EXPERIMENTAL REPORT
RAPPORT D'EXPERIENCE

Programme Committee Proposal Number
N° Projet Comité de Programme

02-02-193

PROJECT TITLE : *TITRE DU PROJET :*

CARTOGRAPHIES DANS L'ESPACE RECIPROQUE DE SUPERRESEAUX D'OXYDES PEROVSKITES $(BaTiO_3/SrTiO_3)_n$

LIGNE :	**D2AM**		**I F**	
INSTRUMENT :	PETITS ANGLES	☐	EXAFS	☐
	7 CERCLES	✕	G M	☐
	F I P	☐	S U V	☐

NUMBER OF RUNS USED
NOMBRE DE SESSIONS EFFECTUEES : 23

STARTING DATE
DATE DE DEMARRAGE : Avril 2002

AUTHORS : *AUTEURS :* Maud NEMOZ, Eric DOORYHEE, Jean-Louis HODEAU
Laboratoire de Cristallographie du CNRS, BP 166, 38042 Grenoble Cedex 09
nemoz@grenoble.cnrs.fr

Catherine DUBOURDIEU, Rémi PANTOU, Hervé ROUSSEL
LMGP, UMR 5628, ENSPG-INPG, BP 46, 38402 St Martin d'Hères

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Abstract: *$(BaTiO_3/SrTiO_3)_n$ multilayers are synthesized by two methods: chemical vapor deposition (CVD) and pulsed laser deposition (PLD). High-angle BM2 diffraction data show the excellent crystallinity and epitaxy of the films. For all $(BaTiO_3/SrTiO_3)_n$ studied we observe a pseudo tetragonal symmetry with no difference between a and b axes, a full relaxation of in-plane strain in BTO and STO layers and a small misfit (<2%) with the substrate.*

Micro-electronic components are increasingly efficient, with decreasing size of the devices. Nevertheless, fundamental physics predicts some limiting factors in the development of the materials and technologies currently used. In capacitors, a rapid charge loss occurs with decreasing thickness of SiO_2 ($\varepsilon = 3.9$). One solution lies in materials with a higher dielectric susceptibility. Thin films and solid solutions of perovskite oxides $BaTiO_3$ and $SrTiO_3$ exhibit a very high dielectric constant ($\varepsilon = 100\text{-}600$) and are studied in view of their integration in capacities and DRAM memories. Superlattices $(BaTiO_3/SrTiO_3)_n$ exhibit a dielectric constant higher than that of the thin films of the respective materials. These properties highly depend on the morphology of the system (thickness, periodicity, Ba/Sr content) and on the structural quality of the deposition (epitaxy, interface rugosity, grain size, strain gradient).

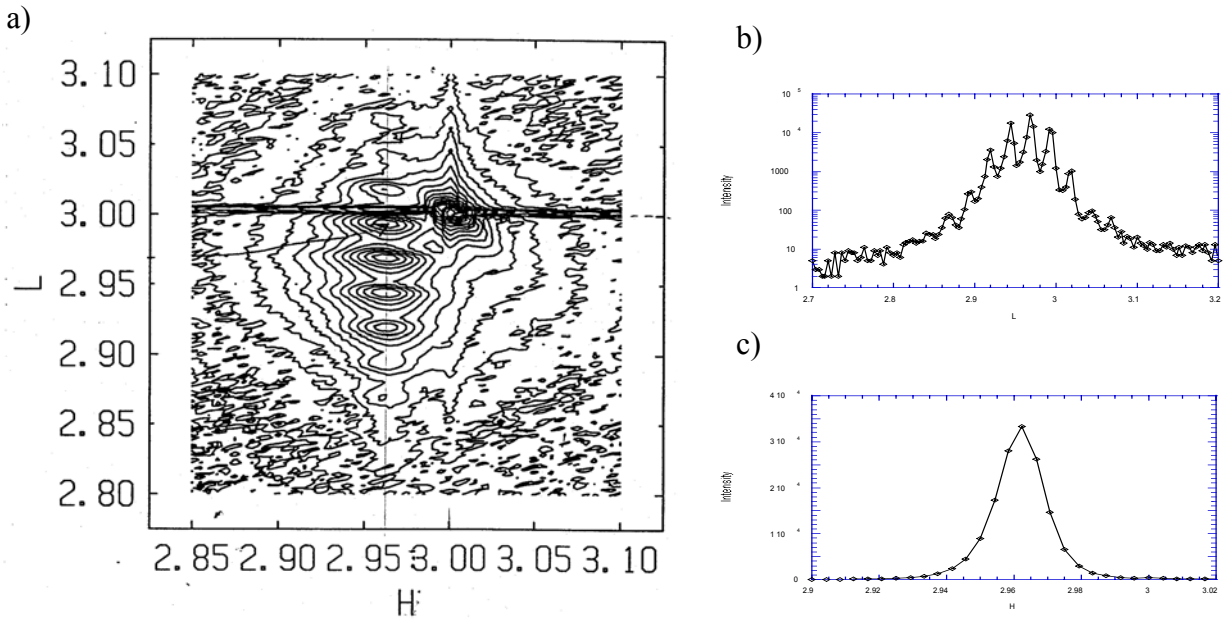
We have studied a series of $(BaTiO_3/SrTiO_3)_n$ epitaxial multilayers synthesized by the chemical vapor deposition of organo-metallic precursors (MOCVD)[1] and by pulsed laser deposition (PLD)[2]. These multilayers have been deposited on c-oriented $LaAl_2O_3$ and $SrTiO_3$ substrates, the thickness of the single layers is varied between 28 Å and 320 Å and the total thickness of the multilayers ranges from 2400 Å to 4800 Å.

During previous experiments (Report 02-02-177) the (00L) diffraction diagrams of these samples were measured. These experiments allow us to determine the strains and the atomic diffusion along the growth axis.

The present experiments consist in the reciprocal space mapping around the (H0L) and (OKL) nodes and give information in plane. They could not be performed in transmission mode because of the absorption of the substrate, therefore the experiments were carried out in asymmetric reflection geometry. The energy was fixed at 8.090 keV. We measured the (003), (303) and (033) peaks by determining the orientation matrix of each sample and then used a hklscan routine.

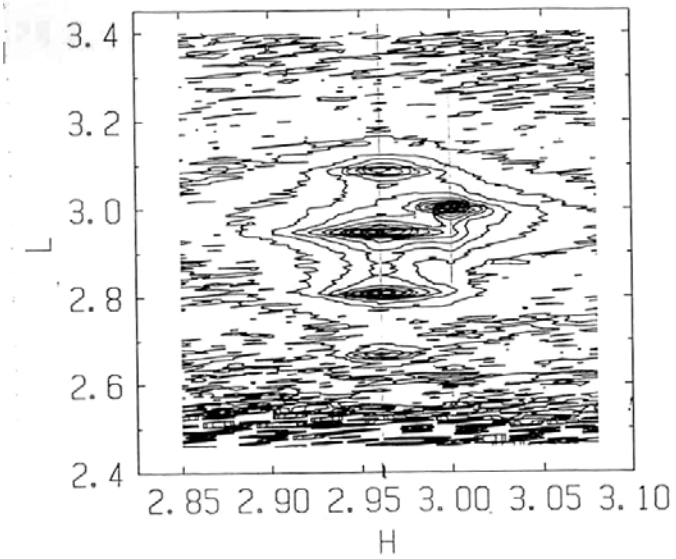
For all $(BaTiO_3/SrTiO_3)_n$ studied we observe a pseudo tetragonal symmetry with no difference between *a* and *b* axes, a full relaxation of strain in BTO and STO layers in the (*ab*) plane and only a small misfit (<2%) with the substrate. One CVD and one PLD sample are detailed above.

Below, an example of a CVD-grown multilayer composed of 15 bilayers of (80 Å STO/ 80 Å BTO): a) the HL map around the (303) peak, b) the extracted L profile and c) the H profile for the main superlattice peak . The map shows aligned peaks along L: therefore BTO and STO sub-layers exhibit the same a (= b) = 3.955 Å parameter, compared to a = 3.905 Å for the STO substrate. This value is closed to the mid value of a for bulk STO and BTO (3.950 Å). The L line shows satellite peaks, whose spacing is determined by the period of the superlattice (Λ = 162 Å). The intensity and breadth of the satellite peaks determine the strain and the interdiffusion along the growth axis (Report 02-02-177 and Ref. 3). The FWHM of the peak along H indicates that the *a* parameter varies between 3.944 Å and 3.966 Å and is due to domain size and angular misorientation between domains.

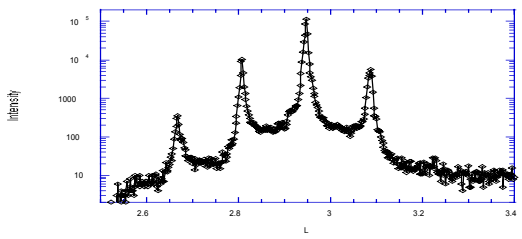


Below, an example of a PLD-grown multilayer of 100 bilayers of (16 Å STO/ 12 Å BTO): a) the HL map around the (303) peak, b) the extracted L line and c) the H line for the main superlattice peak. The lattice parameter for BTO and STO layers is a (= b) = 3.957 Å (value close to that of the previous sample). The period determined on the L profile is Λ = 28 Å and the FWHM along H shows that the variation range of the a parameter is between 3.947 Å and 3.966 Å , that is 15 % smaller than that of the CVD sample.

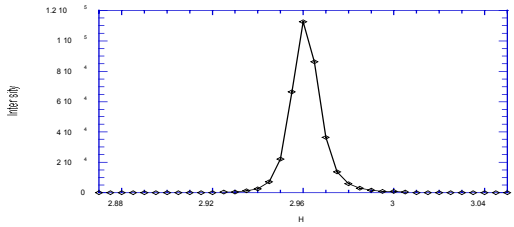
a)



b)



c)



The X-ray diagrams along L are very different. The c parameter varies continuously between 3.905 Å and 4.005 Å for the CVD sample, whereas the c parameter takes only two distinct values (c_{BTO} = 4.053 Å; c_{STO} = 3.920 Å) for the PLD sample. Such a difference was observed on other CVD and PLD samples and is related to the much higher coherence of the PLD layers along the growth axis and of the larger interdiffusion in the CVD superlattices. In the (ab) plane, the relaxation of CVD and PLD samples seems to be similar: for all $(BaTiO_3/SrTiO_3)_n$ studied we observe no difference between a and b axes and a full relaxation of in-plane strain in BTO and STO layers. The common large in plane width of all reflections could indicate that a mirror twinned domain phenomenon occurs due to the quadratic strain induced by the STO substrate.

1 F. Weiss, J. Lindner, J. P. Senateur, *et al*., Surface and Coatings Technology **133-134**, 191 (2000).

2 G. Koebernik, W. Haessler, H.-D. Bauer, *et al*., Integrated Ferroelectrics **33**, 373 (2001).

3 E. Dooryhee, J. L. Hodeau, M. Nemoz, *et al*., Journal de Physique IV **11**, 267 (2001).