Polychromatic Microbeam Diffraction Characterization of Individual ZnO Nanostructures

J.D. Budai,[1] W. Yang,[2] W. Liu,[3] J.Z. Tischler,[1] Z. Pan,[1] Y.W. Heo,[4] D.P. Norton,[4] B.C. Larson,[1] G.E. Ice[1]

[1]Oak Ridge National Laboratory, Oak Ridge, TN U.S.A.; [2]Carnegie Institution, Washington, DC U.S.A.; [3]Argonne National Laboratory, Argonne, IL U.S.A.; [4]University of Florida, Gainesville, FL U.S.A.

Introduction

Recent progress in x-ray focusing optics has generated interest in microstructural investigations with high spatial resolution. In particular, research involving nanostructured materials clearly will benefit from the ability to characterize structures within small, localized sample regions. At XOR/UNI sector 34 of the APS, we have used Kirkpatrick-Baez (KB) mirrors to focus polychromatic x-rays routinely to ~0.5 µm FWHM [1]. We have initiated Laue diffraction studies of individual nanostructures using ZnO fabricated in several different shapes: rods, belts and tapered styluses.

Methods and Materials

In the setup developed at sector 34, KB mirrors are used to focus polychromatic off-axis undulator radiation with an energy bandpass of ~8-23 keV onto the sample. A CCD area detector records the Laue microdiffraction pattern. Analysis provides real-space maps of the **local** lattice structure, crystal orientation, and strain tensor. The microbeam setup implemented on sector 34 is particularly versatile in that a translating double-crystal monochromator is also available, enabling absolute lattice spacing measurements. To test the feasibility of measurements from small volumes, we obtained ZnO samples which had been fabricated in several different shapes and mounted on different substrates [2]. Shapes investigated included cylindrical rods, rectangular belts and tapered stylus rods.

Results

Initial Laue observations using a beam diameter of ~0.5 µm revealed that ZnO reflections could be obtained from cylindrical nanorods as small as ~200 nm in diameter. However, the measurements also showed that strong substrate scattering can easily overwhelm weak ZnO reflections; i.e. experimental limitations generally involved the signal/noise ratio rather than simply the signal. Fig. 1 shows an optical image of a cylindrical ZnO nanorod mounted across metal contacts on a Si wafer. Microfluorescence obtained by scanning the sample in the focused beam provided a spatial map of the sample composition and hence the nanorod location. In Laue patterns, intense scattering from conventional Si wafer substrates caused intensity overflow streaks across the detector image. To reduce substrate scattering, subsequent ZnO nanorods were mounted on thinner Si wafers. Fig. 2 shows a Laue pattern obtained from a single ~200 nm diameter ZnO nanorod mounted on a 25 µm thick Si(001) wafer. In addition to the intense Si peaks, 16 ZnO reflections (e.g. inset) can be observed and indexed to yield the local ZnO lattice and orientation. A hexagonal crystal structure was observed for all ZnO nanostructures. Generally, the ZnO c-axis was found to lie along the long growth axis, but at least one exception was observed. In most cases, the ZnO (10-10) planes lie parallel to the substrate surface, suggesting that the nanostructures possess flat, faceted surfaces. The shape of individual ZnO diffraction peaks was strongly dependent on the size of the nanostructure. Narrow structures (e.g. ~200 nm nanorods) displayed large local angular deviations (mosaic), while structures several microns thick were essentially perfect single crystals (deviations <0.02°). This difference is likely due to the large eleastic flexibility of thin structures.

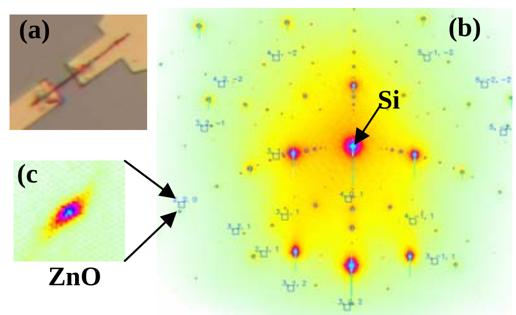

Fig. 1: (a) Optical image of ~200 nm nanorod; (b) Laue pattern from Si substrate and ZnO; (c) enlargement of ZnO(22-40)

Discussion

An important feature of the white-beam Laue approach is the ability to collect full diffraction patterns without rotating the sample. This advantage over monochromatic approaches is extremely useful when the local crystal structure or orientation are not known. In practice, substrate background scattering is an important consideration; thin substrates or samples on TEM grids are suitable. X-ray microdiffraction is complementary to electron microscopy characterization in cases where quantitative measurements over longer length scales are needed. X-ray measurements generally have increased angular resolution and no charging effects, but can be limited by weak scattering from nanostructured materials. At sector 34, improved KB mirrors have recently been used to provide focused demonstration beams as small as ~90 nm, [3] and ongoing improvements at synchrotron facilities worldwide suggest that polychromatic beams with diameter ~20 nm can be achieved.

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