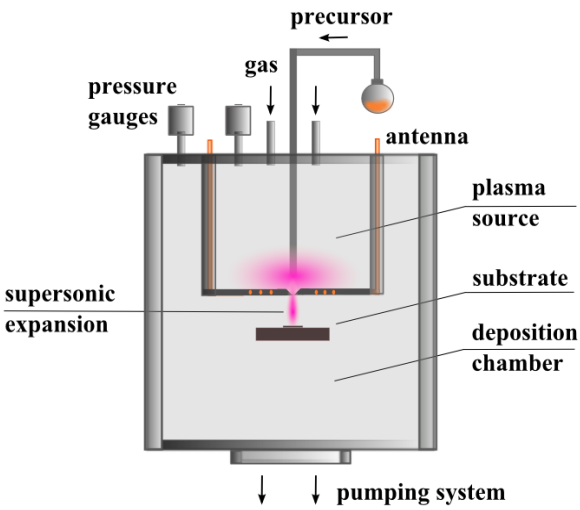
Experimental Characterization of a new Plasma Source for Controlled Deposition of Thin Films

C. Riccardi[1], I.Biganzoli[1], R. Barni[1]

[1]*Dipartimento di Fisica Occhialini, Universita' degli Studi di Milano-Bicocca, p.za della Scienza, 3 I-20216 Milano, Italy*

Thin films find several applications depending on both their morphology and chemistry [1]. In particular the production of nanostructured materials is, currently, one of the fields of more intense research and technological development. Thin films made of oxides, semiconductors or metals are especially interesting in this respect. We have recently implemented a double step deposition process in which film chemistry can be controlled separately from film growth. The molecules of the substance chosen for the deposit are obtained by dissociating an appropriate precursor into an inductively coupled plasma (ICP). Molecules formed during this first phase are then extracted through a nozzle into a lower pressure deposition chamber. A supersonic freely expanding jet is thus produced, until recompression occurs through a shock wave. Before and after the latter, the flow properties and the degree of molecule clusterization are different. Consequently, film growth can be controlled by changing the substrate location. We present the design and properties of this new versatile plasma source for thin film deposition. It is well know that ICP discharges work in the inductive regime (H) only after a transition from the capacitive regime (E), which is obtained if the applied voltage is high enough [2]. This transition has been studied using optical and electrical probes. Optical emission spectroscopy (OES) has been chosen as an easy and non-intrusive tool for studying other plasma properties. We have used a simplified radiative model for argon to evaluate the electron temperature [3]. We have also measured the relative abundance of oxygen atoms, which plays a role in precursor dissociation. When the precursor is injected, the shape of light emission spectra is useful for monitoring the deposition process. A sketched view of the source setup is shown in Fig.1. Our main purpose was to spatially separate the region of the precursor plasma dissociation from the deposition zone, where the substrate is exposed. An ICP was driven by an RF planar coil antenna facing the upper plasma chamber. In correspondence of the coil axis, the transition between the plasma and the deposition chambers consists in a nozzle ending with a rectangular slit. With this choice, a differential pressure exists and the flow out of the plasma chamber assumes the form of a jet. When this pressure difference is high enough, the jet expansion could become supersonic [4]. This pressure ratio R is controlled by the slit conductance and by the effective pumping speed



tuned by partially throttling the gate valve at the bottom of the device, in front of the turbo molecular pump. Our plasma source operates under moderate vacuum conditions (1 ÷ 100 Pa). In our setup, the ratio R can reach a maximum of 38 in argon, largely sufficient for a supersonic jet, which requires R > 2.05 for argon [4].

Fig.1 - Layout of the plasma reactor.

The expansion region then constitutes a sort of plume emerging from the nozzle, laterally limited by oblique shocks and downstream restricted by the so called Mach disk shock. This region is often called zone of silence, being unaffected by the background pressure. Here the Mach number progressively increases with the distance from the slit, allowing to select the velocity of particles and thus to grow films with different characteristics. Moreover, R controls the Mach disk position, and thus the maximum speed achievable. This constitutes the main characteristic of our device, since within this supersonic expansion region, the reduced number of collisions does not favour cluster nucleation and allows to synthesize films with small nanostructures and grains.

In the experiments discussed here plasma was produced from argon and oxygen mixtures. Argon ICPs provide a stable environment, whereas oxygen was selected as the oxidizing agent to chemically attack the organic groups in precursors. Oxygen content directly affects the power level beyond which the truly inductive regine is reached. This was investigated using an high voltage probe to measure the potential at the feeded coil ending, as well as collecting the emission spectrum of the discharge. In Fig. 2a and 2b we report the dependence of both these measurements from the oxygen concentration as a function of the power level. The steep rise in the HV signal at low power is due to the E-mode, and it is followed by a voltage drop, when the regime transition starts and the coupling changes. After the H-mode is fully established, the HV rises linearly with the power level. The addiction of oxygen has only a slight effect on the characteristics of the E-mode. However it delays the onset of the transition to higher power levels. Fully developed H-mode discharges require power levels in excess of 400 W whether oxygen concentration exceeds 25%.

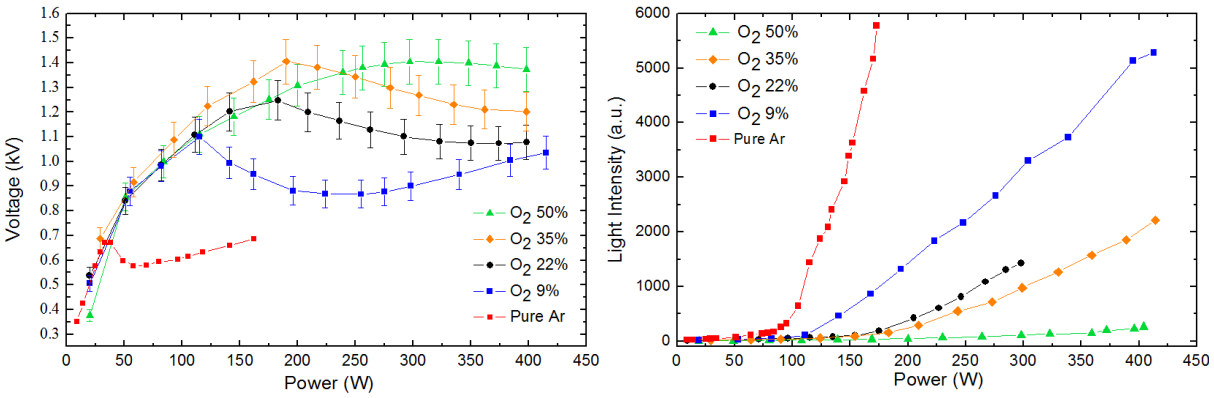


Fig.2 – Coil voltage (a) and intensity of the 751 nm argon line (b), as a function of power for different argon-oxygen mixtures, argon pressure 10 Pa.

The brightest feature in the spectra of such discharges is the 2px system in the Paschen notation, in the red and in the near IR. The transition can be evaluated by considering the intensity of one of these emission lines, as shown in Fig.2b. The transition between E and H-mode in the OES intensity is sharp, at least at the lower oxygen amounts, and broadly consistent with the power levels evaluated from electrical measurements. In the H-regime the intensity rises linearly with the RF power level, with a different slope depending on the oxygen concentration. Under vacuum conditions, the excitation of argon radiatively decaying levels happens mainly through inelastic scattering of argon atoms by high energy electron impact. Under such an approximation the intensity of emission lines is proportional to the product of the electron density and the rate of impact excitation process, which is a function of the electron temperature [5]. This framework can be exploited in the implementation of suitable radiative models, which can be used to extract plasma parameters. This was proposed for argon, using only part of the 2px system and modified by us to increase precision [3]. Here we applied this method to measure the electron temperature. In Fig.3 we report the evaluated electron temperatures as a function of the power level, for different argon-oxygen mixtures. Electron temperatures are almost constant in the H-mode. Their values stay in the 1−1.5 eV range. They are somewhat larger in the E-mode, but this difference cannot explain the sharp transition of the emission line intensity between the E and H modes. This is almost entirely due to a jump in the electron density in the H mode. The variations in the light intensity with the oxygen amount point towards a decrease in the total electron density (at a same power level). This behaviour can be related to oxygen electronegativity, favouring the formation of negative ions and reducing the electron plasma density [5].

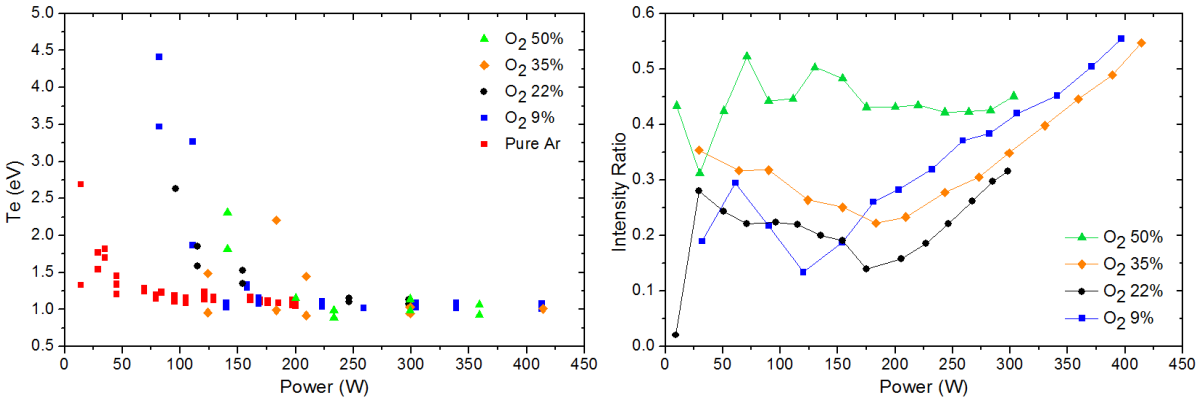


Fig.3 – Electron temperature (a) and intensity ratio between the 777 nm O and the 751 nm Ar lines (b), as a function of power for different argon-oxygen mixtures, argon pressure 10 Pa.

Argon is favourable to OES since its emission line intensity is controlled mainly by electron properties in the plasma. Then the ratio between the intensity of any emission line and that of argon line factors out the electron density. Being the electron temperature variations small in ICPs, the excitation rates introduce only a multiplicative factor between the ratio of intensity and that of emitting particle densities [5]. Here we have employed this procedure in order to compare the dissociation capabilities of different plasma mixtures. In Fig.3b we report the relative abundance of atomic oxygen. The intensity ratio, so the atomic oxygen density, increases with the power level in the H mode, but there it appears to be quite independent from the oxygen percentage.

These observations can be used to assess the oxidizing capabilities of the discharges in argon-oxygen mixtures in our device [6], and will be taken into consideration when deposition processes will be performed using organic precursors.

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