Chemical vapour deposition enhanced by atmospheric microwave plasmas: A large-scale industrial process or the next nanomanufacturing tool?

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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 [1-3]. Various plasma sources have been proposed, including DC arc, corona discharges, dielectric barrier discharges, and microwave excited plasmas. Different reviews were written to describe the specificity of each source. Briefly, a source operates at a specific temperature, ranging from room temperature to several thousands Kelvin. It also works at a specific scale, e.g. for localized surface treatment or over large industrial substrates. 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 can be used in many metallurgical applications. Several possibilities have been used to design microwave sources operating at atmospheric pressure. Sources like surface wave excited plasmas, waveguide-based microwave torches and resonant cavities are widely used. Even split-ring resonator micro-plasmas were recently proposed to create small-scale plasmas (the gap size can be as low as 45 μm) [4].

V. Hopfe *et al.* have made huge progress recently using microwave sources in remote mode [1]. They succeeded in reaching deposition rates in the range 15-100 nm s^{-1} (static) and 0.3-2.0 nm m s^{-1} (dynamic) with properties of the silica thin films close to those of bulk silica. These very high values of the deposition rate 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, V. Hopfe *et al.* suggest changing the excitation frequency or the coupling structure [1]. We propose another idea based on the multiplication of compact microwave sources (Fig. 1). 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 the importance of the control of the flux of the precursor 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.
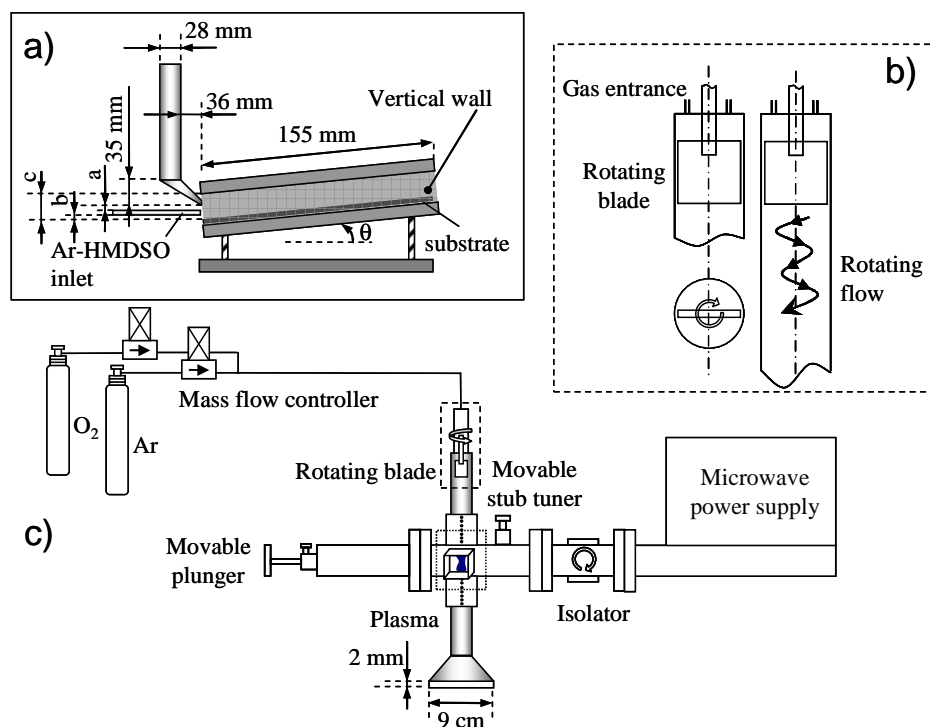
Fig. 1: The experimental set up. a) AP-PECVD reactor. b) Detail of the rotating blade used to centre the plasma and avoid its contact with the wall of the quartz tube. c) Resonant microwave cavity.

If a special attention is paid to the way the precursor is injected with regards to the substrate, it can be understood by Computational Fluid Dynamics how mass transport, *i.e.* forced convection and turbulent diffusion, determines the deposition yield [5]. Indeed, we show that mass transport can be advantageously ensured by convection for the heavier precursor of the coating, the lighter being driven by turbulent diffusion towards the surface. Transport by laminar diffusion is negligible. The use of high flow rates is mandatory to have a good mixing of species. However, strongly turbulent flows have to be avoided to limit volume reaction and powder synthesis.

From these observations, it is possible to increase the deposition rate to unexpected values (~hundreds of µm/s!) by localizing the deposition. Deposition yields can thus be increased up to almost 100%. In recent works [6, 7] performed under reduced pressure with capillary, deposition rates could reach up to hundreds of micrometers per second, *i.e.* about one thousand times faster than the fastest rates ever obtained at atmospheric pressure. These results establish clearly that there is no link between deposition rate and pressure. In these works [6, 7] deposition is defined as "localized." The reactant gas is injected via a capillary through a plasma and deposition builds up as a peak on a substrate kept at a specified distance from the capillary. Deposition is said to be localized when the dimensionality of the deposited features becomes zero dimensional. In this sense, localized deposition differs from thin film deposition.

Several micro-plasma jets were recently developed to synthesize coatings of limited area (down to several tens of micrometers). We develop a remote microwave micro-post-discharge at atmospheric pressure offering the capability to reach high gas temperature (up to 2000 K) over a small area (~several hundreds of µm in diameter) [8]. Hydrodynamic flows can be controlled to

create a "beam of atoms" that can be handled like a pen to "write" directly patterns on surface and that extends over more than 10 cm in the air.

Depending on the excitation conditions of the plasma, self-organization may be observed [9, 10], leading to possible developments in the field of nanoscience. Coating of nanoparticles, synthesis of nanoobjects like nanotubes or nanowires, deposition of nanometer-thick stacks of layers are major fields of study for these processes in the years to come. Self-organization may be defined as simultaneous assembly and functionalization of nanostructures. It can be driven under certain conditions by applying external energy drivers, like electric fields. For instance, in oxidation processes where charged species play an important role, the presence of electromagnetic fields orientate the growth [11]. Microwave excited microplasmas can create strong electromagnetic fields at the processing surface and the field strength patterns contribute to the self-assembly of the surface features.

Self-organization of SiO_2 nanodots can also be obtained by chemical vapor deposition out of hexamethyldisiloxane (HMDSO) and atmospheric pressure remote Ar–O_2 plasma operating at high temperature (1200 K – 1600 K). The dewetting of the film being deposited when it is still thin enough (<500 nm) is found to be partly responsible for this self-organization. When the coating becomes thicker (~ 1µm), and for relatively high contents in HMDSO, SiO_2 walls forming hexagonal cells are obtained on a SiO_2 sub-layer. For thicker coatings (> 1 µm), droplet-shaped coatings with a gaussian distribution in thickness over their width are deposited. The coatings are submitted to high compressive stress. When it is relaxed, "nest-like structures" made of nano-ribbons are synthesized. We still have to assign more accurately the importance of the respective roles of dewetting, CVD growth and stress development to the observed patterns. They role are qualitatively presented in figure 2.
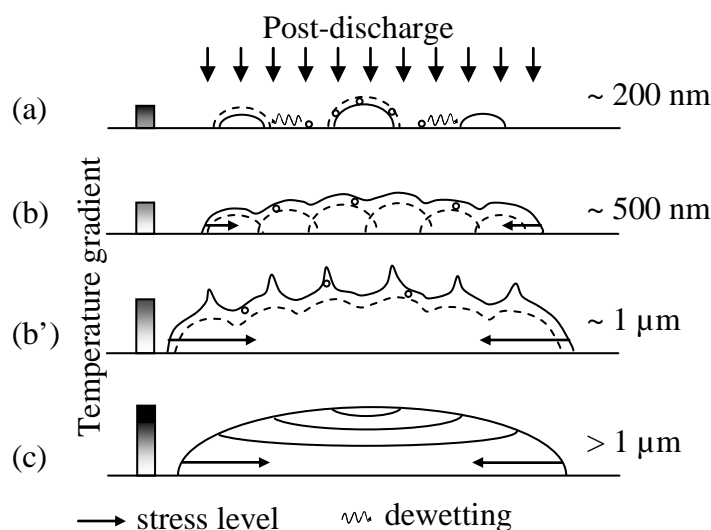

Fig. 2: Schematic of elemental processes leading to patterned surfaces. (a): High temperature (1600 K), weak thermal gradients giving nanodots ; (b) – short time – and (b') – long time –: low temperature (1200 K), weak thermal gradients and high stress level leading to hexagonal cells ; (c): thick films with high compressive stress leading to nest-like structures.

To scale down localized deposition, several strategies may be adopted. Among them, decreasing the size of the capillary seems to be the easiest way. However, it is limited by the rise of the pressure required to enable the flow of the gas through a tiny hole. Recently, works on plasmas in liquids showed the possibility to decrease the characteristic radius of the plasma down

to hundreds of nanometers [12, 13]. These developments may lead to important new fields of applications in biology, optical diagnostics and micromachining.

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