Surface recombination of oxygen atoms on carbon nanowalls

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Abstract: Atomic oxygen loss coefficients on carbon nanowall (CNW) surface were measured. CNW layers were prepared by plasma jet enhanced chemical-vapor deposition using C2H2/H2/Ar gas mixtures. CNW layers consisted of interconnected individual nanostructures with average length of 1.1 µm, average thickness of 66 nm and surface density of 3 CNW/µm². The loss coefficient was measured in a flowing afterglow at different densities of oxygen atoms (up to 1.3×10^{21} m^{-3}) supplied from inductively coupled RF oxygen plasma at different nominal powers up to 900 W. CNW and several different samples of known coefficients for heterogeneous surface recombination of neutral oxygen atoms have been placed separately in the afterglow chamber and the O-atom density in their vicinity was measured with calibrated catalytic probes. Comparison of measured results allowed for determination of the loss coefficient for CNWs which was about 0.57 ± 0.1.

Keywords: carbon nanowalls, oxygen plasma, surface recombination, loss coefficient

1. Introduction
Plasma is often used for tailoring surface properties of various materials. The most important particles in plasma are neutral atoms that readily react with the surfaces exposed to plasma. Neutral atoms may be lost by surface recombination mechanisms. Therefore, plasma reactors are often made from glass which has very low probability for recombination. Neutral atoms may be lost also on the surfaces of treated materials especially in the case of the samples with large specific surface area [1]. Examples of such materials are nanostructured materials. In the case of afterglows the supply of atoms may not be sufficient to cover losses by surface recombination. Large samples are therefore treated non-uniformly – the section close to the atom source is treated more intensively than the rest of the sample. The loss of atoms on treated surfaces therefore represents a major concern and should be known.

2. Experimental section
Plasma was created in 80 cm long glass tube. A copper coil with was mounted onto the tube and connected via a matching network to RF generator (13.56 MHz) with a nominal power up to 1000 W. The distance from the coil to the flange was 35 cm while the distance to the opposite flange (where the pump duct was mounted) was 45 cm. CNW sample was placed 20 cm from the coil towards the pump duct. The loss coefficient was measured at a constant pressure (50 Pa, 70 sccm) in an afterglow chamber and various supplies of atoms from oxygen plasma (different powers). The loss of atoms on CNW was compared to losses observed by placing other samples of identical dimensions to the afterglow chamber. Samples of different known recombination coefficients were used in order to plot a line of atom density versus the recombination coefficient: polytetrafluoroethylene (PTFE) (\(\gamma = 6.6 \times 10^{-4}\)), stainless steel (SS) (\(\gamma = 0.07\)), copper (Cu) (\(\gamma = 0.225\)) and nickel (Ni) (\(\gamma = 0.27\)). The neutral atom density was measured by a catalytic probe with and without the sample inside the tube. The probe was mounted at the position above the sample.

3. Results and discussion
In Fig. 1 is shown SEM image of the CNW sample. It shows an open network of interconnected nanowalls, with average length of 0.74 µm, average thickness of 44 nm, and surface density of 11 CNW/µm².

First, the density of neutral oxygen atoms at the position of the catalytic probe tip was measured for the empty tube (without samples) at several powers. The measured values are presented in Fig. 2a. The measurements performed at the nominal RF powers of 150, 200 and 230 W correspond to the E-mode of the discharge, while those at higher powers (500, 700 and 900 W) correspond to the H-mode. Between the modes the discharge may be unstable so no attempt was made to measure the O-atom density between 250 and 500 W. The O-atom density is of the

Fig. 1. SEM image of carbon nanowalls.
order of $10^{20}$ m$^{-3}$ for the E-mode and above $10^{21}$ m$^{-3}$ for the H-mode.

Fig. 2. The O-atom density in an empty discharge tube (a) and in tube loaded with different samples (b).

The measured values of the O-atom densities at the presence of different samples are shown in Fig. 2b. The O-atom density measurements show dependence on the type of the sample. As expected, the density is the largest for the material with the lowest recombination coefficient (PTFE) and the lowest for nickel which has the highest recombination coefficient among the selected materials. The density of O-atoms for the case of CNW sample is even lower indicating extensive loss of the atoms on the surface of this particular material. The difference between the empty tube and the tube loaded with different samples is almost negligible for the case of PTFE but more pronounced for the catalytic materials (Cu, Ni).

The plot of O-atom density measured at the presence of the samples versus the density measured in the empty chamber is shown in Fig. 3. The results indicate that the loss of atoms due to interaction with the CNW sample is much higher than for other catalytic materials such as Cu or Ni. In Fig. 4 is shown the O-atom density versus recombination coefficient. The plot of the O-atom density shows rather linear behavior. Such dependence allows for estimation of the recombination coefficient for any other material. A solid line is used as the linear fit between points measured for materials with known recombination coefficient (stainless steel, Cu, Ni, PTFE) while the extrapolation is represented with the dashed line. The extrapolation allows for determination of the O-atom loss coefficient for CNW. The plots in Fig. 4 indicate that the coefficient is $0.57 \pm 0.1$.

Fig. 3. The O-atom density measured at the presence of different samples versus the density measured in the empty chamber.

Fig. 4. The O-atom density measured at the presence of different samples versus the recombination coefficient.

4. Conclusions
The loss of neutral oxygen atoms on carbon nanowalls (CNW) sample was determined. The loss of atoms on CNW was compared to losses observed by placing other samples of identical dimensions in the same afterglow chamber. Samples of different recombination coefficients were used in order to plot a line of atom density versus the recombination coefficient. Extrapolation of the line towards high loss coefficients allowed for determination of the loss coefficient for CNW what was found very large at the value of $0.57 \pm 0.1$ [1]. The unusually high value of the recombination coefficient can be explained by trapping atoms into the volume between nanowalls causing numerous surface collisions before an atom is able to leave the gaps between the nanowalls.

5. References

6. Acknowledgements
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