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Impact of the crystallographic structure of epitaxially grown strained sodium–bismuth–titanate thin films on local piezo- and ferroelectric properties

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ABSTRACT

Thin films of different phases of lead-free sodium–bismuth–titanate were epitaxially grown on $SrTiO_3$ and $NdGaO_3$ substrates by metal–organic chemical vapor deposition. Aurivillius phases with $m = 3$, $m = 3.5$ and $m = 4$ and the $Na_{0.5}Bi_{0.5}TiO_3$ perovskite phase were obtained by varying the substrate temperature and the Na/Bi ratio in the gas phase. Investigations of the impact of crystallographic structure and incorporated film lattice strain on local piezo- and ferroelectric properties were carried out by piezoresponse force microscopy experiments using dual AC resonance tracking combined with a tip-sample contact modeling procedure to determine an effective value for the piezoelectric coefficient for each sample. Comparative piezoresponse force microscopy measurements revealed a significant increase of the average effective piezoelectric coefficient d_{zz} when the film structure changed from an Aurivillius phase to the perovskite phase. Films of perovskite phase have also shown the possibility of local tip-induced polarization switching.

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1. Introduction

Recently, functional materials such as ferroelectric thin films have attracted high attention for modern technologic applications and fundamental research. Lead-based compounds like lead–zirconate–titanate (PZT) are up to now the common material for non-volatile ferroelectric memories (NvRAM) and piezoelectric applications (actuators, sensors), because of their outstanding piezo- and ferroelectric properties [1]. However, besides the high amount of lead in PZT based electronics, there are some other major drawbacks such as ferroelectric fatigue and degeneration which negatively affect the reliability in a long term use [2,3]. As an alternative lead-free sodium bismuth titanate (NBT) based compounds of the system $Bi_4Ti_3O_{12} + \times Na_{0.5}Bi_{0.5}TiO_3$ show promising piezo- and ferroelectric properties [4,5]. The members of the considered system exhibit either perovskite crystal structure ($Na_{0.5}Bi_{0.5}TiO_3$) or belong to the Aurivillius family corresponding to the general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, whereby A displays here a Bi^{3+} or Na^+ ion and B the tetravalent Ti^{4+} ion [6,7]. The number m represents the average amount of perovskite units sandwiched between two $(Bi_2O_2)^{2+}$ intermediate layers along the c-direction. Until now, research on these compounds is essentially restricted to the growth of bulk crystals and ceramics [8–12]. Only a few papers report on the deposition and characterization of $Na_{0.5}Bi_{0.5}TiO_3$ and $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ thin films with chemical solution deposition (CSD) [13], pulsed laser deposition (PLD) [14] or the sputtering technique [4]. On the other hand, the metal–organic chemical vapor deposition (MOCVD) is so far practically unexplored for this type of compounds [15], which is caused by the poor availability of suitable and chemically stable Na precursors. Up to now deposition of Na containing ferroelectric films with MOCVD is still challenging. The main advantage of epitaxial layers, in contrast to bulk material, is that strained thin films can be achieved by pseudomorphic growth on substrates with a small lattice mismatch, which is expected to affect their functional properties [16,17].

Recently, piezoresponse force microscopy (PFM) has gained increasing interest in the investigation of ferro- and piezoelectric properties of thin films. PFM studies provide the possibility of revealing the orientation of spontaneously polarized domains and to determine piezoelectric properties of films with high spatial resolution for investigation of the lateral homogeneity [18,19].

In the presented study, NBT films were grown hetero-epitaxially by liquid delivery MOCVD on $SrTiO_3$ and $NdGaO_3$ substrates. Strained films of Aurivillius phase with $m = 3$, $m = 3.5$ and $m = 4$ and the $Na_{0.5}Bi_{0.5}TiO_3$ perovskite phase were realized by changing the deposition temperature and the chemical potential by varying the Na/Bi ratio in the vapor phase. In order to study the impact of crystal structure (or the number m) of NBT films and incorporated film lattice strain on local out-of-plane piezo- and ferroelectric properties, PFM measurements were carried out on the as-grown films. A relative comparison between the local effective longitudinal piezoelectric coefficients d_{zz}, as derived from

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a tip/sample contact modeling procedure based on dual AC resonance tracking PFM, recently developed by Ganepalli et al. [20], is presented. Local switching spectroscopy PFM measurements have also shown the possibility of remnant tip-induced polarization switching in the tip/sample contact area without inserting a conducting buffer layer between substrate and thin film.

2. Experimental

2.1. Thin film deposition

NBT thin films were hetero-epitaxially grown by the liquid delivery MOCVD technique on $SrTiO_3$ and $NdGaO_3$ substrates using Na(thd), Ti(O^iPr)$_2$(thd)$_2$, Bi(thd)$_3$ precursors solved in toluene. While the Bi/Ti ratio was kept constant, the Na/Bi ratio in the source solutions was varied between 0 and 3. After flash evaporation at 230 °C the precursors were transported by a carrier gas (Ar) into the reactor chamber and the films were deposited at substrate temperatures between 600 °C and 800 °C in an Ar/O_2 atmosphere (with 38% O_2) at a constant pressure of 2.7×10^3 Pa. 0.1° off-oriented $NdGaO_3$ (1 1 0) and $SrTiO_3$ (0 0 1) substrates were fixed with silver paste on a Si_3N_4 substrate carrier in order to improve heat contact. To ensure homogeneous deposition conditions the substrate carrier was rotated at 500 rpm. Details of the deposition process have been described elsewhere [15].

2.2. X-ray diffraction technique

The different crystallographic phases of the NBT compounds were characterized by high-resolution X-ray diffraction (HRXRD). After passing a parabolic multilayer mirror the incident beam was collimated (11 arcsec) and monochromatized (λ = 1.54056 Å) by a Ge (2 2 0) channel cut crystal. Slits in front of the sample (typically 0.3 mm × 5 mm) were used to reduce the footprint of the incoming X-ray beam to the sample area and corresponding slits were placed in front of the single channel scintillation detector in order to reduce the scattering background. The out-of-plane strains and thicknesses of the as-grown thin films were obtained by performing θ–2θ scans over a wide angular range. The angular positions of selected Bragg reflections of the films as compared to the positions of the corresponding substrate reflections were used to evaluate the out-of-plane lattice parameter of the film from which the corresponding vertical elastic strain ε can be calculated. Film thicknesses between 30 nm and 130 nm were determined by evaluating interference fringes in the θ–2θ scans. For analysis of in-plane strains X-ray reciprocal space maps were carried out on selected samples. The ratio of the incorporated Na- and Bi-ions was estimated by energy dispersive X-ray spectroscopy (EDX) connected to a scanning electron microscopy (FEI Nova 600 Nanolab) (not shown here, see [15]).

2.3. Piezoresponse force microscopy

For characterization of the film surface morphology an atomic force microscope (AFM, Asylum Research MFP3D standalone) was used in tapping mode under ambient conditions. The PFM setup of the AFM, consisting of two internal digital lock-in and frequency synthesizer units, was used to measure the local piezoelectric and ferroelectric properties of the as-grown films. Stiff Ti/Pt-coated conductive cantilevers (Olympus 240 TM) with spring constants of about 2 N m^{-1}, resonant frequencies of about 74 kHz in air and a cantilever length of 240 μm were used. The local measurements were performed in air at the tip/sample first harmonic contact resonance frequency ($f_{1\omega} \approx 290$ kHz) in dual AC resonance tracking (DART) mode to improve the signal to noise ratio of the PFM images [21].

To determine and compare the local effective piezoelectric coefficients d_{zz} of our films several 5 μm × 5 μm scans were carried out in DART-PFM mode at various positions on each sample. All images were acquired at the same scan rate of 0.3 Hz and AC testing voltage at the tip of 0.3 V. With a spherical tip diameter of (28 ± 10) nm and indentation forces of 100–120 nN the tip sample contact is in the strong indentation regime, as established by Kalinin and Bonnell [18]. The resulting PFM images were evaluated by modeling the tip-sample contact as a driven damped harmonic oscillator (DHO) [20]. This approach allows separating the amplitude and phase of the film surface motion exciting the DHO as well as the natural resonance frequency and the quality factor of the DHO. An average value was then calculated for the obtained driving amplitude images, which gives direct information about the effective piezoelectric coefficient d_{zz} of the film [22]. Since the measurements were carried out locally at the contact resonance frequency a quantitative calibration of the cantilever sensitivity was not possible, due to complex dependencies on the near-resonance mode shapes and the laser alignment. Although an absolute value for the longitudinal piezoelectric coefficient d_{33} could not be determined in this way, a comparison of values effective values d_{zz} can be carried out anyway, because of similar contact resonance frequencies and same experimental conditions for all our NBT films. Local DART switching spectroscopy PFM (SS-PFM [23]) experiments were performed on several spots on each sample. We used the same conducting probes as for the piezoelectric measurements with testing voltages of 0.3 V at the first mode harmonic contact resonance frequency and a DC bias range of ±10 V.

3. Results and discussion

3.1. Crystallographic structure

In Fig. 1 the evolution of the film structure on $SrTiO_3$ substrates with increasing Na/Bi ratio at a substrate temperature of 750 °C is

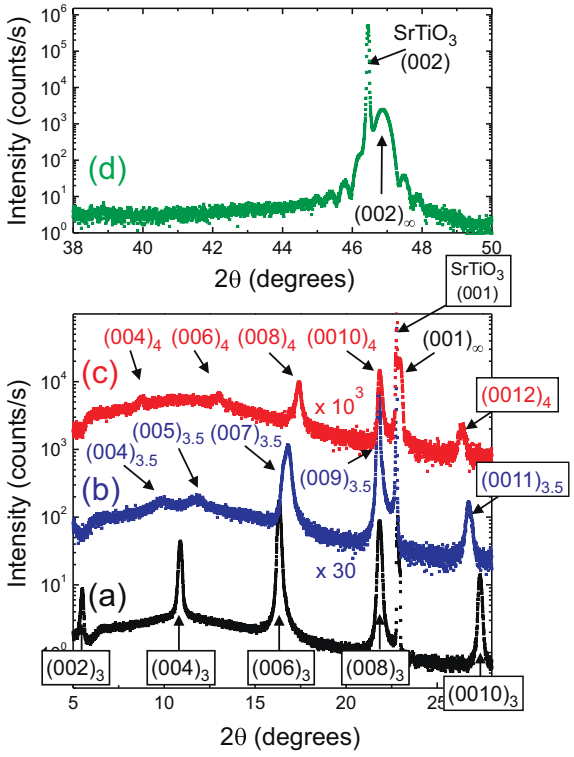

Fig. 1. HRXRD rocking curves (θ–2θ-scans) from films deposited at different Na to Bi molar ratios c(Na)/c(Bi) in the precursor solutions at 750 °C: (a) no Na in the gas phase, (b) c(Na)/c(Bi) = 1, (c) c(Na)/c(Bi) = 2, and (d) c(Na)/c(Bi) = 3.

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