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Atoms, radicals and ions observed in plasmas— their gas phase and surface chemistry

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Abstract: The determination of concentrations, energy distributions, and kinetics of selected atoms, radicals and ions by means of optical observations in RF parallel plate plasma reactors is discussed. O atoms are seen by laser induced two photon excitation near 226nm, and measurements of their concentrations as a function of gas mixture in CF_4/O_2 plasmas show the influence of chemical reactions involving the atoms and fluorocarbon radicals. Optical emission from excited O and, in some cases, F atoms is shown to be a poor measure of the ground state species, and time resolved actinometered optical emission is able to highlight some of the difficulties involved in the use of this technique. Surface loss processes of F atoms in processing plasmas can under some conditions be measured using time resolved observations. Laser induced fluorescence studies of the spatial distribution of radicals in plasmas are shown to reveal both production and loss processes on surfaces. Finally, Doppler resolved linewidth determinations of the velocity distributions of N_2^+ ions in RF plasmas are discussed.

INTRODUCTION

Experimentalists can provide two types of information required for a complete understanding of the chemistry of plasmas. The first, and most obvious one is a set of measurements of the concentrations of the species present in the plasma - atoms, radicals, stable molecules, ions and electrons, spatially resolved where possible, and with their translational and internal energy distributions defined. This is a demanding task, even for the simplest types of plasma in which chemical reactions occur. What is more, such measurements need to be done *in situ*, and with techniques which are ideally non-invasive, or at least do not disturb the plasma to an appreciable extent. The second is the set of cross sections or rate constants for the various processes which take place in the plasma. Many of these can be measured under controlled conditions outside the plasma chamber, but there are some, particularly for the processes describing the interaction of the reactive species with the surfaces of the chamber, which again need to be directly determined.

Optical methods enjoy the widest use as non-invasive diagnostics of plasmas, and are in principle able to provide all of the information required. Techniques are divided into three main types. Absorption measurements have been used in wavelength regions spanning the ir (1) to the vacuum-uv (2), and in particular tunable diode laser techniques, with their high spectral resolution allowing unambiguous molecular species detection, are now set to make a large contribution to plasma chemistry (3). Emission studies are far more common: plasmas glow, and much has been inferred from measurements of the changes in intensities of the emission characteristic of atomic or molecular species observed when plasma parameters vary. The emission is characteristic of the excited species, usually in an electronically excited state, but the ground state, which is present in far higher concentrations, dominates the chemistry. Whether or not the two concentrations are related is a matter of much debate, and will be discussed further below. A third technique, which produces emission, but measures the ground state concentration, is laser induced fluorescence (LIF), and in recent years many studies have appeared of the LIF of atoms, radicals and ions in plasmas (4). This review will concentrate on recent measurements in our laboratory, mainly using LIF,

of each of these types of species. The technique, when used carefully, can satisfy the non invasive requirement of a plasma diagnostic, but it is not the universal solution for all plasma observations: by necessity the species to be observed by the technique must fluoresce, and many, particularly polyatomic radicals and molecules, do not. For species which do, however, the technique delivers the information required, spatially resolved absolute concentrations and energy distributions, and, as we shall see, it can provide data on surface induced processes inside the plasma chamber.

ATOMS

Detection of most atoms involved in plasma systems presents a problem for conventional LIF as the transitions, particularly for light atoms, lie in the vacuum-uv spectral range where lasers are inefficient. Coherent two photon excitation brings the wavelengths required into a more accessible range and has been used for example in plasma studies of H (5) and O (6,7) atoms. We illustrate in Fig. 1 our measurements of the concentration of O atoms in a RF parallel plate plasma chamber containing CF_4/O_2 (a semiconductor etching mixture) as a function of O_2 percentage at constant pressure. The method, two photon excitation of the $2p^3\,{}^3P$-$2p^4\,{}^3P$ transition of atomic O at 226nm, followed by observation of the fluorescence at 845nm from the $2p^3\,{}^3P$-$2p^3\,{}^3S$ transition is not without its pitfalls. Modest laser intensities cause a population inversion to be set up between the pumped $2p^3\,{}^3P$ state and the lower ${}^3S$ level, causing amplified spontaneous emission (ASE) in the direction of the laser beam. The ASE is up to 1000 times more intense than the normally observed fluorescence at right angles to the beam, and shows interesting sub-Doppler narrowing effects. Unfortunately it is not only a dangerous quantitative diagnostic (it behaves non-linearly with almost everything, including O atom concentrations), it also affects the observation of fluorescence, as it effectively depletes the upper fluorescing state. The results of Figure 1 have been necessarily taken with low laser powers, where ASE is absent, and highlight the need for the laser itself to be a non-perturbing diagnostic tool.

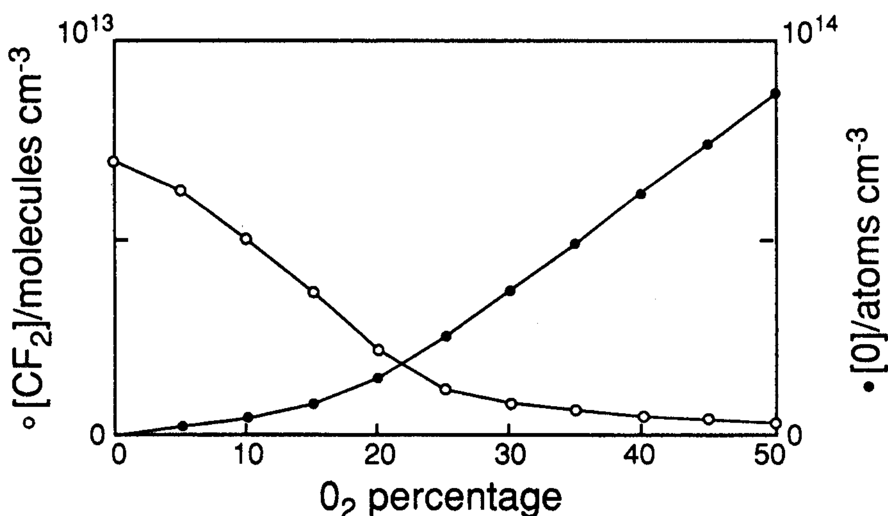

Fig. 1 O atom (●) and CF_2 (O) concentrations in a 50 mTorr CF_4/O_2 plasma as a function of percentage O_2.

Figure 1 shows that the method can be used to measure absolute concentrations, and also shows some chemistry in action: CF_2 concentrations, now measured by conventional one photon LIF are shown for comparison. As the percentage of O_2 is increased, the concentration of CF_2 goes down because of reactions

$$O + CF_2 \rightarrow FCO + F \qquad (1)$$

$$O + FCO \rightarrow CO_2 + F \qquad (2)$$

and the presence of CO_2 is confirmed by observations of ir emission from this species in the plasma (8).

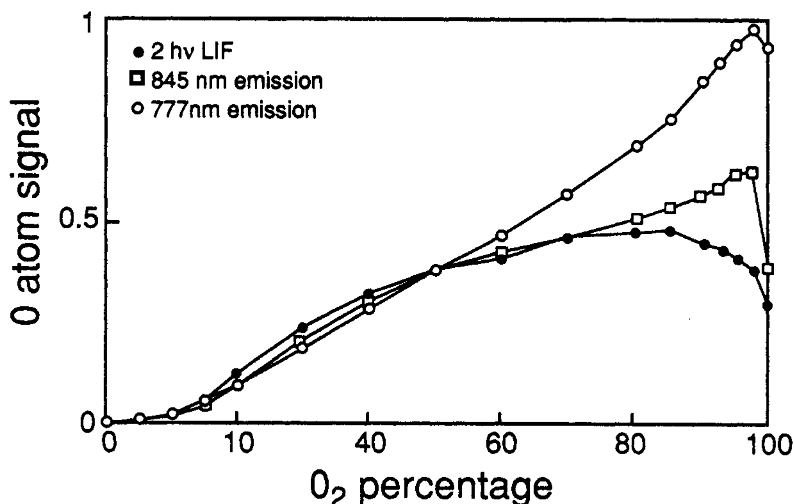

Fig. 2 O atoms observed by 2 photon LIF, and by optical emission at two different wavelengths, as a function of O_2 percentage in a 200 mTorr CF_4/O_2 plasma.

Optical emission from O atoms is easily observed in such plasmas, and the potential danger of the use of its intensity as a measure of the ground state relative concentrations is shown in Fig. 2. Here we have measured O atom LIF and compared it with optical emission (actinometered to allow for changes in the electron distribution in the plasma) at two wavelengths commonly seen in plasmas containing oxygen, as a function of the CF_4/O_2 composition. The data can be seen to be markedly different at high O_2 percentages: such problems have been noted previously (7) and are believed to result from electron impact processes of the form

$$O_2 + e \rightarrow O + O^* + e \qquad (3)$$

where O^* represents the electronically excited species observed. Such processes clearly invalidate the use of actinometered optical emission (AOE) as a diagnostic for the atomic species, and great care must be taken in the interpretation of AOE signals as a result of this.

Some atoms are not easily detected by any laser method, and one of the most important ones present in processing plasmas used in semiconductor manufacturing, F atoms, lies in this category. AOE is routinely used for relative F atom detection, and some checks on its validity have been made by techniques such as EPR (9) and gas phase titration (10). Figure 3 shows the use of a variant of AOE, time resolved actinometered optical emission (TRAOE) to probe F atom behaviour (11). Here the plasma is extinguished at time t=0 and then reignited after a delay time t. The AOE signal instantaneously rises to a value lower than that immediately prior to switch-off, and then rises to its equilibrium value in a non-exponential fashion, and as can be seen in Fig. 3, an increase in t leads to a smaller component of the instantaneous signal. We interpret these instantaneous signals as being due to F atoms still remaining in the chamber

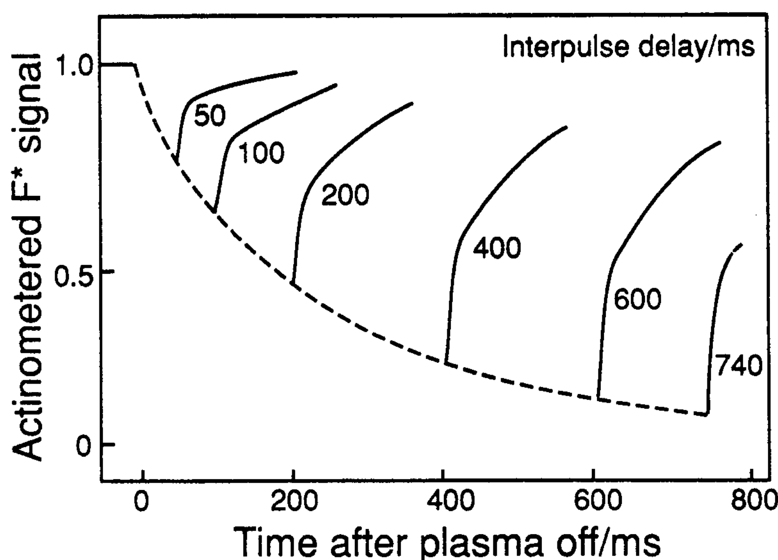

Fig. 3 AOE from F atoms observed in a 50 mTorr CF_4 plasma, switched off for periods of 50, 100, 200 etc ms. The dashed line indicates the decay rate of the ground state atoms.

a time t after switch off, and analyses of their decay curves (eg. the dashed line of Fig. 3) gives the decay rates of the atoms. In this case the decay is largely due to wall loss and from an analysis of the diffusion properties of our reactor we can extract the loss coefficients on the reactor or substrate surfaces.

Loss rates are markedly sensitive to the chamber condition, and need to be measured if any sense is to be made of the plasma chemistry. For example, addition of a small percentage of O_2 to a CF_4 plasma causes the F atom AOE signal to increase markedly. Reactions such as (1) and (2) clearly increase the F atom concentration, but our measurements of absolute radical and O atom concentrations (Fig. 1) have shown their contributions to be small. The effect is explained by measurements of the loss rates on the surfaces. With O_2 present the chamber walls become passivated with respect to O atom loss, the measured loss coefficient drops, and the steady state F atom concentration rises. Quantitative determination of loss rates have also been made with Si wafers present in the chamber, showing the dramatic increase in F atom loss rate due to etching of the substrate surface.

TRAOE, and a variant of it in which the plasma is not extinguished completely, but modulated between two different power levels (12) can provide a great deal of information about the atom chemistry. Some care however is needed. Figure 3 shows that after a long period of plasma extinction the instantaneous signal does not fall to zero, but tends to a constant (in this case ~10% of equilibrium) value. This is due to the minor process

$$CF_4 + e \rightarrow CF_3 + F_* + F_* + e \qquad (4)$$

interfering with AOE, and the figure also shows that TRAOE can measure the component of this interference from the feedstock gas. In other cases this contribution is far greater. Figure 4 shows data for a CHF_3/Ar plasma, a mixture which is used for etching SiO_2. Here two different switch off periods, 250 and 800ms are shown, both of which are long in comparison with the measured F atom decay times. The signal in both cases rises instantaneously to ~50% of its equilibrium value. F atom concentrations are lower than in CF_4 plasmas, and the contribution from the process

$$CHF_3 + e \rightarrow CHF_2 + F^* + e \qquad (5)$$

accounts for half the observed signal, and if not properly allowed for, makes AOE invalid.

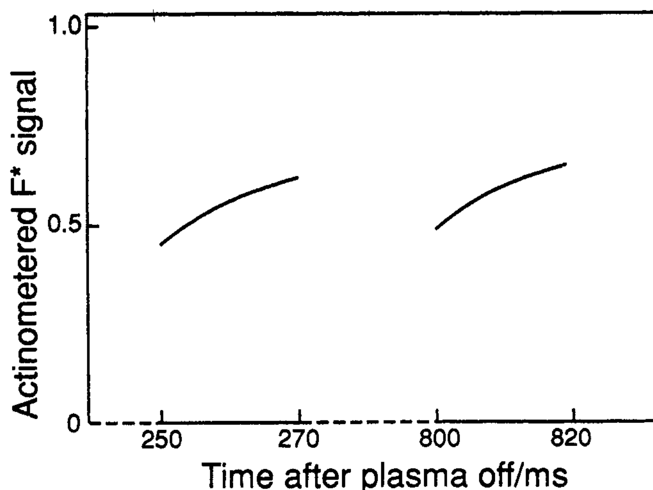

Fig. 4 TRAOE of F atoms in a 200 mTorr plasma of an equimolar mixture of CHF_3 and Ar. At time zero the plasma is switched off, and reignited at times 250 and 800 ms in two separate experiments. Note the large instantaneous F atom signal.

RADICALS

Measurements of the LIF signal from radicals in the plasma as a function of excitation wavelength produce a fingerprint of the internal energies of the species. For rotational levels these energies generally correspond to a temperature in equilibrium with the local translational temperature of the bath gas. Such temperatures, which in our reactor are in the 300-400K range, depending on excitation conditions, are important to know for modelling calculations which include temperature dependent rate constants. Radical concentrations can be measured spatially resolved, and Fig. 5 shows two such sets of data for the CF_2 radical as a function of perpendicular distance from an electrode surface.

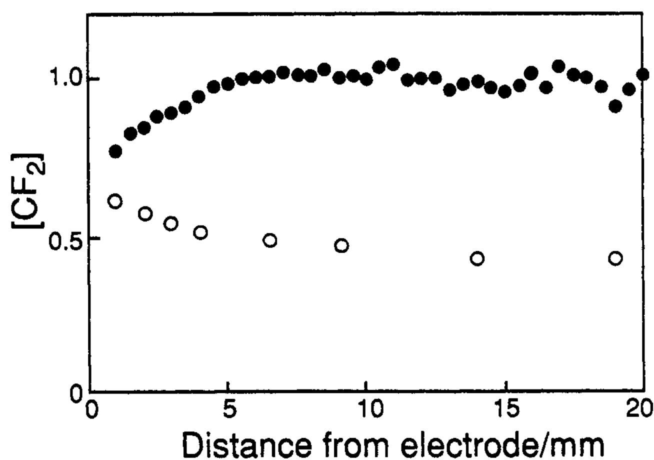

Fig. 5 CF_2 relative concentrations measured as a function of height above the RF driven electrode surface for plasmas of CF_4 (●) and CHF_3/Ar (O) at pressures of 50 mTorr.

In CF_4, the CF_2 concentration is seen to be almost constant throughout the measured region, with a small and reproducible drop near the electrode surface. The data are in sharp contrast with spatial variations of

electronically excited CF_2, which rise sharply with height above the surface and peak in the sheath (about 1 cm from the electrode in these conditions). CF_2 is produced in a non-uniform fashion in the chamber, but its relatively low chemical reactivity in this CF_4 plasma results in diffusive mixing taking place, with loss processes at the electrode causing the drop in concentration observed. Loss coefficients are measured by time resolved LIF (11). In contrast, CF_2 from CHF_3/Ar plasmas shows a rise near the electrode surface. Time resolved measurements in the bulk of the plasma show that in some cases after plasma switch-off the CF_2 concentration initially rises due to diffusion of the higher radical concentrations near the electrode into the bulk region, before the now spatially uniform radical distribution decays to zero. These data are consistent with a production term for CF_2 which peaks at or near the electrode, and this appears due to radical formation by sputtering of polymer which is clearly laid down on the electrode surfaces in plasmas of CHF_3/Ar mixtures.

Differences in the chemistries of the CF radical are also seen in CF_4 and CHF_3 plasmas. In the former case, CF loss rates on plasma switch-off decrease with increasing pressure, and are characteristic of loss of the radical on the surface being the dominant decay process (11). The reverse trend with pressure is seen for the radicals behaviour in a CHF_3/Ar plasma, where the loss rates are considerably faster in the higher pressure regions probed in these studies (~0.5 Torr). Chemical removal processes must occur in the CHF_3 case, and one possible reaction is

$$CF + H \rightarrow C + HF \qquad (6)$$

which has a fast rate constant of 1.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 300K (13). If this process predominates, then the decay rate measurement would provide an estimate of the H atom concentration in the system. Emission from electronically excited H atoms is clearly seen in CHF_3 plasmas, but is not a good diagnostic for the ground state. TRAOE measurements clearly show a substantial contribution from dissociative excitation of the parent CHF_3 molecule, and measurements of the H Balmer α Doppler profiles show widths far in excess of those expected from electron impact excitation of H atoms. Production of H^* by charge transfer or ion-electron recombination processes may explain the latter observations (14). HF can be detected in these plasmas, but not by LIF, as its easily accessible upper electronic states are dissociative. It is however a strong ir emitter, and copious signals can be seen from vibrationally excited HF by time resolved FTIR emission (8,15). Its origins however can be from a multitude of sources in the plasma, and reaction (6) is only one of a variety of production pathways.

IONS

Ion bombardment plays a crucial role in reactive ion etching and plasma treatment of surfaces, and a knowledge of the flux of ions towards a surface, and their velocity distribution is of importance. Velocity distributions can be measured by LIF determination of the lineshapes of transitions, and this can be of distinct advantage over more conventional ion energy analyses in that the LIF method does not introduce a perturbation, for example by a probe, in the plasma. Such measurements have been recently reported for Ar^+ metastables (16) and N_2^+ (17). In Figure 6 we show a LIF spectrum of N_2^+, excited in the A-X transition near 390nm, in a plasma of N_2 at 500 mTorr pressure in a RF driven parallel plate reactor. Under these high pressure conditions with the measurements being taken in the plasma bulk, the rotational distribution is, as expected, in equilibration with the local translational temperature of ~400K. Near the electrode surface in the plasma sheath we observe the ion concentration to drop markedly and the N_2^+ A state lifetime to decrease, similar to observations reported in the literature (18,19). Figure 7 shows the Doppler profile of the R(6) line taken with a high resolution (.04cm^{-1}) dye laser propagating parallel to the electrode surfaces in the plasma bulk. The doublet structure is the result of spin-rotation doubling in the upper and lower $^2\Sigma$ states of N_2^+, and the width of the lines is compatible with a Maxwell Boltzmann velocity distribution parallel to the electrodes and thus perpendicular to the direction of the DC field in the chamber, corresponding to a temperature of ~400K, as expected. N_2^+ concentrations were estimated from observations of their decay by dissociative recombination (19). Their densities are low in such RF powered reactors (between 10^{10} and 10^{11} cm^{-3} in the present case) but we have recently shown that ions in such concentrations can be detected close to (within a mean free path of) the electrode surface, and with a laser beam probing velocity distributions perpendicular to it. We expect that velocity profiling of N_2^+ using this

technique to be feasible in RF powered chambers, to produce information similar to that already demonstrated in the more highly ionised ECR plasmas of nitrogen (17). Such ion velocity profiles can then be compared with those more straightforwardly obtainable from probe measurements near the substrate surfaces.

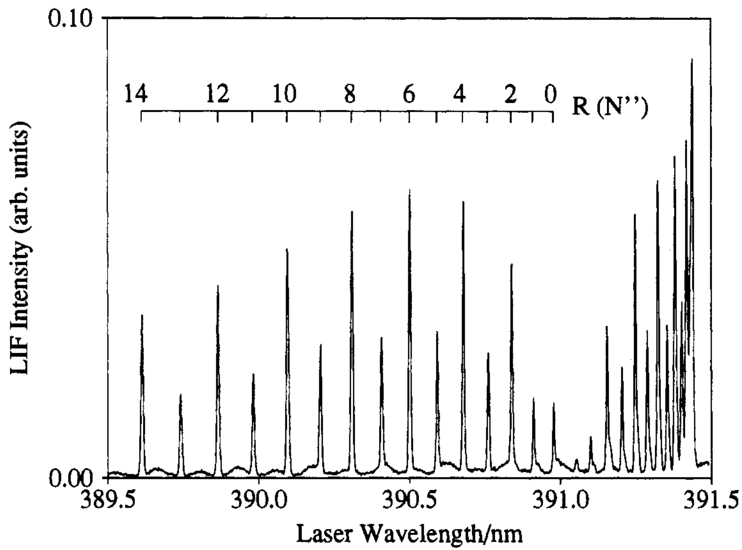

Fig. 6 LIF excitation spectrum of the N_2^+ A-X transition with the ion formed in a RF plasma in 500 mTorr N_2. R branch lines of the $^2\Sigma$-$^2\Sigma$ transition are marked originating from N″ values in the v″ = 0 ground state.

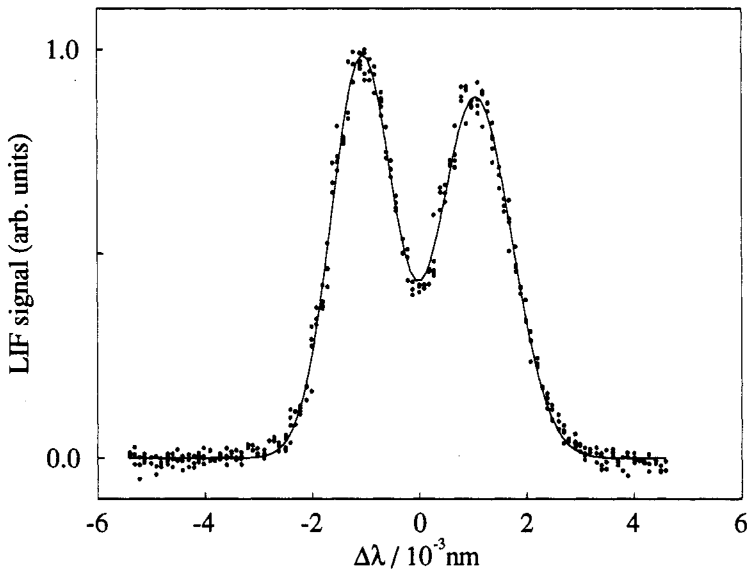

Fig. 7 High resolution scan over the R(6) line of the spectrum shown in Fig. 6. The solid curve is the fitted profile for a velocity distribution corresponding to a 400K temperature.

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