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# Plasma-based ion implantation : a valuable technology for the elaboration of innovative materials and nanostructured thin films

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**Abstract.** Plasma-based ion implantation (PBII), invented in 1987, can now be considered as a mature technology for thin film modification. After a short recall of the principle and physics of PBII, its advantages and disadvantages, as compared to conventional ion beam implantation, are listed and commented. The elaboration of thin films or the modification of their functional properties by PBII are now currently achieved in many application fields, such as microelectronics (plasma doping / PLAD), biomaterials (surgical implants, bio- and blood-compatible materials), plastics (grafting, surface adhesion), metallurgy (hard coatings, tribology), to name a few. The major interest of PBII processing lies, on one hand, in its flexibility in terms of ion implantation energy (from zero to 100 keV), of operating conditions (plasma density, collisional or non-collisional ion sheath), and, on the other hand, in the possibility to easily transfer processes from the laboratory to industry. The possibility to modify the composition and the physical nature of the films, or to change drastically their physical properties over several orders of magnitude makes this technology very attractive for the elaboration of innovative materials, including metastable materials, and the realization of micro- or nanostructures. A review of the state-of-the-art in these domains is presented and illustrated through a few selected examples. The perspectives opened by PBII processing, as well as its limitations, are discussed.

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## **1. Introduction**

Plasma-based ion implantation (PBII) was initially developed in 1987 by Conrad [1,2] in order to circumvent the limitations and cost of conventional implanters. In the PBII technique, substrates are immersed directly in the plasma and biased negatively with high voltage pulses. As the plasma conformably surrounds the substrate, its whole surface is implanted at the same time, so that scanning and manipulation are not necessary. PBII also eliminates the intermediate stages of beam extraction and acceleration.

At the origin, PBII appeared particularly attractive for mass production, in metallurgy, and the first applications were conducted with the objective to improve surface properties of metals and alloys, such as wear or corrosion resistance, adhesion, hardness, or tribologic behaviour (see for instance chapter 11 of [3]). Nowadays, the elaboration of thin films and the modification of their functional properties by plasma-based ion implantation are now currently achieved in many other application fields, such as microelectronics (plasma doping and deuterium/hydrogen implantation) [4], biomaterials (surgical implants, bio- and blood-compatible materials) [5], plastics (grafting, surface adhesion), to name a few. The major interest of plasma-based ion implantation processing lies, on one hand, in its flexibility in terms of ion implantation energy (from zero to 100 keV), of operating conditions (density, collisional or non-collisional ion sheath), of substrate geometry (two- or tri-dimensional shapes), and, on the other hand, in the possibility to easily transfer most of the processes from the laboratory to industry.

The objective of this article is to show that PBII technology is particularly well-suited to the elaboration of thin films of innovative materials and a quite flexible tool for the fabrication of

micro- or nanostructures. Therefore, after a short recall of the physics of PBII and the plasma specifications required, and the description of a plasma reactor able to fulfill most of these specifications, we present an overview of the applications of PBII processing in microelectronics and micro-nanotechnologies. Then, before concluding, we present two examples of modification of the magnetic properties of thin films via PBII, and its application to the fabrication of magnetic micro- or nanostructures.

## **2. Physics of plasma-based ion implantation**

### **2.1. Principle of PBII : interest, advantages, limitations**

The PBII technique has many advantages over conventional implantation, such as high dose rates ( $10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ ), wide ion energy range starting from 0 up to 100 keV, large implant areas, and treatment of 3-D workpieces with complex shapes. However, a few limitations and disadvantages of PBII in comparison to beam-line ion implantation must be pointed out : i) no ion-mass separation : all the ions in the plasma (monoatomic and molecular ions) are implanted; ii) not strictly mono-energetic, mainly depending on gas pressure and pulse shape; iii) in situ dose monitoring is difficult and requires calibration; iv) the production of secondary electrons under ion impact and their acceleration in the sheath leads to high current densities and generation of X-rays. Despite these disadvantages, PBII appears particularly attractive for mass production, in metallurgy, but also for the surface modification of polymers (hardening, producing wettability, adhesion-promotion treatments). However, the difficulty with polymers, and more generally with dielectric materials, lies in their insulating character. Therefore, the main objectives of this article are to discuss the possibility and to identify the limitations of PBII processing of insulating substrates, and then to report the surface modifications achieved on polymers using this implantation technology.

After a brief recall of the basic mechanisms of PBII on conducting substrates, the general hypotheses governing PBII processing of insulating substrates are then presented and analyzed in terms of process limitations and new plasma specifications. Finally, before concluding, the experimental results obtained in the PBII processing of polymers are reported and summarized.

## 2. PBII processing of conductive substrates

### 2.1. Plasma sheath dynamics

When a rectangular negative high voltage pulse is applied to a conducting substrate immersed in plasma, an ion sheath develops around the substrate and the ions are accelerated towards the substrate surface, where they are implanted. The sheath dynamics has already been extensively studied [3-6] and is now well understood. According to the time scale, three different phases can be distinguished : 1) on the time scale of the inverse plasma frequency,  $\omega_{pe}^{-1} = (\epsilon_0 m_e/n_e e^2)^{1/2}$ , electrons are repelled, while ions, much more massive than electrons, remain in place. Therefore, an ion "matrix" sheath, free of electrons is formed around the substrate; 2) on the time scale of the inverse ion plasma frequency,  $\omega_{pi}^{-1} = (\epsilon_0 m_i/n_i e^2)^{1/2}$ , the ions in the matrix sheath close to the substrate are accelerated towards the substrate and the ion current density reaches a sharp maximum, before decreasing (cf. Fig. 1). Then, once the ions in the matrix are collected (the energy distribution of ions of course depends on their initial position in the ion "matrix"), new ions are extracted from the plasma edge, and the plasma sheath expands; 3) on a large time scale, typically tens of  $\omega_{pi}^{-1}$ , the sheath and the current density evolve to a steady state (static sheath) given by the Child-Langmuir law. In the above expressions for the electron and ion plasma frequencies,  $\epsilon_0$  is the permittivity of free

space,  $n_e$  and  $n_i$  are the electron and ion densities, and  $m_e$  and  $m_i$  are their masses, respectively. If the pulse duration is much longer than a few tens of  $\omega_{pi}^{-1}$ , e.g. 100 or 1000  $\omega_{pi}^{-1}$ , the additional ion contribution during the initial transient regime (ion matrix and sheath expansion) can be considered negligible with respect to the total contribution of implanted ions. Therefore, as a first approximation, the ion current density collected on the substrate can be assumed constant during the entire voltage pulse (see Fig.1).

## 2.2. Sheath expansion

Since in PBII, the duration of negative pulses is much longer than the inverse ion plasma frequency, we can generally consider that the sheath thickness,  $g$ , is that given by the steady-state Child-Langmuir law, i.e.

$$g = \frac{2^{5/2} \epsilon_0^{1/2}}{3 \exp(-1/4) e^{1/4} n_e^{1/2} (kT_e)^{1/4}} \frac{V_0^{3/4}}{(kT_e)^{1/4}} \approx \lambda_{De} (eV_0 / kT_e)^{3/4}, \quad (1)$$

where  $-V_0$  is the potential of the substrate during the pulse (as a first approximation, the plasma potential is assumed equal to the ground potential),  $T_e$  is the electron temperature of the plasma,  $k$  is the Boltzmann constant, and  $\lambda_{De}$  the electron Debye length. As shown in Eq. (1),  $g$  is independent of the ion mass, depends little on the electron temperature, and is inversely proportional to the square root of the plasma density. The variation of  $g$  as a function of pulse voltage is shown in Fig. 2, when considering plasmas with densities  $n_e$  from  $10^9$  to  $10^{11} \text{ cm}^{-3}$  and an electron temperature  $kT_e = 1 \text{ eV}$ . For example, the sheath thickness exceeds 40 cm for  $V_0 = 100 \text{ kV}$  and  $n_e = 10^{10} \text{ cm}^{-3}$ . This result has strong implications for the design of PBII reactors.

## 2.3. Plasma specifications

A first specification concerns the volume of the plasma, which must be much larger than the sheath thickness in order to avoid total depletion of the plasma between the substrate and the vessel walls. As an example, at  $V_0 = 100$  kV, the sheath thickness (40 cm) is such that the implantation of a 30 cm horizontal wafer requires reactor dimensions more than one meter in diameter and 40 cm high. The other plasma specification mainly concerns the energy distribution function of the ions (IEDF) being implanted. Since, for a given application, the energy of implanted ions is generally predetermined, control of the energy distribution function is necessary. Implantation of monoenergetic ions using PBII requires that ion transit in the sheath must be collisionless, i.e. an ion mean free path  $\lambda_{in}$  on the order or longer than the sheath thickness,  $g$ . Under these conditions, monoenergetic ion bombardment can be obtained. Otherwise, ion-neutral collisions in the sheath (elastic collisions and inelastic collisions, such as charge-exchange collisions) will significantly reduce the ion energy, well below the expected value. Assuming an overall ion-neutral collision cross-section  $\sigma_{in}$  independent of the ion energy, the threshold condition  $\lambda_{in} = g$  for a collisionless sheath can be simply expressed in terms of gas pressure  $p$ ,  $n_e$  and  $V_0$  according to the relationship

$$p = \frac{kT_0}{\sigma_{in} \lambda_{De}} \left( \frac{kT_e}{eV_0} \right)^{3/4} \quad (2)$$

The evolution of  $p$  in Eq. (2) as a function of  $V_0$  is shown in Fig. 3, when considering an argon plasma with  $n_e$  values ranging from  $10^9$  to  $10^{11}$   $\text{cm}^{-3}$ , an electron temperature  $kT_e = 1$  eV, an overall cross-section of argon ions on atoms  $\sigma_{in} = 6 \times 10^{-15}$   $\text{cm}^2$ , and gas temperature  $T_0 = 300$  K. For example, for  $V_0 = 100$  kV, a collisionless ion sheath requires  $p < 10^{-4}$  torr (1 torr = 133 Pa) for  $n_e = 10^{10}$   $\text{cm}^{-3}$ . This result clearly demonstrates that PBII processing in the high-energy range requires large plasma volumes at very low pressures. Here, the difficulty lies mainly in achieving gas breakdown below  $10^{-4}$  torr. In order to illustrate this challenge,

we must recall that the mean free path for ionization of a 50-eV electron is 11.5 m in argon at  $10^{-4}$  torr, and 115 m at  $10^{-5}$  torr.

## 2.2. Sheath dynamics

## 2.3. Plasma specifications

### **3. Example of PBII facility**

As PBII processing usually requires to generate low-pressure, large-size plasmas, dimension scalability of the different categories of microwave plasmas is of prime importance to estimate their respective interest for PBII. Generally, antenna applicators seem to be superior to transmission-line applicators when one needs to sustain large volume discharges in metal chambers through a dielectric wall. With transmission-line applicators, the transverse extend of the wave field is limited, since microwave power is concentrated along the guided structure. Therefore, only a thin layer of plasma is generated in the chamber, close to the dielectric window<sup>[3]</sup>.

In the same way, although a slight density modulation may appear, plasmas obtained withstanding wave antenna systems are naturally more uniform than with travelling wave systems. The reason is that, for standing wave systems, the microwave power along the propagation direction is distributed uniformly owing to the standing wave pattern.

Because of the difficulty to scale-up quasi-uniform magnetic fields, and also of the anisotropic character of magnetized plasmas, the use of ECR discharges as (very) low pressure plasmas for PBII processing seems strictly limited either to small and planar substrates or to very specific applications. For this reason, multipolar magnetic fields, which can confine and generate low-pressure, large size, isotropic plasmas appear particularly well suited for PBII processing. In addition, the scaling-up of these plasmas is possible up to several cubic meters without any difficulty<sup>[51,52]</sup>.

Among multipolar discharges, those excited at very low pressure by DECR, which can produce a peripheral ionization facing the substrates are perfectly adapted to the treatment of large size and three-dimensional objects with convex shapes. In contrast with hot cathode multipolar discharges, DECR plasmas can operate with reactive gases such as oxygen, fluorine and other corrosive precursors. Thus, sequential processing steps (cleaning, oxidation, etching, CVD deposition) before or after PBII can be achieved with any gas. An example of such a cylindrical DECR plasma reactor, 50 cm in diameter, 60 cm high, with, at its periphery, 24 tubular magnets with diametrical magnetization acting as as many "magnetron" structures excited by standing waves at 2.45 GHz, is shown in Fig. 14.

Finally, multipolar magnetic field structures, when excited by d.c. or r.f. voltages, may act as "magnetron" plasmas designed for direct or reactive sputtering. Such magnetron plasmas, covering the wall of a cylindrical reactor, could also be applied favorably to PBIID processing on three-dimensional substrates.

## **4. Modification of thin film properties via PBII**

### 4.1. Modification of electric properties : plasma doping

### 4.2. Transition of layer properties via PBII

#### 4.2.1. Review

It is well know that ion implantation can be used to change physical properties of a material implantation of interstitial or substitutional elements. This is the case, for example, for the doping of silicon with P, B or As. It is also possible to create new innovative materials, including metastable materials, by creating new phases. Then, physical properties of such new

phases can be quite different from the properties of the initial materials. For example, implantation of nitrogen in aluminium produces aluminium nitride, which is a dielectric material whereas aluminium is metallic. In the same way, the synthesis of the MgB<sub>2</sub> phase by boron implantation in magnesium produces a superconducting material whereas Mg is metallic.

#### 4.2.2. Ni

##### **Experimental**

A nickel film was deposited by direct sputtering assisted by a microwave multi-dipolar plasma. As shown in Figure 1, the plasma is produced by twenty elementary sources at the periphery of the reactor.

Target and substrate are immersed in a low pressure microwave plasma of argon ( $10^{-3}$  mbar) and can be biased independently of microwave plasma generation. The ions present in the plasma can be used firstly to sputter uniformly the target, and secondly to provide ion assistance by bombarding the substrate surface with independent and controlled bias (DC, RF or pulsed bias). The absence of a magnet configuration behind the target allows the use of magnetic materials as target materials, whereas magnetron sputtering of magnetic material is difficult. Good quality thin films can thus be deposited in this experimental set up.

The 60 nm thick nickel film was deposited with a target bias of – 600 V DC in an argon plasma of density  $7-8 \times 10^{10} \text{ cm}^{-3}$ . The silicon substrate was at the floating potential.

Then, by using PBII technique, the nickel film was implanted with the nitrogen ions produced in the microwave plasma reactor previously described [4]. The ion density of the nitrogen microwave plasma was  $2-3 \times 10^{10} \text{ cm}^{-3}$ . The frequency of the highly negative pulses applied to the sample was 50 Hz, time width 40  $\mu\text{s}$  and voltage up to 40 kV. The total implantation time was 10 s at 40 kV and 3 s at 15 kV. The atomic to molecular nitrogen ions current ratio

determined by mass spectrometry was 3.2. The ion dose implanted was calculated using a previous calibration of the process and was approximately  $2.9 \times 10^{17} \text{ cm}^{-2}$ , enough to reach  $\text{Ni}_3\text{N}$  stoichiometry.

## Results

In order to characterize the film before and after the implantation process, X-ray diffraction at grazing incidence (Fig. 2), SQUID susceptometer characterization (Fig. 3) and AFM (Tab. I) were performed. The XRD patterns (Fig. 2) shows that  $\text{Ni}_3\text{N}$  was synthesized with lattice parameters  $a=4.635 \text{ \AA}$  and  $c=4.314 \text{ \AA}$ . This result is in agreement with earlier works [5] which show a crystallization of  $\text{Ni}_3\text{N}$  in a h.c.p. sublattice structure with parameters values of  $a=4.621 \text{ \AA}$  and  $c=4.304 \text{ \AA}$ . Moreover, the FWHM of the diffraction peaks allows to conclude about the nano-crystalline state of Ni and  $\text{Ni}_3\text{N}$ .

The magnetic characterization (Fig. 3) performed by a SQUID susceptometer demonstrates that most of the starting ferromagnetic nickel has been transformed into a non magnetic nickel nitride. A decrease of 98% of the magnetization is observed. The persistence of a small ferromagnetic signal (less than 2% compared to pure Ni) has been assigned to residual non nitrated nickel.

AFM was also used to characterize the topography of the surface. As we can see in Table I, the average roughness of the nickel surface is very low (0.31 nm). After implantation, we observe an increase in roughness that remains in the nanometer range. This roughness however decrease when decreasing the implanted dose. Then, for applications that need very low roughness, decrease in film thickness can be a solution.

In parallel, we used a FLAPW (Full Potential Linearized Augmented Plane Wave) method [6] to determine the theoretical magnetic state of  $\text{Ni}_3\text{N}$ . This method performs DFT calculations using the local density approximation with wave functions as a basis. The Kohn-Sham

equation and energy functional are evaluated consistently using the FLAPW method. These calculations were performed with the crystal structure parameters derived from our X-ray measurements.

The results from the band structure calculations with spin polarized potential taking in the account a ferromagnetic state of  $\text{Ni}_3\text{N}$  led to the total DOS, the partial DOS and the 1-decomposed on the Ni site.

Examination of all these DOS and especially the total DOS provides evidence that no polarization of DOS is found indicating particularly no localized moment on the Ni atom in the  $\text{Ni}_3\text{N}$  ferromagnetic state case. The calculations also show that there is no DOS polarization in the interstitial space. Therefore, one can conclude that neither itinerant nor localized magnetism is present, proving a full paramagnetic state of this material.

#### 4.2.3.Mn

The elaboration of thin films and the modification of their functional properties by PBII are now currently achieved in many application fields, such as microelectronics, biomaterials, plastics, metallurgy, to name a few. Previous investigations in our group have been devoted to hydrogen, carbon or nitrogen insertion in rare earth-transition metal alloys. In this paper, we present the synthesis of  $\text{Mn}_4\text{N}$  by nitrogen implantation in a manganese layer while  $\text{Mn}_4\text{N}$  is usually synthesized by gas-solid reaction [1], MBE [2] or reactive sputtering [3]. Structural and magnetic characterizations have been performed using X-ray diffraction at grazing incidence, XPS and SQUID measurements. In parallel, a FLAPW method has been used to calculate the theoretical state of  $\text{Mn}_4\text{N}$  that is known as a ferrimagnetic material in which the magnetic moments of the  $\text{Mn}^1$  and the  $\text{Mn}^2$  sites are antiparallel (Figure 4). The results are compared to neutron diffraction and saturation measurements.

## II. Experimental

The manganese thin film has been deposited by direct sputtering assisted by multi-dipolar microwave plasma [4]. Target and substrate are immersed in the plasma and the ions produced can be used either to sputter uniformly the target, or to provide an ion assistance on the substrate surface, or both at the same time. The manganese target, built from manganese powder by hot pressing, has been sputtered using an argon-hydrogen plasma to avoid the oxidation of the deposited manganese. In fact, by using a pure argon plasma to sputter the target, even with a good vacuum ( $10^{-6}$  mbar), the oxygen concentration in the deposited layer

can reach 30 atomic % (determined with XPS analysis). When using an Ar-H<sub>2</sub> plasma, the oxygen concentration in the layer drops to 5 %. By adding a -10 V polarization on the substrate, an oxygen concentration of 2-3 % has been obtained. Thus, by using these process parameters, a 50 nm thick film of manganese has been deposited on silicon.

The plasma based ion implantation technique has been used to synthesize Mn<sub>4</sub>N. The Mn layer has been immersed in a nitrogen plasma produced by the microwave plasma reactor previously described [5] and negative high voltage pulses have been applied to it. The frequency of the pulses was 50 Hz, time width 30 μs and voltage up to 35 kV. To calculate the ion dose implanted per time unit, a calibration of the process has been previously performed using Nuclear Reaction Analysis (RNA). Then, using this calibration, 10<sup>17</sup> at. cm<sup>-2</sup> have been implanted to reach the Mn<sub>4</sub>N stoichiometry with a total implantation time of 2.8 s. During the process, the surface temperature has been evaluated to 420 K by thermal simulations.

### III. Results

The structural characterization of the layer before and after the implantation process has been performed using X-ray diffraction at grazing incidence. From the diffraction pattern of the manganese layer before implantation (Figure 1) we can deduce that the film does not contain any manganese oxide phase. Moreover, the peaks' FWHM (Full Width at Half Maximum) allows us to conclude about the nano-crystallized state of the manganese.

After implantation, according to the diffraction pattern, the layer contains several phases (Mn, Mn<sub>4</sub>N, Mn<sub>3</sub>N<sub>2</sub>, MnO ...). In addition, XPS analysis have been performed and have shown a low oxygen concentration in the layer (2-3 %) and a MnO top layer of 20 nm.

Moreover, the left shift of the manganese peaks is typically due to a solid solution of nitrogen in the manganese. It is then necessary to anneal the layer in order to allow the nitrogen in solid solution to crystallize. But, to avoid the diffusion of oxygen from the surface during the annealing, the MnO layer has been previously removed by sputtering. The X-ray diffraction pattern of the cleaned and annealed layer shows that the main phase is Mn<sub>4</sub>N.

The XPS depth concentration profile of the annealed layer shown on Figure 2 confirms that the oxygen concentration in the layer is around 2-3% and that the nitrogen concentration is equal to 20 %. The diffraction peak located at 55° is due to residual manganese or manganese silicides.

Then, a magnetic characterization of this Mn<sub>4</sub>N layer has been carried out using a SQUID susceptometer. The magnetization loop (Figure 3) shows a saturation of 100 emu.cm<sup>-3</sup> whereas the saturation of a pure Mn<sub>4</sub>N powder is between 180 and 190 emu.cm<sup>-3</sup>. The difference is assigned to the impurities, especially the oxygen, embedded in the film.

Moreover, the film exhibits a coercivity of 1000 Oe which is close to the coercivity of  $\text{Mn}_4\text{N}$  thin film deposited by reactive sputtering [3].

$\text{Mn}_4\text{N}$  has been successfully synthesized using the Plasma Based Ion Implantation technique. The saturation magnetization of this  $\text{Mn}_4\text{N}$  layer represents 50-55% of the maximum saturation obtained with pure  $\text{Mn}_4\text{N}$  powders, the difference being assigned to the 3% of oxygen embedded in the layer. In parallel, theoretical magnetic state of  $\text{Mn}_4\text{N}$  has been calculated using a FLAPW method and the results are in agreement with previous experimental measurements.

## **5. Application to the elaboration of magnetic micro- or nanostructures**

## **6. Conclusion and perspectives**

## References

- [1] J. R. Conrad, J. Appl. Phys. **62** (1987) 777
- [2] J. R. Conrad, J. L. Radtke, R. A. Dodd, F. J. Forzala, N. C. Tran, J. Appl. Phys. **62** (1987) 4591
- [3] A. Anders, editor, Handbook of Plasma Immersion Ion Implantation and Deposition, Wiley, New York (2000)
- [4] M. K. Weldon, V. Marsico, Y. J. Chabal, et al., J. Vac. Sci. Technol. B **15** (1997) 1065-1073
- [5] M. Rinner, J. Gerlach, W. Ensinger, Surf. Coat. Technol. **132** (2000) 23-27

**Table I.** Examples of modification or transition of layer properties via implantation.

	<b>Starting material</b>	<b>Implanted element</b>	<b>Results</b>
<b>Mechanical transitions</b>	Steel TiAl6V4 Aluminium	N, C, O, Cr	wear increase friction decrease hardness increase
<b>Electrical transitions</b>	Al (metallic)	N	AlN (dielectric)
	Si (semiconductor)	P, B	Si-n or Si-p (resistivity)
	Si (semiconductor)	N, O	Si <sub>3</sub> N <sub>4</sub> , SiO <sub>2</sub>
	Mg (metallic)	B	MgB <sub>2</sub> (superconductor)

**Table II.** Roughness of the Ni layer before and after the nitrogen PBI process.

	Rp-v (nm)	Rms roughness	Average roughness
Before implantation	2.84	0.38	0.31
After implantation	12.8	1.64	1.3

## Figure captions

**Figure 1.** Theoretical evolution of the reduced ion current density  $J$  with reduced time  $\tau$  (the time unit is the inverse ion plasma frequency  $\omega_{pi}^{-1}$ ) when applying a negative step voltage on a planar substrate (from reference [Lieberman]). The contributions from ion matrix ( $\tau \leq 2.7$ ) and sheath expansion are indicated.

**Figure 2.** Sheath thickness  $g$  as a function of the voltage amplitude  $V_0$  of negative pulses. The electron density of the plasma is  $n_e = 10^{10} \text{ cm}^{-3}$  and the electron temperature  $kT_e = 1 \text{ eV}$ .

**Figure 3.** Transition from collisional to non-collisional sheaths : argon pressure  $p$  as a function of the voltage amplitude  $V_0$  of a negative pulse for the threshold condition  $\lambda_{in}(p) = g(V_0)$ . The sheath thickness is  $g$  and  $\lambda_{in}$  the mean free path for the ion-neutral collisions.

**Figure 4.** Schematic design of an example of PBII facility : 1) high voltage substrate holder; 2) gas inlet; 3) pumping; 4) high voltage pulse generator 100 kV – 100 A using a pulse transformer; 5) 24 magnet bars for multipolar magnetic field confinement and ECR resonance condition; 6) 24 linear microwave applicators running along the magnet bars. The plasma reactor is 60 cm in diameter and 70 cm high.

**Figure 5.** Top view of a nitrogen DECR plasma in the reactor described in Fig. 4.

**Figure 6.** Typical voltage and current waveforms obtained with a 1 mtorr DECR nitrogen plasma using a 100 kV – 100 A pulse transformer. The surface of the stainless steel substrate is 300 cm<sup>2</sup>.

**Figure 7.** Grazing incidence X-ray diffraction pattern of Ni and Ni<sub>3</sub>N.

**Figure 8.** Magnetization loop of Ni and Ni<sub>3</sub>N.

**Figure 9.** Grazing incidence X-ray diffraction pattern of the Mn layer before and after implantation.

**Figure 10.** XPS depth concentration profile of the implanted, cleaned and annealed Mn layer.

**Figure 11.** Magnetization loop of the implanted, cleaned and annealed Mn layer.

**Figure 12.** Successive steps of the elaboration of magnetic nanostructures using photoresist masks.

**Figure 13.** Lithography pattern and SEM image of the photoresist after development.

**Figure 14.** SEM image of the magnetic microstructure after implantation and resist stripping.