Surface Analysis of All Elements with Isotopic Resolution at High Ambient Pressures Using Ion Spectroscopic Techniques*

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SURFACE ANALYSIS OF ALL ELEMENTS WITH ISOTOPIC RESOLUTION AT HIGH AMBIENT PRESSURES USING ION SPECTROSCOPIC TECHNIQUES

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1. Introduction
We have developed a mass spectrometer capable of surface analysis using the techniques of secondary ion mass spectroscopy (SIMS) and mass spectroscopy of recoiled ions (MSRI). For SIMS, an energetic ion beam creates a “collision cascade” which results in the ejection of low kinetic energy secondary ions from the surface being analyzed [1]. The low kinetic energy SIMS ions are very susceptible to charge neutralization with the surface, and as a result, the SIMS ion yield varies by orders of magnitude depending on the chemical state of the surface [1]. SIM spectra contain elemental ions, and molecular ions. For MSRI, a pulsed ion beam induces a binary collision with the surface being analyzed and the surface species are recoiled into the forward scattering direction with a large kinetic energy [2,3]. The violence of the binary collision results in complete molecular decomposition, and only elemental ions are detected. The high kinetic energy MSRI ions are much less susceptible to charge neutralization with the surface than the low kinetic energy SIMS ions. In MSRI, the ion yield typically varies by less than a factor of ten as the chemical state of the surface changes — simplifying quantitative analysis vs. SIMS. In this paper, we will demonstrate that the high kinetic energy MSRI ions are able to transverse high pressure paths with only a reduction in peak intensity — making MSRI an ideal tool for real-time, in-situ film growth studies. The use of a single analyzer for both MSRI and SIMS is unique and provides complimentary information. Additional information regarding MSRI is provided elsewhere in this proceeding [4].

2. Experimental
The experiments reported here were performed in two ultra-high vacuum chambers that differed in: the primary ion source, the analyzer mounting geometry (θ, see Figure 1), and the diameter of the extractor/differential pumping aperture on the analyzer. The first system has an alkali (10 keV K+) ion source, the reflectron analyzer shown in Figure 1 and described in detail elsewhere [3,7] was mounted at a forward scattering angle (θ) of 74 degrees, and the hole in the pumping aperture/extractor was 3.0 mm in diameter. The second system utilizes an Atomica noble gas gun (10 keV Ar+), the reflectron analyzer was mounted at a forward
scattering angle of 60 degrees, and the hole in the pumping aperture/extractor was 1.0 mm in diameter. The second system also contains a Kaufman ion source and a multi-target assembly for thin film deposition. This system is optimized for real-time, in-situ film growth studies [2,5,6]. The pulsed ion beam current for both systems is less than 1nA, which corresponds to the arrival of ~ $10^9$ ions/s.

The MSRI-SIMS analyzer contains six main parts: an ion extractor/pumping aperture, lens assembly, high voltage field free drift region, reflectron stack, ion detector and a neutral (line-of-sight) detector [3,7]. For positive ion analysis, large (up to 15kV) negative potentials are applied to the extractor, the lens, and the field free drift region. The back ring potential is positive. For negative ion analysis, the potentials are inverted. Neutral species are not effected by the potentials used in the reflectron analyzer and shoot straight through to the line-of-sight detector. Additional details regarding this analyzer can be found elsewhere [3,7].

3. Results.

Figure 2 shows positive ion MSRI (top) and SIM (bottom) spectra obtained from a dirty Ge sample using system 1. These spectra were obtained back-to-back such that a direct comparison can be made between the MSRI and SIM spectra. The obvious difference between the MSRI and SIM spectra is the lack of molecular ions and molecular fragments in the MSRI spectrum, making the positive identification of D, N, Al, Cr, and Fe straightforward. In the SIM spectrum, one can not distinguish D from H$_2$, additionally, C$_x$H$_y$ fragments prevent the positive identification of N (vs. CH$_2$), O (vs. CH$_4$), Al (vs. C$_2$H$_3$), Cr (vs. C$_4$H$_4$), and Fe (vs. C$_4$H$_8$). Since the Be feature measured using MSRI and SIMS can not be attributed to any other species, a comparison of the Be MSRI and SIMS yields can be used to estimate the sensitivity of these two techniques. The observation that similar Be yields are obtained using both techniques indicates that the sensitivity for MSRI is comparable with SIMS. The resolution (peak FWHM) is similar for both MSRI and SIMS for peaks with only one component – for peaks with multiple components in the SIM spectrum (i.e., 14 amu, N and/or CH$_2$) the resolution decreases.

The data of Figure 2 indicate that MSRI and SIMS provides complimentary information. In MSRI, only elemental ions are detected whereas elemental ions, and molecular ions are detected in SIMS. SIMS therefore provides clues as the molecular species present on the surface. Elsewhere, it is shown that using the experimental conditions used here, the recoiled MSRI ions have kinetic energies up to ~1keV [3]. Since the MSRI ions leave the surface with a large kinetic energy, they are not as susceptible as SIMS ions to charge neutralization with the surface.
In MSRI, the ion yield varies by less than a factor of ten as the chemical state of the surface changes - simplifying quantitative analysis.

The second chamber was designed and optimized to allow for surface analysis using the ion spectroscopic techniques at high ambient pressures [2,5,6]. This is accomplished by placing differential pumping apertures close to the sample for both the incident (primary) ion beam [2,5,6] and the outgoing (recoiled surface species) ion path in order to minimize the high pressure path length traveled by the ions. Turbo molecular pumps are used to differentially pump these regions.

In Figure 3 we plot the pressure in the MSRI housing (measured using a nude ionization gauge) as a function of chamber pressure (measured using a Granville Phillips Stabil Ion Gauge) when molecular oxygen is added to the main chamber (open data points).

Figure 2. MSRI and SIM spectra obtained from a dirty Ge sample.

These data indicate that the 1mm diameter pumping aperture/extractor located on the analyzer is able to provide a pressure differential of up to 3 orders of magnitude. The H (filled circles), C (filled inverted triangles), and Pt (filled squares) MSRI intensities measured using a dirty Pt foil sample at various pressures of molecular oxygen are plotted in Figure 3. The fact that the slopes for each of these elements is identical indicates that the oxygen background is attenuating the intensities of these three elements equally; the oxygen is not reacting with the surface or the surface contaminants. It is important to note that at high ambient pressures only the peak intensities are attenuated. The MSRI peaks do not move, nor do they broaden at high ambient pressures as illustrated in more detail elsewhere [7]. At chamber pressures up to ~ 2.7x10^-3 Torr of molecular oxygen MSRI spectra revealing the major surface components could be obtained with a data acquisition time of 20 sec. at higher pressures the signal intensity approached zero.

The attenuation of both the incident ion beam and the outgoing beam due to gas phase scattering can be obtained from: 

\[ I = I_0 e^{-\frac{\langle \sigma \rangle (d_1 + d_2)}{kT}} \]

which can be rewritten as: 

\[ \ln\left(\frac{I}{I_0}\right) = -\frac{\langle \sigma \rangle (d_1 + d_2)}{kT} \] 

where \( I \) is the MSRI intensity obtained at a pressure (p), \( I_0 \) is the MSRI intensity obtained under high vacuum conditions (\( p_0 \)), \( d_1 \) and \( d_2 \) are the high pressure path lengths traveled by the primary ion beam (22.8 mm) and the exiting ion beam (49.3 mm) respectively, \( k \) is Boltzmann’s constant, \( T \) is the temperature, \( \Lambda \) is the slope obtained from a semi-log plot of intensity vs. pressure (Figure 3), and \( \langle \sigma \rangle \) is the weighted collision cross...
section \(<\sigma>=d_1\sigma_1+d_2\sigma_2/d_1+d_2\) where \(\sigma_1\) is the collision cross sections for the primary ion beam and \(\sigma_2\) is the collision cross section for the exiting beam [6]. \(\sigma_1\) was measured \((\sigma_1 = 6.62x10^{-20} m^2)\) by placing a line of sight detector 180° from the primary ion beam, removing the sample from the chamber, and recording the primary ion pulse at different molecular oxygen pressures [6]. The values of \(\Lambda\), \(<\sigma_1>\) and \(\sigma_2\) are listed below for H, C, and Pt.

<table>
<thead>
<tr>
<th>Element</th>
<th>(&lt;\sigma_1&gt;) (m²)</th>
<th>(\sigma_2) (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.28 x 10⁻¹⁹</td>
<td>4.20 x 10⁻¹⁹</td>
</tr>
<tr>
<td>C</td>
<td>1.43 x 10⁻¹⁹</td>
<td>5.06 x 10⁻¹⁹</td>
</tr>
<tr>
<td>Pt</td>
<td>1.14 x 10⁻¹⁹</td>
<td>3.42 x 10⁻¹⁹</td>
</tr>
</tbody>
</table>

The cross sections reported here correspond to signal collected in a very small solid angle and do not necessarily correspond to the total scattering cross section. It is worth noting that the collision cross section measured for the Ar⁺ primary ion beam in a molecular oxygen environment in this work \((\sigma_1 = 6.62x10^{-20} m^2)\) agrees well with the Ar⁺/Ar momentum transfer cross section of 2.9x10⁻¹⁹ m² reported in the literature [8].

4. Summary
It has been demonstrated that the analyzer reported here can be for the complementary techniques of MSRI and SIMS. MSRI provides quantitative elemental analysis while SIMS provides clues as to the molecular species present on the surface. It has also been demonstrated that MSRI analysis is possible at high ambient gas pressures allowing for surface analysis of all elements with isotopic resolution under film growth conditions.

References