

On the application of a single-crystal κ -diffractometer and a CCD area detector for studies of thin films

Henrik Hovde Sønsteby,^{a*} Dmitry Chernyshov,^b Michael Getz,^a Ola Nilsen^a and Helmer Fjellvåg^a

^aDepartment of Chemistry, University of Oslo, Postboks 1033 Blindern, Oslo 0315, Norway, and ^bSwiss–Norwegian Beam Lines, ESRF, BP 220, F-38043 Grenoble, France. E-mail: henrik.sonsteby@kjemi.uio.no

A multipurpose six-axis κ -diffractometer, together with the brilliance of the ESRF light source and a CCD area detector, has been explored for studying epitaxial relations and crystallinity in thin film systems. The geometrical flexibility of the six-axis goniometer allows measurement of a large volume in reciprocal space, providing an in-depth understanding of sample crystal relationships. By a set of examples of LaAlO₃ thin films deposited by the atomic layer deposition technique, the possibilities of the set-up are presented. A fast panoramic scan provides determination of the crystal orientation matrices, prior to more thorough inspection of single Bragg nodes. Such information, in addition to a broadening analysis of families of single reflections, is shown to correlate well with the crystallinity, crystallite size, strain and epitaxial relationships in the thin films. The proposed set-up offers fast and easy sample mounting and alignment, along with crucial information on key features of the thin film structures.

© 2013 International Union of Crystallography
Printed in Singapore – all rights reserved

Keywords: synchrotron X-ray diffraction; epitaxial thin films; six-axis κ -diffractometer.

1. Introduction

Thin solid films are playing an increasingly larger part in emerging materials technology by providing the possibility to design materials for a wide range of applications including solar cells (Britt & Ferekides, 1993; Contreras *et al.*, 1999; Ito *et al.*, 2008; Shah *et al.*, 1999), hydrogen storage (Ito *et al.*, 2008; Vermeulen *et al.*, 2006), solid oxide fuel cells (de Souza *et al.*, 1997; Will *et al.*, 2000) and battery technology (Bates *et al.*, 2000; Brousse *et al.*, 1998). Understanding the structure of the thin film, including the interfacial relationship between the substrate and deposited layer, is in this respect of crucial importance. As such films become thinner, the traditional θ – 2θ Bragg–Brentano home laboratory approach becomes ineffective owing to low diffracted photon flux and poor signal-to-noise ratio. Relatively fast mapping over large \mathbf{q} -volumes is imperative for a range of studies, including crystallization dynamics, phase transitions and peak family evaluation. Thus, a flexible geometrical set-up with minimum constraints on space and with an angular movement control that allows studies of thickness variations down towards the single-digit nanometre range would be a very valuable complementary asset to established thin film diffraction set-ups.

Here, we show how this goal can be reached with the means of a multipurpose κ -diffractometer equipped with a CCD area detector. A similar approach has previously been applied using a Nonius Kappa CCD diffractometer to illustrate thin film disorientation (Aubert *et al.*, 2006). Another related approach has previously been used at the Swiss–Norwegian Beam Lines (SNBL) to study Bragg scattering in a polar Nd-doped BiFeO₃ thin film on a MgO substrate and diffuse

scattering on the domain structure in PbTiO₃ films (Leontyev *et al.*, 2011; Mo *et al.*, 2008). A description of the set-up and experimental strategies are provided and the approach is illustrated with 5–100 nm thin films based on Co₃O₄ (Klepper *et al.*, 2007), MnO₂ (Foss *et al.*, 2005) and LaAlO₃ (Sønsteby *et al.*, 2012) deposited by the atomic layer deposition (ALD) technique (Suntola & Antson, 1976).

2. Experimental

The versatile κ -goniometry¹ is widely applied for single-crystal diffraction studies and can be readily adopted for thin film samples. The basic mathematics for the κ -goniometer geometry used has been thoroughly described (Paciorek *et al.*, 1999). Currently, the KUMA6 κ -diffractometer at the BM01A line of the SNBL at the European Synchrotron Radiation Facility is used. The diffractometer operates under control of the *CrysAlis* software (Oxford Diffraction, 2006) that performs angular calculations based on the method reported by Thorkildsen *et al.* (2006). The experimental set-up and software, albeit not optimized for a thin film experiment, possess the necessary flexibility together with an intuitively clear user interface that offers a wide range of geometries for collecting data. The *CrysAlis* software was further used for indexing reflections and inspection of reciprocal space.

¹ The kappa instrumentation was invented by Siem Poot of Enraf–Nonius, and protected worldwide by patents (Poot, 1972).

The monochromatic beam was prepared by the optic system comprising two focusing mirrors and a focusing monochromator. The beam size was routinely set to $\sim 0.5 \text{ mm} \times 0.5 \text{ mm}$ and the wavelength to around 0.7 \AA . The beam is polarized in the horizontal plane (96%); calibration of the wavelength was performed using a LaB_6 NIST 660 standard powder sample and the calibration of the diffractometer was based on measurements of a ruby single-crystal.

2.1. Sample mounting and alignment

Thin films for research purposes are typically deposited on a sample substrate of a material of choice, often covering an area in the range of a few cm^2 . For practical purposes the substrate is oriented horizontally, *i.e.* with the surface normal in the vertical direction for subsequent routine experiments. The sample substrate is mounted on a goniometer head with arcs, so that the thin film plane is almost parallel to the incoming beam. The samples are pre-aligned using an optical microscope and subsequently aligned with the aid of a complementary alignment laser by adjusting the tilts of the goniometer head. Having aligned the sample horizontally, the sample is positioned into the beam by a vertical displacement guided by an optical microscope or by an additional detector set in transmission mode (so called 'X-ray eye').

2.2. Panoramic scan

Orientations matrices and mutual orientations of the substrate and film unit cells are first obtained by mapping a large volume of reciprocal space with a traditional φ -scan for a set of ω -angles. The detector is placed close to the sample, in order to maximize the q -range per frame. Such a data collection results in two sets of reflections assuming both film and substrate are single crystals, one coming from the thin film and the other from the substrate.

There are some pitfalls to be aware of, namely a systematic distortion of the shape for Bragg reflections that is convoluted with the footprint of the beam, and also a small dead zone near the rotational axis. The first problem is minimized by appropriate selection of the initial tilt angle and beam size. To recover reflections positioned near the rotation axis, additional data collection with non-zero κ and ω angles has to be performed.

For the described broad scans with the thin film surface almost parallel to the beam, an important volume in the reciprocal space around the normal axis is unavailable. In addition, scattering in the horizontal plane is not measured optimally due to Lorentz and polarization factors. The missed volume is easily recovered by an ω -scan for the film positioned horizontally. Similar to the scan described above, the detector is set at the closest distance in order to provide the best coverage of the reciprocal space.

These panoramic scans provide complete information on the scattering intensity for a large volume of the reciprocal space, and allow for derivation of the orientational relationships between the film and the substrate, characterization of strain in the film, observation of diffuse scattering and its orientational distributions.

2.3. Single-peak mapping

The panoramic screening may reveal features for single reflections that call for higher resolution mapping. Based on the orientation matrix, the Bragg node of interest can be brought into reflecting position in the vertical plane. An ω -scan with a small angular step (typically $0.01\text{--}0.02^\circ$) and the detector at maximum distance provides the necessary volume information. One should keep in mind the variation of the footprint of the beam with the incident angle, and

corrections may be required for the diffraction intensities. However, the variation is expectedly small if just a small angular range is scanned, and can be neglected for a scan that just maps a single Bragg node and its close neighbourhood.

3. Results

Selected illustrative experiments are described in the following section.

3.1. Scattering from the substrate

Some considerations on the use of substrates are pertinent. Since the algorithm for determining the orientation matrix includes indexing of a large number of reflections from both the substrates and the thin film, it is imperative that the substrate gives well defined Bragg scattering. Thin film diffraction is often less defined due to crystal truncation (Robinson, 1986), surface roughness (Sinha *et al.*, 1988) and structural or chemical defects (Bahr *et al.*, 1995). Thus, by knowing that the substrate in the sample system has well defined scattering, the analysis of the collected diffraction data can routinely be attributed to the correct component of the sample.

For historical (and partly practical) reasons, the most common substrate for deposition of thin films is silicon, typically Si (100) wafers. However, strong thermal diffuse scattering from phonons of the silicon crystal results in high background that contaminates the scattering from the film (Fig. 1*a*). This phenomenon makes the study of crystalline thin films deposited on silicon difficult using the current set-up. A similar result is seen for soda-lime glass (Fig. 1*b*).

Typical substrates of choice during the current model experiments were single crystals of magnesium oxide (MgO), aluminium oxide (Al_2O_3), lanthanum aluminate (LaAlO_3) and strontium titanate (SrTiO_3 ; Fig. 1*c*). Single-crystal substrates of these compounds show very well defined scattering, which makes it easy to determine the crystallographic relationships to the deposited thin film.

3.2. Panoramic scans

Panoramic data collection is a means for determining the orientation matrix of the system, either for the actual thin film, the substrate itself or both. Most frequently one is interested in determining the relative orientation of the thin film to the substrate. Using the *CrysAlis* software, the reciprocal lattices of the two separate parts of the system can be readily superimposed, providing an understandable visualization of the system at hand. In addition, the panoramic data collection can be used to reconstruct planes in reciprocal space. Even though there are some blind areas due to instrumental restrictions, most planes can be inspected [Fig. 2: here

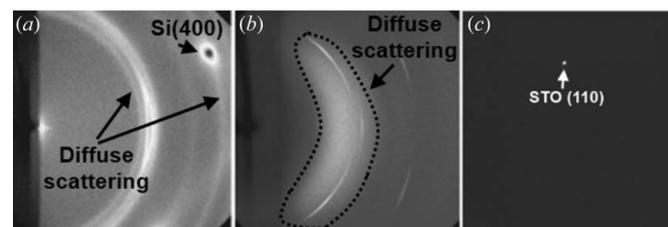


Figure 1

Textured polycrystalline thin films on three different substrates. (a) Polycrystalline ZnO on Si (100), showing strong contribution of thermal diffuse scattering located close to the Bragg reflections of the silicon substrate. (b) Semi-oriented CaCO_3 on soda-lime glass, showing diffuse scattering at low angles making data analysis difficult. (c) A clean SrTiO_3 single-crystal substrate, showing an extremely well defined reflection of SrTiO_3 (110), and no diffuse scattering.

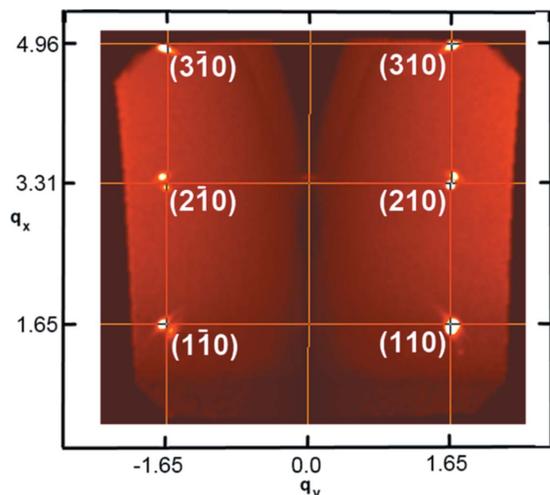


Figure 2
Example of a reconstructed plane spanned by the $[100]^*$ and $[010]^*$ lattice vectors creating a map of the $(001)^*$ plane in a system with a LaAlO_3 thin film on a SrTiO_3 substrate. The very small lattice mismatch in between the SrTiO_3 and the LaAlO_3 lattice cells is still well resolved.

the specular reflection is in a dead zone covering the $(h00)$ reflections].

3.3. Single-peak mapping

The shape and size of single reflections give crucial insight into crystalline properties, *i.e.* size, strain and chemical and structural defects.

An example of the mapping of single reflections is shown in Fig. 3. Here, (100) from both the SrTiO_3 substrate and a 7 nm thin film of LaAlO_3 is shown for two different samples (Fig. 3). The substrate used in Fig. 3(a) is etched with hydrofluoric acid creating a TiO_2 -terminated surface prior to LaAlO_3 deposition. For Fig. 3(b), the substrate was not pre-treated and thus has a random surface termination. An azimuthal integration in 2θ reveals a similar peak intensity and shape for the two samples, pointing out how this would be difficult to quantize using home laboratory equipment. Since the atomic termination of the substrate may influence epitaxial relationships and crystallinity, the possibility to gain insight into such aspects by means of the described measurements becomes crucial.

Another example is shown for the $\text{LaAlO}_3||\text{LaAlO}_3$ system, apparently homoepitaxial as shown by home laboratory X-ray

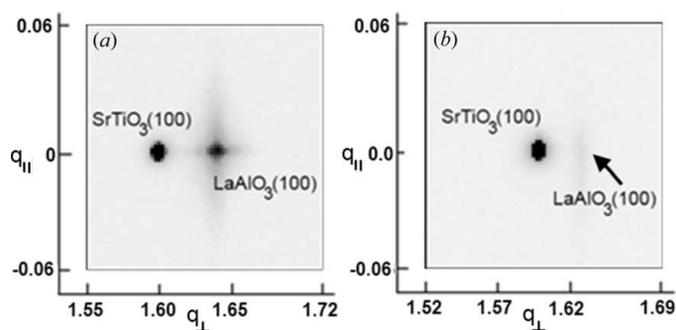


Figure 3
(a) $\text{SrTiO}_3(100)$ and $\text{LaAlO}_3(100)$ in a $\text{LaAlO}_3||\text{SrTiO}_3$ system where the SrTiO_3 substrate is TiO_2 -terminated after hydrofluoric acid etching. (b) $\text{SrTiO}_3(100)$ and $\text{LaAlO}_3(100)$ in a $\text{LaAlO}_3||\text{SrTiO}_3$ system without pre-treatment of the substrate. Both samples are represented by the same intensity scheme for comparison.

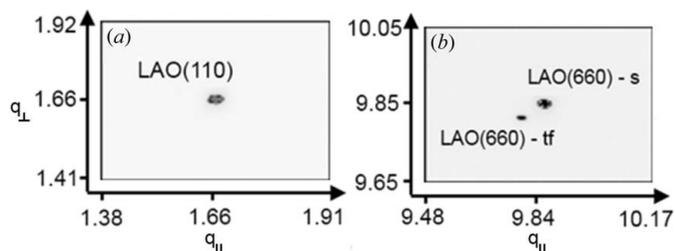


Figure 4
(a) $\text{LaAlO}_3(100)$ in the $\text{LaAlO}_3||\text{LaAlO}_3$ system. The film and substrate cell seems equal, pointing towards perfect homotaxy. (b) $\text{LaAlO}_3(660)$ reflection in the same system. The film (tf) and substrate (s) reflections are clearly split, pointing towards a slight non-homoepitaxial relationship.

diffraction (XRD) and X-ray reflectivity (XRR). When looking at a family of reflections for analysis, a very distinct splitting of the asymmetric $(nm0)$ reflections was observed for high- q reflections (Fig. 4). The splitting corresponds to a lattice parameter shift of less than $+0.01 \text{ \AA}$ for the thin film compared with the substrate. This may possibly be related to the chemical composition, which would be important knowledge for further use of the material. The effect is too small to be observed on home laboratory equipment, owing to the large substrate-to-thin-film signal ratio and because the effect is only outspoken for high- q reflections.

As shown for the LaAlO_3 thin film systems, the possibility to map single reflections using this simple geometry provides possibilities for studying subtle effects in thin film systems. These can be broadening effects, diffuse scattering around Bragg peaks or peak splitting, all being important effects that reveal interesting information about the sample.

4. Conclusions

The single-crystal six-axis κ -diffractometer KUMA6 (BM01A, SNBL at ESRF) has several advantages for retrieving structural information for thin film systems. The few geometrical constraints make it possible to perform a range of studies both *in situ* and *ex situ*. Fast inspection of relatively large volumes in the reciprocal space with very detailed maps of selected Bragg nodes is one option. For powder and polycrystalline thin films, the set-up provides, for example, means to describe preferred orientation and identification of diffuse scattering from the substrates.

Through a set of examples, it has been shown how the proposed instrumentation can be used to gain insight into the structure and crystallinity of thin films. The panoramic scan is used to determine the orientation matrix of the sample, as for the $\text{LaAlO}_3||\text{SrTiO}_3$ system. Furthermore, single Bragg nodes can be studied in detail by increasing the sample-to-detector distance. This has been demonstrated for the $\text{LaAlO}_3||\text{LaAlO}_3$ sample, where a double peak could be identified. In total, the proposed instrumentation can be used to study crystallinity, crystallite size, strain and epitaxial relationships in a thin film sample with fast sample mounting, fast data collection and easy data analysis.

Further development of the set-up is achieved *via* implementation of a fast pixel area detector, Dectris PILATUS2M. Low background, the possibility to suppress fluorescence and fast readout time being augmented with flexible κ goniometry will allow probing of the kinetic processes evolving in a thin film as a function of external fields, and in total provide a very versatile technique for structural characterization of crystalline thin films.

The authors would like to thank Karina B. Klepper for providing some of the samples. We acknowledge the SNBL staff for their great support during the experiments at ESRF.

References

- Aubert, E., Wenger, E., Link, M., Assouar, B., Didierjean, C. & Lecomte, C. (2006). *J. Appl. Cryst.* **39**, 919–921.
- Bahr, D., Press, W., Jebasinski, R. & Mantl, S. (1995). *Phys. Rev. B*, **51**, 12223–12227.
- Bates, J. B., Dudney, N. J., Neudecker, B., Ueda, A. & Evans, C. D. (2000). *Solid State Ion.* **135**, 33–45.
- Britt, J. & Ferekides, C. (1993). *Appl. Phys. Lett.* **62**, 2851.
- Brousse, T., Retoux, R., Herterich, U. & Schleich, D. M. (1998). *J. Electrochem. Soc.* **145**, 1–4.
- Contreras, M. A., Egaas, B., Ramanathan, K., Hiltner, J., Swartzlander, A., Hasoon, F. & Noufi, R. (1999). *Prog. Photovolt.* **7**, 311–316.
- Foss, S., Nilsen, O., Olsen, A. & Taftø, J. (2005). *Philos. Mag.* **85**, 2689–2705.
- Ito, S., Murakami, T. N., Comte, P., Liska, P., Grätzel, C., Nazeeruddin, M. K. & Grätzel, M. (2008). *Thin Solid Films*, **516**, 4613–4619.
- Klepper, K., Nilsen, O. & Fjellvåg, H. (2007). *J. Cryst. Growth*, **307**, 457–465.
- Leontyev, I. N., Yuzyuk, Y. I., Janolin, P. E., El-Marssi, M., Chernyshov, D., Dmitriev, V., Golovko, Y. I., Mukhortov, V. M. & Dkhil, B. (2011). *J. Phys. Condens. Matter*, **23**, 332201.
- Mo, F., Chernyshov, D., Thoresen, L. S., Breiby, D. W. & Tybell, T. (2008). *Acta Cryst.* **A64**, C520–C521.
- Oxford Diffraction (2006). *CrysAlis CCD*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Paciorek, W. A., Meyer, M. & Chapuis, G. (1999). *Acta Cryst.* **A55**, 543–557.
- Poot, S. (1972). US Patent 3 636 347.
- Robinson, I. (1986). *Phys. Rev. B*, **33**, 3830–3836.
- Shah, A., Torres, P., Tscharnner, R., Wyrsh, N. & Keppner, H. (1999). *Science*, **285**, 692–698.
- Sinha, S. K., Sirota, E. B., Garoff, S. & Stanley, H. B. (1988). *Phys. Rev. B*, **38**, 2297–2311.
- Sønsteby, H., Østreng, E., Nilsen, O. & Fjellvåg, H. (2012). *ALD/BALD2012 – 12th International Conference on Atomic Layer Deposition*, Dresden, Germany.
- Souza, S. de, Visco, S. J. & De Jonghe, L. C. (1997). *J. Electrochem. Soc.* **144**, L35–L37.
- Suntola, T. & Antson, J. (1976). Instrumentarium Oy, Finland. DE2553048A1.
- Thorkildsen, G., Larsen, H. B. & Beukes, J. A. (2006). *J. Appl. Cryst.* **39**, 151–157.
- Vermeulen, P., Niessen, R. & Notten, P. (2006). *Electrochem. Commun.* **8**, 27–32.
- Will, J., Mitterdorfer, A., Kleinlogel, C., Perednis, D. & Gauckler, L. J. (2000). *Solid State Ion.* **131**, 79–96.