Commissioning and Performance of Five-circle Kappa Diffractometer at DND-CAT: Epitaxial Oxide Films

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Introduction

A new five-circle "kappa" diffractometer has been installed and commissioned at the 5-ID-C surface studies hutch of the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) at APS. Kappa geometry was chosen to provide space around the sample for a solid-state fluorescence detector and to allow a beam pipe to easily be installed when the downstream 5-ID-D hutch is in use. The high-resolution theta axis of the diffractometer is used for fine scanning through perfect-crystal rocking curves, as needed in x-ray standing wave (XSW) experiments. The fifth vertical axis was included to permit surface x-ray diffraction (SXRD) experiments at grazing incidence. The diffractometer (Fig. 1) was built by Huber and sits on a kinematic table. Initial diffractometer tests were performed with samples of epitaxial thin-film oxides on semiconductors.

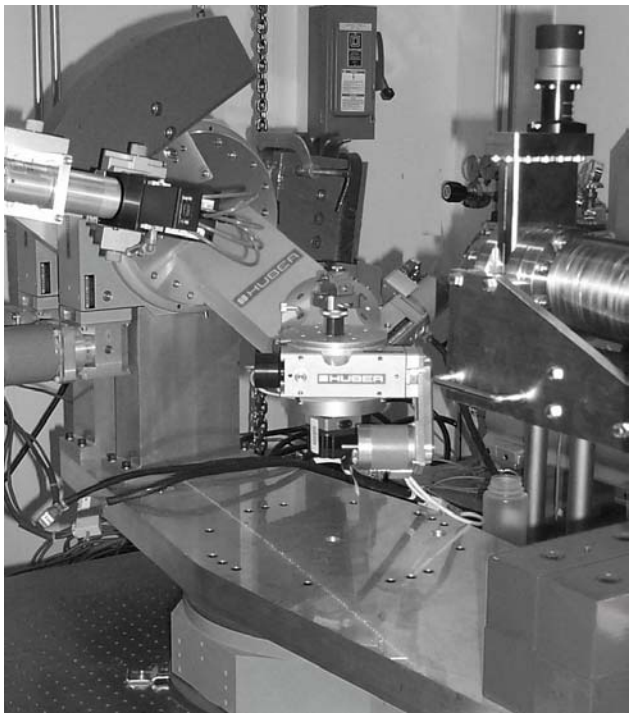

FIG. 1. The new five-circle kappa diffractometer installed in DND-CAT hutch 5-ID-C. On the right is the snout of a solid-state detector used to collect fluorescent x-rays.

Methods and Materials

Two sets of measurements were performed on samples grown at ORNL [1]. SXRD measurements were performed on a 6-monolayer (ML)-thick (three unit cells or 16.4 Å) film of $Ba_{0.75}Sr_{0.25}O$ (BSO) on Si(001). Molecular beam epitaxy (MBE) growth of the lattice-matched BSO film began with 1/4 ML of Sr to form a silicide layer. The BSO film was capped with a 95-Å $SrTiO_3$ (STO) film. To measure diffraction along the specular reflectivity and a small number of crystal truncation rods (CTRs) in this preliminary study, 14.5-keV x-rays were used. The sample was held in an evacuated Be dome to minimize air scattering. The CTR data were collected at a 0.5° angle of incidence.

XSW measurements were performed on a thin film of two unit cells of $BaTiO_3$ (BTO) grown on Ge(001). Growth of the BTO began with 1/4 ML of barium germanide and terminated with a TiO_2 plane. XSW measurements using the bulk Ge(004) Bragg reflection were performed on this sample by using 8.0-keV x-rays. A pair of Si(004) channel-cut crystals were used to condition the beam for the proper divergence. The sample was surrounded by a very thin He-filled bag to reduce Ar *K* fluorescence. While scanning in an angle through the Ge(004) Bragg rocking curve, the fluorescence spectra were collected with a seven-element Ge solid-state detector.

For the SXRD measurements, the diffractometer was controlled by the program SPEC [2], which was recently updated to include the five-circle kappa geometry. By use of pseudoangles, the diffractometer can be operated in Eulerian geometry (utilizing the more traditional theta, chi, and phi angles). The XSW measurements were performed with custom SPEC macros designed to simultaneously collect the reflectivity and fluorescence spectrum.

Results

For the BSO/Si(001) sample, data along one of the CTRs are presented in Fig. 2. Structure factors along the (20*L*) rod, corrected for Lorentz and polarization factors, are shown, as are best fits to a few simple models. Clearly, the data do not exhibit the oscillations that should be present if 6 ML of BSO scattered coherently (dotted line). However, the data cannot be described with a simple Si bulk truncation either (dashed line). The best fit

(solid line) consists of one silicide layer above the Si(001) surface. The silicide layer was modeled as containing a weighted mix of Ba and Sr; its lateral position was found to be above the second-highest Si layer after comparing fits for each of the four high-symmetry sites. Specular reflectivity scans (not shown) clearly showed STO film peaks, but there was no sign of the BSO(002) peak, despite extensive searching. The STO peaks do not appear in the CTR scans (such as Fig. 2), since their in-plane lattice parameter does not match that of the substrate.

XSW results for the BTO/Ge(001) sample are shown in Fig. 3. The modulation of the Ba $L\beta 2$ fluorescence yield was fit to XSW theory to determine the coherent fraction f_{004} and coherent position P_{004} of Ba atoms relative to the bulk Ge(004) planes. A coherent fraction f_{004} = 0.13 ± 0.01 and a coherent position p_{004} = 0.57 ± 0.03 were measured. The other Ba L lines nearly overlap the Ti K lines, so an XSW measurement for the Ti atoms is not feasible without a higher-resolution spectrometer, such as a wavelength-dispersive spectrometer.

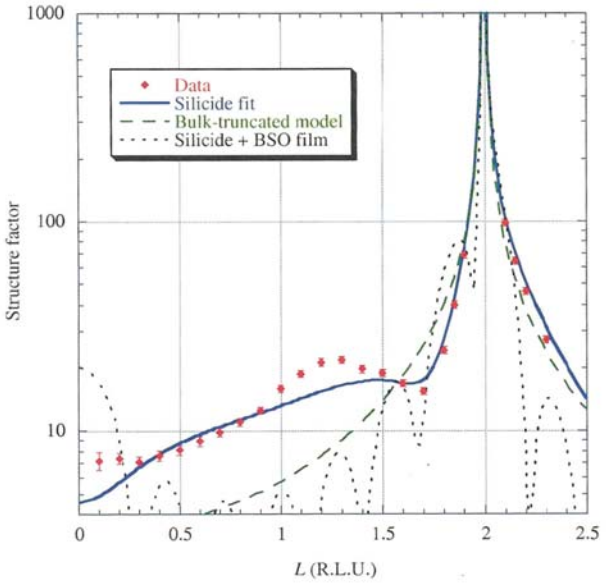

FIG. 2. Surface diffraction along the (20L) crystal truncation rod of the MBE grown heterolayer structure 95 Å of $SrTiO_3$/16 Å of $Ba_{0.75}Sr_{0.25}O$/Si(001).

Discussion

The new five-circle kappa diffractometer performed well in both grazing-incidence diffraction experiments and rocking-curve measurements. A more stringent test of angular resolution, the Si(008) rocking curve at 12.5 keV, again yielded data matched by dynamical diffraction theory [3]. However, both oxide films exhibited significantly more disorder than expected. There was no

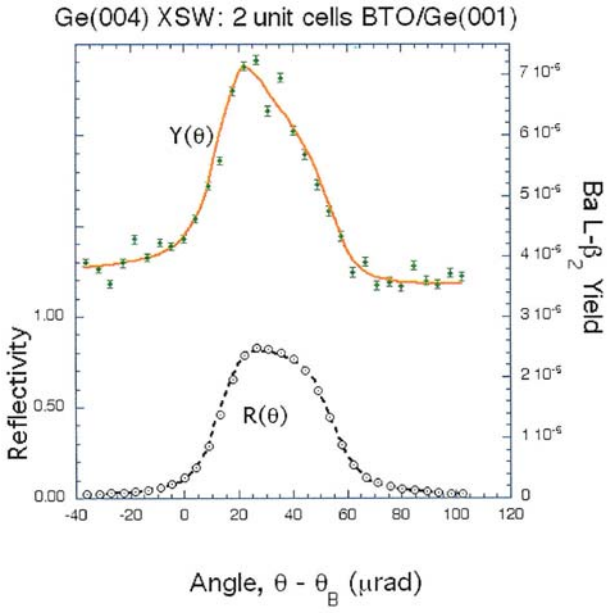

FIG. 3. X-ray standing wave results for two unit cells of $BaTiO_3$ on Ge(001). Normalized data of the Ge(004) rocking curve and Ba $L\beta 2$ fluorescence yield are shown vs. angle θ, as are the corresponding theoretical fits.

sign of an epitaxial BSO film in the SXRD measurements of the first sample. The coherent fraction of the BTO sample was much lower than expected; a basic model, including a reasonable Debye-Waller factor and a geometric correction based on the BTO layer spacing, yields an estimate of f_{004} of ~0.65. Possible explanations include sample degregation due to atmospheric exposure, a reaction at the silicide or germanide interface, or defects in the oxide film due to atomic steps on the semiconductor surface [4]. Both x-ray techniques perform ensemble averages over the sample surface and are thus sensitive to defects that may not always appear when microscopy techniques are used. Further experiments, such as collecting diffraction data along additional CTRs or XSW data at additional Bragg reflections, should shed more light on these samples.

Acknowledgments

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