Chapter 2

A new time-of-flight instrument capable of in-situ and real time studies of plasma-treated surfaces

Abstract: We introduce a new time-of-flight (TOF) instrument that has been constructed to study the dynamics of plasma-surface interactions. The instrument uses a well-defined ion beam at a grazing incidence as a surface probe. Real-space and real-time profiles of scattered particles are created from the output of a position-sensitive detector. The set-up permits the recording of energy and angular distributions of scattered ions and neutrals. Changes in energy and angular distribution as a function of time can be used to monitor real-time and in-situ the interaction between plasma and surfaces. The performance of the set-up is tested and illustrative spectra for Ar$^+$ scattering from Si (100) surfaces subject to different pre-treatments are shown.

2.1 Introduction

Plasma etching, plasma-enhanced chemical vapor deposition and plasma/wall interactions generally involve a variety of physical and chemical processes at surfaces [1-3]. The complex and highly coupled nature of plasma-surface interactions makes the study of dynamics difficult in a plasma environment and as a consequence the mechanisms of the processes are unclear. Grazing-incidence ion scattering has been used to determine surface structure and, in particular, the geometry of first layer adsorbate atoms [4]. It may prove a good technique for monitoring plasma-surface processing in real-time. To our knowledge, there are no groups employing such a combination in a single apparatus. Motivated by this demand, we have built an experimental set-up designed to investigate plasma-surface interactions in-situ and in real time. It utilizes Time-Of-Flight Low Energy Ion Scattering (TOF/LEIS) and Direct Recoil Spectroscopy (DRS) to characterize adsorbed species and to monitor the electronic structure and topography of the sample surface [5]. These techniques are emerging as viable surface analysis tools with particular strength for in-situ monitoring during low-pressure thin film processing [6]. TOF/LEIS can be very useful for determining electronic structure and surface composition through charge-exchange analysis, and long-range crystalline order through scattering profile analysis. Detection of recoiled atoms provides a means of monitoring low concentration of adsorbed species on the surface.
2.2 The In-Situ Spectrometer System

The new system is constructed from a combination of custom-made and commercially available components. It is shown schematically in figure 1 and consists of several distinct elements: (a) main chamber; (b) preparation chamber; (c) pulsed ion beam source; (d) cascaded arc plasma source; (e) the position-sensitive detector (PSD) for scattered particles.

(a) Main Chamber: In the main chamber, where the base pressure is in the $10^{-10}$ mbar range with the plasma off [7], the sample is mounted on a three-axis manipulator in the centre of the chamber [8]. The position of the sample is controlled by computer. The sample manipulator can be rotated through $360^\circ$ around the vertical axis of the chamber (polar rotation). In addition, $360^\circ$ spin rotation of the sample around the surface normal axis can be obtained (azimuthal rotation). X- and Y- translations of the sample holder with respect to the centre of the chamber have a travel of ±15mm with an accuracy of 0.1 mm. The manipulator has a Z-translation of 200 mm. The sample can be tilted $90^\circ$ backward (sample facing up) and $20^\circ$ forward (sample facing down).

The bulk of the tools available in the main chamber are on a single horizontal measurement plane. This plane contains the plasma and ion sources, the multi-channel plate (MCP) based detection system, the exchange point for the preparation chamber, a sputter gun, and a quadrupole mass spectrometer (QMS). The QMS is supplied by ABB-Extrel (type MEX060 2.9C3/P8: ¾ inch (19.05 mm) rods, 2.9 MHz 300W Q-head, off-axial cross-beam ionizer in pulse counting mode). It is mounted on the lid of the vacuum system with the ion extraction region centered in the measurement plane. The lid has a differentially-pumped system that allows it to be rotated while maintaining UHV. Consequently, the ion extraction region of the QMS can be rotated around the measurement plane. The QMS can be used to characterize the plasma source (species and energy distribution) directly and to detect plasma particles scattered from the surface.

(b) Preparation Chamber: In the preparation chamber (base pressure $5\times10^{-11}$ mbar), samples can be cleaned by ion sputtering and/or annealing to more than 1000K. The cleanliness of the surface can be characterized by X-ray photoelectron spectroscopy (XPS). The surface order can be monitored by low energy electron diffraction (LEED). This chamber can hold multiple samples at one time. The samples can be transferred by a linear translator, under vacuum, to the three-axis manipulator in the main chamber.

(c) Ion Source: An ion source, oriented at a low incident angle with respect to the plasma-facing surface, is used for LEIS and DRS studies [9]. The ion beam is produced in a Colutron ion source with a low energy spread (<0.2 eV) [10]. Ions can be created with energies up to 4keV. A Wien filter (Colutron model 600-B) allows the removal of undesired ions from the beam. A $10^\circ$ bend in the ion beamline eliminates neutrals and light originating from the source. The selected ions are focused using a series of einzel lenses and accelerated or decelerated to achieve the required energy.

TOF measurement can be performed by pulsing the ion beam with a high-resolution electrostatic chopper. This chopper consists of two plates pulsed symmetrically by a low voltage pulse generator, producing pulse widths down to ~25ns. In this way, the beam is rapidly swept in front of the injection aperture at the end of the beam line. The pulse generator can be operated a pre-determined frequency (10kHz-10MHz), or through an external trigger source. Thus, the START time (t0) is well defined and an associated trigger time is sent to the acquisition chain.
(d) **Plasma Source:** As shown in figure 1, the plasma beam is created in a differentially pumped beam line. The plasma source is a cascaded arc [11]. A current is drawn from three cathodes to the anode nozzle through a channel with diameter of typically few mm and a length of several cm. The channel consists of a stack of isolated water-cooled copper plates. The plasma beam can be modulated by means of a mechanical chopper. The ion beam pulse can be synchronized to this chopping frequency. Hence, if the presence of the plasma is cumbersome for the ion scattering, the scattering can be performed when the plasma is not exposed to the surface. Additionally, TOF studies of the energy distribution of the arc output and scattering plasma particles can be performed using the rotatable QMS.

(e) **Position-sensitive Detector:** In the previous sections, we outlined the main vacuum system in detail. In this apparatus the central measurements are based on position-sensitive detection of ions and neutrals. The detector is capable of real-time and in-situ two-dimensional imaging.

The configuration of the ion scattering/detection system can be seen in figure 1. On the lower side, the incident beam is injected at grazing incidence through a small aperture. On the opposite side, the scattered projectiles are collected by a position sensitive detector (PSD). The center of the PSD is positioned in the measurement plane. The detector is mounted on an XYZ translator, allowing for fine-tuning of its position. The whole system is built on a CF250 flange. The detector can be mounted in one of two fixed geometries, corresponding to...
Figure 2: Schematic representation of the data acquisition system. The outputs of the two choppers are converted to ECL. The three charge outputs of the detector are amplified by a charge preamplifier and sent to a charge-to-time converter (QTC). The STOP time signal (T) is extracted from the second micro-channel-plate (MCP), amplified by a preamplifier, and sent to a fast discriminator. This signal is converted to ECL and used to trigger the multi-hit time-to-digital converter (TDC). This also provides the COMMON STOP (channel 0) for the acquisition. T is also used to trigger the integrating gate for the QTC. All of the MQT300A outputs are sent to TDC to be maximum scattering angles of 8° and 16°. Deflecting plates with a 2 mm wide slit can be moved in front of the detector to allow determination of the charge fraction of scattered and recoiled particles.

Several types of position sensitive detector are available that use different methods of position determination. We utilize a wedge-and-strip based detection system supplied by Roentdek [12]. The computer-based data acquisition system was developed in this laboratory and is schematically outlined in figure 2.

To get sufficient amplification, a stack of two MCPs is employed. They have an active diameter of 40 mm and a thickness of 1 mm. They are mounted in front of a ceramic disk with a germanium layer on the side facing the MCP and with wedge, strip and meander anodes on the opposite side. The input of the first MCP is biased at a voltage of −1500 V. A grid biased at a small positive potential is placed in front of the PSD. Its main function is to repel low energy positive particles originating from the plasma source when the plasma is injected into the main chamber. The impact of a single particle on the front MCP results in a charge pulse at the output of the back MCP. This is collected by the germanium layer, which is biased at a small positive potential with respect to the back of the MCP stack. This charge pulse induces a current in the electrically isolated anodes on the opposite side of the ceramic disk.

Three charge signals are collected from the wedge (Qw), strip (Qs), and the meander (Qm) anode contacts, amplified and sent to a wide range, high precision charge-to-time converter (LeCroy MQT300A). The position of a particle arriving at the first MCP is
determined by comparing the relative amounts of charge collected from wedge, strip and meander. The impact time signal (STOP time, T) is derived from the charge pulse on the second MCP via a built-in UHV compatible isolation transformer and is then amplified by a charge sensitive amplifier (ORTEC 9306 1 GHz Preamplifier).

The STOP time signal and the three charge signals are sent through a 16-twisted pair flat cable to a multi-channel time-to-digital converter (TDC 767 by CAEN) located in a Versa Module Europa (VME) crate. The TDC records the arrival time of the 64 channels with a 0.8 ns resolution during a set time window. The digitized signals ($Q_w$, $Q_m$, $Q_s$, $t_0$ and $T$) are transferred to a first-in-first-out (FIFO) buffer memory in the TDC board, allowing a maximum accumulation of 32 Kwords. The data in the buffer memory can be read out to a host computer via VME (as single data, block transfer and chained block transfer) in a completely independent way from the acquisition itself.

The position of the detected particles is encoded by the three charge signals and can be easily transformed from the digitized signals into Cartesian coordinates ($x, y$) by the following algorithm:

$$x = \frac{Q_s}{Q_s + Q_w + Q_m}, \quad y = \frac{Q_w}{Q_s + Q_w + Q_m}$$

### 2.3 Experimental Results

A number of measurements involving interactions of low energy ions with surfaces were performed to test the new system. Here we present data obtained for scattering of Ar$^+$ at grazing incidence from Si (100) surfaces to illustrate the performance that can be obtained.

#### 2.3.1 Ar$^+$ Scattering at Grazing Incidence

The sample is placed such that it partially intersects the ion beam. The spot at the bottom of the image arises from the part of the direct beam that misses the sample. The spread image is caused by the scattered particles. In the profile, the horizontal direction represents the azimuthal distribution of scattered particles. The vertical direction represents the polar distribution of scattered particles. Consequently, impacts on the MCP appearing directly above the direct-beam spot represent atoms scattered in-plane (no azimuthal scattering). Impacts to the left and right of this vertical line are due to atoms which are scattered out-of-plane (i.e. experience both polar and azimuthal deflection). Since the MCP plates are circular, the PSD represents the base of a scattering cone. All particles that are scattered within this cone will be detected by the PSD provided the impact initiates an electron cascade. The combination of the MCP active radius and the sample detector separation give a cone half-angle of $\sim 3^\circ$ (i.e. the PSD can detect a 6$^\circ$ spread of scattered particles, excluding edge effects).

During a typical scattering experiment, the acquisition system stores the time and magnitude of several key parameters. The main quantifies acquired are the chopper trigger (START time), the charge pulse on the second MCP (STOP time) and the magnitude of the three charges collected on the wedge-and-strip anode. By correlating the data, a flight-time can be assigned to each individual impact registered on the wedge-and-strip anode. Hence, TOF distributions of the scattered particles can be derived from the xy distributions. For example, post-acquisition analysis allows a TOF distribution to be constructed for particles impacting on strips associated with the different polar scattering angles shown in figure 3. The resulting TOF spectra are converted to energy loss spectra as shown in figure 4.
Figure 3: Example of the measured xy distribution for 2 keV Ar+ scattering from Si (100) at an incidence angle of 1.75° with respect to the surface plane. The lighter regions represent higher intensity. The distribution in x plane corresponds to the azimuthal distribution. The distribution in y plane corresponds to the polar distribution. The polar angles given are only accurate for $\phi_s = 0^\circ$. The angles indicated on the figure refer to the midpoint in the y-plane of the corresponding strip.

Unsurprisingly, particles scattered through the largest angles have undergone the largest energy loss. In addition, the width of the energy loss distribution and the length of the low energy tail increases for larger scattering angles.

The energy loss as a function of the scattering angle is plotted in figure 5. The anticipated loss based on a single binary collision model is also shown in the figure. The data points for the energy loss are based on the peak values of the energy loss distributions shown in figure 4. The energy loss observed is far greater than can be accounted for on the basis of simple elastic collision losses. The discrepancy can be attributed to additional inelastic energy loss processes and defects in the surface during the close interaction of the projectile with the surface atoms. Careful measurement of the energy loss distributions combined with theoretical modeling should provide a means of tracking electronic structure changes during plasma processing of surfaces.

2.3.2 Ar$^+$ Scattering and Recoiling From contaminated Si (100)

A TOF spectrum obtained from a partially cleaned Si (100) surface is shown in figure 6. From the figure, similar flight times are observed for Ar and recoiled particles, indicating that all final velocities are very similar. Scattered Ar and recoiled Si peaks are observed. The
A new time-of-flight instrument

**Figure 4:** Energy loss spectra extracted from figure 3 for 2 keV Ar⁺ scattering from Si(100) surface at an incidence angle of 0.75° with respect to the surface plane.

**Figure 5:** Energy loss spectra based on the peak values of the energy loss distributions shown in figure 4.

**Figure 6:** TOF spectra obtained by scattering 3 keV Ar⁺ from a contaminated Si (100) surface at an incidence angle of 8° with respect to surface plane. (Inset: details of the contaminants).

**Figure 7:** TOF spectra obtained by scattering 3 keV Ar⁺ from an annealed (smooth) and a sputtered (rough) Si (100) surface at an incidence angle of 8° with respect to surface plane.

Emergence of recoiling peaks from carbon, oxygen and hydrogen are due to contamination of the surface. At grazing angles, the incident projectile spends a relatively long time close to the surface. Consequently, ion scattering is very sensitive to contaminants on the surface. The ability to detect hydrogen atoms illustrates that the new system may provide a means to characterize the concentration and adsorption sites of hydrogen atoms on surfaces. Hydrogen deposited by a Ar/H plasma from the cascaded arc could be detected in this way.
2.3.3 \textit{Ar$^+$} Scattering from rough Si (100) surface

The width of the distribution on the PSD and the energy loss profile can be used to monitor the surface smoothness. For example, the width of the TOF distribution shown in figure 7 increases after sputtering by 600eV Ar$^+$ at normal incidence angle. The smooth curve is the total TOF curve (based on T taken from the second MCP) for Ar scattered from a recently annealed Si (100) surface. After sputtering, the observed TOF distribution is significantly broader. In addition, both the leading edge and the peak maximum have shifted corresponding to an increase in the energy lost during the collision.

The above results indicate that the new system should be capable of monitoring structural changes on surface during plasma processing. For example, monitoring the rate of change of the disorder parameter and the degree of reconstruction on the surface.

2.4 Conclusion

A new TOF instrument based on the low energy ion scattering has been designed and constructed. The system allows grazing scattering of atomic or molecular ions from surfaces and the monitoring, real-time and in-situ, of the reaction dynamics of plasma with surface. The preliminary experiments show that this instrument allows surface composition analysis, studies of electronic interaction between projectiles and surface atoms and surface topography.

References