Mass and energy spectrometry of processing plasmas

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Introduction

Plasmas contain complicated mixtures of charged and neutral species. It is clearly important for the design and control of any surface engineering process that the user has as much information as possible about the constituents of a given plasma, about how the behaviour of these constituents changes as the electrical conditions of the plasma are varied, and about the interactions that occur between the plasma constituents and the target and substrate surfaces that are exposed to them. We will outline the application of a mass/energy analyser in diagnostics of a range of processing systems.

The measurements to be described were made using a Hiden mass/energy spectrometer, the most common form of which is shown in figure 1. The main parts of the instrument are its ion-sampling region, the internal ionisation source (which is turned off when sampling ions from a plasma), the cylindrical, electrostatic energy analyser, the quadrupole mass selector, and the channeltron ion detector and pulse counting circuitry. Other forms of the spectrometer are also in use, the most recent being that in which the analyser is incorporated in the Hiden HPR60 instrument which is designed for sampling from plasmas operated at atmospheric pressures.

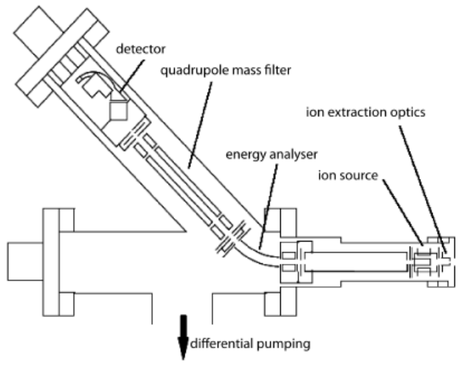
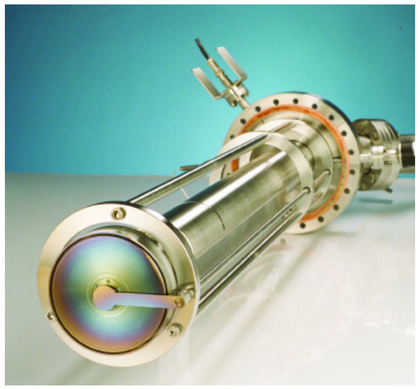


Figure 1: *Hiden mass/energy analyser*

Experimental investigations



a) Neutral species.

The simplest measurements for any reactor are the mass-identification of the neutral species present, firstly in the absence of a plasma and then with the plasma operating. Fragmentation of the working gas and the generation of new species in the plasma or through its interaction with the walls of the reactor or target and substrate surfaces are readily identified. To improve the accuracy of the measurements, it is sometimes advisable to arrange for the sampling to be done via a doubly or triply differential pumping geometry incorporating a 'chopper' arrangement to improve the discrimination between the required plasma signal and competing background effects. (1,2).

It is possible to add considerably to the information derived about the neutral species produced in a plasma if the energy of the electrons used in the source of the mass spectrometer can be varied. It is then possible to study, usually near the threshold ionisation energy, changes in the populations of particular ions generated in the source as the sampled neutral population is altered by changes in the plasma conditions. Figure 2 shows typical data from a Hiden HPR60 instrument used to examine a plasma needle discharge operated in a mixture of air and helium (2).

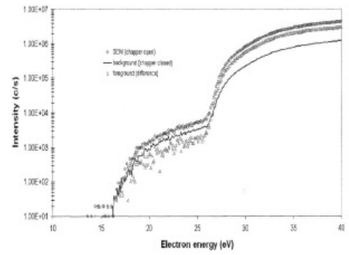


Figure 2: *Ion signals as function of electron energy in mass spectrometer source.*

Since many of the processing gases, particularly for semi-conductor etching and the deposition of DLC and optical coatings, are electro-negative, (oxygen, sulphur hexafluoride, methane, and carbon dioxide, for example), it is often useful to operate the ionisation source of the mass spectrometer to produce negative ions, (3,4,5). Even if the dominant negative ion formed from two different parents is the same, as for instance in the case of carbon dioxide and nitrous oxide, both of which give O- as their dominant negative ion, the variations in production of the ion with electron energy are very distinctive.

b) Ion species.

For the identification of the positive and negative ions produced in a plasma, and arriving at the surface of a substrate, the ionisation source of the Hiden analyser is turned off and the plasma ions are directly sampled. For mass-selected ions it is then possible to determine their energy distributions, which are well known to strongly influence the adhesion, hardness, and other properties of deposited films such as titanium nitride, titanium oxide, diamond-like carbon, and other compounds. It is often helpful if the measurements of the relative abundance and energies are made on ions sampled at a point which is directly equivalent to one on the substrate being processed. This can be done by incorporating the sampling orifice of the mass/energy analyser in the surface of the substrate holder, or in the surface of another electrode if this is in a directly equivalent electrical condition.

As an example, figure 3 shows the energy distributions measured for N^+ions arriving at the cathode of a DC plasma when it was maintained at potentials of between –600 and –750V.

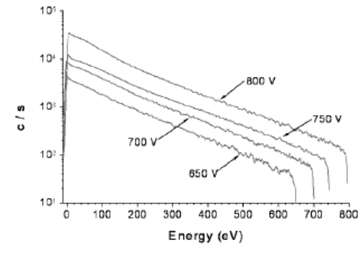


Figure 3: *Energy distributions of N+ from a nitrogen discharge for cathode voltages of 650, 700, 750 and 800 V, obtained at a pressure of 50 Torr.*

Variations in the relative abundance of particular ions in a reactor, and their energies, with changes in the plasma conditions can be correlated with the resulting changes in the properties of a deposited film. For example,data for a titanium nitride deposition system employing a combination of a D.C. magnetron and an inductively-coupled (ICP) source, used to increase the amounts of N+ and N2+, showed (6) that the addition of a small amount of helium to the I.C.P source increased the nitrogen ion signals appreciably and gave a positive correlation with improvements in the tribological properties of the TiN films. Similar experiments for the growth of optical-quality titanium dioxide films were also reported

It is increasingly common to operate magnetron deposition reactors in a variety of pulsed modes. Recent measurements. by Lin et al.(7) using a Hiden mass/energy analyser attached to a dual magnetron system for the deposition of CrAlN films have shown how the ion energy distributions in such systems are strongly influenced by the exact waveforms of the pulsed voltages applied to the two magnetrons. Figure 4 shows a sample of the energy distributions measured. The distributions, and their correlation with the properties of the deposited films, are described further in the paper TF1-2 by Lin et al. at this meeting. Other work which includes time-resolved measurements with a Hiden instrument for a pulsed magnetron reactor has been described by Bradley and his collaborators (8).

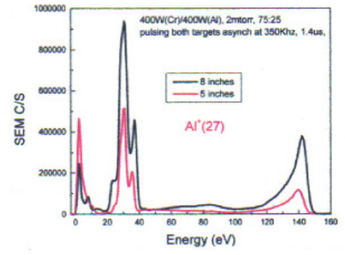


Figure 4: *Ion energy distributions for A1+ as a function of probe position.*

The most recent development in magnetron deposition has been that of so-called HIPIMS (high power impulse magnetron sputtering) systems in which the emphasis is on creating large numbers of ionised metal ions in the vicinity of the magnetron. Various groups are again examining the ion populations and their energy distributions with Hiden mass/energy analysers. Ehiasarian et al. (9,10) have shown their HIPIMS reactor to deliver between four and five times more reactive titanium and nitrogen ions than a more conventional magnetron system with energies around three times higher. Vicek et al (11) have found the ion flux to their substrate to consist of up to 92% copper ions with energies up to 45eV relative to ground potential. Correlation of the energy distributions with the waveforms of the voltages applied to the magnetron electrodes help considerably in the interpretation and design of the operating conditions.

Conclusions

It is clear that the measurement of mass and energy distribution spectra for the ions and neutral species present in a wide range of processing plasmas is of considerable assistance in improving the design and operation of reactors. The Hiden mass/energy instrument has found wide-spread use for such measurements and in conjunction with a molecular beam sampling system is now being applied to plasmas operated at atmospheric pressures.

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