Available online at www.sciencedirect.com
ScienceDirect
Vacuum 81 (2007) 1088–1093
VACUUM
SURFACE ENGINEERING, SURFACE INSTRUMENTATION & VACUUM TECHNOLOGY
www.elsevier.com/locate/vacuum

Oxygen atom density in microwave oxygen plasma

Alenka Vesel[a,*], Miran Mozetic[a], Marianne Balat-Pichelin[b]

[a]Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[b]CNRS-PROMES, Laboratoire Procédés, Matériaux & Energie Solaire, UPR 8521, 7 rue du Four Solaire, F-66120 Font Romeu, Odeillo, France

Received 24 November 2006; received in revised form 2 February 2007; accepted 12 February 2007

Abstract

We determined the density of neutral oxygen atoms in microwave plasma using a fiber-optics catalytic probe (FOCP). Plasma was created within a quartz tube with an outer diameter of 5 cm by a 2.45 GHz microwave generator with an output power up to 1000 W. The oxygen flow was varied between 4 and 20 l/h. The O-atom density was found to increase monotonically with the increasing discharge power, and it decreased with the increasing flow rate. The degree of dissociation of oxygen molecules in the plasma column depended largely on the flow rate. At the oxygen flow of 4 l/h, it was about 18% but it decreased to about 6% at the flow of 20 l/h.

Keywords: Oxygen plasma; Plasma characterization; Microwave discharge; O-atom density; Degree of dissociation; Catalytic probe (FOCP)

1. Introduction

Low-pressure oxygen plasma is usually a rich source of neutral oxygen atoms. The density of atoms depend on various parameters including the type of discharge, the discharge power, pressure, the size and shape of discharge vessel, the type of plasma-facing material, the temperature of discharge chamber, etc. Oxygen plasma can be created in different discharges, but high-frequency electrodeless discharges seem especially suitable as the entire discharge chamber is made from glass with a low recombination coefficient for the surface reaction $O+O \rightarrow O_2$. While inductively coupled radiofrequency discharges often create plasma in the entire discharge chamber, microwave discharges are often well limited to a small volume within the microwave cavity.

The methods for determination of the O density in oxygen plasma include NO titration [1–4], actinometry [5–8], optical absorption spectroscopy [9–11] and catalytic probes [12–16]. The latter seems particularly suitable as it is rather simple and reliable. The probe does not disturb the original concentration of atoms too much, and by moving the probe one can measure possible O-atom gradients in plasma. A definite drawback of the probe is that it often interacts with the high-frequency electromagnetic (EM) field. This is fatal in the case of rather dense microwave plasmas where the EM field interacts strongly with the probe tip. Eventually, the probe tip can be melted by the action of the field itself.

A simple way to avoid interaction of the probe tip with EM field is by placing the probe in the flowing afterglow away from the plasma region, measure the O density in the near vicinity of the probe and then calculate the O density in plasma itself. A way of doing so is presented in this paper.

2. Experimental

2.1. The catalytic probe

The catalytic probe for measuring the O density in a flowing afterglow of oxygen plasma was described to details elsewhere [12,13,15]. Due to completeness of the paper let us briefly present it here. A fibre-optics catalytic probe is shown in Fig. 1. An optical fibre with a diameter of 0.2 mm made of quartz glass is mounted into the Al housing as shown in Fig. 1. The tip of the fibre was placed into an Ar arc in order to melt it. Since the surface energy of quartz is large, a perfect sphere with a diameter of

*Corresponding author. Tel.: +386 1 4773502; fax: +386 1 4773440.
E-mail address: alenka.vesel@guest.arnes.si (A. Vesel).

0042-207X/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2007.02.003

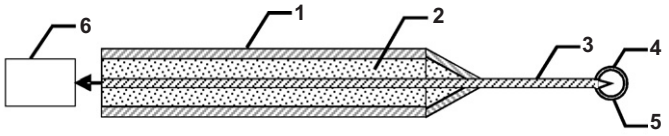

Fig. 1. Schematic of the fiber-optics catalytic probe (FOCP): 1—aluminum housing, 2—Araldite, 3—optical fiber, 4—fiber tip, 5—catalyst coating, 6—optoelectronic detection system.

0.4 mm was formed on the fibre tip as shown in Fig. 1. The probe tip is covered with a catalyst material. In our case we used nickel, since the recombination coefficient for nickel foil was measured rather accurately. It was found that the recombination coefficient did not depend on temperature (at least from 400 to 900 K) and had a value of 0.27 ± 0.04 [17]. The other side of the optical fibre leads to the optoelectronic detection device. The device measures the gray body radiation from the hot nickel catalyst. Since the albedo of the oxidized nickel is not precisely known (and may also depend on its temperature), the probe is calibrated prior the experiments. Calibration is performed by placing the probe tip in a very small furnace with the precisely adjusted temperature. The temperature in the furnace (and thus the catalyst temperature) is slowly changing in the range between the room temperature and 1000 K. The gray body radiation from the catalyst is measured simultaneously. The resultant variation of the probe signal (i.e. radiation) versus the probe tip temperature is stored in the software. During the application of the probe for measuring in oxygen plasma or afterglow, the software automatically transforms the probe signal to temperature. The accuracy of the temperature measurement is extremely good at high temperature, but even at 500 K it is about 1 K. The probe signal is measurable from about 370 K. At lower catalyst temperature it is below the detection limit of the device.

When the probe is immersed into an O-rich atmosphere, extensive surface recombination of the O atoms takes place. Due to the energy dissipation on the surface of the catalyst, the probe temperature rises well above the ambient temperature. The probe is heated at

$$P_{\mathrm{H}} = \frac{1}{4} n v \left(\frac{W_{\mathrm{D}}}{2}\right) \gamma A, \tag{1}$$

where n is the density of O atoms in the vicinity of the probe, v is the average thermal velocity of O atoms ($v = \sqrt{8kT/\pi m_{\mathrm{o}}}$), W_{D} is the dissociation energy of an oxygen molecule, γ is the recombination coefficient for O atoms on oxidized nickel surface and A is the area of the catalyst. After igniting the discharge the probe temperature rises until it reaches a constant value (Fig. 2). Since the thermal capacity of the probe is small, a constant temperature is obtained in few seconds. As the constant temperature is reached, the discharge is turned off and the

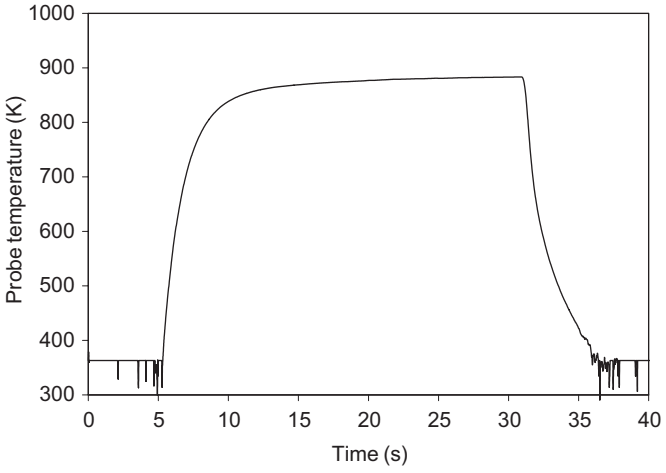

Fig. 2. A typical evolution of the probe temperature versus time at an oxygen flow of 12 l/h and at a discharge power of 750 W.

probe temperature decreases. The cooling rate is

$$P_{\mathrm{C}} = m c_{\mathrm{p}} \frac{\mathrm{d}T}{\mathrm{d}t}. \tag{2}$$

Here, m is the mass of the probe tip, c_{p} is its specific heat capacity, and $\mathrm{d}T/\mathrm{d}t$ is the time derivative of the probe temperature just after turning off the discharge. At the constant temperature the heating and cooling rates are equal ($P_{\mathrm{H}} = P_{\mathrm{C}}$), which means that after rearranging (1) and (2) we obtain an expression for the density of the O atoms (n):

$$n = \frac{8 m c_{\mathrm{p}}}{v W_{\mathrm{D}} \gamma A} \frac{\mathrm{d}T}{\mathrm{d}t}. \tag{3}$$

2.2. Experimental set-up

Schematic of the system is shown in Fig. 3. The system is pumped with a one-stage oil rotary pump with the pumping speed of 12 m^3/h in the pressure range between 50 and 500 Pa. The flow of oxygen through the system is adjusted with a volume flow controller, and the pressure is measured with an absolute vacuum gauge. In the range between 4 and 20 l/h, the pressure increases roughly linearly with increasing gas flow. The effective pumping speed at the exhaust of the discharge tube was estimated to about 4–8 m^3/h, depending on the pressure. The experimental chamber is a quartz cylinder with a length of 50 cm and an outer diameter of 5 cm. Plasma is created within a microwave cavity at 2.45 GHz and the power adjustable between 0 and 1200 W. In our experiments, we used powers between 300 and 1000 W. Inside the quartz tube there is a quartz sample holder. At present experiments it is placed at the lower end of plasma (Fig. 3). The glass tube has a side arm with an outer diameter of 2.6 cm, placed 10 cm below the upper end of the sample holder as shown in Fig. 3. The tip of a nickel fiber-optics catalytic probe is mounted 10 mm inside the side arm in order to prevent probe degradation.