

Asbestos Abatement

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The energy, technology, and environmental research activities which fall into the category of applied science sometimes directly address important problems facing society. Success in such projects can have an immediate positive impact on the public, and thus garner a considerable amount of favorable attention from the general population and press.

A striking example was announced during the fall of 1997 in a press release issued by W.R. Grace and Co. The collaborative venture between Grace and BNL resulted in the development of a polymer foam which can be applied to asbestos as part of an abatement strategy. The foam chemically attacks the asbestos crystal structure, leaving behind a residue of minerals which can continue to act as a fire retarder/insulator.

One important aspect leading to the success of the W. R. Grace and Co./BNL CRADA (Cooperative Research and Development Agreement) on Asbestos

Abatement was the ability to accurately and reliably determine the quantity of asbestos in treated materials. The current EPA-recommended method is fiber counting using Polarised Light Microscopy. However, at the low levels of asbestos that the Project Team was concerned with, this method was believed to be insufficiently accurate and alternatives were explored.

Quantitative X-ray powder diffraction (QXRPD) is a well-established tool for the analysis of mixtures of crystalline powders. One type of QXRPD analysis is the so-called ratio method, where a known quantity of an internal standard is mixed with the analyte and the intensities of a peak from the phase of interest is compared with that of the added internal standard. An exact weight percent can then be determined by comparison to a calibration curve produced from carefully prepared standard samples. Work led by Dr Ruizhong Hu at W. R. Grace and Co. focussed on the use of this method

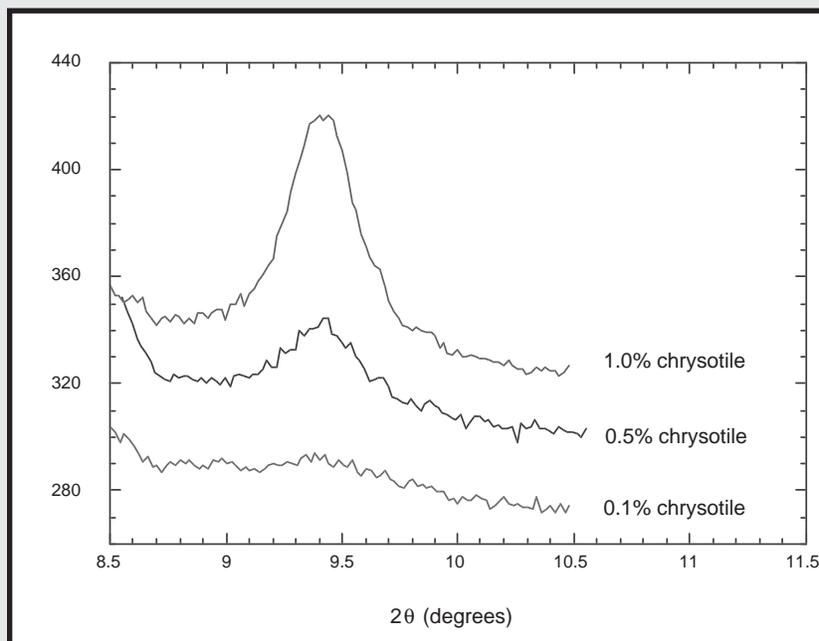


Figure A-1:
Diffraction spectra
around the chrysotil
(0 0 2) peak for low
concentration sam-
ples of asbestos in
alumina.

with a sealed tube X-ray source^[1]. A suitable method was developed to quantify low levels of chrysotile asbestos in chrysotile/gypsum/vermiculite (CGV) mixtures, a typical asbestos-containing material.

One potential drawback of this method is that it requires a pre-treatment to remove the gypsum in order to allow accurate quantification at very low (< 1%) levels. Proof that this did not affect the asbestos fibers (and hence complicate the quantification procedure) was achieved, in part, through the use of synchrotron X-ray powder diffraction at beam line X7A. Further work at X7A by Joe Hriljac, Cahit Eylem (then both in DAS), and Qing

Zhu (then in Physics) extended the use of QXRPD to allow quantification of low levels (0.25-0.5%) of asbestos in the same CGV mixtures without any pre-treatment^[2]. A plot of the diffraction data around the most intense peak of chrysotile in an alumina matrix is in **Figure A-1**. ■

[1] R. Hu, J. Block, J. A. Hriljac, C. Eylem, and L. Petrakis, *Analytical Chemistry* **68**, 3112-20 (1996).

[2] J. A. Hriljac, C. Eylem, Q. Zhu, R. Sabatini, L. Petrakis, R. Hu, and J. Block, *Analytica Chimica Acta* **350**, 221-29 (1997).

NEXAFS Microscopy of Polymers: Phase Separation and Dewetting in Polymer Thin Films and Bilayers

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In many applications, the physio-mechanical properties of polymeric systems can be tailored by altering the chemical and morphological structure. In most cases, the polymer system of interest is not a homogeneous or single-component system, but is a blend, composite, or copolymer. Sophisticated analytical methods are required for their characterization. Amongst them is the recently developed technique of Near Edge X-ray Absorption Fine Structure (NEXAFS) microscopy. It has an advantage of about three orders of magnitude over the equivalent electron microscopy technique in being able to spectroscopically analyze and image small sample areas of radiation sensitive materials such as polymers^[1]. In NEXAFS microscopy, excitations of core electrons into unoccupied molecular orbitals provide sensitivity to a wide variety of chemical functionalities in polymers. This sensitivity complements and resembles that achieved in infrared (IR) spectroscopy. Although NEXAFS spectra are not as specific and "rich" as IR spectra, the spatial resolution achieved in NEXAFS microscopy is about 50 nm^[2,3], and thus much superior to that achieved in IR microscopy. In addition, x-ray linear dichroism microscopy can determine orientation of chemical moieties at higher spatial resolution. These inherent advantages of x-ray microscopy have opened up new avenues for the characterization of polymers.

We will exemplify the impact of NEXAFS microscopy to the analysis of polymer systems by focusing our discussion on the characterization of phase separation and dewetting in polymer thin films and thin bilayers. Compared to bulk properties, relatively little is known about the properties of polymer thin films and surfaces, even though polymer films have considerable technological significance and technological applications, such as coatings and dielectric films. A detailed understanding of thin film properties and possible deviations from bulk properties is highly desirable and numerous studies on blends and bilayers have been undertaken in the recent past. While a variety of patterns that evolve during the phase separation process in polymer thin films have been observed, the two dimensional composition has never been directly determined. Often indirect methods, such as the use of selective solvent extraction for one of the phases in conjunction with AFM microscopy is utilized. However, the dissolution process can lead to ambiguities or artifacts. While qualitative details of the subsurface morphology might be revealed with electron microscopy techniques, NEXAFS microscopy provides quantitative equivalent thickness maps of each constituent polymer, which if summed together yield total thickness maps equivalent to AFM topographs. NEXAFS microscopy will thus allow for

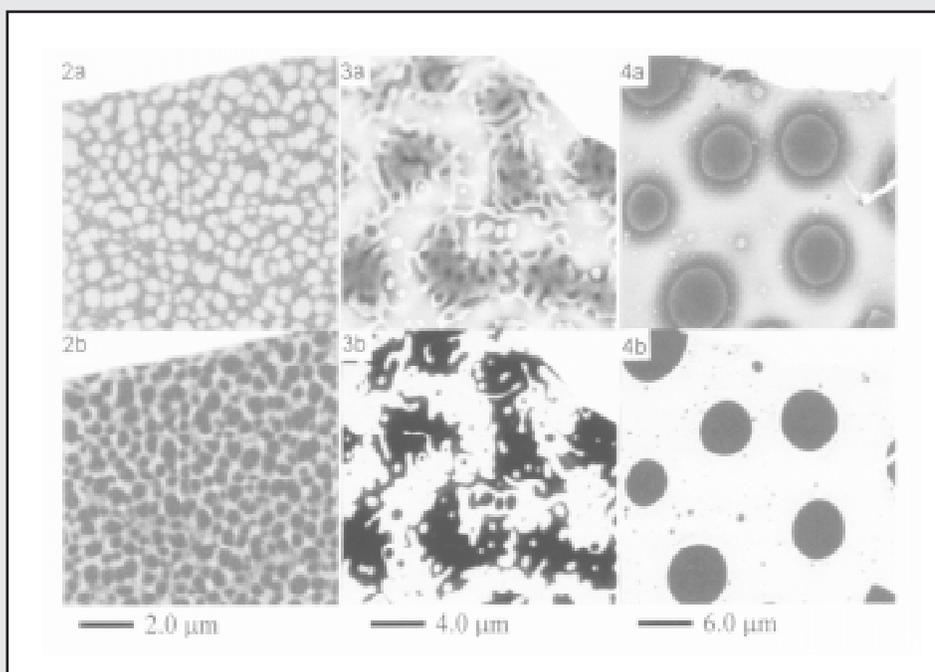


Figure A-2: As cast thin film of 50/50 weight percent PS/PMMA blend imaged at (a) 289.2 eV, and (b) 285.2 eV

Figure A-3: Same as above, but annealed for 10 min.

Figure A-4: Same as above, but annealed for one week.

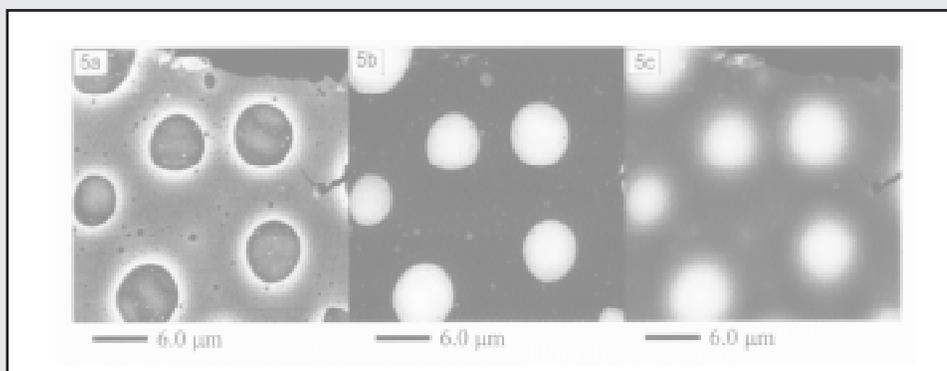


Figure A-5: Quantitative equivalent thickness map of sample annealed for one week. (a) PMMA map, (b) PS map, and (c) total thickness map.

quantitative investigation of the composition of phases and the dynamics of polymer phase separation.

We investigated films composed of a 50/50 weight percent blend of polystyrene (PS) and poly(methyl methacrylate) (PMMA) spun cast onto silicon substrates to a thickness of 146 nm. The films were then annealed for varying times and subsequently transferred to TEM grids for STXM investigation. A series of X-ray micrographs are acquired in the same sample area at energies coinciding with characteristic NEXAFS peaks

of the constituent components. For example, **Figures A-2a, A-3a, and A-4a** were acquired at the C 1s to π^* carbonyl peak at 289.2 eV and emphasizes PMMA, while **Figures A-2b, A-3b, and A-4b** were acquired at a photon energy of 285.2 eV, which is almost exclusively absorbed by PS. Darker regions indicate higher x-ray absorption at the particular photon energy and yield qualitative information on the component composition. The samples imaged in **Figures A-2, A-3 and A-4** were annealed for 0, 10 min, and one week, respectively. Initial phase

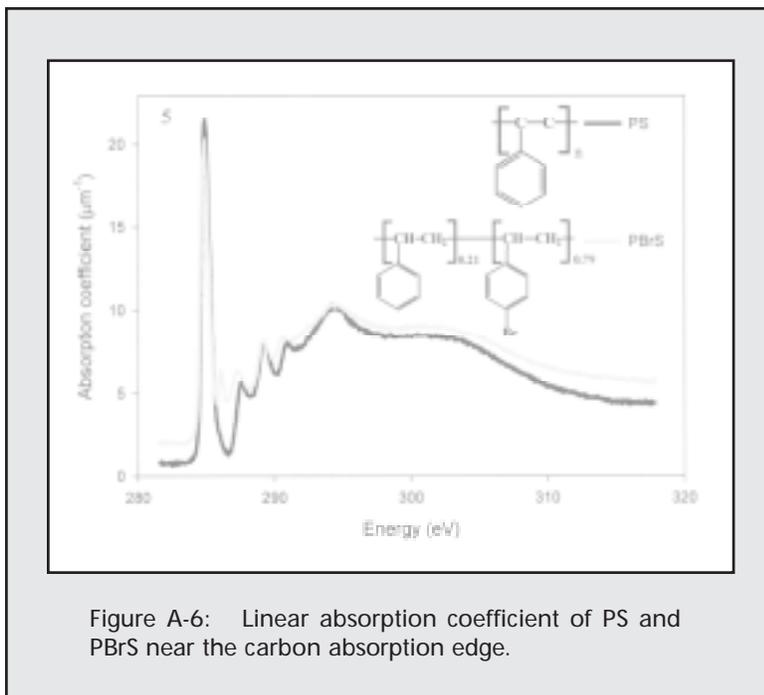


Figure A-6: Linear absorption coefficient of PS and PBrS near the carbon absorption edge.

separation during the spincasting into small domains is observed. After 10 minutes of annealing, intricate filamentary structures and inclusions are observed, with the system evolving towards the formation of large and thick PS domains with a PMMA interconnection layer after one week of annealing. The phase separation process is primarily driven by minimization of the interfacial free energies. In order to differentiate the effects of the relative absorption of the individual polymers, we employ a singular value decomposition method to extract thickness maps of individual components. **Figure A-5** shows the results of using this technique for the sample annealed for one week. **Figure 5a** is the projected thickness map of PMMA, **Figure A-5b** is the map for PS, and **Figure A-5c**

is the sum of **5a** and **5b**, and provides the total thickness map. The thickness map is equivalent and consistent with AFM topographs of these samples. The NEXAFS micrographs provide insight into the structure of the polymer interface formed.

A related issue to phase separation in thin films of polymer blends is the wetting and dewetting in thin polymer films. We have thus investigated a polystyrene/brominated polystyrene (PS/PBrS) bilayer model system with the Stony Brook STXM and employed the method described above to achieve quantitative thickness maps of PS and PBrS, respectively. The initial structure was a 30 nm thick layer of PBrS on top of a 40 nm thick PS layer prepared by spin casting each film and then floating the PBrS layer on top of the PS layer. After annealing, which initiates dewetting, the sample was transferred to a TEM grid for STXM analysis.

Images were acquired of the same sample area at four energies. Each image contains combined information about the PS and PBrS composition and thickness, with the weight governed by the linear absorption coefficient of the two polymers (**Figure A-6**). See inset for chemical structure of PS and PBrS). **Figure A-7** shows the resulting component thickness maps and underlying thickness profiles. Polystyrene has formed thick walls along a network of spines of PBrS that form as PBrS dewets. There is only a pure PS interconnecting thin film between the spines. The total thickness map is consistent with AFM topographs. We attempt to measure the contact angle in these systems as an indirect measurement of the interfacial energies. The NEXAFS data clearly shows thought that a contact angle of the

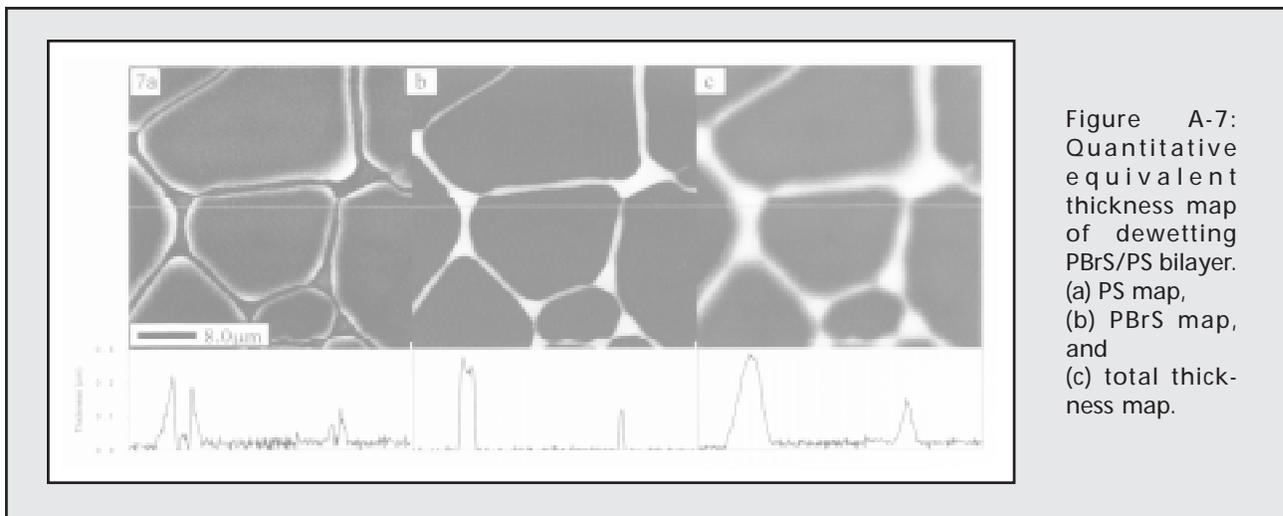


Figure A-7: Quantitative equivalent thickness map of dewetting PBrS/PS bilayer. (a) PS map, (b) PBrS map, and (c) total thickness map.

filamentary structures as measured with the AFM is only indirectly related to the PBrS profiles and the AFM measures primarily the PS walls. The STXM data suggests furthermore that the PBrS is actually completely encapsulated by PS after annealing. This would be consistent with SIMS and Photoelectron Emission Microscopy (PEEM) data that indicate that there is no or little PBrS at the very surface of the sample.

In both cases presented, NEXAFS microscopy provides new quantitative insight into the composition and morphology of the samples investigated, and we believe to be at the very beginning of NEXAFS microscopy making contributions to the science of polymer thin films. A variety of other applications are pursued by some of us and other researchers at beamline X1A. These include the characterization of dispersed phases in complex polyurethane polymers and the initial measurements of the partial miscibility of polycarbonate (PC) and poly(butylene terephthalate) (PBT) in PC/PBT blends. NEXAFS microscopy is also making contributions to polymer materials that were prepared via the non-equilibrium processing technique of mechanical alloying.

The morphology of blends produced in this way from polymers such as poly(ethylene terephthalate) (PET), Vectra (75/25 mol% oxybenzoate/2,6oxynaphthoate), ethylene-propylene rubber (EPR) and PMMA can be readily visualized due to the chemical sensitivity of NEXAFS microscopy. NEXAFS microscopy of polymers has matured as a technique and is now systematically applied to a wide variety of materials. ■

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[3] X. Zhang *et al.*, Nucl. Instrum. Meth. in Phys. Res. **A347**, 431-435 (1994).

[4] Data acquired with the X1A STXM developed by the group of Janos Kirz and Chris Jacobsen at SUNY@Stony Brook, with support from DOE and NSF. Zone plates made by S. Spector and C. Jacobsen (Stony Brook) and D. Tennant (Lucent Technologies/Bell Labs) with support from NSF. HA, DAW and APS are supported by NSF Young Investigator Award (DMR-9458060). SQ, SG, MR and JS are supported by NSF.

Microbeam Diffraction Studies of Interfacial Strain

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Modern integrated circuits may have millions of transistors and a comparable number of passive circuit elements connected by submicron wide metal lines. The total length of these fine wires may exceed hundreds of meters. In general, this wiring is distributed over several levels, separated by dielectric material to prevent shorts. Millions of metal-filled holes (vias) provide the interconnections between these levels. To achieve (typical) failure rates below one chip per thousand, the on-chip structures must be built to very exacting specifications; a few atoms of a contaminant in the wrong place may cause failure. In addition, significant material problems must be solved, often at a basic level.

The thermal expansion coefficient mismatch between different materials may cause stresses that can

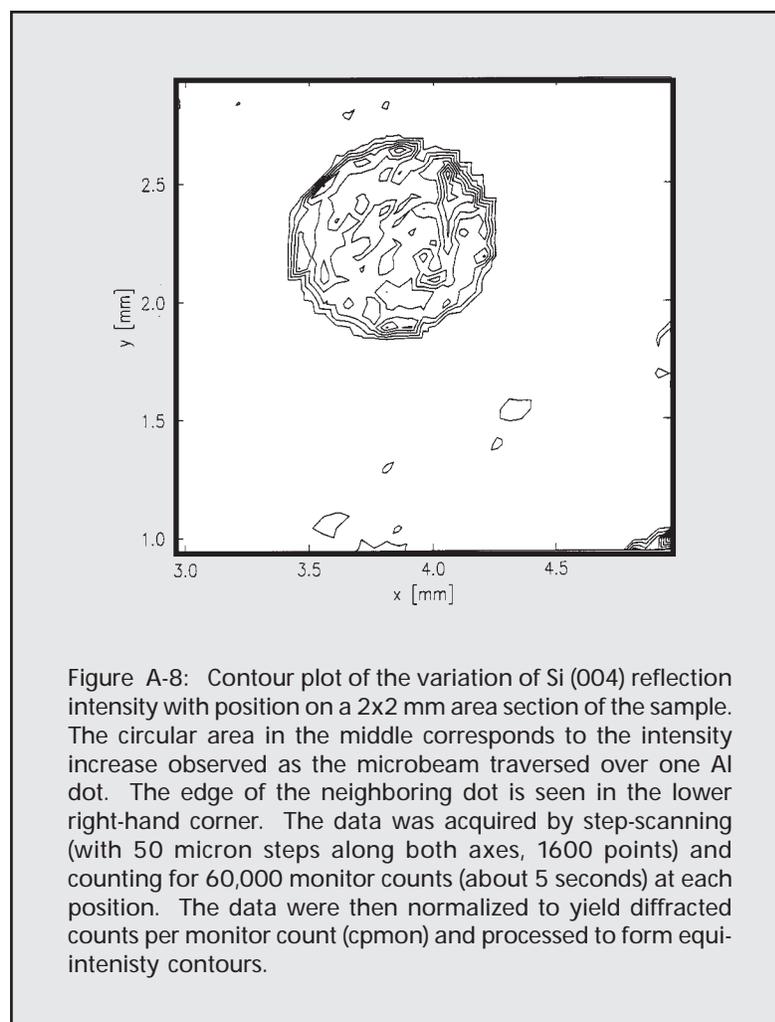
result in fractures in the wiring or in the passivation levels that insulate them. In addition, the tremendous current densities seen by the fine metal wires (in excess of 10^6 amps/cm²) may result in electromigration, where the electron flux knocks atoms from the wiring lattice and sweeps them along, causing voids at the cathode end. The displaced atoms aggregate close to the anode end of the wire (which is terminated by a via with different metallurgy) and cause very large compressive stresses that can actually rupture the passivation. The basic design principles that are used to overcome these problems are based on continuum mechanics with corroborating data from large specimens. These formulations may not be appropriate for the small domains encountered in microelectronic devices; in some cases the material is too

close to an edge such that edge effects dominate and, in other cases, there simply are not enough atoms around to yield a continuum. Microdiffraction is used to obtain the basic boundary conditions to develop the deformation mechanics of small domains and, in addition, to yield structure and phase information.

The first monochromatic x-ray microbeam diffraction experiments at Beamline X20A have been made by IBM scientists in Fall 1997. For this purpose a dedicated endstation which had been under construction during 1997 at Beamline X20B was used. This system is based on a two-circle Huber Goniometer and it uses tapered capillary optics for focussing the beam, micrometer precision sample-stages for specimen positioning, and energy-dispersive, linear and/or single channel detectors.

Beam sizes ranging from 2 to 25 microns have been used to characterize the orientation and strain distribution on a variety of thin-film samples. In this first set of experiments, the applicability of continuum equations (which are based on global averages or large homogeneous volumes) to domains containing limited volumes of material was investigated.

One case in particular is the interfacial strain state of patterned thin Al films on



single-crystal Si wafers^[1]. In this experiment an array of 1mm-diameter, 850nm-thick Al dots evaporated on a 001 Si substrate was examined. A micro-beam topograph of the Si 004 reflection was constructed by mapping the integrated intensity as a function of position on the wafer. An example is shown in **Figure A-8**. The intensity contours corresponding to the region under the Al dot are 2x higher than the intensity from the bare Si substrate. This intensity enhancement is due to the transition from dynamical to kinematic scattering since the thermal stresses between Al and Si distort the Si under the thin film features^[2,3]. A high-resolution scan of the Si 004

reflection across an Al dot (**Figure A-9**) shows multiple maxima and minima on a length scale much larger than the beam size (60-250 micrometers vs. 2x10 micrometers). In contrast, the strain state expected from the continuum “Shear Lag” formulation^[4] predicts only two maxima at each end of the film, which decay smoothly down to the base (dynamical) intensity at the “critical length” as one moves closer to the center. The multiple extrema observed experimentally indicate that the strain transfer is periodically interrupted! This result has significant implications in the analysis of adhesion and stress transfer at thin film/substrate interfaces. It also

shows that common assumptions about thin film properties may be invalid on a local scale. Microbeam x-ray diffraction provides a tool for testing these assumptions by providing data on a small length scale with minimal sample preparation. ■

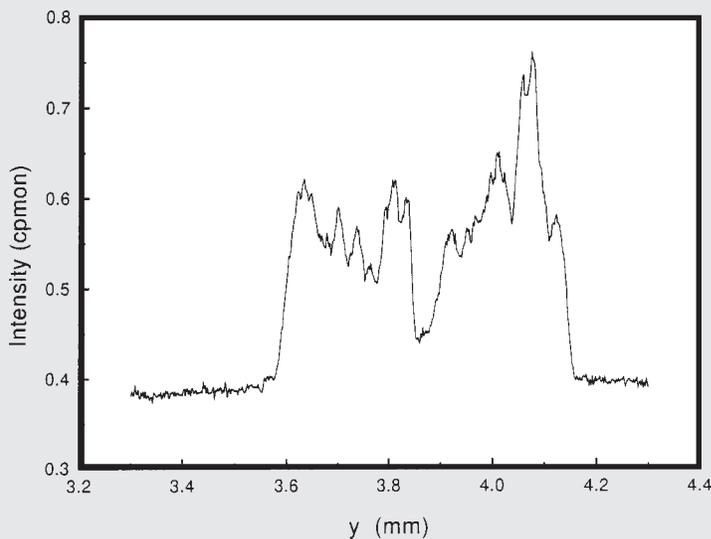


Figure A-9: The variation in Si (004) intensity across an Al dot. The step size is 2 microns. Note that the “baseline” is actually significant intensity from the bare Si wafer. The intensities are normalized to the monitor counts (cpmon). Error bars are not shown because of the high density of data points, but are approximately +/- .006 cpmin.

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