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Fluorine-based plasmas: Main features and application in micro-and nanotechnology and in surface treatment

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ABSTRACT

Fluorine cold plasmas produced by an electrical discharge in SF_6, CF_4, CHF_3 or C_4F_8 gases, principally, have two main fields of application. The first and historical application is etching of materials for microelectronics and later for micro- and nanotechnology. The second concerns the modification of surface properties, mostly in terms of reflectance and wettability. After an introduction to cold plasmas and plasma–surface interaction principles, the article aims at presenting successively the evolution of fluorine plasma etching processes since the origin with respect to other halogen-based routes in microelectronics, the important and raising application in deep etching and microtechnology, and finally some examples in surface treatment.

1. Introduction to plasmas, cold plasmas and plasma–surface interactions

Plasmas, which are also called the fourth state of matter, are defined as a partially ionised gaseous medium. Physicists usually classify plasmas according to the characteristics of the charged particles, their number density and their average kinetic energy, the latter being frequently expressed as an average temperature (Fig. 1).

Man-made cold plasmas, which are used for material processing, have the specificity to be out of thermodynamic equilibrium: average energy of the electrons (Te) typically ranges from 0.1 to 10 eV (~10^3–10^5 K), whereas the neutral and ionised species are at "room" temperature (300–600 K, i.e., 0.025–0.050 eV) or close to it. Typical density (i.e., electron density, Ne) is in the range of 10^{14}–10^{18} m^{-3}. Depending on the mode of plasma generation and the application, the operating pressure is usually between 0.1 mTorr and 1 atm (~10^{-1}–10^5 Pa).

In plasma processing, the plasma is used as a chemical reactor providing the desirable species and some others. The energy fed to the electrical discharge is gained by the electrons, which allows them to initiate dissociation, ionisation or attachment reactions with the molecules, radicals or atoms for the sake that their energy is above the corresponding cross-section threshold. As an example, Fig. 2 presents cross-sections for various electron-induced processes on CF_4 [2]. Typical reactions are as follows:

$$\text{Dissociation:}\ CF_4 + e \rightarrow F + CF_3 + e$$

$$\text{Ionisation, often dissociative:}\ CF_4 + e \rightarrow CF_3^+ + F + 2e$$

$$\text{Attachment, often dissociative:}\ CF_4 + e \rightarrow CF_4^- \rightarrow CF_3^- + F$$

A plasma created from polyatomic molecules is thus composed of the mother molecule, atoms, radicals,

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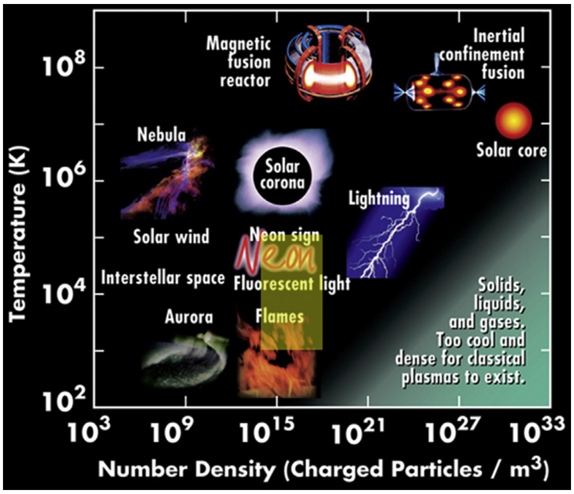

Fig. 1. Plasma temperature versus number density diagram. Man-made cold plasma region is indicated by the yellow box. Adapted from Ref. [1]. Copyright 2010, Contemporary Physics Education Project.

electrons, positive ions, and eventually negative ions. Generally, the produced species are not in their fundamental states, so the system glows in the UV–visible–IR range due to the photons emitted by radiative de-excitation of the excited species. In the volume of the plasma, the overall system is electrically neutral as the number of positive ions equals to the number of negatively charged species (electrons + negative ions). Comparing the electronic excitation and ionisation cross-sections to a typical electron energy distribution (Te = 3 eV) allows one to specify an important feature:

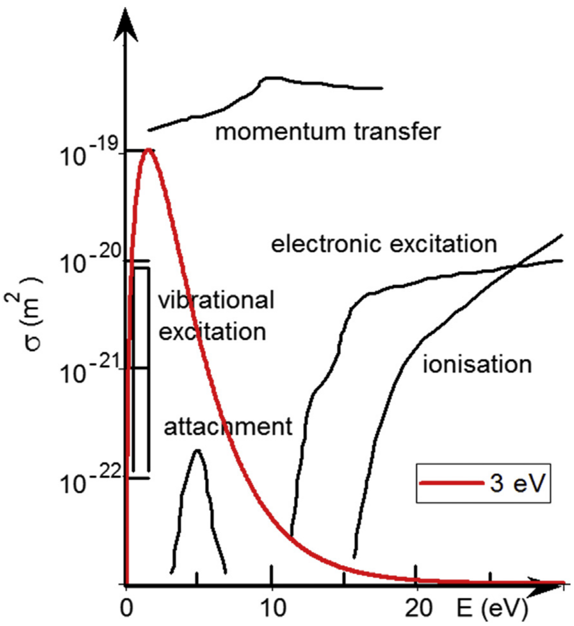

Fig. 2. Electron-induced cross-sections for CF_4. Also shown is an energy distribution for Te = 3 eV electrons. Adapted from Winters et al. [2]. Copyright 1982, APS Publishing.

plasma chemistry is induced by the few electrons of the high energy tail of the distribution. The low energy electrons control the collective behaviour of the plasma and the equilibrium with the surfaces. Information on the plasma composition and electrical characteristics can be obtained by means of mass spectrometry [3–7], optical spectroscopy (emission [4–6] or absorption [8]) and electrostatic probes [6,7,9].

The way the plasma species interact with the sample material defines the dominating operating process. For example using a CF_4 plasma, fluorocarbon radicals (CF_x) can generate a fluorocarbon layer; alternatively fluorine atoms will etch silicon via the formation of volatile SiF_4. Another important element is the (positive) ion bombardment at the surfaces. Due to the difference in the mobility between electrons and positive ions, the collective behaviour of the plasma leads to a positive potential of the plasma volume with respect to all surfaces. A space charge sheath is thus formed between the plasma and the surface, in which the average electrical field accelerates the positive ions towards the surface and repels the electrons. Biasing the sample holder using an rf bias at a frequency (usually 13.56 MHz) higher than the ion plasma frequency allows us to control the average voltage drop (denoted as self-bias) between the plasma and the material, and thus the average energy of the bombarding ions. The result of the interaction between the plasma and the material to be treated will thus depend on the following main features [10]:

- the nature of the species produced by the electron-induced processes through the choice of the feed gas;
- the flux of these chemical active species onto the sample via the pressure and power fed to the discharge;
- the flux of positive ions via the power fed to the discharge and the operating pressure;
- the energy of the bombarding ions via the bias power applied to the sample and the operating pressure.

Potential applications range from thin film deposition, etching features using a mask to protect part of the surface that should not be etched and surface treatment. The latter domain is very broad as it includes engineering of surface morphology (roughening, smoothing, nanostructuring, etc.), engineering of surface chemistry (cleaning, grafting, etc.) or in-depth chemistry (ion implantation) and biomedical applications (sterilisation of surgical tools, tissue and wound healing, etc.). Characterisation of the plasma process makes use of numerous techniques. Imaging techniques such as secondary electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy are commonly used to gain information about the surface and pattern morphology and topography. Surface analyses such as X-ray photoelectron spectroscopy (XPS) [11–15], Auger electron spectroscopy [16,17] and energy dispersive spectroscopy coupled with TEM bring information on the surface chemistry. Secondary ion mass spectrometry, Fourier transform infrared spectroscopy [18], Raman spectrometry and ellipsometry [19] provide information on thin film composition and structure, and in-depth modification of the material.

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