MICRO-XRF

Fast crystal domain screening using the energy dispersive Laue mapping technique

Application Note # XRF 463

Introduction

The M4 TORNADO is a spatially resolving energy dispersive X-ray fluorescence (XRF) spectrometer. The instrument was developed for high speed 2D elemental analysis and visualization. It combines state-of-the-art detector technology with fast sample handling and powerful data processing tools. The method is non-destructive and requires no special sample preparation.

Diffraction peaks are often considered as a bothersome artifact interfering with the XRF information. However, diffraction peaks provide information on the nature of the sample as they are related to the crystal orientation. This lab report describes a new approach to identify high and low angle grain boundaries as well as twin boundaries in crystalline materials.

The detection and visualization of grains or subgrains gives valuable information about the microstructure, which is crucial to evaluate the quality of single crystals and the properties of polycrystalline materials.

Functional principle

Due to the wavelength range of the used X-ray source, the energy dispersive spectra of crystalline samples commonly show various diffraction peaks in addition to the XRF signal of the elements which are present in a sample. These diffraction peaks are caused by constructive interference. The crystal "reflects" specific wavelengths best in a certain direction when the respective photons hit the crystal planes under just the right angle and the Bragg condition

$$n\lambda = 2d \sin\theta$$

is fulfilled. This effect was found by William Lawrence Bragg in 1912, who was subsequently awarded the Nobel Prize for this discovery.

The new method described here is the **e**nergy **d**ispersive **L**aue **m**apping, **EDLM** (Guguschev et al. (2015), Ganschow et al. (2016)).

It has analogies to the classical Laue backscattering method for the determination of crystal orientations based on point measurements on a crystal.

However, the Bragg diffraction peaks are not evaluated by their orientation-dependent diffraction pattern with flat panel detectors but instead by use of a smaller energy-dispersive silicon drift detector (SDD) which allows to collect photons in the spectral range between 0.7 keV and 40 keV.

Using the new energy dispersive Laue mapping technique, the information obtained permits the visualization of crystal domains and changes in crystallinity of a sample, even if it is not yet sufficient to determine the crystal orientation.

Samples

Two different samples were investigated:

1) A cut slab of a multicrystalline silicon wafer with a surface area of 156 x 156 mm². More than 80 % of the surface area was measured without previous polishing.

2) A cut cross section of a twinned $NdGaO_3$ crystal with a diameter of ~ 17 mm. The sample was mounted using commercially available plasticine, which contains Ca-rich compounds.

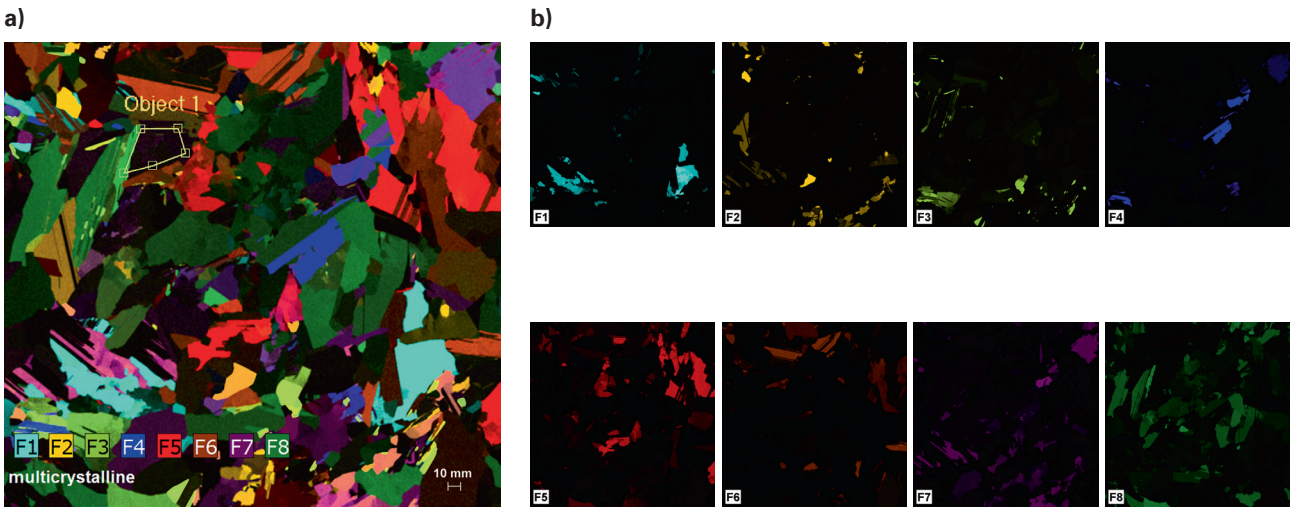
Measurement conditions		
	Multicrystalline silicon wafer	**$NdGaO_3$**
Mapping area / mm	140 x 140	18.2 x 18.4
Number of pixels	1,960,000	551,600
Pixel size / µm	25	26
Time per pixel / ms	10	10
Total time / h:min	6:34	1:55
Tube high voltage / kV	50	50
Tube current / µA	600	600
Chamber pressure / mbar	20	1

Table 1
Measurement conditions

Measurement conditions

The measurements were performed with a Bruker M4 TORNADO equipped with Rh tube and a polycapillary lens using the parameters compiled in Table 1. The spectrometer combines high spatial resolution with fast data processing and a high speed motorized xyz-stage for sample positioning.

Figure 1
(a) Superimposed color coded diffraction intensity plots of all selected Bragg peaks for the scanned surface area of 140 mm x 140 mm, (b) area distribution of selected diffraction peaks in the regions F1–F8 individually shown over the scanned surface area.



Visualization of crystal domains in a silicon wafer

The silicon wafer was measured to explain the principle of Bragg peak identification and visualization. With HyperMap, Bruker's unique position tagged spectroscopy, a full spectrum of each measured pixel is saved. In particular, it allows to select spectral regions (F1–F8) and displays the intensity variations in these regions as color coded map. The area distributions of these features can be visualized superimposed (Figure 1a) and individually (Figure 1b).

Some silicon grains were found to show no diffraction peaks in any of the selected spectral ranges. A closer inspection can then be performed by selecting the respective area from the map. The software allows the selection of any arbitrary shaped object in the map to examine the sum spectra of all pixels in that area.

The overall sum spectrum of the silicon wafer can be compared to the sum spectrum of a selected area "Object 1". Figure 2 displays the diffraction peaks in the regions F1–F8 which were selected for crystal domain identification. "Object 1" appears dark in the element map in Figure 1, hence none of the selected diffraction peaks shows significant intensity in that area.

The sum spectrum of Object 1 (red spectrum) shows intense peaks at energies which were not previously selected (11 keV and 13 keV). Another peak at 9 keV is not much more intense than the average diffraction in this region (black spectrum) and, therefore, shows no extra intensity for the marked object (region F7).

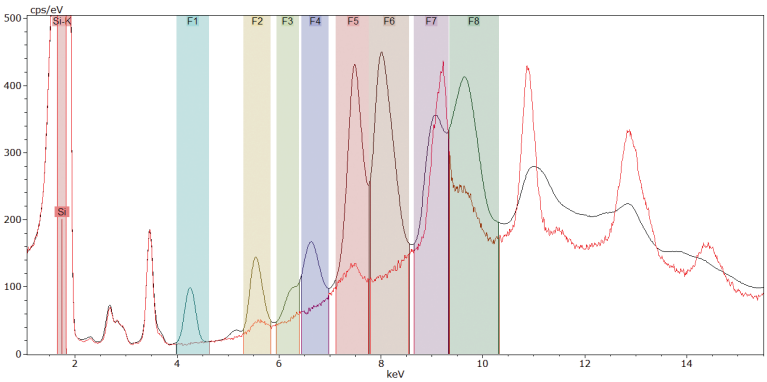


Figure 2

Comparison of the sum spectra of the multicrystalline silicon wafer (black) and the selected "Object 1" in Figure 1 (red).

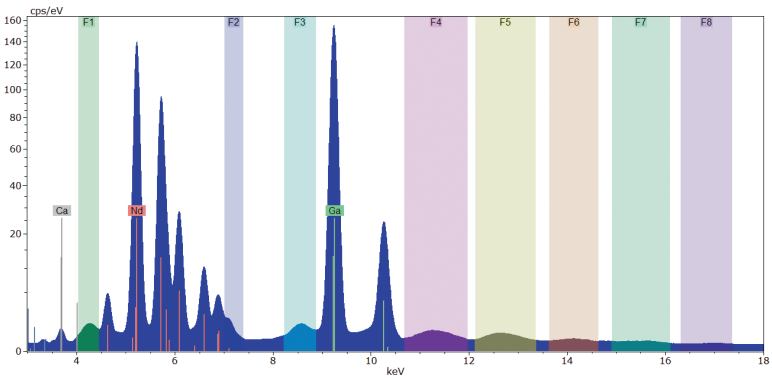


Figure 3

Sum spectrum of the embedded twinned NdGaO3 crystal with selected diffraction peaks (F1–F8) for crystal domain identification.

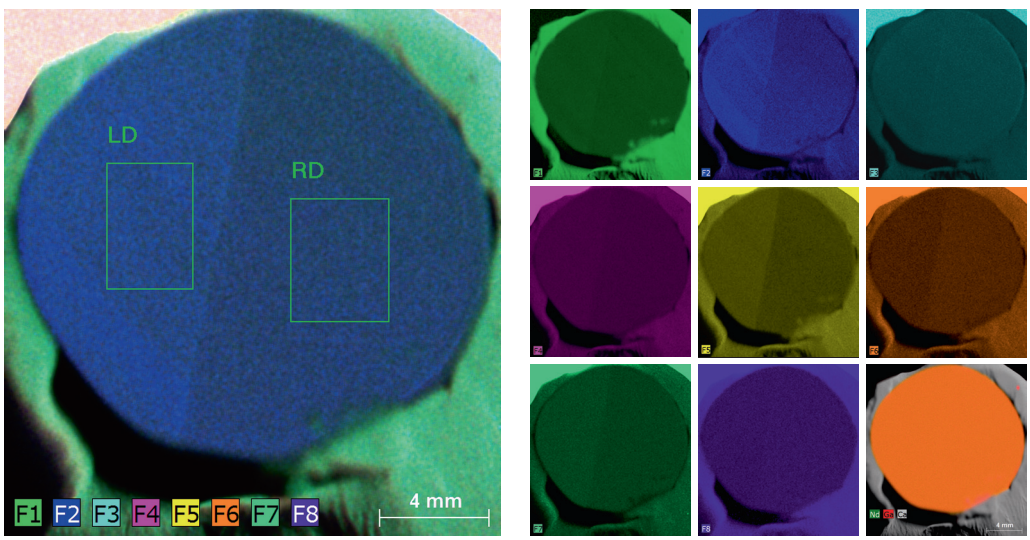


Figure 4

Color coded crystal domain map of $NdGaO_3$ and visualization of the Ga and Nd distribution and of the diffractions peaks (F1–F8).

Detection and characterization of twinning in $NdGaO_3$ crystals

The $NdGaO_3$ sample was investigated to visualize and localize the twin boundary between individual single crystalline domains. Figure 3 shows the measured sum spectrum of the $NdGaO_3$ crystal with several diffraction peaks in the regions F1–F8 that were selected for crystal domain identification.

As can be seen in the crystal domain maps in Figure 4, several diffraction peaks, e.g. all regions except F8, show visually different intensities along the sample. Superimposing the intensity distribution of all regions (large image in Figure 4) clearly reveals two crystal domains, even though the Nd and Gd are perfectly homogeneous (bottom right image). Thus, the observed differences are not related to a change of the sample's elemental composition but are caused by different crystal orientations.

The two green frames represent the selected areas LD and RD over which sum spectra were calculated.

Figure 5 shows the extracted corresponding spectra of the two distinct crystal domains. It reveals the minute changes of the sample properties. The intensity of the F2 pattern changes as would be expected from the map. Moreover, there are significant differences in other regions. Most notably in region F4 and F5 the diffraction peaks of the LD spectrum are shifted to lower energies. In the regions F7 and F8 the intensities revert between LD and RD.

The energy shift of diffraction peak maxima (see regions F4 and F5 in Figure 5) implies that the two domains are tilted against each other at a small angle and are not oriented in a completely different way. Additionally performed Laue backscattering measurements confirm a tilting angle of about 1.5°. These results show that even small changes in the crystal orientation can be reliably identified by the EDLM technique without the need of sample polishing.

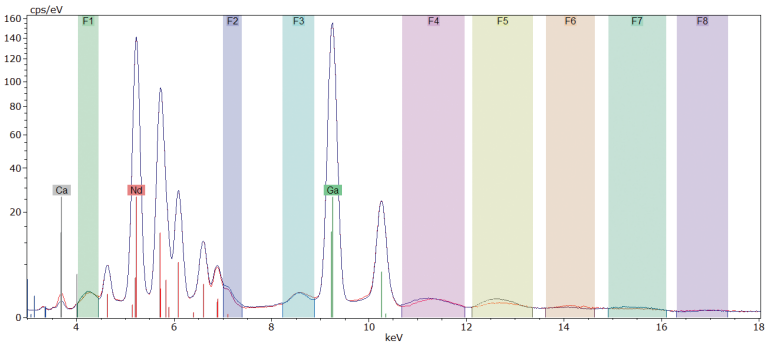


Figure 5
Sum spectra of the regions LD (blue spectrum) and RD (red spectrum) representing the left and right crystal domain. The differences are mostly pronounced in the regions F4 and F5.

Conclusion

The M4 TORNADO allows the fast measurement of the spatial distribution of diffraction peaks and the identification of crystal domains in crystalline materials. It combines highspeed measurements and full sample area coverage with a high spatial resolution.

The new energy dispersive Laue mapping (EDLM) technique is a powerful non-destructive tool for the identification of single crystalline grains in polycrystalline materials, for the detection of twins and to study subgrains in bulk single crystals.

References

Guguschev, C., Tagle, R., Juda, U., Kwasniewski, A., (2015): Microstructural investigations of SrTiO3 single crystals and polysilicon using a powerful new X-ray diffraction surface mapping technique, Journal of Applied Crystallography, 48, 1883-1888.

Ganschow, S., Kwasniewski, A., Klimm, D., (2016): Conditions for the growth of Fe1-xO crystals using the micro-pulling-down technique, Journal of Crystal Growth, 450, 203-206.

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