

GRAZING INCIDENCE IN-PLANE X-RAY DIFFRACTION IN THE LABORATORY

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ABSTRACT

The laboratory implementation of grazing incidence in-plane X-ray diffraction, using an unmodified commercial diffractometer, is described. Low resolution, high intensity measurements are illustrated in the study of the in-plane lattice parameters and texture of a thin polycrystalline ZnO film on glass, the in-plane order in Cd arachidate Langmuir-Blodgett films, and the depth dependence of lattice parameter in graded Si-Ge epilayers. Use of an asymmetrically cut Ge crystal to compress and monochromate the beam provides a high resolution setting, appropriate to measurement of the in-plane mosaic of mismatched epilayers such as GaN on sapphire.

INTRODUCTION

Grazing incidence in-plane diffraction (GIIXD) [1] is a mature technique which has been extensively applied to problems in surface science. Much use has been made of the technique to study surface reconstruction and to determine the crystallographic relationships between such structures and that of the bulk. It has also been exploited to study the in-plane structure of quantum wires and dots [2]. The method exploits the limited depth penetration of the evanescent wave set up when there is total reflection of X-rays incidence at grazing angle to the surface. Below the critical angle, typically between $\frac{1}{4}^\circ$ and $\frac{1}{2}^\circ$, the totally externally reflected wave penetrates only a few nanometres into the material, giving extremely high surface sensitivity. When, as in the geometry shown in Figure 1, the specimen is oriented to satisfy the angle for Bragg diffraction in the plane of the sample, a strong diffracted beam can be observed emerging at the same grazing angle as the incident beam. In such an arrangement, Bragg planes normal to the sample surface are probed. Thus rocking curves, consisting of scans of the sample about the ϕ axis normal to the specimen surface, measure either or both the in-plane mosaic and correlation length. The in-plane lattice parameter (in-plane strain) can be measured by performing either a scan of the detector about the specimen surface normal or a ϕ - 2θ of sample and detector. It is important to note that the Bragg angle is never quite satisfied; the scattering vector (which is the vector difference between the exit and incident scattering vector) always points out of the sample and can never be set exactly equal to the reciprocal lattice vector of the Bragg planes. The scattering vector therefore cuts the crystal truncation rod of the reciprocal lattice point being probed. The requirements for GIIXD are different to those for high resolution X-ray diffraction or reflectivity. In order to access an appreciable component around an in-plane reciprocal lattice feature (truncation rod), the incident beam must include a small amount of divergence, although

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this divergence must be small enough to produce a distinct diffraction peak. A minimum divergence of about one μrad is acceptable [3].

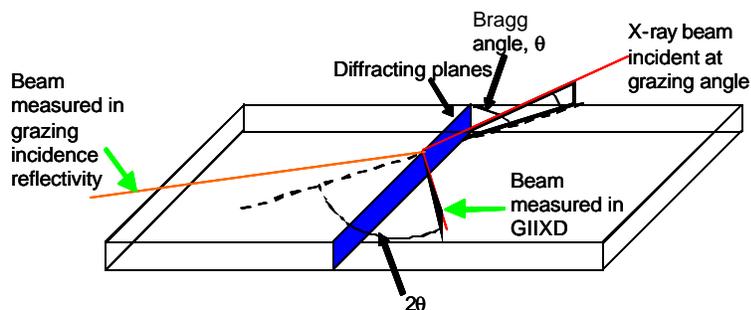


Figure 1. Schematic diagram of the GIIXD geometry, showing the incident and diffracted beams and the specularly reflected beam that is measured in standard grazing incidence reflectivity.

The penetration depth varies very rapidly just beyond the critical angle, providing for example a depth-sensitive technique for X-ray fluorescence [4]. Pietsch and co-workers [5] have used a position-sensitive detector and a beam that is divergent normal to the specimen surface to perform depth-sensitive GIIXD. Beyond the critical angle, the depth penetration can reach several micrometres, still retaining significant signal in the GIIXD diffraction peaks. An example of data taken beyond the critical angle is shown in Figure 2, which shows a map of the in-plane scattering from the 220 peak in a (001) epitaxial layer of Si-Ge, grown with an increasing Ge concentration on a (001) Si wafer. The in-plane specimen rotation measures the in-plane mosaic, whereas the in-plane scattering angle probes the Ge composition and associated relaxation. The in-plane mosaic increases with increasing Ge concentration; the width of the scatter (to the left of the image) on rotating the sample in-plane increases as the angle of the diffraction peak falls.

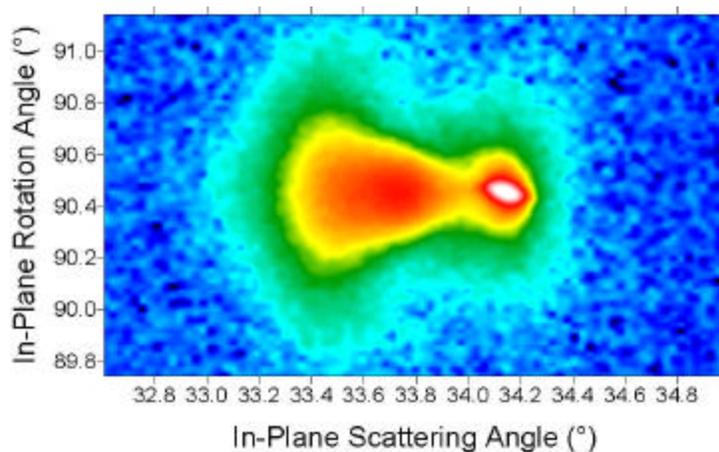


Figure 2. In-plane map of the GIIXD scattering from a graded Si-Ge layer on Si. Scatter from epilayer is to the left of the substrate peak. Data taken on beamline BM28, ESRF, Grenoble.

IMPLEMENTATION OF GIIXD IN THE LABORATORY

To date, most of the applications of GIIXD have been at synchrotron radiation sources and the weak scattering has made laboratory work impracticable. The few reports to be found in the literature show low signal and poor signal to noise ratio [6]. Recently, however, we have shown that use of a microfocus X-ray source and coupled optic can provide a beam of sufficient collimation and intensity to perform such experiments in the laboratory [7]. Initial experiments were performed with a standard commercial dual source Bede D1 diffractometer and focusing optic, an ellipsoidal MicromirrorTM (Reflex s.r.o.). Excellent agreement was found between in-plane rocking curves taken with this system and on beamline BM28 at the ESRF in Grenoble.

HIGH INTENSITY LOW RESOLUTION CONFIGURATION

The experiments described below were performed on a dual source Bede D1 diffractometer, fitted with a Microsource[®] microfocus X-ray generator and focusing optic in addition to a standard sealed source and Bragg reflection optics for high-resolution diffraction. No modification to the commercial system was undertaken. The Cu target microfocus X-ray generator was run at a power of 80W (40kV, 2mA), the beam being focused onto the sample using low divergence polycapillary optics from X-ray Optical Systems Inc. These had a divergence of 3 mrad at the sample in both horizontal and vertical directions. The beam diameter varied from 1.5 to 4mm, depending on the particular optic used.

A set of Soller slits, with the blades vertical, determines the angular resolution of the detector and a Ni foil behind the polycapillary optic removes the CuK β line. The configuration delivers a high intensity beam to the sample with a divergence of typically 0.15°. Compared with a parabolic graded multilayer mirror and a conventional sealed source, the intensity is increased by over an order of magnitude [8]. Note that the detector scans in the horizontal plane, not quite in the plane of the sample (which is tilted at a small angle to the horizontal X-ray beam.). For the measurements described below, the wide aperture of the detector (and of the vertical Soller slit attachment) allows the diffracted beam to be collected by the detector without translating or rotating the detector out of the plane of the wafer surface. However, this configuration both sets an upper limit on the grazing incidence angle and also integrates intensity over the vertical aperture of the detector. The intensity that is recorded at the detector corresponds to the length of the truncation rod in reciprocal space.

The simple setting has a polychromatic beam, limited only by the high energy cut-off of the polycapillary optic. For large range ϕ -2 θ scans the effect of the Bremsstrahlung on the signal background is deleterious, sharp step changes being observed as harmonics switch in. The background can be dramatically suppressed, with loss of signal by only a factor of two, through use of a graphite monochromator before the detector.

An example of the application to measurement of the in-plane lattice parameter and texture of a polycrystalline film is shown in Figure 3. This shows a portion of a ϕ -2 θ scan from a 200 nm ZnO film deposited on float glass. The signal to noise ratio for the weaker Bragg peaks is sufficient to deconvolve the overlapping 11.2 and 20.1 peaks, despite the signal being only a few

counts per second. The 10.3 peak is well defined with a peak height of only 2 c.p.s. (at 30 seconds count time per point).

The Bragg peaks index to in-plane lattice parameters of $a = 3.2674 \pm 0.0016 \text{ \AA}$ and $c = 5.234 \pm 0.037 \text{ \AA}$ revealing the presence of substantial in-plane strain. From the peak widths we deduce an in-plane grain size of $160 \pm 50 \text{ \AA}$. Use of GIIXD permits the strain to be measured independently of the out-of-plane strains in the film and without complex analysis because it is sensitive only to Bragg planes normal to the specimen surface. Specimen scans about the ϕ axis at fixed detector position revealed absence of significant texture in the film, the only intensity variation resulting from the sample surface being slightly misaligned from the plane of rotation.

A second example of the data quality is in the study of the in-plane order of Langmuir-Blodgett (L-B) films. Figure 4 shows an out-of-plane grazing incidence scan of the specular reflectivity of a typical Cd arachidate L-B film. There is excellent order out of plane with well-defined Kiessig thickness fringes visible in addition to many orders of Bragg reflection associated with the length of the Cd arachidate molecule. However, the rocking curve (specimen scan) through a Bragg peak indicates that the in-plane order is relatively poor. The distribution of diffuse scatter varies slowly with angle and this absence of significant peaking in the diffuse scatter is indicative of a very short in-plane correlation length.

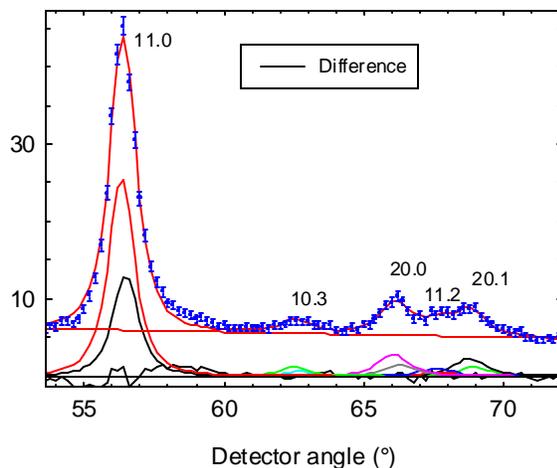


Figure 3. In-plane $f-2q$ scan of a polycrystalline ZnO film on float glass

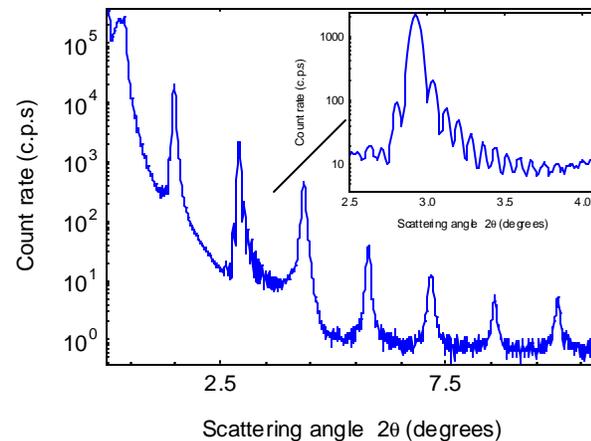


Figure 4. Grazing incidence reflectivity scan of a Cd arachidate L-B film

GIIXD measurements enable the in-plane order of the L-B films to be probed. Almost all measurements of this have, to date, been performed at synchrotron radiation sources. Figure 5 shows a GIIXD detector scan, taken in the laboratory, of a 20 layer L-B film of cadmium arachidate. The three peaks index to the rectangular herringbone structure reported previously with $a = 4.89 \pm 0.01 \text{ \AA}$, $b = 7.51 \pm 0.01 \text{ \AA}$. The data quality is comparable to that from the ELETTRA synchrotron radiation source and the lattice parameters are comparable to those reported by Kumar *et al* [9]. From the large width of the Bragg peaks ($\Delta\theta \approx 0.8^\circ$) we see immediately that the ordering is poorer in the plane of the film than out of the plane. From the peak widths we find an in-plane diffracting domain size of $110 \pm 10 \text{ \AA}$, consistent with the short in-plane correlation length deduced from the diffuse reflectivity rocking curve.

A final example of the application of the low resolution arrangement is in the use of GIIXD above the critical angle. Here the beam penetrates to a depth of microns, giving a larger diffracting volume, but the increased incidence angle means that the reciprocal lattice truncation rod is cut further away from the reciprocal lattice point. The scattering power consequently decreases. However, with only the focusing optic conditioning the incident beam, there is enough intensity to obtain good GIIXD signals from depths approaching 2 μm . In a series of ϕ - 2θ scans as a function of grazing angle from a linearly graded Si-Ge epitaxial layer grown on (001) silicon, the position of the maximum of the 220 Bragg peak from the epilayer (Figure 2) moved linearly towards larger angles. The shift arises from the increase in Ge concentration towards the top of the layer.

HIGH RESOLUTION GIIXD

High resolution GIIXD can be achieved by further conditioning the incident beam to limit both the wavelength bandpass and the divergence in the horizontal plane. This was achieved by use of an asymmetrically cut Ge 004 beam-conditioner set in a grazing exit geometry, giving beam compression to a 300 $\mu\text{m} \times 2$ mm spot on the sample. The dramatic effect on the resolution on insertion of the Ge monochromator crystal after the polycapillary optic is seen in Figure 6. There is loss of a factor of 30 intensity upon monochromatisation, but only the $\text{CuK}\alpha_1$ line reaches the sample and the full width at half height maximum (FWHM) of the 220 rocking curve (ϕ) scan of a single crystal (001) Si sample is reduced from 0.15° to 0.01° . As with all Bragg reflection optics, beam divergence and monochromaticity are coupled and the effect of the Ge crystal is to reduce both intensity and input beam divergence. Table 1 shows the comparison of rocking curve widths and peak intensity between various combinations of source and beam conditioner.

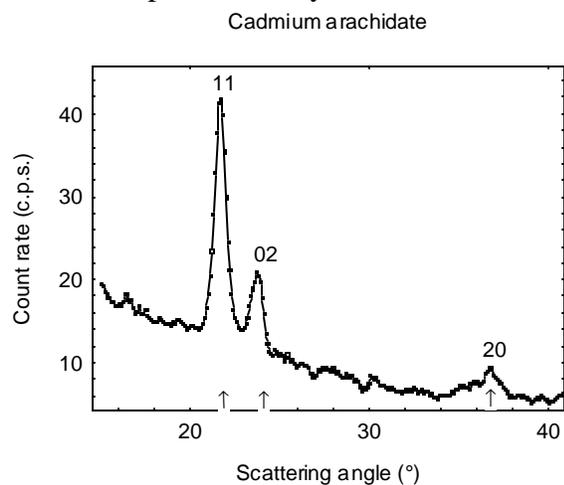


Figure 5. GIIXD detector scan of a Cd arachidate L-B film. Indexing is to the rectangular herringbone structure.

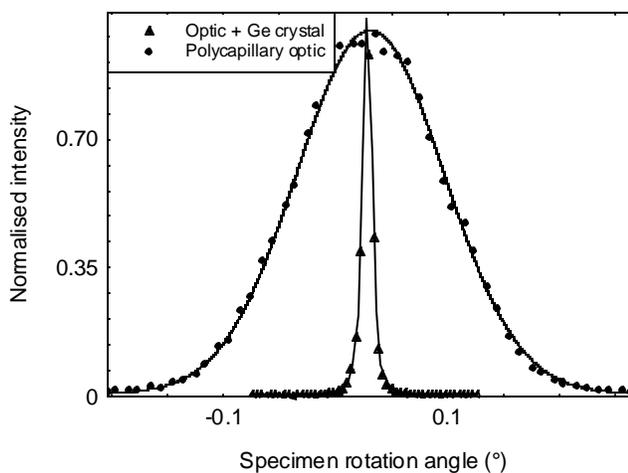


Figure 6. f scans of a Si wafer (about surface normal), detector set for the 220 reflection, with and without the Ge monochromator crystal. Solid lines are fits of Voigt functions.

The high resolution setting has been used to study the changes in the twist mosaic of GaN as a function of epilayer thickness [10], growth temperature [11] and AlN barrier thickness [12]. In all the samples and reflections studied to date, the GIIXD rocking curve width has been larger than

that of the symmetric out-of-plane reflections. This has not been resolution limited and it appears generally that the threading edge dislocation density (associated with twist mosaic) is a few times that of the threading screw dislocation density (associated with tilt mosaic).

Table 1

Sample	D1 Microsource® 4 mm diameter Polycapillary optic		D1 Standard Source 2 mm width Gutman optic		D1 Microsource® 4 mm Polycapillary optic Asymmetric Ge crystal	
	<i>FWHM</i> (°)	<i>Count Rate</i> (kcps)	<i>FWHM</i> (°)	<i>Count Rate</i> (kcps)	<i>FWHM</i> (°)	<i>Count Rate</i> (kcps)
200mm (001) Si wafer, 220	0.15	42	0.05	1.4	0.01	1.4
(00.1) GaN epilayer 110	0.31	>800	0.27	14.7	0.25	4.1

CONCLUSIONS

Using recent developments in X-ray sources and optics, it is now feasible to undertake a range of grazing incidence in-plane diffraction experiments in the laboratory. Because of the high intrinsic width of the Bragg peaks in highly mismatched systems such as GaN on sapphire the quality of the data approaches that obtained at synchrotron radiation sources. The technique appears therefore appropriate for transfer to the industrial research laboratory.

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REFERENCES

- [1] I. K. Robinson and D. J. Tweet, Rept. Prog. Phys. **55** (1992) 599
- [2] V. Holý, U. Pietsch and T. Baumbach, *High Resolution X-ray Scattering from Thin Films and Multilayers*, Springer Tracts in Modern Physics **149** (1999) Springer: Berlin
- [3] D. Rose, U. Zeimer, and U. Pietsch, J. Appl. Phys. **81** (1997) 2601
- [4] K Sakurai, Spectrochimia Acta B **54** (1999) 1497
- [5] D. Rose, U. Pietsch, A. Förster, H. Metzger, Physica **B198** (1994) 256
- [6] K. Kobayashi, A. A. Yamaguchi, S. Kimura, H. Sunakawa, A. Kimura and A. Usui, Japan. J. Appl. Phys. **38** (1999) L611
- [7] M. S. Goorsky and B. K. Tanner, Cryst. Res. Technol. **37** (2002) 647
- [8] T. A. Lafford, P. A. Ryan, D. E. Joyce, M. S. Goorsky and B. K. Tanner, Phys. Stat. Sol (a) **195** (2003) 265
- [9] N. P. Kumar, S. Major, S. Vitta, S. S. Talwar, P. Dubcek, H. Amenitsch, S. Bernstorff, V. Ganesan, A. Gupta and B.A. Dasannacharya, Colloids and Surfaces A **198-200** (2002)75
- [10] T. A. Lafford, P. J. Parbrook and B. K. Tanner, Phys Stat Sol (c) **0** (2002) 542
- [11] T. A. Lafford, B. K. Tanner and P. J. Parbrook, J. Phys. D: Appl. Phys. **36**, (2003) A245
- [12] T. A. Lafford, P. J. Parbrook and B. K. Tanner, Appl. Phys. Lett. **84** (2004) in press