Modern Microscopy on the Light Side
Analyzing Chemical States and Phases

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The McCrone Group

As an industrial consulting laboratory specializing in small particle, thin film, and surface analysis, instrumental techniques to solve problems involving contamination, failure analysis, processing control, and materials research are used on a daily basis. In many cases, elemental analysis for samples is sufficient to pinpoint problems and suggest solutions. However, some cases require a more detailed understanding of chemical states and phases in small particles and films than that typically obtained from light and electron microscopy and x-ray microanalysis.

The chemical states and phases in crystalline particles and thick films can be analyzed with several techniques found in many laboratories, including polarized light microscopy, x-ray diffraction, and electron diffraction. In combination with elemental analysis, these techniques oftentimes provide a very detailed understanding of the chemistry of particles and films. However, amorphous particles and thin films and surface treatments require different techniques for chemical state analysis.

Applications requiring chemical state determination in small, amorphous particles and thin films include the measurement of metal oxidation states, important in catalysis and mineralogy; thin film chemical bonding, particularly in electronics; carbon bonding, for surface treatment analysis; and, characterization of particle chemistry, for a variety of uses. Although many wet chemical and instrumental analysis techniques exist for bulk crystalline and amorphous samples, small particles and thin films require techniques with high spatial and depth resolution.

Three techniques useful for the chemical state analysis and the imaging of particles and thin films are x-ray photoelectron spectroscopy (XPS or ESCA), Auger electron spectroscopy (AES), and electron energy loss spectroscopy (EELS). In many cases these techniques are used solely for elemental analysis, but all three spectroscopies measure electronic transitions that are sensitive to the chemical environment of the target atoms. Changes in chemical state and environment are manifested as changes in peak position and peak structure. Although the changes are often small and subject to substantial peak overlap, quantitative chemical state information can be obtained by curve fitting or multivariate analysis techniques.

XPS is perhaps the best developed of the techniques, with extensive databases and theoretical models for peak positions and structure. XPS is surface sensitive, with photoelectron elastic escape depths of 5-40 Å. An important advantage of XPS is that nonconductive samples can be analyzed with no major problems; thus, XPS has been widely used for polymer and mineral samples. New small area and imaging systems greatly extend the capabilities for the techniques for small samples and particles.

AES is used extensively in surface science and in some AEM instruments, but primarily for elemental analysis. Although many species exhibit AES chemical shifts equal to or greater than XPS, the complicated structure of AES spectra and the use of derivative spectra have prevented the widespread use of AES for chemical state analysis. With newer systems using electron-counting data collection and improved spectral processing routines, AES can be just as useful as XPS for chemical state determination on many samples. AES has the same surface sensitivity as XPS, and excellent spatial resolution and imaging capabilities, particularly with field emission sources.

EELS, performed in a TEM or STEM, is similar to XPS, but involves the measurement of energy lost by electrons passing through a thin sample. Thus EELS is less surface sensitive than XPS or AES, which can be an advantage in the analysis of particles that might have surfaces altered by oxidation or other processes. Spatial resolution can be as good as or better than AES, depending on the sample. The near-edge structure of edge profiles can be treated by a variety of methods to obtain bonding information, particularly for transition metals. Improvements in data reduction methods should lead to a greater use of EELS for chemical state termination.

Two recent examples from our laboratory that required instrumental measurement of chemical states involved the analysis of bonding in a mixed metal nitride thin film and the quantitative determination of iron oxidation states in clay particles. In the first case, a protective nitride film, containing aluminum and other metals, on a vanadium alloy substrate was analyzed by XPS. Although elemental analysis showed nitrogen in the film, the manufacturer was not certain that under his deposition conditions he was producing the desired aluminum nitride film. Measurements of the aluminum photoelectron and Auger peak energies showed that the film was primarily aluminum nitride and confirmed that the client's process was working correctly.

The second example was a research project designed to determine the feasibility of quantitative measurement of Fe(II)/Fe(III) ratios in clays and other silicate minerals. Iron oxidation state ratios are important in controlling clay properties such as brightness and swelling. Although several techniques, including XPS and EELS, were shown to be able to measure iron oxidation states in clays containing several wt% iron, EELS proved most useful, due to its superior spatial resolution, probing depth, and sensitivity. Further refinements could allow EELS to complement Mössbauer and other bulk techniques for quantitative transition metal oxidation state determination in clays and other minerals.

These examples illustrate that chemical state determination by high spatial and depth resolution instrumental techniques can be used to answer a variety of questions beyond the realm of elemental analysis, even for amorphous samples and ultrathin films. Improvements in source brightness and spot size, multichannel detectors, and data reduction strategies will increase the ease and applicability of chemical bonding analysis by electron emission and energy loss spectroscopies.

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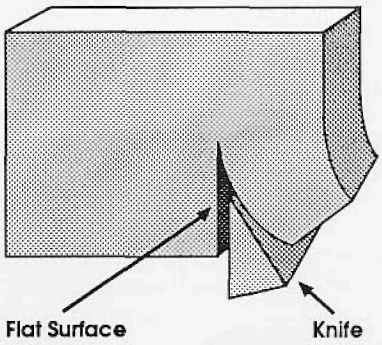

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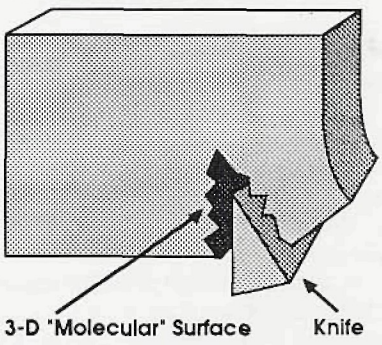

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✓ Nov 15/19 '93: **40th Annual Symposium of American Vacuum Society.** Orlando, FL. Marion Churchill: (212)661-9404.

✓ Nov 19 '93: **Optical Microscopy Sample Preparation and Image Processing Seminar** (Sponsored by ASM Chicago Electronic Materials Chapter). Schaumburg, Il. Anita Brandes. (708)205-2525.

✓ Nov 29/Dec 3 '93: **MRS Fall Meeting.** Boston, MA: (412)367-3003.

✓ Jan 18/20 '94: **TEM Sample Preparation Short Course/Workshop.** Arizona State Univ., Tempe, AZ. Dr. Farhad Shaapur: (602)965-0399.

✓ Feb 27/March 4 '94: **PITTCON '94.** Chicago IL Alma Johnson (412)825-3220.

✓ Mar 14/18 & 21/25 '94: **Practical Aspects of Scanning Electron Microscopy.** (Univ. of MD 4.5 day short courses). College Park MD. Tim Maugel: (301)405-6898.

✓ April 5/7 '94: **MRS Spring Meeting.** San Francisco CA. Mary E. KLaufold: (412)367-3036.

✓ May 7/12 '94: **Food Structure Annual Meeting.** Toronto, Canada. Dr. Om Johari: (708)529-6677.

✓ May 17/20 '94: **SCANNING '94.** (FAMS & SEEMS) Charleston SC. Mary K. Sullivan: (201)818-1010.

✓ June 13/23 '94: **Lehigh Microscopy Short Cources.** Bethelem, PA. David B. Williams. (215)758-5133.

✓ June 16/18 '94: **Current Trends In Immunocytochemical Protocols.** Geo. Washington Univ. Medical Ctr. Washington, DC. Fred G. Lightfoot: (202)994-2881.

✓ June 26/30 '94: **10th Annual Molecular Microspectroscopy Short Course.** (Miami University) Oxford, OH. (513)529-2873.

✓ July 11/15 '94: **41st International Field Emission Symposium (IFE '94).** Rouen, France. Prof. D. Blavette and A. Menand. Tel.: (33) 35 14 66 51, Fax: (33) 35 14 66 52.

✓ July 17/22 '94: **13th International Congress on Electron Microscopy.** Paris, France. Secretariat ICEM 13, 67 rue Maurice Gunsbourg, 94205 Ivry sur Seine cedex, France.

✓ Sept 12/15 '94: **MICRO 94 - International Microscopy and Image Analysis.** London, UK (***)

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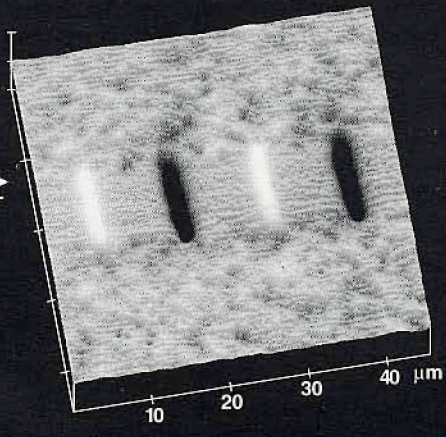
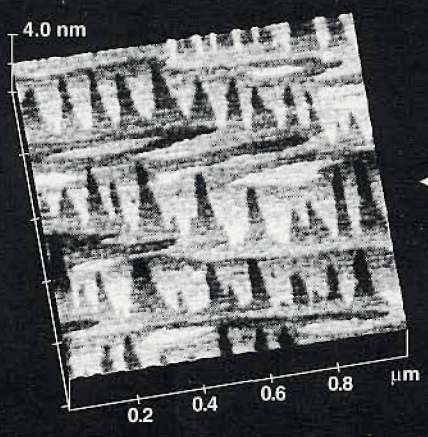


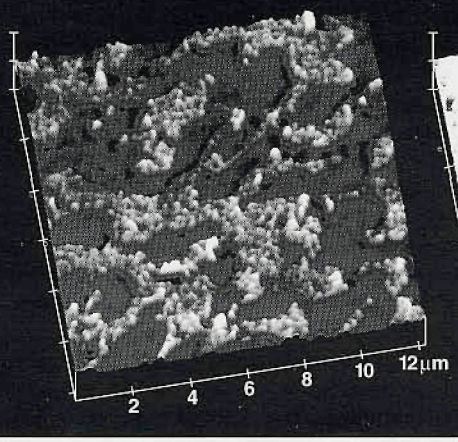
Magnetic Force Gradients ▶

These hard disk bits were written with alternating polarity and a slight skew. The speckle above and below the recorded track is due to the disordered magnetic domains in the virgin media.



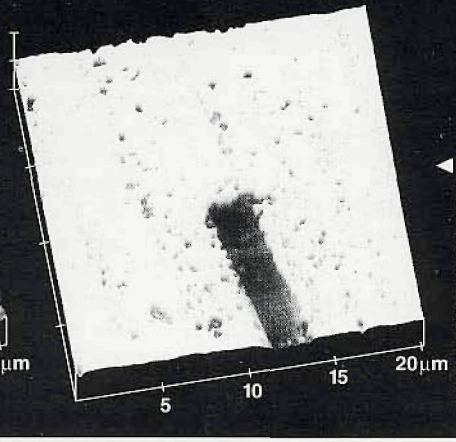
◀ *TappingMode™ AFM Topography*

These 1.6Å-high terraces of epitaxially-grown silicon were imaged using the NanoScope Large Sample Stage. Only the AFM probe touched the top surface of the intact 8in wafer.



Lateral Force (Friction) ▶

A mixture of EPDM and natural rubber scanned with a Si_3N_4 tip shows regions of higher friction (lighter color) and lower friction (darker color). These regions probably correspond to the two different types of rubber.



◀ *Electric Force Gradients*

A voltage applied to a broken metallization line on a GaAs test structure is shown. The image clearly indicates that the line is open at the break. This capability is another example of Digital Instruments innovation.

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