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The Use of X-ray Microbeams in Materials Science

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ABSTRACT

Most materials are heterogeneous on mesoscopic length scales (tenths-to-tens of microns), and materials properties depend critically on mesoscopic structures such as grain sizes, texture, and impurities. The recent availability of intense, focused x-ray microbeams at synchrotron facilities has enabled new techniques for mesoscale materials characterization. We describe instrumentation and experiments on the MHATT-CAT and UNICAT undulator beamlines at the Advanced Photon Source which use micron and submicron-size x-ray beams to investigate the grain orientation, local strain and defect content in a variety of materials of technological interest. Results from a combinatorial study on epitaxial growth of oxide films on textured metal substrates will be described to illustrate x-ray microbeam capabilities.

INTRODUCTION

Synchrotron-based x-ray microbeam techniques for investigating the structure and dynamics of materials have been progressing for more than 25 years.¹⁻⁵ A variety of approaches have been developed for creating microbeams, including pinholes, Fresnel zone plates, Kirkpatrick-Baez (K-B) mirror pairs, and tapered capillaries.⁶⁻⁸ As the brilliance of synchrotron sources and the precision of x-ray optics have improved, the beam-size of useful x-ray probes has decreased to the point where now both monochromatic and white-beam experiments can be carried out at third-generation sources with $\leq 1 \mu\text{m}$ spatial resolution.

Finely-focussed x-ray beams provide spatially-resolved structural information such as the local strain, grain sizes and orientation, and compositional profiles for a wide range of technologically important materials.⁹⁻¹² In addition, the penetrating power of x-rays enables measurements that are complementary to more surface-sensitive electron-beam probes. Since most materials are heterogeneous on the mesoscopic length scale, x-ray microbeam investigations will provide fundamentally new information needed for understanding many classic processes in materials such as grain growth, fracture and creep.

As evidenced by this workshop, microbeam investigations already cover a diverse spectrum of active disciplines at the Advanced Photon Source (APS). Researchers from ORNL and collaborators have initiated several materials science investigations using micron and sub-micron size x-ray beams at the APS. Our studies include: grain-by-grain strain determination in Al interconnects on Si; local deformation induced by nano-indentation; depth-dependent diffuse scattering studies of ion-implantation defect clusters in single-crystal Si; and epitaxy of oxide films on textured metal substrates.

INSTRUMENTAL

Measurements for the various investigations are being carried out using two different experimental setups on undulator beamlines at the APS: monochromatic beams produced using Fresnel zone-plate optics (obtained in collaboration with SRI-CAT at the APS) at UNICAT, and white/monochromatic beams produced using K-B mirrors at MHATT-CAT. The zone-plate setup is well suited for single-crystal studies or other experiments where a monochromatic beam is effective, and it has achieved a spatial resolution of $\sim 0.6 \mu\text{m}$ with a flux in the $10^9/\text{sec}$ range at 9 keV. The K-B mirror-based setup at MHATT-CAT is more versatile in that it is capable of alternating between white and monochromatic modes with a fixed beam position using the components shown schematically in Figure 1.¹³ This versatility is a key feature for studying polycrystalline samples because the motions on conventional diffractometers are not coincident to $\leq 1 \mu\text{m}$. In this arrangement, the double-crystal monochromator is mounted on a stage allowing it to be translated into or out of the white beam.¹⁴ Slits guarantee colinearity of the beams when switching between white or

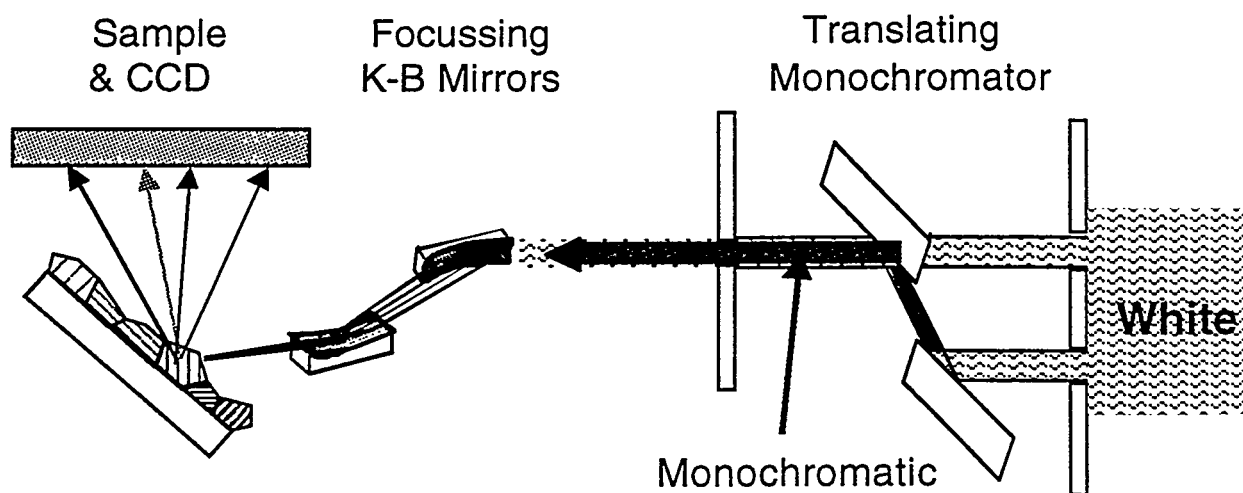


Figure 1 Schematic diagram of x-ray microbeam optics used at MHATT-CAT.

monochromatic modes. A pair of K-B mirrors then focuses either the white or monochromatic beam onto a sample and diffracted beams are measured using a CCD detector. This setup has achieved spatial resolutions of $\sim 0.8 \mu\text{m} \times 1.6 \mu\text{m}$, and smaller beams are expected with mirrors fabricated with improved precision. In white-beam mode, the CCD records a Laue pattern, which is analyzed using an automated indexing program.¹⁵ This arrangement is presently capable of measuring angular deviations of $\sim 0.01^\circ$ and strain resolution $\Delta d/d \sim 10^{-4}$.

RESULTS

We have initiated fundamental research in four areas of mesoscale materials science based on x-ray microbeam investigations. 1) Interconnect Strains - Controlling thermal and electromigration-induced stresses in metal interconnects represents one of the most important reliability concerns in the microelectronics industry. We have combined white and monochromatic beam measurements from individual grains in Al microchip interconnects to obtain maps of the triaxial inter- and intra-granular strain with $\sim 1 \mu\text{m}$ spatial resolution. 2) Nanoindentation Deformation - The dynamics of deformation and microstructural evolution represent some of the most complex physical processes to characterize at mesoscale length scales. We have made initial microbeam measurements of local residual strain associated with nanoindents in copper. These studies demonstrate the potential for fundamental deformation investigations using a combination of x-ray microbeam and nanoindentation techniques. 3) Ion-Implantation Defects - On the micron scale, the depth dependence of the size, concentration, and type of ion-implantation induced defect clusters has until now been outside the realm of x-ray diffraction investigations. We have used Fresnel zone plate x-ray optics to perform submicron resolution cross-section diffuse-scattering measurements of MeV Si ion-induced damage in Si. 4) Vicinal Epitaxy - The current-carrying ability of high- T_c superconductors is suppressed by orders of magnitude by weak-link high-angle grain boundaries. We are studying the grain-by-grain orientation of oxide superconducting films during epitaxial growth on textured metal foils.

To illustrate x-ray microbeam capabilities, we describe here results only from the last area, a combinatorial study of crystallographic tilting during epitaxial growth of oxide films. Since early studies of high-temperature superconducting materials such as YBCO revealed that high-angle grain boundaries act as weak links for the critical current density, substantial efforts have been directed towards the fabrication of long lengths of crystallographically-aligned superconductors. One approach has been to induce alignment using the epitaxial growth of oxide films on rolling-assisted biaxially-textured substrates (RABiTS).¹⁶ Rolled Ni

substrates are recrystallized under conditions that lead to a high degree of biaxial $\{100\}\langle 100 \rangle$ cube texture. Conventional x-ray ω - and ϕ - scans typically show that the Ni substrate is three-dimensionally aligned to within $\sim 7^\circ$ FWHM. Subsequent growth of epitaxial oxide buffer layers (typically YSZ/CeO₂ as a chemical barrier) and then superconducting YBCO preserves the alignment, enabling high critical current densities, $J_c > 10^6/\text{cm}^2$. Although the feasibility of this approach has been demonstrated in small samples, reliably controlling microstructure for scale-up to km lengths is a significant challenge. Understanding the details of processes such as epitaxial growth and stress-cracking under different conditions are essential for the fabrication of superconducting wires.

Figure 2A shows a schematic diagram of a YBCO/YSZ/CeO₂/Ni(001) multilayer sample. Since the substrate grains are typically $\sim 50\ \mu\text{m}$ in diameter and the x-rays penetrate the epitaxial layers, the x-ray microbeam is ideally suited for measuring the structure and orientation of each layer on a grain-by-grain basis. Figure 2B shows a typical CCD image consisting of white-beam Laue patterns from the different layers within a single grain. It reveals that the successive layers are not exactly aligned. Instead, the [001] poles of the YSZ/CeO₂ buffer layers are tilted towards the surface normal when compared with the substrate Ni[001]. Similarly, the YBCO (001) planes are tilted further in the same direction.

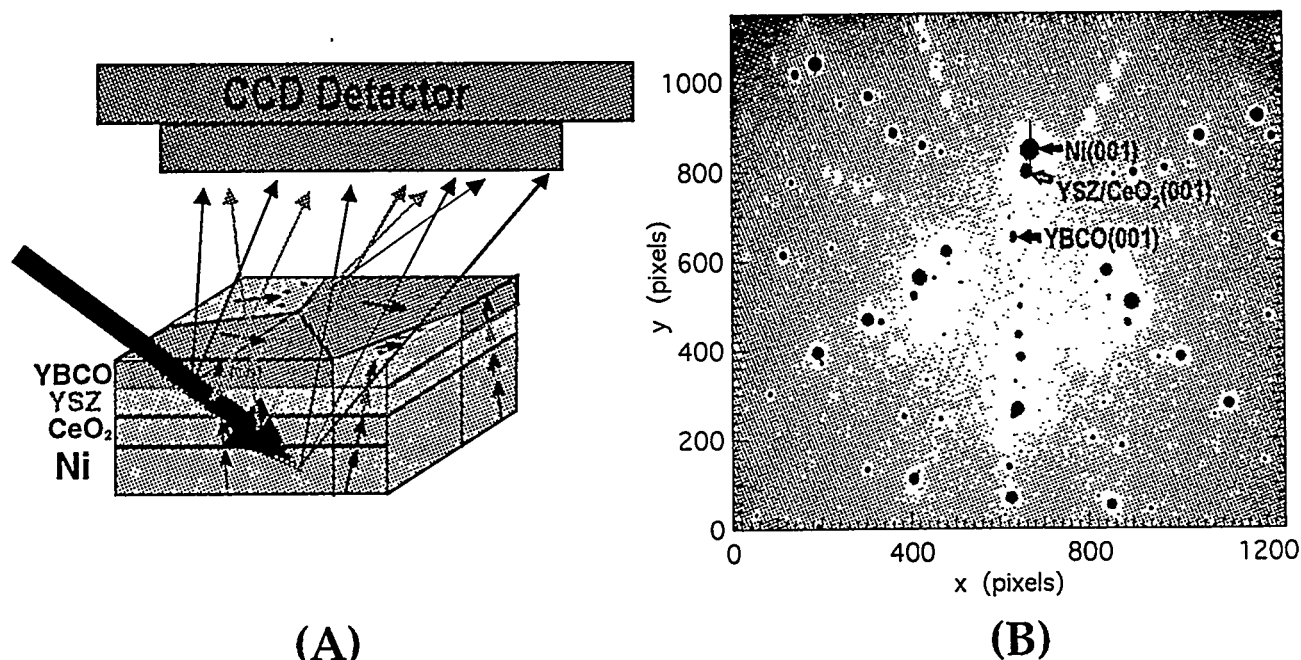


Fig. 2A) Schematic of oxide films grown epitaxially on rolling-textured Ni foil.
 Fig. 2B) CCD image showing separate (001) Laue patterns from YBCO, buffer layers and Ni.

We find this form of tilting to be a general result for RABiTS samples prepared under normal conditions. Typically, we find a linear relation between the tilt of a heteroepitaxial layer and the miscut angle of a particular substrate grain.

Examples of crystallographic tilting of heteroepitaxial films on vicinal surfaces have been reported previously.¹⁷⁻²⁰ Semiconductor films are often observed to grow tilted with respect to miscut single-crystal substrates. Although many of our observations are in qualitative agreement with a geometrical model based on mismatch at surface steps proposed by Nagai,¹⁷ we find that the quantitative value for the slope in the linear relation can depend on processing conditions, and that deviations from a linear relation can occur. Discovery of these effects has been made possible by the x-ray microbeam. To our knowledge, all previous investigations used large single-crystal substrates; that is, they required that a new sample be grown for each miscut angle. Thus, studies were limited to a small number of observations and were susceptible to errors introduced by changes in processing conditions. The use of the x-ray microbeam and textured substrates eliminates these limitations. Films grown under identical conditions on a large number of grains with a distribution of miscut angles can easily be measured from a single sample. In effect, the x-ray microbeam enables a combinatorial approach with greatly improved statistics to the measurement of heteroepitaxial growth.

SUMMARY

The availability of intense, $\leq 1\text{ }\mu\text{m}$ diameter, white and monochromatic x-ray beams at third generation synchrotron sources has enabled a broad range of materials science investigations. Direct measurements of local structure, strain and orientation at mesoscale length scales have not been previously available by any experimental technique. This new information, in conjunction with advances in theoretical modeling, will provide a foundation for the future understanding and development of materials and processing techniques.

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