short to the top electrodes. Blocking behavior is observed for the $PZT/ZnO/Al_2O_3$ sample, with typical leakage currents in the range of 10^{-9}–10^{-8} A. Leakage becomes significant in these capacitors near an applied voltage of 12 V and above. The polarization versus applied electric field (P–E) characteristics were measured using a Radiant Technologies 66 A Ferroelectric Test System. The high leakage current for the $PZT/Pt/SiO_2/Si$ samples prevented P–E measurements for voltage loops above 2 V. At low voltages, linear P–E characteristics were observed with no clear hysteresis behavior. The lack of hysteresis for the $PZT/Pt/SiO_2/Si$ capacitors may be attributed to the poor crystalline quality of the PZT thin films. The P–E characteristics for varying applied voltage