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Thin-film disorientation measurement using the single-crystal Nonius Kappa CCD diffractometer

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The experimental procedure for the determination of disorientation of thin films relative to their substrate using the dedicated single-crystal Nonius Kappa CCD diffractometer is presented in this paper. This setup is applied to the analysis of polycrystalline ZnO films deposited on silicon, where the inclination of the piezoelectric film relative to the substrate is related to excitation of the shear wave mode in these resonators. Care must be taken with harmonic contamination arising from the sealed tube. Diffraction patterns were analysed with dedicated programs written in Fortran77.

1. Introduction

ZnO thin films are used in a variety of microsystems, ranging from radio-frequency filters and oscillators, to sensors and actuators. They allow the excitation of bulk and surface acoustic waves with high electromechanical coupling coefficients. Films in which the *c* axis is inclined with respect to the surface normal are of interest with respect to the excitation of the shear wave mode. Compared with the longitudinal wave mode, the shear wave mode features higher coupling coefficients (Foster *et al.*, 1968) and allows operation in liquids, such as in applications where film bulk acoustic resonators (FBAR) are used as sensors (Link *et al.*, 2006*a*). The growth of polycrystalline ZnO films with inclined structure is difficult, since the trend of the ZnO to crystallize in the perpendicular direction must be overcome and the polar *c* axes of all different grains must point in the same direction. Inclined ZnO thin films have been fabricated by using various physical and chemical vapour deposition methods (Link *et al.*, 2006*b*). In order to obtain information about the *c*-axis inclination and assess the expected acoustic properties, we present here X-ray diffraction (XRD) measurements performed on a Nonius Kappa CCD single-crystal diffractometer. This paper reports on the method and the development of the analytical tools used to analyse the recorded data from this diffractometer, which is routinely used in single-crystal structure determination and charge density studies (see, for example, Aubert *et al.*, 2003).

2. Experimental

The sample was a multiple-layer thin film composed of platinum electrodes (~100 nm thick), ZnO (400 nm), alumina (~100 nm) acting as an insulator, followed by another layer of platinum. All these materials are deposited on silicon (110) substrate (~400 µm thick) (Fig. 1). Whereas silicon is single crystalline, Al_2O_3 is amorphous, Pt electrodes are polycrystalline, and one expects an orientation distribution of the ZnO film.

The aim of the study is to determine the average inclination of the *c* axis of the ZnO film (Wurtzite structure, $P6_3mc$, $a = b = 3.24$ Å, $c = 5.20$ Å; ICSD-Fiz-Karlsruhe, 2005) relative to the substrate normal Si(110).

A small (~1 mm^2) fragment was cut from the parent wafer and mounted with the face opposite to the thin film glued to the extremity of a glass capillary in order to allow the largest possible rotation around the normal Si(110) (Fig. 2) and minimize diffusion by the sample holder when placed on the diffractometer [radiation source: graphite (002) monochromated, Mo *Kα* sealed tube; goniometer: Kappa geometry; detector: Princeton Instruments 625 × 576 pixels in binned mode]. The Mo *Kα* sealed tube was operated at 30 kV (60 kV nominal), despite the heavy loss in intensity, in order to remove harmonics which were shown to be rather significant (mostly the λ/2 contamination). Typical exposure time for quantitative analysis was around 120 s $(^\circ)^{-1}$, which is a compromise between noise and ZnO signal.

The orientation matrix of the sample was then determined using the sharp diffraction spots of the silicon substrate recorded with the Nonius Kappa CCD (*HKL* software; Otwinowski & Minor, 1997) (see Fig. 3). Then the option 'orientation and single scan' of the single-crystal software suite *Collect* (Nonius BV, 1999) allowed the silicon substrate to be oriented with its normal in the equatorial plane and perpendicular to the incident X-ray beam. ZnO(002) is thus anywhere around a cone centred on Si(110), the thickness of which

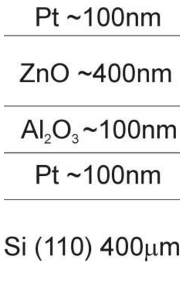


Figure 1
Composition of the thin-film sample.

depends on the orientation distribution (Fig. 2), and is brought into the equatorial plane by trial-and-error rotations around Si(110) (defined as the ψ axis). The required orientation was achieved when the ZnO(00±2) direction [*i.e.* the line going from ZnO(00$\bar{2}$) to its Friedel pair ZnO(002) on the diffraction pattern] is aligned with Si(±2±20) on ω-scan diffraction frames (orientation defined as ψ = 0°; Fig. 2). The inclination of ZnO(002) relative to Si(220) is then obtained by recording such diffraction patterns, but with the sample rotated at ψ = 90° around its normal Si(110) with the detector centred at θ = 0° (Fig. 3). The ZnO(00±2) direction is therefore in the vertical plane. Due to the fact that the distribution of ZnO *c*-axis orientation is rather spread, large ω scans are required; an amplitude of 40° for all scans was finally chosen after several tests.

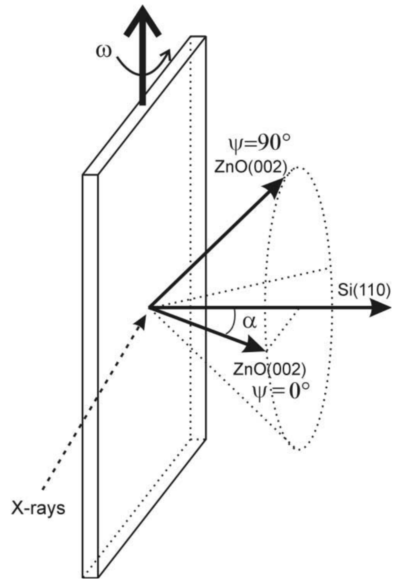


Figure 2
Orientation of the sample on the diffractometer and disorientation angle α of the ZnO thin film relative to the silicon wafer.

Table 1
Bragg diffraction angles (°) of low-resolution non-zero reflections for Si, Pt and ZnO for Mo $K\alpha$ wavelength.

Compound	h	k	l	$\theta_{\rm Mo}$
Si	1	1	1	6.50
ZnO	1	0	0	7.26
ZnO	0	0	2	7.86
ZnO	1	0	1	8.26
Pt	1	1	1	9.01
Pt	0	0	2	10.42
Si	0	2	2	10.65
ZnO	1	0	2	10.73
Si	1	1	3	12.52

3. Data analysis

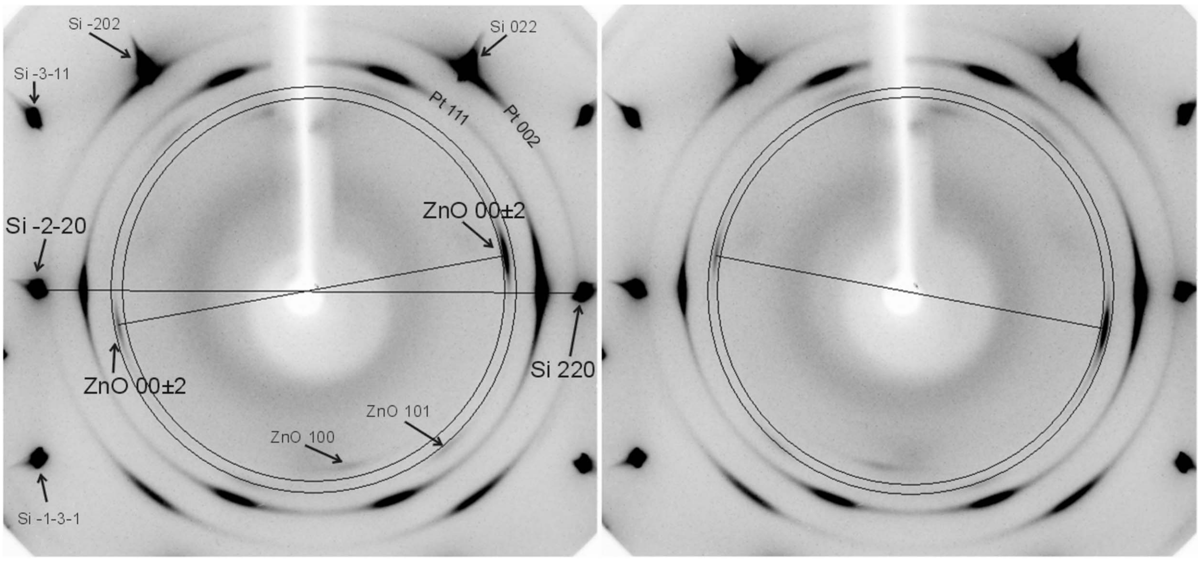
The diffraction patterns were recorded using ω scans ($\Delta\omega$ = 40°) with the CCD detector placed at θ = 0° with Δt = 120 s $(°)^{-1}$ integration time (generator set at 30 kV, 55 mA). The crystal to detector distance (80 mm) was chosen to be as large as possible in order to have the highest precision in the determination of the angular position of ZnO, but small enough to be able to use sharp Si spots as rough orientation references.

On a typical diffraction pattern, such as Fig. 3(*a*), sharp diffraction spots arise from the single-crystalline silicon wafer, whereas Pt and ZnO films appear as spreading arcs, reflecting their polycrystalline character (Table 1). The intensity asymmetry observed between ZnO 00±2 reflections arises from the asymmetry of the sample: the weak signal is related to the incident and diffracted beams that have to propagate through the entire thickness (400 µm) of the Si wafer, whereas the strong one comes from reflection of X-rays from the ZnO-coated side of the sample.

Because of the curvature of the Ewald sphere, the inclination angle α of the ZnO thin film is related to the angle β between the directions ZnO(00±2) and Si(±2±20) by

$$\sin\alpha = \sin\beta\cos\gamma,$$

where γ = 7.9° is the ZnO(002) Bragg angle.



(*a*)

(*b*)

Figure 3
Diffraction patterns (without ‘zingers’ and hot pixels) taken at θ = 0° [Δt = 120 s $(°)^{-1}$, $\Delta\omega$ = 40°; generator set at 30 kV, 55 mA]. (*a*) Orientation ψ = +90°. (*b*) Orientation ψ = −90°. The deviation 2β is defined as the angle between the two oblique ZnO(00±2) directions. The horizontal line links Si(220) to Si($\bar{2}\bar{2}0$) diffraction spots. The integration rings (6 pixels width) for intensity extraction of ZnO(00±2) are superimposed. Sharp diffraction spots arise from the Si substrate, whereas strong diffuse signals come from the polycrystalline Pt layers.

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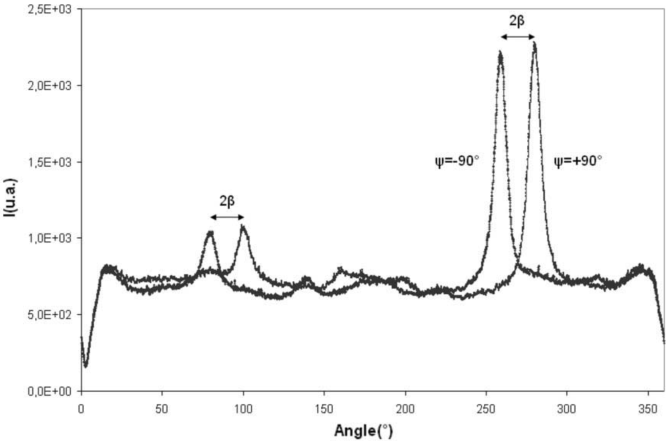

Figure 4
Intensity profiles of the ZnO(00±2) signals recorded at $\psi = \pm 90°$. The deviation 2β is defined as the angle between the maxima of the two profiles and is determined by correlation of the profiles.

As the ZnO film is rather thin compared with the silicon substrate, the diffraction spots of Si(220) are easily saturated in order to achieve a good signal-to-noise ratio for ZnO. Thus, in practice, it is not useful to use Si(±2±20) as an orientation reference. On the other hand, we cannot use the horizontal axis of the detector as it may be rotated by a certain amount around the primary beam direction. This can lead to β not being the correct angle between ZnO(00±2) and the horizontal line on the diffraction frame. To overcome this difficulty, we determined the 2β angle between the ZnO(00±2) directions on two diffraction frames taken at $\psi \pm 90°$ (Fig. 3).

The exposure time per frame being rather long (~1 h 20 min), zingers and hot pixels markedly affect the diffraction patterns. Because recording a dark image would take the same amount of time and because hot pixels are observed to change during that long period, we dealt with these bad signals by recording two successive frames and comparing the pixel intensities extracted from the Nonius.kcd file using a program developed in our laboratory.[1]

On the two $\psi = \pm 90°$ diffraction patterns, the ZnO(00±2) profiles are circular (because the detector is centred at $\theta = 0°$) and were extracted using another Fortran routine, the starting rough estimates of the coordinates of the two centres being taken from visual examination of the patterns using *DigitalMicrograph* software (http://www.gatan.com/). In order to increase the signal-to-noise ratio, the extracted profiles are radially integrated over a few pixels (typically 6), as shown by the rings displayed in Fig. 3. The best centres of these rings are determined by calculating the autocorrelation curve of each profile $p(x)$,

$$I_{\rm ac}(y) = \int p(x)p(x+y)\,{\rm d}x,$$

which has to display a single peak at 180° angular position, *i.e.* the angle between the ZnO(002) and ZnO(00$\bar{2}$) signals. The sensitivity of this method appeared to be better than one pixel.

Finally, the deviation angle 2β is obtained by determining the position of the maximum in the correlation curve between the two ZnO(00±2) profiles recorded at $\psi \pm 90°$ [$p_{\pm 90}(x)$] (Fig. 4):

$$I_{\rm c}(y) = \int p_{-90}(x)p_{90}(x+y)\,{\rm d}x.$$

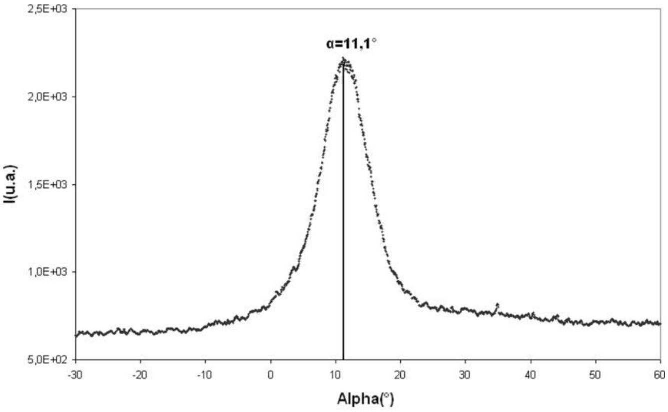

Figure 5
Final intensity profile showing the disorientation α of the ZnO thin film relative to the silicon substrate.

For that particular sample, the disorientation of the ZnO thin film relative to the silicon substrate was thus estimated to be $\alpha = 11.1°$. The final profile is shown in Fig. 5.

4. Conclusions

It is shown that single-crystal X-ray diffractometers dedicated to crystal structure analyses and equipped with area CCD detectors could be used for the determination of disorientation of thin films relative to their substrate. In this example, it is made possible by the high versatility of the Nonius Kappa CCD goniometer and the powerful sample orientation procedure implemented in the standard single-crystal software. Nevertheless, this requires development of non-standard data analysis tools (here written in Fortran77) and care must be taken with respect to λ/2 contamination from the sealed tubes.

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References

Aubert, E., Porcher, F., Souhassou, F. & Lecomte, C. (2003). *Acta Cryst.* B**59**, 687–700.

Nonius BV (1999). *Collect*, data collection software, Nonius BV, Delft, The Netherlands.

Foster, N. F., Coquin, G. A., Rozgonyi, G. A. & Vannatta, F. A. (1968). *IEEE Trans. Son. Ultrason.* **SU-15**, 28.

ICSD-Fiz-Karlsruhe (2005). Inorganic Crystal Structure Database, http://icsdweb.fiz-karlsruhe.de.

Link, M., Schreiter, M., Weber, J., Gabl, R., Pitzer, D., Primig, R., Wersing, W., Assouar, M. B. & Elmazria, O. (2006*b*) *J. Vac. Sci. Technol. A*, **24**, 218–222.

Link, M., Schreiter, M., Weber, J., Primig, R., Pitzer, D. & Gabl, R. (2006*a*). *IEEE Trans. Ultrason. Ferroelec. Freq. Control*, **53**, 492–496.

Otwinowski, Z. & Minor, W. (1997). *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology*, in *Macromolecular Crystallography A*, Vol. 276, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

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[1] The Fortran77 routines discussed in this paper are available from the IUCr electronic archives (Reference: HX5046). Services for accessing these data are described at the back of the journal.

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