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High-rate deposition by microwave RPECVD at atmospheric pressure

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ABSTRACT

The post-discharge of a microwave resonant cavity working at atmospheric pressure is used to enhance deposition of SiO_x thin films from HMDSO by chemical vapor deposition. Maximum static deposition rates are close to 150 µm h^{-1} for low power consumption per unit of coated width (~100 W/cm). Dynamic deposition rates are close to 3.5 nm m s^{-1}. The distribution of the coating thickness is heterogeneous over an area of 150 × 90 mm^2. The influence of the main parameters of the process is systematically studied to show how the key reactions, i.e. gas phase synthesis of powders and surface deposition, are correlated.

1. Introduction

Recent works in the field of plasma enhanced chemical vapor deposition at atmospheric pressure have demonstrated the capability of these processes to coat substrates at high rates [1–9]. Various plasma sources have been proposed, including DC arc [1,4], corona discharges [5], dielectric barrier discharges [5], and microwave excited plasmas [1,3]. Different reviews were written to describe the specificity of each source [7–9]. Briefly, a source operates at a specific temperature, ranging from room temperature [5] to several thousands Kelvin [10]. It also works at a specific scale, *e.g.* for localized surface treatment [5] or over large industrial substrates [1]. In continuous flow processes, a source can be set-up on a production line more or less easily.

Because of their high temperature (typically, above 1000 K and up to 5000 K), microwave plasmas at atmospheric pressure ought to be used in metallurgical applications. Several options were proposed to design microwave sources operating at atmospheric pressure. Sources like surface wave excited plasmas [11–15], waveguide-based microwave torches [9,16–21] and resonant cavities [10,22–25] are widely used. Even split-ring resonator micro-plasmas were recently proposed [26] to create small-scale plasmas (the gap size of the gap required to launch the microwaves can be as low as 45 µm).

V. Hopfe and collaborators made huge progress recently by using microwave sources in remote mode [1,3]. They reached static and dynamic deposition rates (as discussed in Appendix A) in the range 15–100 nm s^{-1} and 0.3–2.0 nm m s^{-1} respectively with properties of the silica thin films close to those of bulk silica. These deposition rates are very high and make it possible to deposit thin films in continuous flow processes with moving substrates past the plasma source at several meters per minute.

To scale-up their plasma source, Hopfe et al. suggest changing the excitation frequency or the coupling structure [3]. In this work, we propose another idea based on the multiplication of compact microwave sources. Since post-discharges can be easily handled by controlling their hydrodynamics, resorting to these neutral media provides an easier way to adapt this deposition process to on-line processes. On the other hand, we want to emphasize in this work the importance of the control of the precursor flux with respect to the flux of active species from the plasma. Precursor dissociation and subsequent synthesis of intermediates have to occur in the vicinity of the surface of the substrate. Diffusion being strongly limited at high pressure, one may play principally on the convective flows of the precursors. The important time scale to be controlled is the residence time required for active species to reach the surface. For long time scales, homogeneous nucleation occurs. Powders are synthesized and deposition rates decrease.

2. Experimental setup

The experimental setup is shown schematically in Fig. 1. Experiments are carried out in the post-discharge of a microwave

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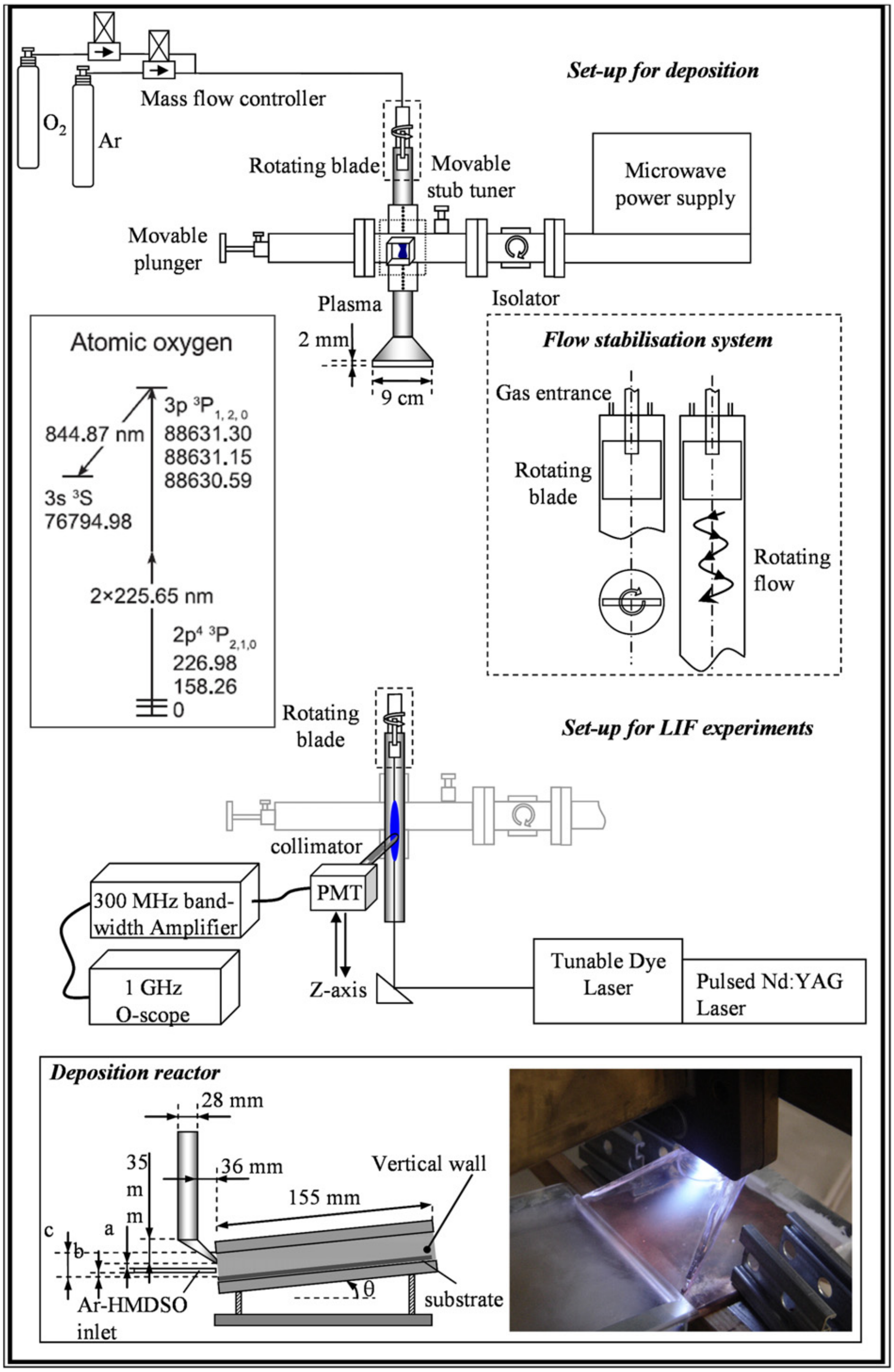

Fig. 1. The experimental setup for deposition and the experimental arrangement used for TALIF measurements. The fan used to centre the argon filament on the tube axis is depicted. The deposition reactor is described. Detail of the transition used to probe the $O(2p^4\ ^3P)$ state.

plasma generated in a resonant cavity working at 2.45 GHz and at atmospheric pressure. The resonant cavity consists of a discharge tube (27 mm inner diameter) made of fused silica going through a WR 340 rectangular waveguide. A standing wave is established between the moving short-circuit and the three-stub tuner, to get maximum electric field intensity on the tube axis. The absorbed microwave power varies from 600 to 1000 W depending on the incident power and the discharge gas composition. A rotating fan is used to centre the plasma on the tube axis and to avoid its contact with the walls.

All gas flows are controlled by mass flow controllers. The gas injection system consists of two independent lines. The first one is used for the discharge gas mixture and the second is used for the precursor injection in post-discharge. The discharge gas mixture is made of argon (purity 99.997 vol.%) and oxygen (99.995 vol.%). The total gas flow rate in the discharge is set typically at 10 standard liters per minute (slm) for diagnostics and 50 slm for deposition experiments and the oxygen partial pressure in the gas mixture is 10 vol.%. Under these conditions, the plasma operates in glow mode. The nozzle of the quartz tube (Fig. 1) is designed to create through a rectangular slit (typically 2 mm in height) a sheet of active species impinging the surface of the substrate with a controlled angle. To limit the number of parameters to study, we chose to set some distances: $a = 1$ mm, $b = 2$ mm and $c = 10$ mm (Fig.1).

We used hexamethyldisiloxane (HMDSO-$Si_2O(CH_3)_6$) as precursor. In the precursor injection line, partial pressures of