

Synchrotron X-ray imaging applied to solar photovoltaic silicon

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Abstract. Photovoltaic (PV) cell performance is dictated by the material of the cell, its quality and purity, the type, quantity, size and distribution of defects, as well as surface treatments, deposited layers and contacts. A synchrotron offers unique opportunities for a variety of complementary X-ray techniques, given the brilliance, spectrum, energy tunability and potential for (sub-) micron-sized beams. Material properties are revealed within in the bulk and at surfaces and interfaces. X-ray Diffraction Imaging (X-ray Topography), Rocking Curve Imaging and Section Topography reveal defects such as dislocations, inclusions, misorientations and strain in the bulk and at surfaces. Simultaneous measurement of micro-X-Ray Fluorescence (\(\mu\)-XRF) and micro-X-ray Beam Induced Current (\(\mu\)-XBIC) gives direct correlation between impurities and PV performance. Together with techniques such as microscopy and Light Beam Induced Current (LBIC) measurements, the correlation between structural properties and photovoltaic performance can be deduced, as well as the relative influence of parameters such as defect type, size, spatial distribution and density (e.g [1]). Measurements may be applied at different stages of solar cell processing in order to follow the evolution of the material and its properties through the manufacturing process. Various grades of silicon are under study, including electronic and metallurgical grades in mono-crystalline, multi-crystalline and mono-like forms. This paper aims to introduce synchrotron imaging to non-specialists, giving example results on selected solar photovoltaic silicon samples.

1. Survey of synchrotron X-ray techniques

1.1. X-Ray Diffraction Imaging (X-Ray Topography) and Rocking Curve Imaging

In all the X-ray diffraction imaging techniques described here, deviations from perfection in the sample result in a change in intensity (light or dark “contrast”) in the diffracted image. A perfect sample would result in a uniformly illuminated diffraction spot. For details on topography, see [3].

1.1.1. White beam topography. White beam topography uses all the energies in the incident beam. Different sets of diffracting planes in the sample select the appropriate energies from the beam to diffract at the corresponding Bragg angles, in accordance with Bragg’s Law, \(\lambda = 2d_{hkl}\sin\theta\); \(n\) is the order number, \(\lambda\) is the wavelength of the X-rays, \(d_{hkl}\) is the effective spacing between planes for the reflection \(hkl\) and \(\theta\) is the angle between the incident beam and those planes. Several diffraction spots are seen simultaneously, each one a topograph of the part of the crystal illuminated (Figure 1). The distribution of the spots on the detector reflects the symmetry of the crystal (cf. stereographic
Defects cause long-range distortion fields in the sample, and diffraction occurs over a wider angular and/or energy range than for a perfect crystal, giving intensity contrast and/or displacement of [parts of] the diffracted spot. Effective misorientations $\delta \theta$ down to $\sim 10^{-6}$ to $\sim 10^{-7}$ rad can be observed under suitable conditions.

White beam topography is useful in itself for visualising e.g. dislocations, stacking faults, twins, larger inclusions, precipitates, grains, growth sector boundaries, growth striations and scratches. It also gives an "overview" of the sample before moving to monochromatic beam techniques. Film is typically used as the 2D detector - the field of view is many cm while spatial resolutions may be a few $\mu$m. Cameras + optics giving pixel sizes of a few $\mu$m generally have fields of view of only a few mm.

### 1.1.2. Monochromatic beam topography and Rocking Curve Imaging

Working at higher energies and higher $hkl$ with a highly monochromated incident beam (e.g. $\Delta E/E \sim 10^{-4}$) enhances the strain sensitivity of the diffraction imaging, enabling effective misorientations down to $\sim 10^{-8}$ to $\sim 10^{-9}$ to be imaged under suitable conditions. The sample may be oriented for transmission geometry or reflection geometry, the latter offering a greater surface sensitivity while the former gives information through the bulk of the specimen. The sample must be at exactly the correct angle to the beam to diffract from a specific set of planes $hkl$. If $d_{hkl}$ is not the same as in the monochromator, or the planes are not oriented parallel, then the configuration is "dispersive" and only part of the beam is diffracted at a given sample angle. (However, in some cases, this may be overcome by bending a suitable monochromator crystal [4]). An integrated image may be collected while rocking the sample through its angular diffracting range, or many separate images may be collected at different points across the rocking curve (Figure 2, Figure 3). The latter is called "Rocking Curve Imaging", and a camera is practically essential. Analysing the many images together numerically gives local quantitative information. As long as the sample is not too distorted, the signal in a single pixel can be considered to come from a particular physical location in the sample. Each pixel then contains the rocking curve corresponding to a different location on the sample. Using software such as Visrock [4] maps of, for example, integrated intensity, full-width at half-maximum (FWHM, often a measure of the crystalline quality) or peak position may be generated.

### 1.1.3. Section Topography

Thus far, topographs collected in transmission geometry have given 2D images of defects present in the whole volume of the sample. Section topography distributes the images of defects as a function of their position through the depth of the sample (Figure 4).

The incident beam size is drastically reduced in one direction. Diffraction then occurs across a section of the sample within the "Bormann fan". Images of defects at different depths appear distributed across the diffraction spot. The use of multiple slits, sufficiently separated that the diffraction images do not overlap, has been applied to studies of 3D deformation in ice [6].
1.2. X-Ray Fluorescence (XRF), X-ray and Light Beam Induced Current (XBIC and LBIC)

XRF is a means of identifying the elements within a specimen. An incident monochromatic X-ray beam excites atoms within the sample such that they emit characteristic X-rays (at lower energies). Scanning an area on the sample allows the 2D localization of the chemical elements. The sample is oriented in reflection geometry and the resolution in the thickness of the sample is directly linked to the energy of the incident and fluorescent beams. The detector is placed close to the sample for maximum solid angle of collection and because low energy X-rays are rapidly absorbed if working in air. For this reason, XRF measurements are often carried out in vacuum.

The ESRF beamlines ID22 or ID21 produce sub-µm and µm-sized beams with high intensities. Scanning the sample across the beam produces high-resolution XRF maps [7]. At the same time, on a solar cell, which has electrical contacts, XBIC can be measured (Figure 5), giving direct correlation between the PV performance and the composition locally. Combined µ-XRF and µ-XBIC has been used to demonstrate a link between e.g. precipitates and electrical pre-breakdown in solar cells [8].

Off-line, LBIC measurements using multiple visible wavelengths are combined with light reflectivity measurements to produce maps of minority carrier diffusion length and lifetime.

2. Example results

Example results are shown in Figure 6, Figure 7. The topographs were collected at BM05, ESRF, the white beam topograph being collected on Agfa Structurix D3 film. Section rocking curve images were recorded using an ESRF FReLoN camera with optics giving a 0.75 µm pixel size; the beam was monochromated at 20 keV using a double Si (111) monochromator, and multiple 10 µm slits were positioned ~1.5 m before the sample. µ-XRF and µ-XBIC data were collected at ID22 at 17 keV with a beam probe 1.3 µm (V) × 7 µm (H). LBIC data were collected at INES using a Semilab WT2000.
Figure 6: From left: A sample (~20 mm × ~10 mm) from a "mono-like" Si solar cell, showing the front, textured surface with Ag electrical contact lines; a crystallographic "twin" is seen, surrounded by smaller, misoriented grains; the Al backplane is behind. LBIC map of minority carrier diffusion length around the twin (from red (40 µm) to blue (140 µm)). White beam topograph, 220 reflection; misorientation of the Si by the Ag lines is seen, plus an "orange-peel" effect due to the effect of the rough Al backplane, on top of regions of higher dislocation density. Integrated intensity rocking curve section topographs of a "bad" PV region (from the red area of the LBIC map) and a "good" region (blue on the LBIC map) - images 1.5 mm across; distortion of the Si by the Al backplane is seen in the enhanced intensity at the lower edge of each section.

Figure 7: Left: Monochromatic beam integrated intensity rocking curve image of a micro-electronic-grade Si solar cell. The Ag contact lines on both sides of the sample, and cracks, induce misorientations which show bright yellow. There is no Al backplane. Middle below: LBIC minority carrier diffusion length map of selected area (resolution 62.5 µm). Middle above: µ-XBIC map collected simultaneously with the µ-XRF map showing the distribution of Pb and Ti (above right) - .

3. Conclusions
A brief overview of synchrotron radiation imaging techniques has been given, together with illustrative data on selected solar photovoltaic silicon samples. The capabilities of diffraction imaging (topography) for revealing crystallographic defects within the bulk and at the surface of samples has been shown, as well as the possibility of direct correlation between element identification and photovoltaic performance via simultaneous µ-XRF and µ-XBIC mapping. Application of complementary methods such as Light-Beam Induced Current measurements adds to the characterisation and understanding of such photovoltaic samples, which are an important contribution to addressing the needs for sustainable energy sources.

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