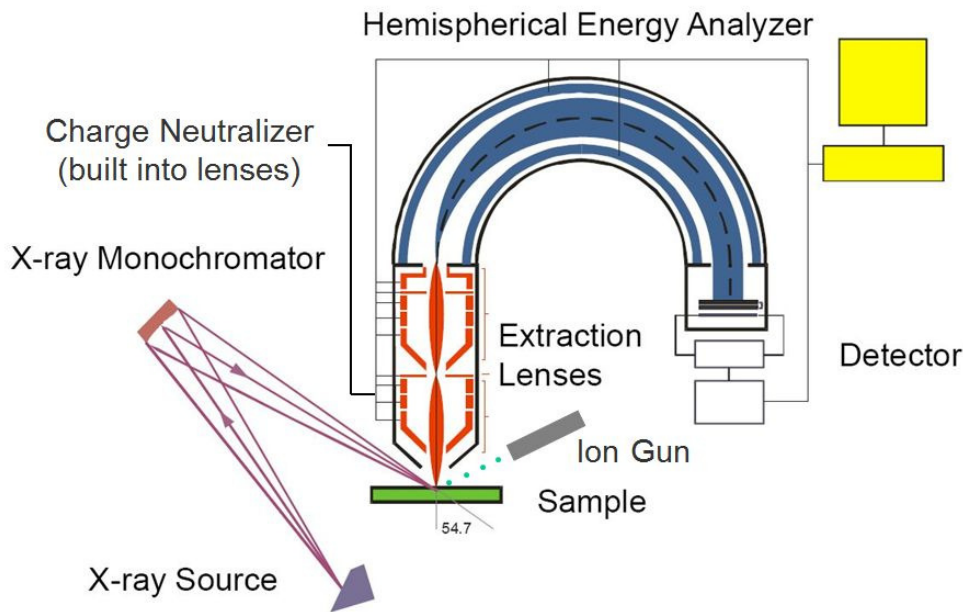# RRC-EMS: Surface Analysis

In addition to Electron Microscopy EMS provides access to a number of other surface sensitive techniques including X-Ray Photon Spectroscopy and Raman Spectroscopy.

X-Ray Photon Spectroscopy (XPS)

(Kratos AXIS-165)

*Schematic diagram of major components of an XPS system*

X-ray photoelectron spectroscopy, also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a surface-sensitive analytical technique that relies on the Photoelectric Effect explained by Einstein (Nobel Prize 1921). It is a semi-quantitative method (10-15% error) for obtaining composition and chemical state information. It is a surface-sensitive technique as the photoelectrons generally have low kinetic energies and hence short escape depths, and XPS experiments must be conducted in an ultra-high vacuum (UHV) environment ($10^{-9} – 10^{-10}$ Torr).

X-rays of a fixed wavelength irradiate the specimen and the energies of photoelectrons generated are measured using a hemispherical analyzer. Given that the binding energy of each element's orbitals is unique and is dependent on bonding environment, it can act as 'fingerprints' for identifying elements and chemical compounds. The photoelectrons that give rise to the spectra come from depths of 3-10 nm from the specimen surface.

XPS can identify all elements and compounds, except H and He. It can determine oxidation states (e.g. Ti^{3+} or Ti^{4+}) and identify types of chemical bonds (e.g. Si-O or Si-C). It is non-destructive for most materials with a detection limit of 0.1-1at%.

The RRC instrument has an argon ion gun which can remove material from the surface allowing a depth profile to be measured. The ion gun is particularly useful for removing contamination on the surface of the specimen revealing the specimen below. Angle resolved XPS can also give depth information to be acquired without sputtering the specimen.
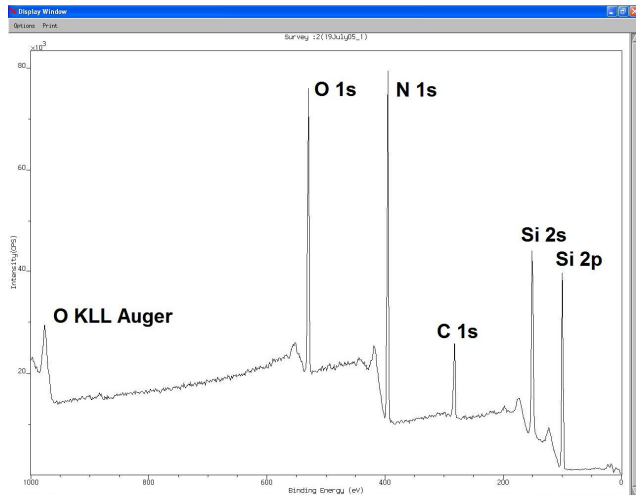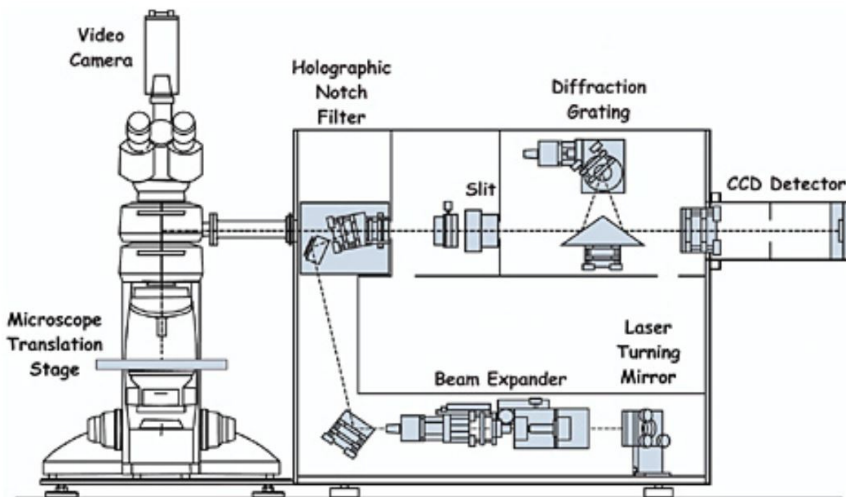
XPS survey spectrum from a silicon oxynitride surface
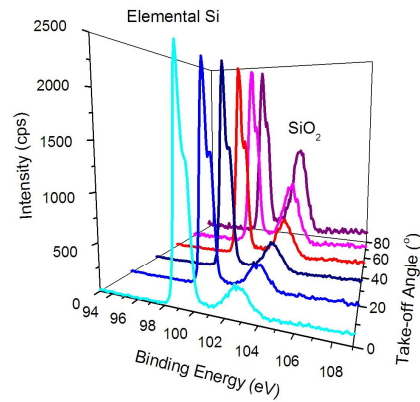
Angle resolved XPS of a silicon wafer (Si 2p) showing the oxidation of the surface

Raman Spectroscopy

(Renishaw inVia Reflex)

Schematic of a Raman Spectrometer

Raman spectroscopy (named after C. V. Raman) is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons shifted up or down in energy. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar, but complementary, information. The Raman Spectrometer in the EMS uses a 532nm Green laser or a 633nm Red laser.

Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light. The EMS Raman spectrometer employs edge filters for laser rejection, and CCD detector.

Raman spectroscopy offers several advantages for microscopic analysis. Since it is a scattering technique, specimens do not need to be fixed or sectioned. Raman spectra can be collected from a very small volume (< 1 µm in diameter); these spectra allow the identification of species present in that volume. Water does not generally interfere with Raman spectral analysis. Thus, Raman spectroscopy is suitable for the microscopic examination of minerals, materials such as polymers and

ceramics, cells and proteins. A Raman microscope begins with a standard optical microscope, and adds an excitation laser, a monochromator, and a sensitive detector (such as a charge-coupled device (CCD)).

Raman spectroscopy is used to identify molecules, since vibrational information is specific to the chemical bonds and symmetry of molecules. The fingerprint region for organic molecules is in the (wavenumber) range 500–2000 cm^{-1}. Raman active fibers, such as aramid and carbon, have vibrational modes that show a shift in Raman frequency with applied stress. Polypropylene fibers also exhibit similar shifts. The radial breathing mode is a commonly used technique to evaluate the diameter of carbon nanotubes. In nanotechnology, a Raman microscope can be used to analyze nanowires to better understand the composition of the structures.
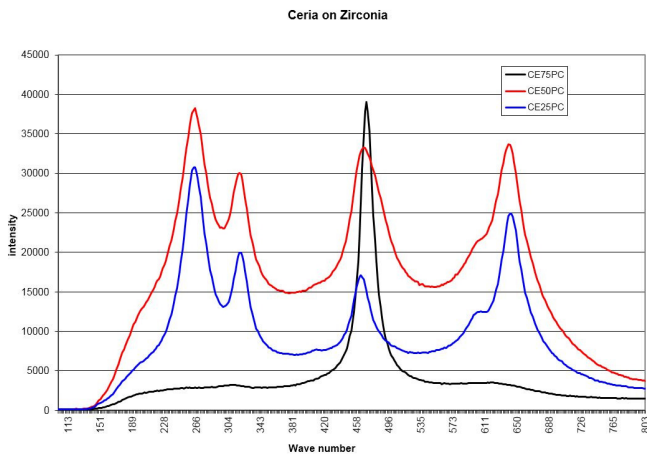
Raman spectra from three mixtures of Ceria and Zirconia. Ceria, which is cubic, only has one Raman peak (465cm-1), zirconia which is tetragonal has six peaks of which five are visible in the spectra (265, 313, 460, 600 & 645cm-1)
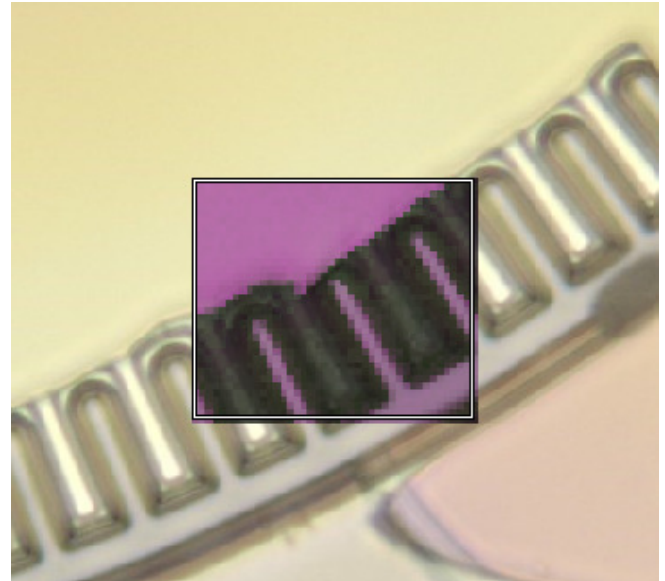
Streamline HR map of Si 520nm signal across a MEMS device collected in parallel giving drastically shorter total acquisition times compared to conventional Raman imaging. Map consists of data from 1512 spectra acquired in 160 seconds

The Surface Science Laboratory in Chemistry also operates an **Omicron variable temperature, ultra high vacuum scanning probe microscope (UHV-SPM)** which is located in EMS space and is available to other users. It was purchased in 2006 as a complete system and is equipped with a combined STM/AFM unit with a sample stage that permits images to be obtained, in principle, over the temperature range of 25 to 1500 K. The system is also equipped with a reverse view LEED instrument and with a metal evaporator. The STM uses a standard tube scanner with an electrochemically sharpened metal tip whereas AFM images are obtained with a needle-sensor based on a miniature quartz resonator. Sample introduction and tip exchange are achieved without breaking vacuum using a load lock system. The STM tip and AFM needle-sensor are readily interchangeable. The capabilities of the STM function of this instrument has been demonstrated by images of the Si(111)-7x7 surface obtained by the surface Science Group.