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# Data and modeling of negative ion transport in gases of interest for production of integrated circuits and nanotechnologies

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**Abstract**

We review techniques to prepare, evaluate and apply sets of cross section and transport data for negative ions that are required for the modeling of collisional non-equilibrium plasmas used for processing of microelectronic circuits. We collect and discuss the transport coefficients and cross section sets.

We have compiled data for negative ions in $CF_4$ and $CF_4$-related negative ions in rare gases. In addition, we consider data for $F^-$ and $CF_3{}^-$ in rare gases. Furthermore, we analyze the cross sections of halogen negative ions in rare gases and other molecules. This is followed by the data for $SF_6$ related ions in $SF_6$ and in rare gases. The cross section for scattering of $O^-$ in $O_2$ has been derived from the transport data and used to make calculations of the transport properties. Finally we give a brief discussion of the availability of the data for $H^-$ ions in $H_2$. We have derived cross sections in several cases but the basic aim is to show the basic features of transport coefficients. In particular we discuss the need to represent properly some details such as the non-conservative nature of transport coefficients and the anisotropy of diffusion. Application of approximate theories and representations of cross sections are also discussed.


*Keywords:* Negative ions; Monte Carlo; Transport coefficients; Swarm data; Plasma processing; Plasma modeling; Halogen ions; $SF_6$; Oxygen; Hydrogen; Molecular ions

## 1. Introduction

Plasmas used in the production of integrated circuits and nanostructures invariably involve electronegative gases [1,2]. The non-equilibrium nature of plasma is required to achieve functionality of anisotropic plasma etching. It implies that plasmas are dominated by collisions and dependent strongly on the nature of the feedstock gases. The theory of non-equilibrium collisional plasmas is based on the transport theory of charged particles which has been used for many years to analyze swarm experiments and to convert swarm data into scattering cross section sets [1,3].

When swarm data for plasma modeling are considered, usually only electron and positive ion transport and cross section data are discussed. In general, only a few surveys and critical evaluations of the negative ion data exist in the literature. In this paper we shall try to present a review of the availability of transport data and collisional cross sections for the negative ions of interest for plasma processing. In addition, some aspects of the negative ion transport in plasma modeling will be described.

Typically, mixtures of fluorocarbons and argon are used in plasma etching. The obvious choice is $CF_4$, but awareness of environmental issues has resulted in a drive to reduce the use of gases with a potential for inducing global warming. Yet the data for $F^-$and $CF_3{}^-$ in $CF_4$, Ar and other fluorocarbons, are the primary target of the data base. In addition, one needs data for negative ions in Cl and Br bearing molecules such as $Cl_2$, HCl, $BCl_3$, HBr either pure or in mixtures with rare gases. Although

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$SF_6$ has a considerable global warming potential, it is still a possible option in many related technologies and should be considered in our evaluation. For plasma ashing oxygen or oxygen argon mixtures are the usual choices and for the etching of organic low-k dielectrics one uses mixtures of $H_2$, $N_2$ and/or $NH_3$. All of these gases produce negative ions and plasmas in most of them have predominantly electronegative characteristics.

Normally, consideration of negative ions is limited to the fluid description since these ions are assumed to be trapped in the bulk of the plasma. However, the application of the two-frequency pulsed-plasmas includes a possibility to use double layers to inject negative ions into nanostructures [4] to reduce charging of dielectrics [5]. This has led to a greater need for negative ion cross section data at higher energies. Collisional processes of negative ions may actually be quite complex since they are subjected to a number of ion–molecule reactions that change their identity and produce a large number of different ions. In addition, detachment also acts as a non-conservative process and it has been shown that it leads to non-linear phenomena in collision dominated plasmas [6].

There is a general shortage of data for most ions of interest for plasma processing. Even for the cases where some data exist, one may need either to repeat the measurements or extend the range of $E/N$. As for the cross sections there is a general shortage of data and therefore a considerable effort in extending the date base is required. On the other hand a very detailed knowledge of the ion molecule reactions is available in the literature, but this issue is beyond the scope of this article [7].

### 1.1. On the role of negative ions in rf plasmas used for IC processing

The presence of negative ions in gas discharges and in particular in rf plasmas alters the distribution of charges and the mobility of negative charge carriers [8]. Thus, not surprisingly the effects on the plasma anatomy and maintenance mechanisms are quite pronounced [9]. For example, the thickness of the sheath changes. In inductively coupled plasmas (ICP) it was found that two separate mechanisms of heating electrons occur [10] in electropositive gases and one of the two is missing in electronegative gases, presumably due to a different sheath thickness. On the other hand, in capacitively coupled plasmas (CCP) new mechanisms are opened due to a large field in the bulk which is required to overcome the losses due to attachment, and also due to the formation of double layers [11] which become the most important source of ionization for electronegative plasmas. Distribution of fields and regions of ionization changes considerably in electronegative plasmas and one of the reasons is that detachment plays a role of the source of electrons which can sometimes even compete with the ionization by free electrons and may also lead to non-linearities [6]. In addition it was also shown that the presence of an electronegative gas in the plasma reactor leads to a higher sensitivity of the plasma on the local electric field which unfortunately leads to more pronounced non-uniformities [12].

Negative ions have a special role in pulsed-plasmas. It was found that, in the afterglow, the number of negative ions increases while electron density is reduced [13]. Consequently, afterglow conditions allow formation of ion–ion plasmas [14]. Two-frequency operation of plasma sources also involves an application of a lower frequency power source which is used to control the energy of ions. In that respect, it is preferable to separate the roles of biasing and plasma maintaining power supplies and the presece of electronegative gas in the reactor was shown to improve the functional separation between the two sources [15]. Negative ions will also play a considerable role in the abatement of the perfluorcarbon gases from the exhaust of the plasma processing reactors [16].

One of the issues that has been opened is the control of the density and energy of negative ions [17]. Another issue is whether the negative ions may be regarded as thermal. Some recent studies indicate that the mean energy of negative ions in standard two-frequency rf plasmas may be considerably larger than expected [18,19] (e.g. higher than the energy of positive ions in the bulk of the plasma).

Negative ions may be used for implantation and sputtering (under high voltage acceleration) in the same way as positive ions and even secondary electron emission may become significant under those conditions [20]. Recent attempts to use neutral beams to reduce charging in plasma etching [21,22] have also led to an idea to produce the fast beams by neutralizing the negative ion beams obtained from an rf plasma [23].

It has been suggested that secondary electron production by positive ion bombardment may proceed by a release of a negative ion that subsequently decays by releasing electron [24]. The presence of negative ions will lead to instabilities in breakdown[25], dc discharges and in rf plasmas [26].

An extreme case of negative ions are the dust particles which are, under normal circumstances (low flux of UV radiation), negatively charged and which often display the same properties and transitions as those in electronegative plasmas [27]. Stefanović et al. [28] have taken advantage of the well established explanation of the anomalous Doppler broadened profile of $H_\alpha$ radiation [29] that is due to the excitation by fast neutrals formed in charge transfer collisions. They have followed the $H_\alpha$ profiles during formation of dust particles and during their subsequent deposition on the surfaces, leaving the discharge in pristine buffer gas without dust particles (i.e. without negative ions). The width of the $H_\alpha$ lines revealed the different nature of the electronegative and electropositive rf plasmas through a very different sheath thickness which, in the electronegative case did not allow enough length to lead to considerable Doppler broadening by fast neutrals. Dusty plasmas may have a large degree of complexity (self organization) partly due to their electronegative nature [30].

In atmospheric discharges, the presence of oxygen leads to formation of negative ions that may dominate some discharge regimes. This is the case in corona discharges at atmospheric pressure where electrons are efficiently converted into negative ions that dominate the discharge at later times after the initiation of the pulse [31].