

**UNRAVELING THE IMPORTANCE OF
SURFACE ASSOCIATION TO THE FORMATION OF
MOLECULES IN A RECOMBINING N₂/O₂ PLASMA**

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1. INTRODUCTION

The interaction of reactive species, like atomic or molecular radicals, with a surface is a very general phenomenon. In plasma processing it is this interaction that leads to the modification of surfaces, i.e. deposition or etching (van de Sanden et al. 1998, Martinu and Poitras 2000). But also in the plasma assisted conversion of gases the surface plays an important role (Rousseau et al. 2006, Tanaka et al. 1994). In interstellar space it has been recognized that ice or dust particles act as third body in association processes in which not only hydrogen molecules are formed, but also larger molecules (Vidali et al. 2006). How to control the very fast erosion of the carbon tiles due to the plasma-surface interaction in the divertor region of Tokamaks, is one of the most important research questions still to be answered in thermonuclear fusion research (Shimomura 2007).

Next to studies on technological plasmas, also more fundamental studies have been performed to obtain detailed insight in the interaction of radicals with surfaces. In these studies different surface materials are exposed to well-defined atomic and molecular radicals. For example, already in 1971, the formation of NH₃ at different types of surfaces in a plasma created from mixtures of N₂ and H₂ was studied by Eremin et al. (Eremin et al. 1971). They compared the catalytic conversion into NH₃ in a barrier discharge in the presence of metallic palladium, platinum, iron, copper or nickel with clean glass. Differences of a factor of four of production for the various materials is observed. Detailed studies on the plasma assisted ammonia formation from N₂ and H₂ mixtures have been performed also by Vankan (2002) and van Helden

(2007). More recent are studies on photo-catalytic processes, as reported for example by Thevenet et al. (2006). Another example is described by Gatilova et al. (2007), where the formation of NO in a low pressure discharge is investigated. The authors focus mainly on the gas phase formation of NO, but recognize the importance of the surfaces of the plasma reactor. Also Castillo et al. (2005) conclude in their studies that mainly heterogeneous processes are responsible for the formation of NO.

To unravel the contribution of surface related processes to the total kinetics in a low pressure recombining plasma created from mixtures of N₂ and O₂, we measured the abundance of the stable molecules NO, N₂O and NO₂ in the plasma by means of IRMA, which is an IR tunable diode laser absorption system (Röpcke et al. 2000), and mass spectrometry (N₂ and O₂). A simulation, developed in CHEMKIN (2004), is used to investigate the effect of radical-surface interactions on the conversion of the feedstock gases.

2. RESULTS

A plasma expansion is created from a flow of 3000 standard cubic centimeters per minute (sccm) argon through a cascaded arc plasma source. A total power of 5 kW ($I = 75$ A) is used to create the Ar plasma in the arc channel of the source. This plasma expands from the exit of the arc channel into the reactor, which is kept at a pressure of $p = 20$ Pa or $p = 100$ Pa. A total flow of 1800 sccm of mixtures of N₂ and O₂ is injected directly into the reactor. The molecular abundances of the species formed in the plasma vessel are investigated as function of the ratio of admixed O₂ flow over the total flow of O₂ and N₂.

In Figure 1 the symbols denote the measured mole fractions of Ar, N₂, O₂, NO, N₂O and NO₂, which are plotted on a semi-logarithmic scale. All the species are measured with the quadrupole mass spectrometer, while NO and N₂O are also measured by infrared absorption spectroscopy, using the IRMA system (Röpcke et al. 2000). The results of both the mass spectrometry measurements and tunable diode laser absorption spectroscopy measurements showed good agreement (within 10%). For both pressures the molecules N₂ and O₂ are dominantly present. The abundance of the other types of molecules (NO, NO₂ and N₂O) is at least one to three orders of magnitude lower. Remarkable is the maximum abundance of NO: for both pressures it is close to a mole fraction of 10^{-2} . Furthermore, the abundance of N₂O and NO₂ decreases significantly with an increase of pressure. During the presentation it will be shown that the abundance of NO increases with increasing O₂ admixture only for admixed O₂ fractions higher than 10%. This onset is much more pronounced at a pressure of $p = 100$ Pa than at $p = 20$ Pa.

In Figure 1 the lines denote, except for argon, the simulations performed with CHEMKIN (2004), a chemical kinetics model. During the presentation results will be shown that clearly indicate that, especially for the formation of NO₂ and N₂O, the presence of surfaces is essential to explain the observed abundances in the plasma. Also, the rate of surface production of NO was calculated to be the highest for almost all the studied conditions and was found in the same order as the primary dissociation rate of injected gases. The best agreement between calculations and measurements was found for low activation energies and desorption energies of the surface processes and low calculated surface coverage. It will be shown that these results can be explained by assuming that the processes take place on a mobile surface layer.

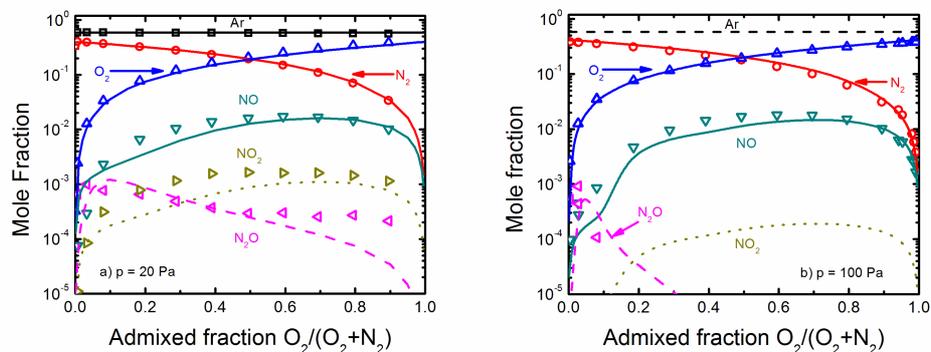


Figure 1: The measured (symbols) and calculated (lines) mole fractions of the molecules in the plasma at two different pressures as a function of the ratio of the flow of O_2 to the total flow of the injected gas mixture of N_2 and O_2 . The expanding plasma is generated from 3000 sccm of argon. The total flow of the injected mixture is 1800 sccm.

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