MAKING MORE-PERFECT THIN FILMS

X-rays reveal the structure of things we cannot otherwise see, like leg bones, and even tiny objects, like DNA chains, viruses, and individual atoms. As the size of the material being x-rayed shrinks, the individual objects that it comprises become more difficult to distinguish. X-ray images of extremely tiny materials are best when the materials are composed of identical objects arranged in a precise order, like a perfect crystal. These images can also be used to calculate statistical averages of disorder, but not to locate individual disorders. Researchers working at the APS have developed a new way of using coherent x-rays, specifically heterodyne mode x-ray photon correlation spectroscopy (XPCS), to study surfaces, interfaces, and bulk defects in thin films as the films are being grown. Mixed bulk and surface x-rays can pick out the speeds of small groups of atoms, providing a measure of the velocity of surface and subsurface features, such as voids and other defects. Once they are found, improved industrial techniques can be developed to create thin films with fewer imperfections.

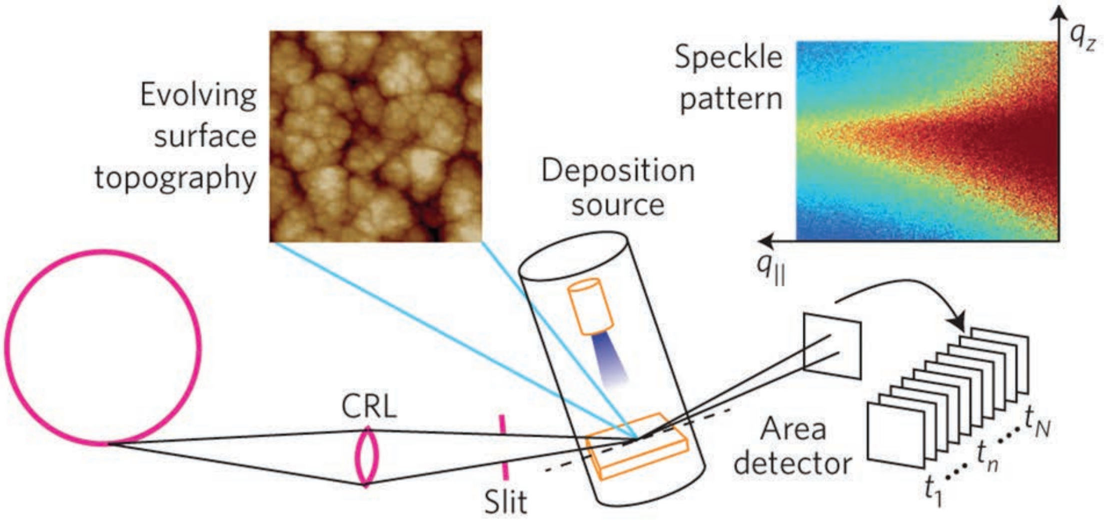

Fig. 1. X-rays from the APS are focused by a compound refractive lens (CRL) and a collimating slit system into an ultrahigh-vacuum sample enclosure. An amorphous thin film is deposited, which causes the surface to advance at the growth velocity and also induces random fluctuations in the surface roughness. Scattered coherent x-rays form a speckle pattern that corresponds to the detailed configuration of the surface, which is recorded versus time by a high-resolution photon-sensitive x-ray area detector. From J.G. Ulbrandt et al. Nat. Phys. **12**, 794 (AUGUST 2016). © 2016 Macmillan Publishers Limited, part of Springer Nature. All rights reserved.

Thin films are layers of materials that may be only fractions of nanometers in thickness, grown by deposition in a vacuum chamber. In one common technique for creating thin films, known as "sputtering," a plasma knocks material from target atoms and onto the film surface. Thus far, researchers have been unable to monitor the deposition of atoms on the film during deposition because the atoms are too small to be imaged, but it is important to understand the interactions of surface and buried defects in thin films so that better ones can be created. X-rays have the potential to probe both surface and interior defects since they are highly penetrating and sensitive to features measuring mere nanometers. However, thus far x-ray patterns of thin films have been blurry because the arrangement of their atoms is complex and disordered, and subsurface study is extremely difficult, especially in real time as the films are being grown.

The researchers in this study, from the University of Vermont, Boston University, and Argonne, employed XPCS at XSD beamline 8-ID-I of the APS. Their approach improves x-ray scattering techniques by imposing order on the x-rays so that they can detect disorder in the material. Two types of defects are common in thin films: nanocolumns that grow with the film surface as the layers are being deposited, and voids that form at the surface and are trapped. In XPCS, a scattered x-ray wave bounces off the surface of the thin film in response to nanocolumns. These waves mix with scattered waves of x-rays bouncing off the disordered defects, which are voids at and beneath the surface. The mixed x-rays indicate the motion of the voids and nanocolumns. Waves that bounce off the surface determine speed, because the rate at which the film was deposited is known. Waves that bounce off interior defects in the subsurface develop oscillations because the irregularities cause the atoms to go different speeds. Once the defects are observed, they can be left to grow into the film or be eliminated. Even more important is that the XPCS technique can be used to monitor atoms in motion, even if they are moving independently and erratically, while the thin film is being made.

This new technique can lead to the creation of thin films that are smoother with fewer defects and voids. Increasing the quality of thin films improves their usefulness in a range of industrial, medical, and consumer

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A NEW IMAGING MODE USING A GERMANIUM ENERGY-DISPERSIVE STRIP DETECTOR

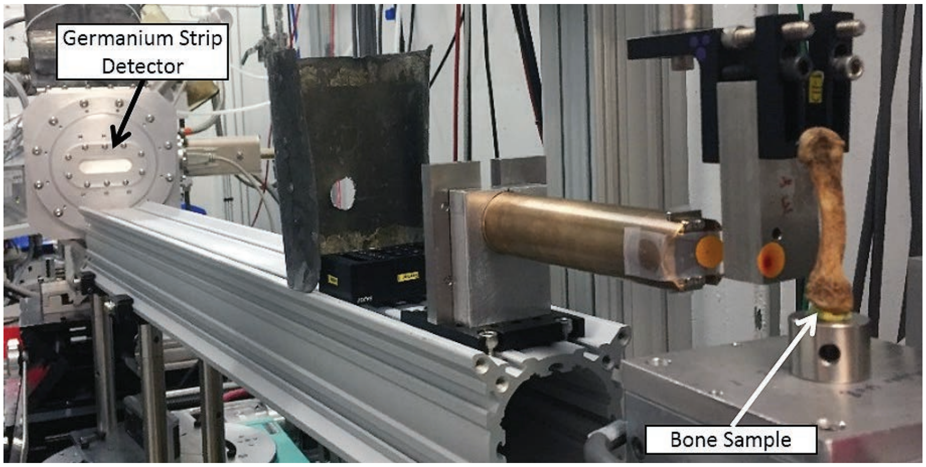

Fig. 1. The new germanium strip detector at 6-BM-A,B is located at the far left in the photograph. A human second metacarpal bone from the Roman-era cemetery in the UK is at near right of the photo.

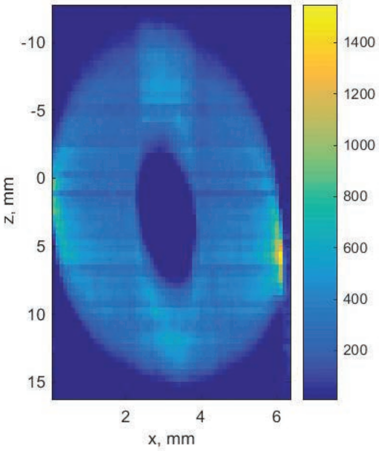

Fig. 2. The energy dispersive real space reconstruction of a hydroxyapatite (hAp) bone phantom is shown to the left. Several diffraction peaks were reconstructed and peak intensity from one is shown here (hAp 004 reflection). The shape including empty central region is correctly reconstructed.

X-ray diffraction provides a wealth of information including crystallographic phases comprising a material along with the strain and texture states of those phases. There is great interest in measuring these properties in a spatially-resolved fashion, within a sample cross-section. Several monochromatic x-ray techniques have been developed recently at the APS, using area detectors and a sample rotation.

A team of detector developers from the APS and from the National Synchrotron Light Source-II (NSLS-II) at Brookhaven National Laboratory together with scientists from the APS and Northwestern University have developed a new and complementary imaging technique using white-beam radiation and a germanium strip detector. The use of high-energy x-rays from an APS bending magnet allows measurements on up to centimeter-sized specimens. It also does not require sample rotations to extract cross-sectional information, so it can be used to image a wider array of geometries than with standard tomography techniques (namely high-aspect-ratio samples) with target areas including batteries, bone implants, and aerospace components.

The heart of the technique is the germanium detector developed by the APS and NSLS-II detector groups, which combines low-noise readout electronics with a high-quality germanium sensor to provide position and energy resolution. The first-generation detector (Fig. 1) consists of a 3-mm-thick germanium sensor with 64 strips on a 0.5-mm pitch. An energy spectrum is measured from each strip simultaneously; the energy resolution is 400-500 eV. Currently, the maximum energy is limited to 50 keV. Further detector developments will enable energies to ~100 keV to be imaged, allowing thicker and/or higher-z materials to be investigated.

The new imaging mode was accomplished with a slit and single translation across the sample, and applied to a three-dimensional printed bone "phantom" to confirm accuracy. Several diffraction peaks were reconstructed; peak intensity from one is shown in Fig. 2. The peak centers from each phase present can also be reconstructed to yield strain information.

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This effort is the work of detector developers from APS (Jonathan Baldwin, Antonino Miceli, Orlando Quaranta, Russell Woods) and NSLS-II (Anthony Kuczewski, Joseph Mead, Abdul Rumaiz, Peter Siddons) as well as scientists from the APS (Jonathan Almer, John Okasinski) and Northwestern University (Stuart Stock).

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products, such as cell phone screens, thin-film solar cells, drug delivery systems, and even potato chip bags.

— Dana Desonie

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