PROPRIETĂȚILE FILMELOR SUBȚIRI DE $BaTiO_3$ OBȚINUTE PRIN ABLAȚIE LASER

PROPERTIES OF $BaTiO_3$ THIN FILMS GROWN BY LASER ABLATION

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$BaTiO_3$ thin films with a tetragonal symmetry were grown on (001) $SrTiO_3$ single crystal substrates by pulsed laser ablation (PLD). The evolution of the growth front was monitored in-situ and in real time by means of high-pressure reflection high-energy electron diffraction (RHEED), while atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to analyze the surface morphology. The films microstructure, substrate-film interface properties, and the type and level of epitaxial strain were determined by X-ray diffraction (XRD) studies. RHEED data showed that under optimum deposition conditions the films grow following a Stransky-Krastanov mechanism. The films morphology and microstructure is strongly dependent on the deposition and post-deposition vacuum annealing parameters, as well as on the substrate-film interface properties.

Filme subțiri de $BaTiO_3$ cu structura tetragonală au fost crescute prin ablație laser pe suporturi din $SrTiO_3$ orientat (001). Evoluția frontului de creştere a fost monitorizată in-situ şi in timp real prin intermediul difracției prin reflexie de electroni cu energie înaltă (DREEI) la presiuni mari, iar morfologia suprafeței a fost analizată prin microscopie de forță atomică (MFA) şi microscopie electronică de baleiaj (ME). Microstructura filmelor, proprietățile interfeței substrat-film şi informații despre stresul epitaxial au fost determinate prin studii de difracție de raze X (DRX). Datele DREEI au arătat că pentru condiții optime de depunere, filmele cresc conform unui mecanism tip Stransky-Krastanov. Morfologia şi structura filmelor depind de parametrii de depunere şi de condițiile tratamentului termic post-depoziție, precum şi de caracteristicile interfeței substrat-film.

Keywords: *$BaTiO_3$, pulsed laser ablation, reflection high-energy electron diffraction, X-ray diffraction*

1. Introduction

Ferroelectric $BaTiO_3$ thin films are intensively studied due to their potential application for the next generation of semiconductor memory [1,2]. They were successfully grown on $SrTiO_3$ substrates by means of pulsed laser ablation [3] or molecular beam epitaxy [4,5]. The critical thickness d_c (related with the strain relaxation) of a ferroelectric thin film when the ferroelectricity becomes thermo-dynamically unstable is an issue of interest from a scientific as well as a technological point of view [6]. Most experimental work on this topic has been done using indirect methods, such as piezoelectric and/or structural measurements [7,8], however no consensus have been reached on the d_c values yet.

Following the above considerations, we present in this paper the results of studies on the interdependence between structural/morphological properties and deposition/cooling parameters of c-axis oriented $BaTiO_3$ thin films grown by PLD on (001) $SrTiO_3$ substrates, as well as the implications of the deposition and post-deposition annealing parameters on critical thickness for films' strain relaxation.

2. Experimental details

$BaTiO_3$ thin films with thickness in range of 30-55 nm were epitaxialy grown by means of PLD on (001) $SrTiO_3$ single crystal substrates using a commercially available polycrystalline target. The growth studies were done on a computer controlled PLD system equipped with *in-situ* high-pressure (up to 0.50 mbar) RHEED. Before deposition each substrate was cleaned in organic solvents (acetone and ethanol) and then chemically etched in a NH_4OH buffered HF solution (pH=4.5) following the procedure described in Refs. [9] and [10]. In order to recrystalize the substrate surface, the chemical etching was followed by a thermal treatment in oxygen flow (300-400 cm^3/min) at temperatures of 950-1000 ^oC. The substrates were then attached to the heating stage using Ag paste.

For deposition of the $BaTiO_3$ films a substrate temperature of T_s=700-850 ^oC, a pressure of P_d=(1-10)×10^{-2} mbar O_2, a laser repetition rate of f=2 Hz, and an energy density on target of E_d=1.50-2 J/cm^2 were used for a substrate to target distance d_{ts}=65 mm. A post-deposition vacuum annealing step at P_a~10^{-7} mbar for 0.5-1 h was performed in order to improve the films' surface morphology and to obtain partial relaxation of the strain [11]. The films were then characterized with AFM and SEM, in order to check their surface morphology, and by XRD for structural analysis.

3. Results and discussions

The evolution of the intensity of the RHEED specular spot showed that $BaTiO_3$ grows following

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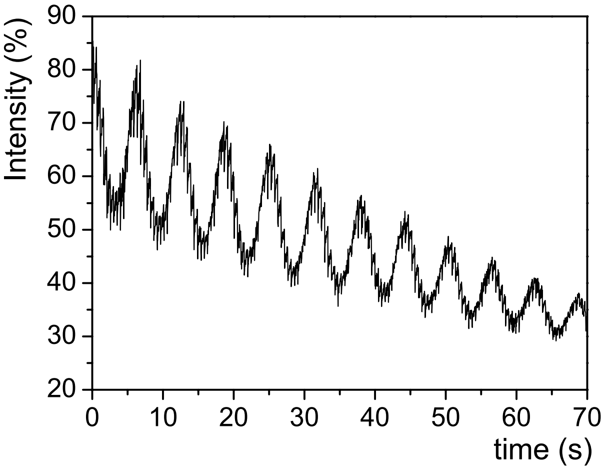


Fig. 1 - Evolution of the intensity of the RHEED specular spot (oscillations corresponding to 11 unit-cells) at the initial stages of $BaTiO_3$ thin film grown on (001) $SrTiO_3$. The continuous decrease of the RHEED intensity indicates roughening of the film surface with thickness. Deposition parameters: T_d=800 °C, P_d=2 Pa O_2, E_d=1.75 J/cm^2. / *Evoluția intensității fasciculului DREEI (oscilațiile corespund depunerii a 11 celule atomice) la începutul creşterii filmului de $BaTiO_3$ pe $SrTiO_3$ (001). Scăderea constantă a intensității semnalului DREEI indică o creştere a rugozității suprafeței filmului cu grosimea acestuia. Parametrii de depunere: T_d=800 °C, P_d=2 Pa O_2, E_d=1.75 J/cm^2.*

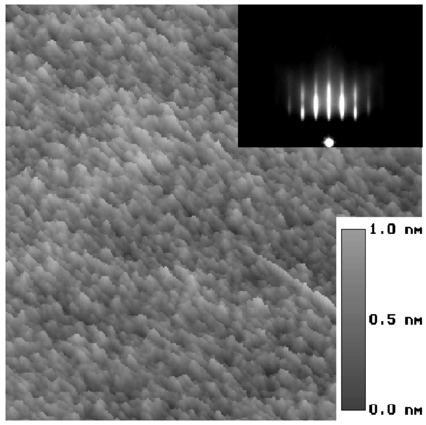


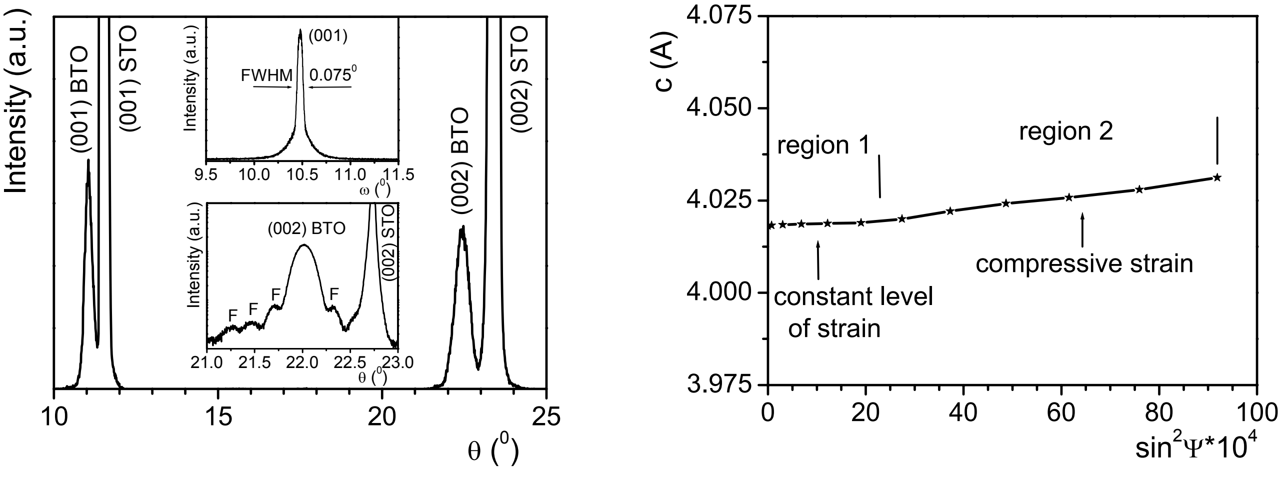
Fig. 2 - AFM image (2×2 μm^2) of a 55 nm thick $BaTiO_3$ thin film grown on (001) $SrTiO_3$ showing a terraced structure of the surface. The corresponding RHEED pattern confirms the atomically smooth surface. Deposition parameters: T_d=800 °C, P_d=1 Pa O_2, E_d=1.60 J/cm^2 / *Imagine de la MFA (2×2 μm^2) a unui film de $BaTiO_3$ cu grosimea de 55 nm crescut pe $SrTiO_3$ (001) indicând o structură în terase a suprafeței. Spectrul DREEI confirmă formarea unei suprafețe cu rugozitate redusă. Parametrii de depunere: T_d=800 °C, P_d=1 Pa O_2, E_d=1.60 J/cm^2.*

a Stransky-Krastanov mechanism, i.e., at the initial stages of deposition the film follows a 2D (layer-by-layer) growth mode (see Fig. 1) for a critical thickness d_c up to about 30-40 nm, then the film relaxes and, due to increased step density at the surface, a 3D (islands) growth mechanism takes place after relaxation.

However, due to relatively high mobility of the ad-atoms on the surface, for films with thickness up to 55 nm (the upper limit for our films) the AFM and the corresponding RHEED data showed a relatively flat surface, with terraces of no more than few units cells height, as confirmed by the AFM image of an optimally grown layer and by the presence of streaky RHEED pattern (Fig. 2).

For the upper limit of E_d (2 J/cm^2) the SEM analysis showed the presence on the surface of droplets, which were not observed for lower values of E_d, i.e., E_d=1.5-1.75 J/cm^2, a too high laser energy resulting in transport via the plasma of particulates from the target. This problem may be avoided by increasing the d_{ts} distance or by decreasing the laser energy, so that the E_d value reaches the optimum (in the 1.5-1.75 J/cm^2 range). The XRD data showed that the $BaTiO_3$ films were epitaxially grown, c-axis oriented, with a tetragonal symmetry due to the presence of epitaxial strain. The cell parameters are determined by the deposition and the annealing parameters, as well as by the film thickness (due to differences in strain level with thickness), and were calculated from the ω-2θ scans around several (*00l*) and (*h0l*) planes. The resulted values were a~3.98-3.99 Å and c~4.03-4.12 Å, with larger a-axis and smaller c-axis values for lower P_d and/or higher T_d. These values indicate incomplete relaxation of the $BaTiO_3$ layer and that the films are under compressive strain. Fig. 3a shows a ω-2θ XRD scan of a single-phase, 40 nm thick $BaTiO_3$ thin film grown at T_d=800 °C, P_d=0.10 mbar O_2, and annealed in vacuum (10^{-7} mbar) for 30 min at T_d. For the film, only the (00*l*) reflections can be observed, confirming the c-axis orientation, with no secondary phases. The ω-2θ scan of (002) reflection (insert of Fig. 3a, bottom image) shows the presence of fringes, an indication of high crystallinity of the film. The ω scan of the (001) reflection (insert of Fig. 3a, upper image) shows a peak with two parts: a thinner component, corresponding to the un-relaxed section of the film - the upper part of the peak with a full width at half maximum (FWHM) of ~ 0.075°, and a larger one, corresponding to the bulk-like, relaxed part of the film. For films with thickness lower than the d_c value the later component of the peak is not detected, as the film is not relaxed.

The type and level of epitaxial strain was determined by XRD from variation of the out-of-plane cell parameter (*c*) value with the sample tilt angle (φ), as presented in Fig. 3b. The result indicates the presence of two regions along the c-axis direction with different level of strain: one with



a b

Fig. 3 - a) XRD 2θ-ω scan of a c-axis oriented, single phase $BaTiO_3$ thin film grown on (001) $SrTiO_3$ showing the presence of only the (00*l*) reflections. Insert: (bottom image) the (002) $BaTiO_3$ peak; (upper image) omega scan of (001) $BaTiO_3$ reflection; b) evolution of the in-plane epitaxial strain with film thickness. BTO=$BaTiO_3$, STO=$SrTiO_3$ / *a) Spectrul DRX (scan 2θ-ω) al unui film monocristalin de $BaTiO_3$ crescut epitaxial cu axa c perpendiculară pe suprafața substratului de $SrTiO_3$ (001) indicând prezența numai a liniilor de difracție (00l). Insert: (jos) linia (002) a $BaTiO_3$; (sus) spectrul DRX în direcția omega corespunzător planului cristalografic (001) al $BaTiO_3$; b) evoluția stresului epitaxial cu grosimea filmului. BTO=$BaTiO_3$, STO=$SrTiO_3$.*

a constant level of strain (region 1) and the second one indicating a compressive strain (region 2) due to the mismatch between the cell parameters of $SrTiO_3$ (a=3.905 Å) and of the $BaTiO_3$ layer (a~3.97-3.99 Å).

The reciprocal space map (rsm) of the $BaTiO_3$ (001) plane (Fig. 4) indicates a relatively rough substrate-film interface, as can be concluded from the short diffraction streak (the short tail in the ω/2θ direction, for negative region of ω/2θ range in Fig. 4). This may be due to the presence of a high level of compressive strain at the interface and/or due to the presence of structural defects, such as dislocations, which were observed before for thin films of this material [3]. In order to obtain a better relaxation of the strain, several films were annealed at 950°C in vacuum, for 0.5-1h. However, after this thermal treatment the interface properties did not improve (no clear improvement of the interface roughness seen on the rsm scans), while the film become very rough, most probably as a result of formation of $BaO_{1-\delta}$ precipitates on the surface due to high vacuum annealing temperature. Therefore, we concluded that a high-temperature vacuum annealing for the $BaTiO_3$ thin films grown under the conditions used in this study should be avoided, as it does not clearly improve the interface properties, while it has a negative impact on the films morphology.

4. Conclusions

High quality, single phase c-axis oriented $BaTiO_3$ thin films were grown by laser ablation on (001) $SrTiO_3$ single crystal substrates. The surface morphology of the films has been investigated by means of high-pressure RHEED, AFM, and SEM, while the structural properties were studied by XRD. Deposition under optimum conditions produces films with smooth surface, with a terraced morphology, free of large islands or droplets, as confirmed by AFM and SEM data. The growth is governed by the film-substrate interface properties due to presence of compressive strain. The critical thickness value d_c at which the $BaTiO_3$ thin film relaxes depends on the deposition temperature and pressure, increasing for higher T_d and/or lower P_d values. When the surface mobility is no longer high enough to support 2D growth, a transition to islands growth takes place driven by strain

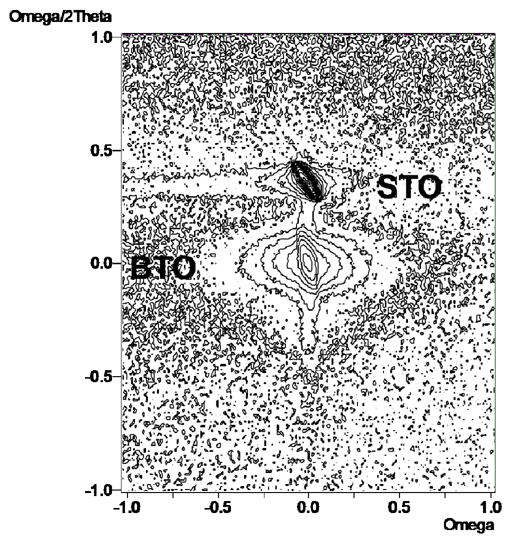


Fig. 4 - XRD rsm of (001) planes for a $BaTiO_3$ film and the $SrTiO_3$ substrate. / *Harta în spațiu reciproc al planelor cristalografice (001) pentru un film de $BaTiO_3$ şi a substratului de $SrTiO_3$ obținută prin difracție de raze X. STO=$SrTiO_3$, BTO=$BaTiO_3$.*

relaxation. Due to the epitaxial strain the unit-cell shows a tetragonal symmetry (as compared with a cubic symmetry of the bulk $BaTiO_3$), with cell parameters values determined by the deposition and post-deposition annealing conditions.

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