Plasma Analysis
EQP Application Note 229

EQP
Radicals sampled from a plasma

Summary

The measurements described in this note were carried out using an EQP instrument to examine the radicals produced in a plasma generated in a small test cell by a capacitively coupled 13.56MHz supply. The electrodes of the discharge cell were a 5cm diameter electrode and the front electrode of the EQP instrument. A glass cylinder was used to help confine the discharge between these two parallel surfaces.

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Method

The front orifice plate of the EQP was grounded and sampling was carried out through its 100 µm orifice. A positive potential of around 50 volts was applied to the 'Extractor' electrode placed behind the orifice plate to prevent positive ions generated in the plasma from entering the EQP system. Neutral species produced in the plasma entered the EQP from the test cell and were ionised in the instrument's electron-impact ionisation source. The data presented here are the ionisation efficiency curves for the various species examined.

The present measurements were obtained using CCl_2F_2 as the test gas. The ions produced in the EQP's ionisation source from the radicals generated in the plasma were:

CF^+, Cl^+, CF_2^+, CF_3^+ and $C\,Cl\,F_2^+$

The gas pressure in the plasma cell was .04 mbar and the RF-driven electrode acquired a self-bias of -100 volts.

Figure 1 shows the data for M = 50, i.e. for the production of CF_2^+ ions.

Two features are readily observed:

- the additional ions produced for electron energies of between 14 and 20 eV when the plasma is on, and
- the lower signal obtained at high energies when the plasma is on.

The 'plasma off' curve is presumed (at this stage) to correspond to the process

$$e + CCl_2F_2 \rightarrow CF_2^+ + ? \qquad (1)$$

while with the plasma on, additional CF_2^+ ions are produced by

$$e + CF_2 \rightarrow CF_2^+ + 2e \qquad (2)$$

and/or

$$e + CClF_2 \rightarrow CF_2^+ + Cl^- + e \qquad (3)$$

where the CF_2 and $CClF_2$ are produced in the plasma. (There may be other possible reactions also).

The fact that the CF_2^+ signal is lower at high electron energies, with the plasma on, than with the plasma off is presumably attributable to the depletion of the CCl_2F_2 in the gas sampled from the plasma chamber when the plasma is running. The two curves should perhaps be normalised to each other at, say, 40 eV.

Figure 2 shows data for M = 69, i.e. for the production of CF_3^+ ions. There is clearly a very large difference in the signals recorded with the plasma on and off. This is not surprising - the signal recorded with the plasma off is essentially noise since the process

$$e + CCl_2F_2 \rightarrow CF_3^+ + ? \qquad (4)$$

seems very unlikely to occur in the EQP source. On the other hand, with the plasma on, CF_3 radicals can be produced which when ionised in the EQP source give CF_3^+ ions.

$$e + CF_3 \rightarrow CF_3^+ + 2e \qquad (5)$$

It should be noted that CF_3^+ ions are known from work on positive ion sampling to be produced in the plasma, but these ions are excluded by the +50 volts on the extractor. The M = 69 ions seen in figure 2 must have been produced by ionisation of neutral fragments. Fragments other than the CF_3 shown in reaction (5) cannot be excluded at this stage.

Figure 3 shows data for M = 31 (CF^+). Clearly large amounts of the CF radical are sampled from the plasma, which in this case was running in a .05 mbar atmosphere, with a self-bias for the driven electrode of -200 volts.

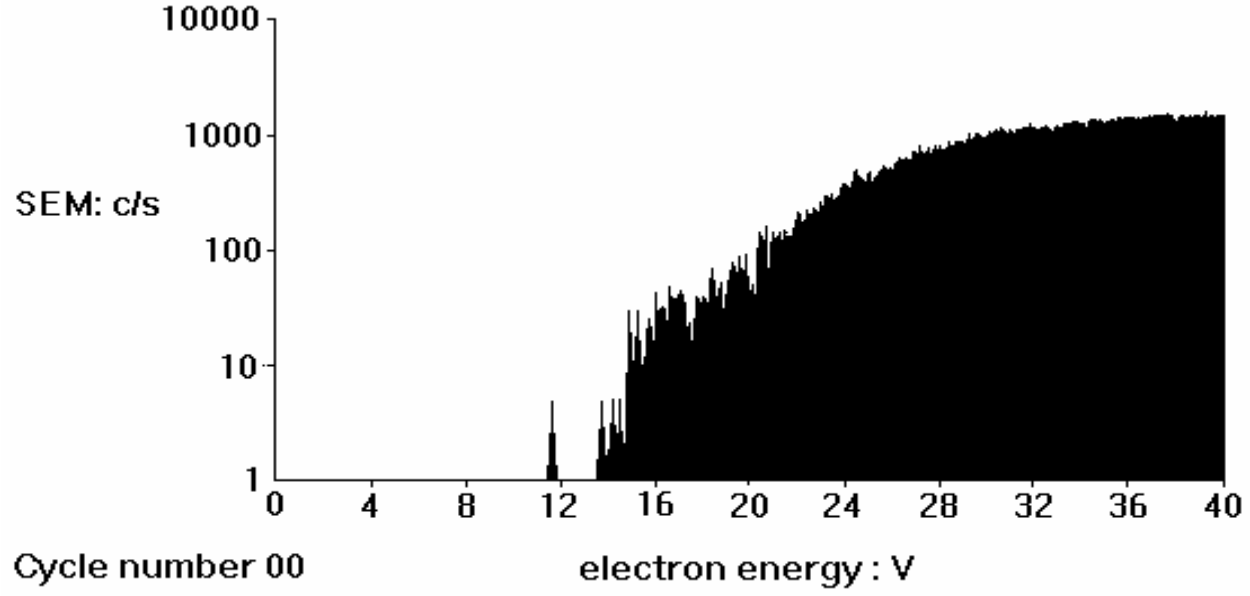
The data for CF^+ with the plasma on are re-plotted on a logarithmic scale in figure 4. Comparison with the corresponding data obtained with the plasma off suggests that the region between electron energies of 14 and 20

eV should be examined carefully for both ‘plasma on’ and ‘plasma off’ conditions.

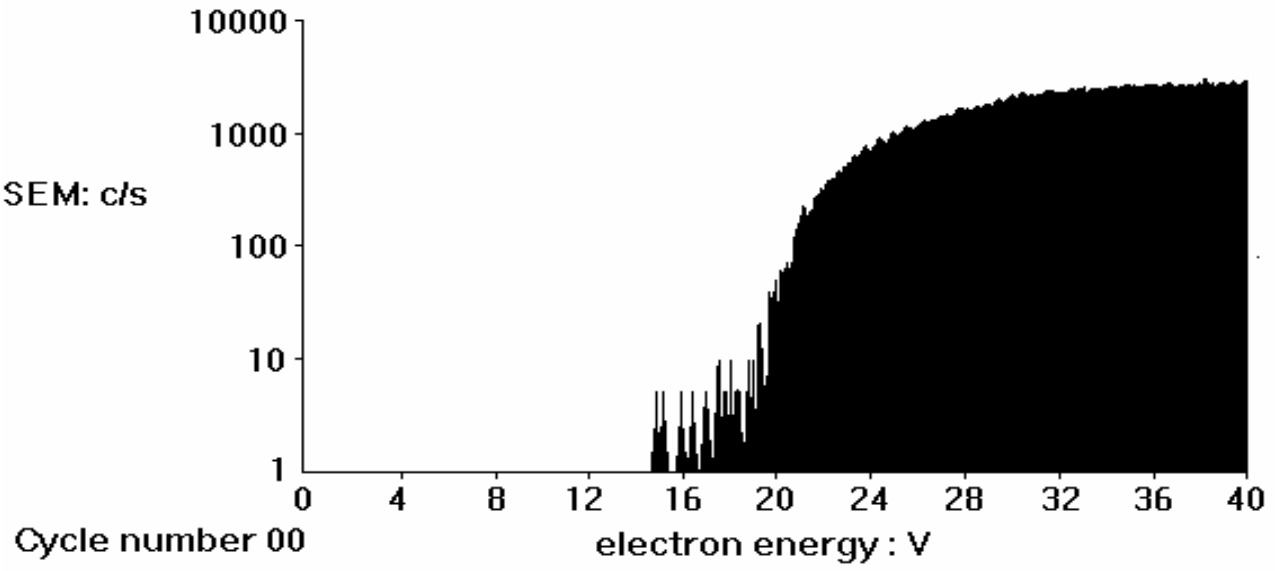
Figure 5 shows data for M = 85 ($CClF_2^+$). There appears to be a marked difference (≈ 3 eV) in the threshold onset energy which requires further study. As was the case for M = 50, at higher electron energies the recorded signal was higher for the ‘plasma off’ conditions. This is presumably due to depletion of the parent CCl_2F_2 when the plasma is on.

Conclusions

The above data show how the EQP may be used to examine the radicals produced in plasmas. The detailed interpretation of the ionisation efficiency curves can lead to information on both the abundance of particular radicals in the plasma and on their state of excitation. The variation of the ionisation efficiency curves with the plasma conditions would clearly be of interest if the radicals involved are expected to play a major part in the surface modification process for which the plasma is intended.

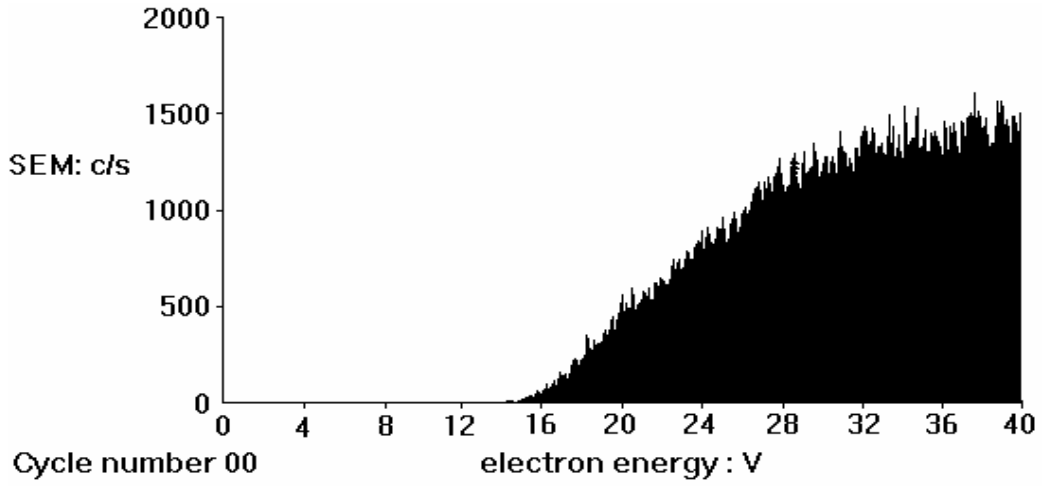


Plasma on

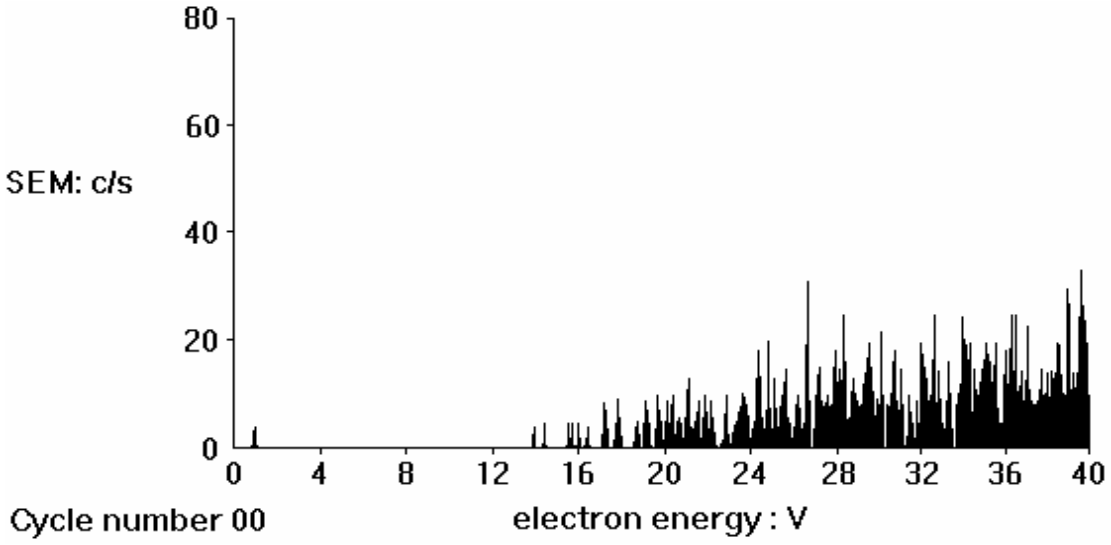


Plasma Off

Figure 1



Plasma On



Plasma Off

Figure 2

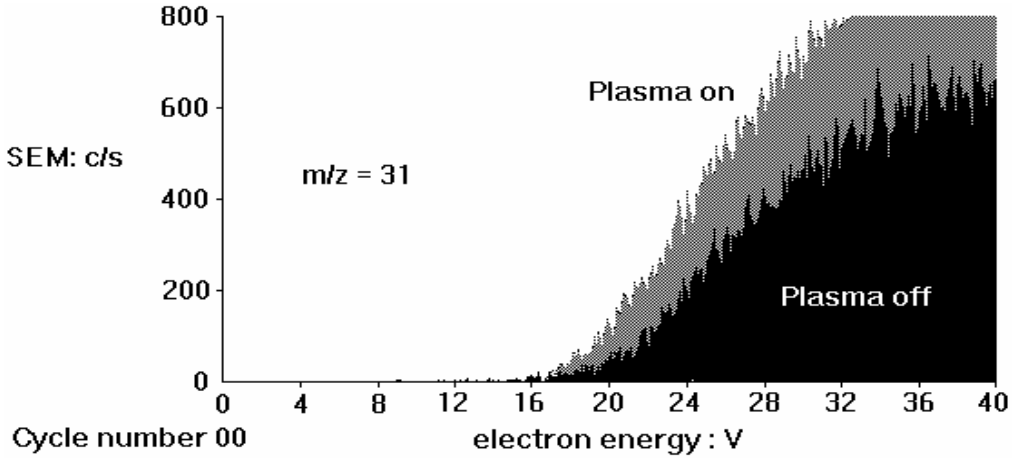


Figure 3

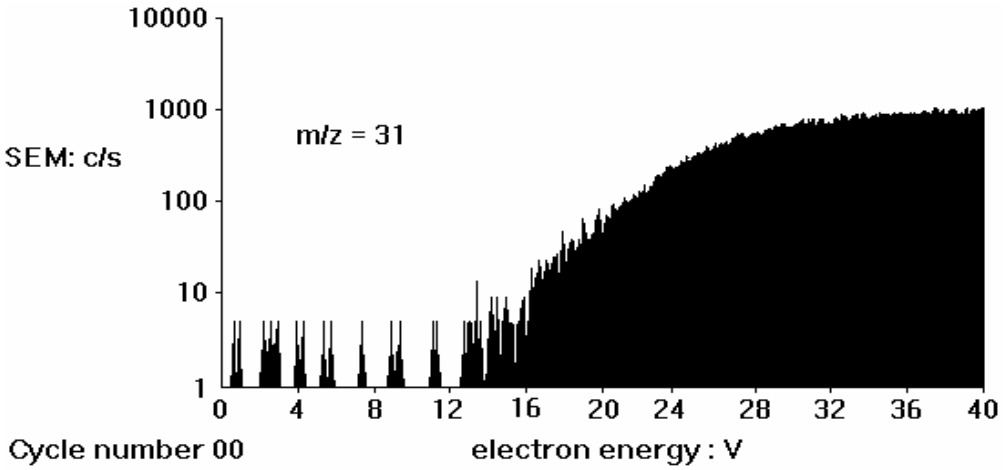


Figure 4

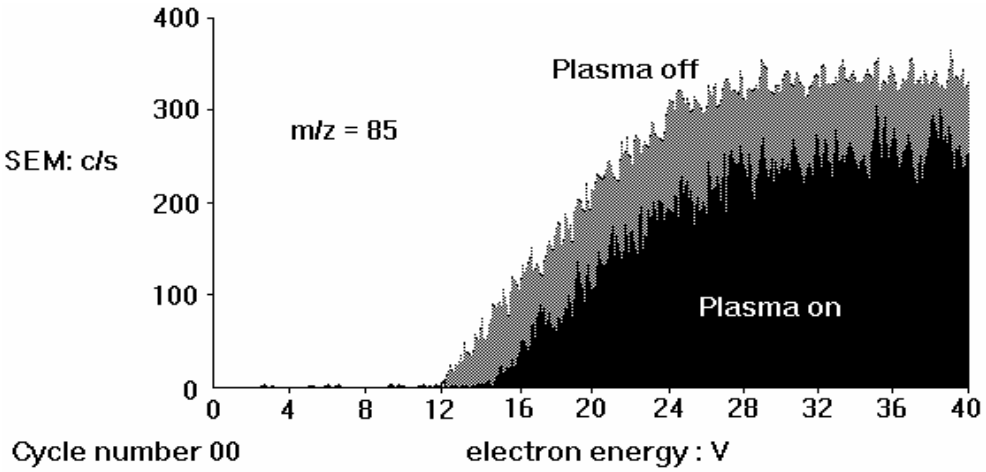


Figure 5