Probability of Heterogeneous Recombination of Atomic Hydrogen on Fine-Grain Graphite Surface

A. Drenik [1], A. Vesel [1], M. Mozetič [1]

1 Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
(*) aleksander.drenik@ijs.si

The recombination coefficient of fine grain graphite EK98 was determined for neutral hydrogen atoms. The source of hydrogen atoms was an inductively coupled radiofrequency discharge in hydrogen. The values of the recombination coefficient were determined by measuring spatial profiles of the neutral hydrogen atom densities. The measured values were of the order of 10^{-2} and increased sharply at samples with higher grades of surface roughness.

Plasma based technologies have become indispensible in moder sufrace engineering applications as they provide an environmentally friendly and more cost-efficient alternative to classical wet chemical treatments. The application of plasma in surface processing ranges from very beningn surface activation[1] which has no long-lasting effect on the surface to erosion[2] and permanent modification of the chemical composition of the surface[3, 4].

In many cases, the key plasma species are neutral atoms, stemming from the dissociation of source-gas molecules. They exhibit high chemical reactivity while at the same time their kinetic energy is seldom above the thermal kinetic energy of the source gas, which makes such plasmas very suitable for surface processing, where the induced chemical changes are limited to the topmost atomic layers of the surface while the bulk material is left intact[5].

In such plasmas, the rate and efficiency of the processes are chiefly determined by the density of atomic species. The density of atomic species is, in turn, determined by the efficiency of loss mechanisms. At low pressures, the loss mechanisms are mostly limited to surface reactions and one of the strongest contributions to the atom loss is heterogeneous recombination, in which atoms join and form molecules. The probability of the recombination reaction depends on many surface and plasma parameters[6], and is summarized in a quantity called the recombination coefficient, e.g. the probability that an impinging atom will find a partner on the surface and leave the surface as a part of the newly-formed molecule. The recombination coefficient of solid materials can strongly infuence the density of atomic species in the plasma reactor. Not only do the structural materials have a major impact but the processed materials can also be a major source of atom loss through recombiantion.

In this contribution we present our study of the recombination coefficient of neutral hydrogen atoms on surfaces of fine grain graphite. The graphite samples used in our experiment were constructed from fine-grain graphite EK-98, and different types of surface finishing. This resulted in samples with three different grades of surface roughness. The recombination coefficient of the samples was determined by observing the spatial profile of atomic hydrogen density in the presence of the graphite samples. The experiments were performed in the spatial afterglow of a weakly ionized hydrogen plasma. The plasma was ignited by means of an indutively coupler radiofrequency generator, operating at 27.12 MHz, at the output power of 120 W. Hydrogen of commercially avaliable purity was leaked in the reactor through a needle valve, at pressures between 30 Pa and 175 Pa. The density of hydrogen atoms in the afterglow chamber was measured by means of a Fiber Optic Catalytic Probe[7] (FOCP) and was determined to reach up to $6 \cdot 10^{21}/m^3$.

The density profiles were recorded by moving a FOCP along a closed side-vessel of the afterglow chamber. A graphite sample was affixed around the probe which effectively terminated the side-vessel and was moved together with the probe, as seen in Fig. 1. The value of the recombination coefficient was calculated using a diffusion model first published by Smith [8] and used and modified by several other authors[9, 10].
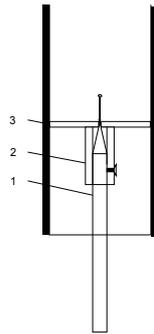
Fig. 1: Mounting of the sample and the probe in the side-vessel. 1 – FOCP, 2 – sample holder, 3 – sample

The experimentally obtained values of the recombination coefficient are plotted in Fig. 2 as a function of the effective surface. The recombination coefficient exhibits a disproportionate increase regarding the effective surface – as the effective surface increases for 12 %, the recombination coefficient increases from $6 \cdot 10^{-3}$ to $12 \cdot 10^{-3}$. We attribute this discrepancy to the fact that the effective surface may not be determined accurately enough, and that an increase of surface roughness leads to an increased probability of multiple collisions – the probability that an impinging atom will collide with the surface more than one time before it can eventually be reflected into the gas phase.
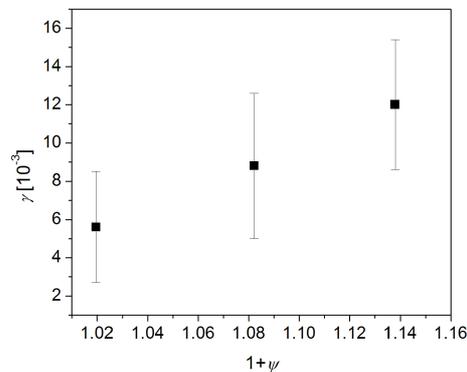

Fig. 2: Experimentally determined values of the recombination coefficient vs. the effective surface. The x axis shows the relative surface increase, defined as $1 + \psi = A_{\text{effective}}/A_{\text{geometric}}$.

We have shown that an increase in the surface roughness can have an important impact on the recombination coefficient. Since changes of the surface roughness may be caused by plasma treatment[11], this could lead to significant changes in densities of atomic species and thus changes in the kintecis of the plasma process.

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