Enhanced deposition rates in plasma sputter deposition

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Abstract. Langmuir probe and emission spectroscopic measurements are performed in a high frequency (100 MHz) argon plasma used for the sputter deposition process of thin films of palladium (dedicated to catalysis applications). The metal source is a helicoidal palladium wire which is negatively biased with respect to the plasma potential. This induces sputtering by the ions present in the plasma. The probe results show that the presence of the helicoidal wire in the chamber does not affect the total ion flux at the substrate location. However, as the bias voltage on the wire and/or the argon pressure are increased, a secondary direct current (DC) discharge is created inside the helicoidal wire which follows a Paschen-like law; the breakdown voltage is lower than in the case of a conventional Ar discharge, probably as a result of the presence of primary electrons generated by the main high frequency (HF) plasma. This second discharge is characterized by a strong Ar⁺ flux peak inside the helicoidal wire, which probably arises from a hollow cathode type discharge. From emission spectroscopy and deposition analysis, it is shown that this secondary plasma causes an increase of the sputtered Pd atom number and, consequently, an enhanced deposition rate.

1. Introduction

Over several years we have developed a plasma process dedicated to the synthesis of heterogeneous catalysis systems such as supported metal aggregates [1, 2]. Our aim is to develop an alternative method to the commonly used techniques: vapour phase deposition [3–6] which has the drawback of UHV technology, and liquid phase processes such as impregnation or exchange [7, 8], which take a long time so as to avoid organic contamination. The first results obtained with the plasma synthesis method were encouraging because they showed that the metal deposits were composed of small pure aggregates of the size (15–200 Å) required for catalysis application [2, 9]. Moreover, these systems exhibited a high catalysis activity when tested with butadiene hydrogenation, equivalent to that usually obtained with atomic beam deposited samples.

In the present system, the metal atom source is a helicoidal wire (HW) placed in the chamber, negatively biased with respect to the plasma potential, and thus sputtered by the ions present in the plasma. In previous works, we have studied the influence of the HW bias voltage and of the gas pressure on the main characteristics of the film formation, i.e., deposition rate and morphology [2, 9]. The HW bias voltage is expected to play an important role in the metal sputtering process, because it defines the energy gained by ions accelerating through the sheath around the HW and, as shown later, creates, under certain circumstances, a secondary discharge which increases the ion flux impinging onto the wire. The gas pressure is also a major parameter because it governs the diffusion of the Ar⁺ ions from the antenna to the HW, as well as the diffusion of the ejected metal atoms and ions towards the substrate [10, 11].

Initial results concerning the deposition rate were not easy to explain, especially at high pressures and voltages, conditions leading to surprising large rate values [1]. They revealed that the influence of both parameters on the deposition rate is more complex than expected, and needed to be closely studied. Therefore, a systematic plasma characterization has been performed, firstly by emission spectroscopy in order to determine the presence of sputtered metal atoms. Earlier work presented in [1] has shown the existence of a direct current (DC) auxiliary plasma inside the HW (intense Pd line emission), in experimental conditions for which high deposition rates are measured. The creation of this secondary plasma was not well understood at that time, but it was thought to follow the Paschen law. Its presence seems to increase the sputtering process, leading to high amounts of metal being deposited on the substrate.

In order to complete the plasma study and to better understand the role of the secondary discharge in the deposition process, Langmuir probe measurements have
been performed in the deposition system along the main axis. The ion saturation current is used to estimate the flux of argon ions responsible for the sputtering process. The deposition rate on the substrate is measured for different HW bias voltages and gas pressures and the results are correlated to the plasma characteristics.

2. Experimental details

The experimental set-up has been fully described in [1], and the main features are summarized in figure 1(a). Owing to its well known high catalytic activity and selectivity (CO oxidation [8, 12], butadiene hydrogenation [7, 13]), palladium has been chosen for this study. The metal source is a 1 cm in diameter palladium helicoidal wire located 1 cm away from the antenna, and connected to a DC voltage generator operating in the $-350$ to $+350$ V range. In deposition configuration, the substrate is placed 3.5 cm away from the HW which is normally negatively biased with respect to the plasma potential, forming a positive ion sheath which accelerates the Ar ions to sufficient energy to induce Pd sputtering. The metal atoms and ions diffuse away from the wire, some of them reaching the substrate.

The high frequency (HF, 100 MHz) power to the antenna is fixed at about 5 W, the argon pressure ($P$) ranges from 1 mTorr to 200 mTorr and the Pd HW bias voltage ($V_{HW}$) is varied from $-350$ to $+200$ V. Deposits on Si wafers are carried out at $-100$ and $-350$ V HW voltages and different Ar pressures. From 2 MeV He$^+$ particle Rutherford backscattering spectroscopy (RBS) the average area density of Pd is measured [9]. The deposition rate is then calculated by dividing by the deposition time which is fixed at 5 minutes for all samples.

The Langmuir probe tip consists of a 2 mm long and 1 mm in diameter tungsten wire. For the experiments, the probe is placed on a translating device which replaces the substrate holder (figure 1), and is connected to a DC voltage supply. The aim of this work is to determine the flux of Ar$^+$ ions responsible for the sputtering process, and consequently the Langmuir probe is biased to a sufficiently negative voltage so as to be well away from electron collection and to be sure that only ions would be collected. As primary measurements gave a plasma potential ($V_p$) of 80–100 V and a mean electron energy in the range 2–4 eV (section 3, table 1), the probe is biased to $-40$ V, which is more than $10kT_e$ below $V_p$. Since the floating ($V_f$) and plasma potentials do not vary significantly over the present experimental conditions, this bias voltage remains the same for all the measurements. It is important to note that since we move from a collisionless to a collisional sheath as the Ar pressure is increased from 1 mTorr to 200 mTorr, precise interpretation of ion saturation current to give plasma density would be ambiguous. Nevertheless, at a constant pressure, the curves of $I_{sat}$ are proportional to the ion density. At the biased probe voltage ($-40$ V) the total ion energy is low (less than 150 eV), and the part of $I_{sat}$ that can be due to secondary electron emission is not greater than 10% [14].

Langmuir probe measurements were carried out in three different configurations: without the HW, with the HW at the same position as in deposition configuration and with the HW at this axial position but withdrawn slightly off the main axis (figure 1(b)). For all three configurations, the ion saturation current ($I_{sat}$) was measured along the experimental axis for different HW bias voltages and argon pressures.
in a quasi-homogeneous plasma. As the argon pressure take place in a large volume of the chamber resulting diffuse easily in the whole chamber. The ionization events I the exponential part; the floating potential was measured at 100 mTorr. The high plasma potential (table 1) was unexpected. A possible explanation is that measured at 100 mTorr. The high plasma potential (table 1) was unexpected. A possible explanation is that the inner surfaces of the chamber are not good conductors and the walls to charge up [15]. This was tested by earthing the top plate which resulted in a lowering of Vp and Vf by 10 V. The lack of matching network may also contribute to this effect.

Having estimated the range of the main Ar plasma parameters, only the ion saturation current was studied in the following experiments. Isat is attributed to Ar+ ions because double charge species are unlikely to be created in the low density plasma conditions described here, and because Pd+ ions have never been clearly evidenced by emission spectroscopy [1]. Nevertheless, these ions may exist in small quantity especially inside the HW when the secondary discharge is created.

### 3. Plasma characterization

In initial Langmuir probe experiments, the current–voltage curves were recorded at 1 mTorr and 100 mTorr for HW bias voltages of 0 V, −100 V and −350 V. For these measurements, the probe was located at the substrate position, 3.5 cm away from the HW. The measured parameters (plasma and floating potentials, electron temperature) are presented in table 1 for an HW bias voltage of −100 V. The plasma potential was obtained from the knee in the current–voltage curve and kT_e from the exponential part; the floating potential was measured at I_{probe} = 0. These parameters were found not to vary with the HW bias voltage, but changed with the argon pressure. The plasma density was estimated from the ion saturation current using orbital motion limit theory (cylindrical probe) and was between 10^9 and 10^{10} cm^{-3} for all pressures. The electron temperature measured at 1 mTorr is about twice that measured at 100 mTorr. The high plasma potential (table 1) was unexpected. A possible explanation is that the inner surfaces of the chamber are not good conductors and allow the walls to charge up [15]. This was tested by earthing the top plate which resulted in a lowering of V_p and V_f by 10 V. The lack of matching network may also contribute to this effect.

| V_p (V) | 60 | 100 |
| V_f (V) | 80 | 100 |
| kT_e (eV) | 3-4 | 2 |

#### Table 1. Main plasma parameters determined from the I(V) curves obtained with the Langmuir probe situated at the substrate location for V_{HW} = −100 V (floating top plate).

### 3.2. With HW

In order to study the effect of the presence of the biased HW on the main plasma characteristics in the reactor. At this pressure the mean free path \( \lambda \) of the electrons is large [14] (≈ several tens of cm), and they diffuse easily in the whole chamber. The ionization events take place in a large volume of the chamber resulting in a quasi-homogeneous plasma. As the argon pressure is increased to 10 mTorr, the mean free path decreases and the ionization zone becomes more localized near the antenna. At 100 mTorr (\( \lambda \approx 0.5 \) cm) the plasma is confined in the antenna as shown by the peak in \( I_{\text{sat}} \) present in this zone. The argon ions created in the antenna expand into the chamber leading to a decrease of \( I_{\text{sat}} \) towards the substrate. Consequently, the characteristics of the plasma at the substrate position will vary with pressure. Since the values for \( I_{\text{sat}} \) at the substrate position are similar for 1 mTorr and 10 mTorr, only 1 mTorr and 100 mTorr pressure conditions will be analysed below.

Figure 2(b) shows the evolution of \( I_{\text{sat}} \) versus pressure at the substrate (\( x = 4.5 \) cm) and HW (\( x = 8 \) cm) positions. A peak is observed at about 5 mTorr for both positions on the axis. For \( P < 5 \) mTorr the mean free path is large and an increase of the pressure causes the collision frequency to rise and results in more effective ionization. For \( P > 5 \) mTorr the mean free path decreases and we enter the diffusion region. The maximum of the curve corresponds to the optimum coupling between the input power and the ionization development in this particular plasma.
Figure 3. Argon plasma characterization when the HW is set in the deposition configuration position. (a) $I_{\text{sat}}$ along the experimental axis at 1 mTorr, $-100$ V and 100 mTorr, $-350$ V, (b) $I_{\text{sat}}$ evolution as a function of the bias voltage, at 1 mTorr and 100 mTorr. The Langmuir probe is located at the substrate position.

chamber, the HW is then introduced into the chamber and centred in front of the antenna (deposition configuration, figure 1(b)). Its axis is perpendicular to the experimental main axis, and parallel to the substrate surface.

3.2.1. HW on main axis (deposition configuration). The evolution of $I_{\text{sat}}$ along the main axis at 1 mTorr, $-100$ V and 100 mTorr, $-350$ V, is presented in figure 3(a). The plasma is strongly perturbed near the biased HW. The ion flux drops sharply inside the HW, showing the existence of an ion sheath which, for the present parameters, would have a width of almost 1 cm. About 1 cm away from the HW, the plasma is not modified at either pressure and, for $x \leq 6$ cm, $I_{\text{sat}}$ is as previously measured (figure 2(a)).

Figure 3(b) shows the variation of $I_{\text{sat}}$ at the substrate position as a function of the HW bias voltage for two argon pressures. At 1 mTorr the current is constant for all voltages below the plasma potential (table 1). Above $V_p$, the plasma is strongly perturbed in the whole chamber for both pressures. At 100 mTorr for bias voltages between 100 and $-200$ V there is little change in $I_{\text{sat}}$. For more negative values of the voltage, $I_{\text{sat}}$ increases slightly. It is important to note that this rise coincides with the secondary discharge appearance inside the wire.

Figure 4. Evolution of the saturation current along the axis for a bias voltage of $-350$ V, at 1 mTorr and 100 mTorr gas pressures.

Nevertheless, as this last rise at 100 mTorr is rather small, it can be concluded that the major perturbation of the biased HW is localized, producing only a minor variation of $I_{\text{sat}}$ at the substrate position. Hence, the Ar$^+$ flux bombarding the substrate during the deposition is approximately the same whatever the HW bias voltage.

3.2.2. HW off main axis. In order to characterize the plasma inside the HW when the secondary discharge is initiated, and the area between the wire and the antenna, the HW is subsequently retracted from its previous position (figure 1(b)). Even if $I_{\text{sat}}$ is expected to be lower at the HW extremity than in the middle, it will be possible with this set-up to show the ion flux evolution along the axis from $x = 0$ to the antenna position.

Figure 4 shows the evolution of $I_{\text{sat}}$ along the axis for a constant HW voltage of $-350$ V and for 1 mTorr and 100 mTorr pressure conditions. The decrease of $I_{\text{sat}}$ around the HW, shown in figure 3(a), is verified but a great difference between low and high pressure can be seen (figure 4). Indeed, at 100 mTorr, there is a peak in $I_{\text{sat}}$ at the centre of the HW. This phenomenon coincides with the observation of an intense luminous area inside the HW, and is attributed to the creation of a secondary DC discharge [1] which will be discussed below in section 3.2.3.

At 1 mTorr, this luminosity is not observed and $I_{\text{sat}}$ remains low inside the HW. This particular behaviour can be explained by comparing the sheath thickness to the HW diameter. From Child–Langmuir theory the sheath thickness was estimated as 0.6 cm and 0.3 cm at $-350$ V and $-100$ V respectively. As the diameter of the HW is about 1 cm, the sheath will almost take up the whole volume inside, and the plasma will be excluded. The existence of a slight increase of $I_{\text{sat}}$ in the centre of the HW (figure 4) evidences that the plasma is about to penetrate inside. Although the interpretation of Langmuir probes is problematical within sheaths, this confirms that the sheath widths are indeed of the order of a few mm in agreement with many other experiments in sheaths [16]. A schematic of the sheath formation around and within the HW and of the subsequent density and potential profiles across the HW is shown in figure 5 for low and high pressure.
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The initiation of the secondary discharge was investigated by measuring the variation of $I_{sat}$ in the centre of the HW as a function of the bias voltage (figure 6). The area around the HW is shown on an expanded scale, at both Ar pressures and for $-100$ and $-350$ V HW bias voltages in figure 7(a), (b).

Figure 6 shows that the variation of $I_{sat}$ as a function of bias has opposite trends for 1 mTorr and 100 mTorr. At 100 mTorr, for large positive voltages ($> V_p$), the increase is probably due to the ionization caused by electrons drawn to the probe. For bias voltages more negative than $-50$ V, the increase of $I_{sat}$ is caused by the initiation of the secondary discharge. Indeed, in figure 7(b) the $I_{sat}$ peak inside the HW is visible at $-350$ V and $-100$ V, whereas it does not exist at $+50$ V. For voltages below $V_p$, the minimum observed at about $-50$ V in figure 6 corresponds to the minimum voltage required for the ignition of the secondary discharge at 100 mTorr argon pressure. This effect qualitatively follows the Paschen law [16–18]. The low breakdown voltage measured for our experimental conditions (50 V instead of several hundreds of volts) is likely due to the presence of primary electrons generated by the main HF plasma.

For 1 mTorr argon pressure, the perturbation of the plasma induced by either bias voltage on the HW only extends a distance of about 1 cm (figure 7(a)). This can be simply interpreted as the formation of an ion sheath which increases in size as the bias is made more negative. This results in a decrease of $I_{sat}$ inside the HW, as shown in figure 6.

3.2.3. Secondary discharge. The secondary discharge has also been observed by emission spectroscopy as shown in figure 8. In this experiment the volume of the plasma contributing to the optical signal is located around the HW [1]. For pressures above 50 mTorr, increasingly negative bias voltages cause an increase of the Pd line emission (340.4 nm). This phenomenon takes place when the secondary discharge appears inside the HW.

The high luminosity of the secondary discharge is probably caused by suprathermal electrons as the increase in the emitted light is much greater than the increase in $I_{sat}$. If we consider that this discharge is caused by secondary electrons produced by ions striking the HW, it is possible...
to estimate some characteristic parameters. The ionization cross section for electrons of about 400 eV colliding with argon is about $3 \times 10^{-16}$ cm$^2$ [14] which at 100 mTorr yields a mean free path of 1 cm. For the present plasma conditions it has been shown before that the sheath width is a few mm allowing sheaths to form inside the HW with a small volume of plasma of diameter a few mm in the centre (figure 5). The pitch of the HW is sufficiently small that the sheaths can join up axially along the HW giving a geometry similar to a hollow cathode. An electron liberated from some portion of the HW will be accelerated into the centre of the HW, ionize, produce a second electron while losing some of its own energy and become trapped between the sheaths forming the boundary of the plasma inside the HW. As is well known, this will increase the plasma density in this ‘hollow cathode’ by a factor of 2 or so and dramatically increase the light output [20, 21]. At lower voltages, the secondary electron emission coefficient decreases as does the ionization (and excitation) cross section.

4. Deposition rate

For these experiments, the variation of $I_{sat}$ inside the HW is recorded as a function of the pressure for HW bias voltages of $-100$ V and $-350$ V (figure 9). For pressures lower than about 50 mTorr, the evolution of $I_{sat}$ is the same as that measured without the HW in the chamber (figure 2(b)). The strong current increase observed at $-350$ V for pressures above 50 mTorr is correlated with the Pd line emission increase observed in figure 8 and is attributed to the presence of the secondary discharge. For comparison, two series of deposits have been performed for different Ar pressures and HW bias voltages of $-100$ V and $-350$ V.

Deposition rates deduced from RBS are plotted in figure 10. For the 1 mTorr to 50 mTorr pressure range the Pd deposition rate follows the same evolution as $I_{sat}$ (figure 9). In this pressure range, the deposition rate of Pd strongly depends on the HW bias voltage and is about 2 or 3 times larger at $-350$ V than at $-100$ V. For $P \leq 5$ mTorr, the variation of the sputter rate can be explained simply by considering the flux and energy of the ions impinging onto the HW. Supposing a non-collisional sheath in this low pressure range [14], we can estimate that the energy of the ions striking the HW equals $V_p - V_{HW}$ (with $V_p \approx 80$ V), which leads to 430 eV and 180 eV for bias voltages of $-350$ V and $-100$ V, respectively. The corresponding sputtering yields obtained from [14] in the case of a Pd target sputtered by Ar$^+$ ions, are 2 and 1. Including the difference in the measured flux of a factor of approximately 0.9 at 1 mTorr (figure 9), we can deduce a mean factor of about 2 between Pd sputtering efficiency at $-350$ V and $-100$ V. This is similar to the mean value of about 2.5 obtained from the RBS results at 1 mTorr (figure 10).

For higher pressures ($P > 5$ mTorr), both the ion flux and mean free path decrease leading to a decreasing ion flux impinging onto the HW and a decreasing ion energy as charge exchange collisions occur in the sheath. Hence a direct correlation between the $I_{sat}(-350$ V)/$I_{sat}(-100$ V) ratio and the corresponding deposition rate ratio cannot be simply established for these higher pressures.

When the pressure is above 50 mTorr the experimental results obtained for bias voltages of $-100$ V and $-350$ V strongly differ (figures 9, 10). For low bias voltage ($-100$ V), there is no strong secondary discharge in the HW and the Pd deposition rate and $I_{sat}$ show similar trends, which is the general evolution of ion flux in the chamber (figure 2(b)). The ions involved in the sputtering of the
5. Conclusion

The HF argon plasma used in the deposition of Pd has been characterized, as well as the secondary DC discharge that is initiated inside the palladium HW for large bias voltages and gas pressures. At low pressure (<5 mTorr) the electron mean free path for ionizing collisions is of the order of the system dimensions and the plasma density is uniform; at high pressure (>5 mTorr) diffusion occurs from the excitation antenna (where the ionization is localized) to the walls and substrate.

When the biased metallic HW is added in the chamber, the argon plasma is only locally perturbed due to the formation of a sheath with a width of few mm. At low pressures a well is observed in the ion flux in the centre of the HW since the sheath width is close to the diameter of the HW. For higher gas pressures a secondary plasma is created inside the HW below a \( V_{HW} \) threshold value (−50 V at 100 mTorr) and a peak in the ion flux is observed. This suggests the presence of a hollow cathode type discharge where electrons are trapped inside the sheaths of the HW. This phenomenon is accompanied by an intense rise of the Pd line emission from the plasma and of the deposition rate on the substrate. Hence, when present, the secondary discharge in the HW determines the sputtering process and leads to large deposition rates. Since the presence of the HW does not affect the Ar\(^{+}\) ion flux onto the substrate, the ion energy during deposition (\( V_p - V_f \)) is given by the primary discharge created by the antenna and is independent of the HW bias voltage.

The plasma characterization (Langmuir probe, optical emission spectroscopy) has lead to a better understanding of the sputtering process and of the resulting deposition rate on the substrate. Still the surface morphology of the deposited film will also depend on the plasma characteristics and this will be pursued further in later work.

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References