Application Note

Growth direction and orientation analysis of nanostructures by EBSD

Introduction

Nanoscale crystalline materials play a key role as active components in a wide range of advanced technologies, such as nanoelectronics, optoelectronics, and chemical sensing. Following the discovery of carbon nanotubes in 1991, a large world-wide effort has been devoted to the synthesis of high aspect ratio inorganic nanotubes, nanowires and nanorods with well defined structural and electronic properties. The synthesis of high aspect ratio crystalline nanostructures can be achieved using several approaches that allow some degree of control over dimensions, morphology, and uniformity of the product [1,2]. However, in order to fulfil the promise of nanotechnology and achieve reliable components for different applications, it is essential to control the crystallographic orientation of the wires, their relationship with the substrate used for the growth, and the nature of the exposed surfaces.

Although transmission electron microscopy (TEM) is the most powerful and widely used method for the crystallographic characterization of nanostructures, it is not ideal for statistical and large scale studies because of its destructive and time intensive nature. EBSD is proving a valuable tool for the study of nanowires and nanostructured materials, giving fast and accurate crystallographic information on individual structures imaged directly on the substrates on which they were grown.

Traditionally the EBSD technique has been used for polished flat ‘in-surface’ sample analysis. However in the examples discussed here, high aspect-ratio ‘out of surface’ nanostructures were analyzed by EBSD to determine whether there is a preferential growth direction. In particular we are presenting results concerning ZnO structures grown by an aqueous solution technique, as well as about CdSe and Si nanowires synthesized by chemical vapour deposition on Si substrates. The growth direction of the Wurtzite CdSe, on a small number of structures, was verified with TEM analysis.

The EBSD technique confirmed this information allowing a very efficient in-line identification of the orientation of the nanowires. Moreover, to exploit the full potential of high resolution secondary electron imaging and EBSD, the software developed at Oxford Instruments combines the information from crystal orientation and

crystal morphology. In such an investigation it is difficult to conclude the exact growth direction from a 2D image, which is a projection of a 3D object (unless there are two images from different angles from the same object). Therefore the crystallographic directions can be classified into two types of candidates of, ‘can be’ and ‘can not be’, where with more statistics the ‘can be’ candidates showing the same result, would be classified as the ‘most likely’ crystallographic direction. Such investigations were done on nanowires down to 80nm in diameter.

EBSD Conditions

Sample preparation	None. The samples were analysed as grown
SEM Type	FEG-SEM
EBSD system	HKL Channel5 and Nordlys II with low kV Phosphor screen
Accelerating voltage	10kV
Probe current	1nA
SEM conditions	High vacuum, 5 to 6 mm working distance and 70 degrees stage tilt with no tilt correction on the SEM images

Results

This is a preliminary study, where three examples are discussed in this report. In the first example the multilayer, pancake-like, ZnO structures were grown on a single crystal Silicon substrate with {111}<110> orientation. ZnO was found to crystallize in the Wurtzite structure (hexagonal, space group P63mc) with lattice parameters of a=3.25Å and c=5.2Å. Figure 1a shows the SEM image of the pancake stacks, which have a hexagonal section with diameters ranging between 1.5 and 2.5µm. The stacks are built up of individual hexagonal platelets 50 to 80nm thick, and their total length varies between 5 to 8 µm. The

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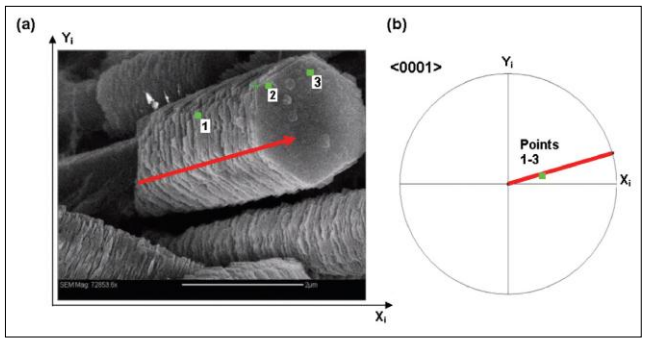
hexagonal platelets within a stack are uniformly aligned and were calculated to have a misorientation of up to 3 degrees in the basal plane. The alignment is shown by the red arrow superimposed on the SEM image in figure 1a. There was no tilt correction applied to the image in order to retain the true directions of the 'out of surface' stacks with respect to the image plane. The red arrow indicates the trace of the growth direction of the stacks in a 2D-projection. In a 2D-projection (image plane), the growth direction of a 3-dimensional object can only be estimated within a partial plane, here referred to as the 'object plane'.

The software developed at Oxford Instruments can be used to determine the crystal orientations in the growth directions for these 'out of surface' nano-objects. The example in figure 1b shows how a red arrow representing a set of possible directions of the stacks in real space is plotted as a partial great circle in the pole figure. This segment of a great circle – or mathematically called 'orthodrome'- is a projection of the possible directions in the 'object plane' with an angle ranging between 0° and 90° to the image plane (this is an arbitrary choice and a different range can be selected by the user). The software allows the user to plot the pole figures in the image or the acquisition surface coordinate systems. Here the pole figure is in the image coordinates (X_i, Y_i), and the 'object plane' is identified and depicted as a thick red line, which is also parallel to the red arrow drawn in the SEM image in figure 1. For a set of equivalent directions <uvw> the result can be the one with minimum angle between the object plane and any of the directions. For a cluster of orientation data the software automatically calculates the mean minimum angle between the crystal directions for the data points and the 'object plane', ranks the solutions for a defined number of low-indexed directions, and allows the user to plot pole figures along the corresponding axes. Here the minimum angle (1.39 degrees) between the experimental orientation data and the stack's growth direction was found for the <0001> direction, see table 1. This can also be seen in the <0001> pole figure (1b) from the overlapping of the 'object plane' (thick red line) and the green points which represent the c-direction of the Wurtzite cell for the three points in the SEM image. Therefore the growth direction can be <0001> direction, although there are three other candidates below 5° angle, <10-14>, <2-1-14> and <10-13>. However the other directions above 5° angle can not be considered, because the deviation is above any errors that may be present in the results.

Pole	Mean minimum angle (°)
<0 0 0 1>	1.39
<1 0 -1 4>	3.05
<2 -1 -1 4>	4.15
<1 0 -1 3>	4.41
<2 -1 -1 3>	5.59
<1 0 -1 2>	6.81
<2 -1 -1 2>	7.73
<2 0 -2 3>	8.79
<4 -2 -2 3>	9.13
<3 0 -3 4>	9.96
<2 -1 -1 1>	12.21
<3 -1 -2 4>	12.39
<1 0 -1 1>	13.44
<4 0 -4 3>	14.81
<3 -1 -2 3>	15.1
<3 0 -3 2>	15.49
<3 -1 -2 2>	18.44
<2 0 -2 1>	18.6
<4 -1 -3 4>	18.7
<4 -1 -3 3>	21.65

Table1: The table shows the mean angular deviation between the orientation data points and the 'object plane', shown in figure 1. The solutions are ranked for a defined number of low-indexed directions, where 'can be' candidates are in orange and 'can not be' candidates are in grey.

Figure 1: The EBSD investigation of the ZnO structures are shown with the a) analysed points and the arrow indicating the growth direction on a secondary electron image and b) the orientation analysis and the 'object plane' in a <0001> pole figure in image coordinate system.



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Some of the error may be originating from the accuracy of the orientation analysis and indication of the growth direction (object plane), which are not expected to be above 5° in total. The errors in such an analysis is a subject that needs to be discussed more elaborately in a separate report and is beyond the scope of this report.

A second example is of a branched CdSe nanostructure with a complex shape grown without a catalyst on a Si substrate with {001}<110> orientation, which is shown in figure 2. The CdSe was found to be crystalline with a Wurtzite structure (hexagonal, space group P63mc) with lattice parameters of a=4.30Å and c=7.02Å. The individual branches are nanowires of about 80 to 200nm diameter and up to 2µm in length. In figure 2a the three main directions of the branches are shown as three arrows in different colours. The three points of EBSD analysis are also shown in figure 2a. In each branch the minimum angle (below 3 degrees) between the experimental orientation data and the directions of the branches was found that it can be for the <0001> direction. Thus the same result was found for all the three branches, which is seen from the cumulative <0001> pole figure showing the crystal directions and the corresponding 'object planes' for the three directions of the branches, hence making the <0001> direction the most likely candidate. From this it can be easily inferred that the growth direction of all the branches is most likely aligned with the c-axis, even though the branches grow in different spatial directions.

In figure 2b, the mean angle between the three growth directions was measured to be about 120°, which corresponds to the angles between the a (and b) axes in a Hexagonal crystal structure. This is an indication of possibly the presence of a back-bone in the structure, where the branches are growing from with the c-axes of the branches perpendicular to the a (or b) axes of the back-bone, which is as expected in a dendritic type of structure.

The third example is of a Au catalysed Si nanowire grown on a Si substrate with {001}<110> orientation, which is shown in figure 3a. The Si nanowire is about 80nm in diameter with the gold catalyst particle at the tip. Si has a cubic (diamond) structure with a=5.43Å and Au is face-centred cubic with a=4.07Å. It was found that the crystal axis in the Si nanowire can be the <111> direction aligned along the wire axis or wire growth direction with a minimum angle of 0.24 degrees, as shown in the <111> pole figure in the image coordinate system in figure 3b.

Comparison of the pole figures in figure 4, in the acquisition surface coordinate system (X1, Y1), show that the Au tip and the Si nanowire have a common <111> rotation axis with 35° misorientation.

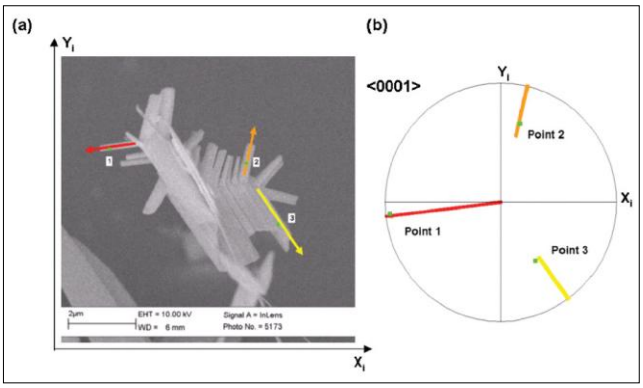

Figure 2: The EBSD investigation of the CdSe nano-structures are shown with the a) analysed points and the arrows indicating the growth direction on a secondary electron image and b) the orientation analysis and the 'object planes' in a <0001> pole figure in image coordinate system.

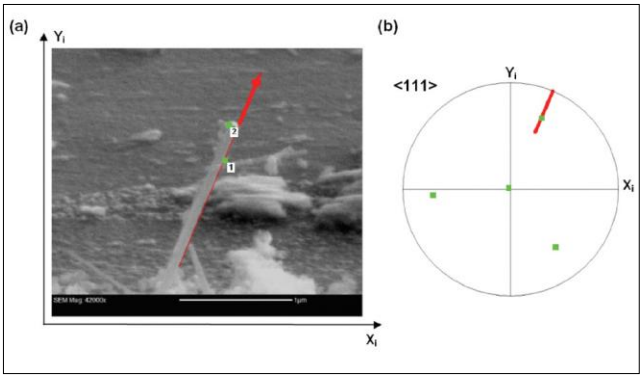

Figure 3: The EBSD investigation of the Si nano-wire and the Au catalyst particle at the tip are shown with the a) analysed points and the arrow indicating the growth direction on a secondary electron image and b) the orientation analysis and the 'object plane' in a <111> pole figure in image coordinate system.

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Conclusions

EBSD has been successfully applied for the study of high aspect-ratio 'out of surface' nanostructures in the SEM, extracting information from features down to 80nm in size. The EBSD software developed at Oxford Instruments enables the user to correlate crystal morphology and crystallography, to find the 'can not be', 'can be' and with more statistics the 'very likely' candidates of crystallographic directions, for the growth directions of various nanostructures, and hence answering fundamental questions essential for the control of the structural and physical properties at the nanoscale. Here examples are given for ZnO, CdSe and Si, showing how the growth direction most likely corresponds to the c-axis for Wurtzite structures, whereas for Si the preferential direction for growth can correspond to the <111> direction. It is also shown that it is possible to use the software to analyse interphase relationships, such as between the Au catalyst and the Si nanowire.

The EBSD technique is a fast and accurate method to investigate nanostructures from large areas, with good statistics in the as-grown condition without any sample preparation. EBSD has the advantage of enabling the analysis of individual nanostructures, unlike XRD, accessing a size range precluded to TEM. This makes the EBSD technique a versatile and valuable tool for nanoscience and nanotechnology.

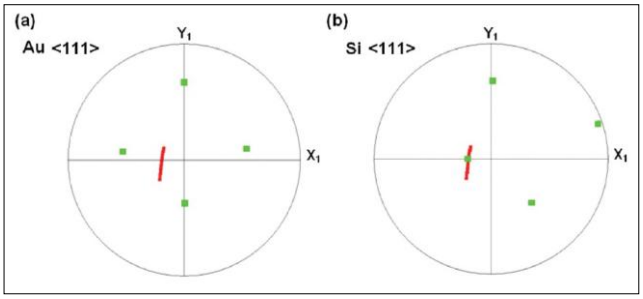

Figure 4: The orientation analysis and the 'object plane' in <111> pole figures in acquisition surface coordinate system for a) Au and b) Si.

Acknowledgements

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References

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[2] Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., Gates, B., Yin, Y., Kim, F. & Yan, H. 2003 One-dimensional nanostructures: synthesis, characterization and applications. Adv. Mater., 15, 353-389.