

## Recent developments in X-ray Diffraction Analysis



As an attendee/organizer of diffraction meetings and an editor/coeditor of X-ray journals for many years, I find two of the most exciting and important developments for X-ray diffraction in recent years are the application of graded multilayer optics for X-ray diffraction and residual stress depth profiling in thin films. These two developments greatly expand the capabilities of X-ray diffraction analysis using laboratory X-rays.

### **GRADED MULTILAYER MIRRORS**

An intense X-ray beam can be obtained from a laboratory X-ray source (i.e., a sealed-off X-ray tube or a rotating anode X-ray generator) using graded multilayer “Bragg” reflecting mirrors as X-ray beam conditioners. Three types of graded multilayer optics used in X-ray diffraction are parabolically curved multilayer mirrors for parallel-beam optics, elliptically curved multilayer mirrors for focusing optics, and planar multilayer mirrors for divergent-beam optics. With these newly developed multilayer mirrors, a number of important X-ray diffraction applications can be dramatically improved.

Parabolically curved multilayer mirrors can condense a divergent incident X-ray beam from a laboratory X-ray source with more than  $1^\circ$  opening into an intense parallel beam with only a few tenths of arc-minute divergence. Up to 80% of the incident Cu  $K\alpha$  X-rays impinging on the parabolic mirror is reflected. Using such an intensive parallel incident beam from a laboratory X-ray source in powder diffraction, the well-known instrumental broadening and specimen aberrations caused by surface displacement, flat specimen, specimen transparency, etc. commonly occur in a conventional diffractometer with para-focusing optics are eliminated. Powder diffraction analysis using parabolic mirrors greatly improve the accuracy and precision of an analysis including phase identification, quantitative analysis, stress measurement, texture determination, line broadening analysis, etc. This also makes possible for measurements of irregularly shaped objects (such as ceramic art and archeometry, as well as on parts with corrosion protective or surface hardening layers etc.) and low-absorption organic materials (pharmaceuticals, polymers, etc.), which are very difficult, if not impossible, to be measured by a conventional diffractometer. A parabolic mirror positioned close to an X-ray source condense the photo flux into a narrow parallel incident beam and greatly improve the intensity for grazing incidence diffraction and reflectivity analyses of surfaces and thin films. Such an intense parallel beam has also been used successfully in high-resolution X-ray diffraction for the characterization of epitaxial films. A gain of nearly two orders of magnitude in intensity was reported. It was also reported that a two-dimensional parallel beam can be obtained from cross-coupled graded multilayer mirrors. Such a system which gives six times or more intensity than that from a 2-D total reflection mirror system has been used successfully for laboratory protein crystallography.

Elliptically curved multilayer mirrors can focus a divergent beam emerging from a laboratory X-ray source onto a sample or a detector. A capillary/fiber diffractometer using an elliptically bent multilayer mirror gave about 9 times

more intensity than a conventional transmission diffractometer equipped with a Johansson monochromator. This is particularly beneficial for the analysis of small samples and for microdiffraction.

Planar multilayer mirrors are used in divergent beam optics. A conventional diffractometer equipped with an incident beam planar mirror has been shown to be an alternative to a curved Johansson monochromator. It has the advantages of much shorter X-ray beam path and easy wavelength selection.

The development of using graded multilayer mirrors for X-ray analysis has generated a great deal of excitement in the scientific community, and many more reports on its applications can be expected in the near future.

## DEPTH PROFILING OF RESIDUAL STRESSES

It is well-known that an X-ray beam can penetrate deep into a sample with an X-ray path length up to hundreds of  $\mu\text{m}$  for normal incidence with a large incident angle. The beam can also be limited to tenths of angstroms under the sample surface for grazing incidence with a small incident angle near the critical angle for total reflection. Residual stresses determined from an X-ray diffraction measurement are the average values over the X-ray penetration depths inside the sample (called  $\tau$ -profile). Since there is now considerable evidence that residual stress gradients are present in many samples and thin films, it is, therefore, necessary to obtain an actual stress depth profile stress beneath the sample surface (called z-profile). One approach for obtaining the stress depth profile is by layer removal. This approach is, however, destructive and requires corrections for new penetration depths after top-layer removal.

The new approach involves a measurement of the  $\tau$ -profile averaged from different depths obtained by grazing-incidence asymmetric diffraction with a conventional X-ray source. The actual stresses at different depths below a surface (i.e., z-profile) are, then, mathematically extracted from the measured average stresses from the  $\tau$ -profile, without the need for the difficult task of top-layer removal. Two data-reduction techniques for extracting a z-profile from the measured  $\tau$ -profile proposed the Predecki's group are the inverse Laplace transform and the numerical inversion methods.

These techniques have been applied to determining the actual stress depth profiles for sputtered Mo and W films deposited on glass substrates,  $\text{Al}_2\text{O}_3/\text{SiC}$  (whisker) composite in an  $\text{Al}_2\text{O}_3$  matrix, etc. Results show that the average and the actual in-plane stresses (i.e.,  $\tau$ - and z-profiles) were the same at large depths inside the bulk of the films and the  $\text{Al}_2\text{O}_3$  matrix, but differed significantly, however, at small depths as the surfaces were approached. For an 1- $\mu\text{m}$  thick Mo film the z-profile decreased monotonically with thickness, and its actual stresses changed from tensile in the bulk to compressive as the depth decreased below 400 Å from its surface. On the opposite, the actual tensile stresses in the  $\text{Al}_2\text{O}_3$  matrix increased first to a maximum and then decreased rapidly toward zero as the sample surface was approached.

The intense parallel incident X-ray beam produced by parabolic multilayer mirrors can be used for residual stress measurements, and this will greatly improve the speed of the experiments and the accuracy/precision of stress depth profiling results.

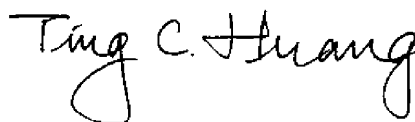
It should be noted that the actual in-plane stresses at depths within a few tens or less angstroms from the sample surface can not be obtained by X-ray diffraction because the X-ray penetration depths are practically the same for incident angles below the critical angle for total reflection.

## SUMMARY

Graded multilayer mirrors have the amazing ability of converting a divergent beam from a laboratory X-ray source into an intense parallel, focusing or divergent  $K\alpha$  X-ray beam. Such an intense X-ray beam has a wide variety of applications in powder diffraction, surface and thin-film characterization, as well as single-crystal structure determination. Stress depth profiling analysis allows the determination of the actual stress distribution and stress

gradients from near the surface to inside the bulk of a sample. These two exciting developments will make X-ray diffraction analysis using a laboratory X-ray source better and faster.

During my visit to the Rigaku Corporation in March 1998, I was delighted to learn that Rigaku has successfully developed techniques using graded multilayers in its produces for better and faster Xray diffraction analysis.

A handwritten signature in black ink that reads "Ting C. Huang". The signature is written in a cursive style with a large, looped initial 'T'.

Ting C. Huang

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