

PREFACE

Non-Destructive Depth-Profiling of X-ray Powder Diffraction Information



This year marks the 100th anniversary of Roentgen's wonderful discovery that gave birth to the X-ray field and its diverse applications. It is appropriate therefore to take stock of at least one part of the field and its relation to current developments in other areas of science and technology, to try to envisage what the future may hold.

In the technological arena, we are in the midst of an accelerating trend toward the development of micro to nano-scale structures in the form of films, multilayers, columns, clusters and particles, in which a significant fraction: >1% of the atoms are associated with interfaces such as grain or phase boundaries. Such structures are finding applications in a wide range of devices for many reasons. From a materials standpoint:

- in metals and ceramics, decreasing the crystallite size increases yield strength and toughness,
- in semiconductors, the band structure is altered affecting the bandgap the electronic transitions and the optical properties,
- in multilayers, alternating layers of various materials produce improvements in mechanical properties and the capability of tailoring electrical, magnetic and optical properties,
- in nanophase materials assembled from atom clusters, there is evidence that a wide variety of unique or improved physical and chemical properties can be attained.

From the device standpoint, the potential of micro electromechanical devices (MEMS) is being realized, while with IC's, the insatiable demand for increased speed, integration and memory density continues unabated.

In X-rays it seems that God has provided a tool well-suited to investigating these structures, specifically: (1) X-ray wavelengths are in the right range (0.01-10 nm) to measure scattering from these structures at readily accessible angles, (2) penetration depths (a few nm to a few hundred μm) are in the range of the dimensions of most films, surface treatments, clusters and MEMS and (3) X-rays are largely non-destructive and non-invasive allowing measurements to be made at high temperatures, pressures, in hostile environments, on rotating machinery etc.

Most X-ray diffraction measurements are presently made assuming specimens to be homogeneous and uniform, however, in the real world this is seldom the case. In particular, various structural and physical quantities can vary with depth from the surface. With the increasing interest in nano-scale structures, such depth gradients, whether intentional or not, assume a much greater importance than with bulk materials. The ability to control X-ray penetration depth by varying the incidence angle with the aid of parallel-beam optics, together with the intensity and wavelength range available from synchrotron sources have opened up the possibilities of obtaining non-destructively the depth-profiles of most quantities measurable by X-rays. Such grazing incidence diffraction (GIXD) measurements are also possible with laboratory sources, albeit with greater difficulty and longer count times. The recent demonstration of a many-fold increase in intensity and decrease in divergence attainable with a graded multilayer parabolic mirror inserted in the incident beam of a laboratory source promises to make depth-profile measurements much more accessible. A tentative list of the quantities that could be measured as a function of depth, together with the pertinent analysis or measurement method(s), might read as follows:

- phase structure (cell parameters and contents) — *Rietveld refinement*
- phase volume fraction — *Rietveld refinement*
- phase texture — *Rietveld refinement*
- crystallite size and shape — *peak profile analysis*
- surface island size and shape — *grazing incidence SAXS*
- crystal defects (point, line, plane, volume) — *peak profile analysis, SAXS, diffuse scattering*
- rms strain — *peak profile analysis*

macro strain/stress — *peak shift, peak profile analysis*
micro (or pseudo-macro) strain/stress — *peak shift, peak profile analysis*
elemental composition — *XRF, Rietveld refinement*

The measurements could be made using any of three geometries: asymmetric with grazing incident beam (for increased intensity), asymmetric with grazing diffracted beam (for increased spatial resolution) or symmetric with grazing incident and diffracted beams (which requires no refraction correction). Since a grazing incident beam of small divergence is also required for X-ray reflectivity measurements, one can envisage a single instrument in which all of these measurements can be made. If in addition an energy dispersive X-ray detector is used, one could simultaneously obtain depth profiles of elemental composition by measuring the XRF. By introducing some process-specific modifications it should be possible to adapt such instruments for *in situ* monitoring of the deposition and processing steps in the fabrication of thin film and multilayer devices.

A difficulty arises with the interpretation of the depth-profile data obtained by these methods because X-rays are absorbed exponentially with depth provided X-ray absorption in the specimen obeys the Beer Law. Thus what is varied as one varies the incidence angle is the $1/e$ penetration depth τ . The profiles measured are therefore functions of τ , whereas what is preferred for correlation with physical and chemical properties are the true depth profiles or z-profiles. The relation between the two for diffraction from a phase in a layer of thickness D is:

$$\langle Q(\tau) \rangle = \int_0^D q(z) e^{-z/\tau} dz \int_0^D e^{-z/\tau} dz$$

where $\langle Q(\tau) \rangle$ is the measured τ -profile of any quantity in the list above and $q(z)$ is the corresponding z-profile. Analytical (inverse Laplace) and numerical methods have been developed to extract $q(z)$ from the above equation with reasonable success. Further difficulties are encountered if X-ray absorption does not follow the Beer Law, as when significant concentration (or density) gradients are present in the specimen. The linear absorption coefficient, the structure factor and the cell volume all become functions of z and must appear in the above equation. Numerical extraction of $q(z)$ may still be possible but may require independent determination of the elemental composition profile, e.g., by XRF.

In addition to depth profiles, recent developments in capillary optics will make X-ray measurements possible with sub-micron lateral spatial resolution. Such measurements when coupled with the depth profiles mentioned above will provide a comprehensive characterization of the microstructure and stress state of the structures discussed.

The possibilities outlined above stem from the creative insight and persistent work of many individuals — too many to mention here. The future of the X-ray powder diffraction field depends critically on such efforts and on our willingness to increase the "exposure" of students and new users to X-rays, without, of course, intending any biological harm. With this thought in mind we can confidently embark on the next 100 years.



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