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 mole-
cular 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
UNRAVELING THE IMPORTANCE OF SURFACE ASSOCIATION TO THE FORMATION OF MOLECULES...

(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 N\textsubscript{2} and O\textsubscript{2}, we measured the abundance of the stable molecules NO, N\textsubscript{2}O and NO\textsubscript{2} in the plasma by means of IRMA, which is an IR tunable diode laser absorption system (Röpcke et al. 2000), and mass spectrometry (N\textsubscript{2} and O\textsubscript{2}). 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 (scm) 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 scm of mixtures of N\textsubscript{2} and O\textsubscript{2} 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 O\textsubscript{2} flow over the total flow of O\textsubscript{2} and N\textsubscript{2}.

In Figure 1 the symbols denote the measured mole fractions of Ar, N\textsubscript{2}, O\textsubscript{2}, NO, N\textsubscript{2}O and NO\textsubscript{2}, which are plotted on a semi-logarithmic scale. All the species are measured with the quadrupole mass spectrometer, while NO and N\textsubscript{2}O 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 N\textsubscript{2} and O\textsubscript{2} are dominantly present. The abundance of the other types of molecules (NO, NO\textsubscript{2} and N\textsubscript{2}O) 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\textsuperscript{-2}. Furthermore, the abundance of N\textsubscript{2}O and NO\textsubscript{2} decreases significantly with an increase of pressure. During the presentation it will be shown that the abundance of NO increases with increasing O\textsubscript{2} admixture only for admixed O\textsubscript{2} 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 NO\textsubscript{2} and N\textsubscript{2}O, 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.

References