Plasma-based ion implantation and deposition:

A review of physics, technology, and applications

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Abstract

After pioneering work in the 1980s, plasma-based ion implantation (PBII) and plasma-based ion implantation and deposition (PBIID) can now be considered mature technologies for surface modification and thin film deposition. This review starts by looking at the historical development and recalling the basic ideas of PBII. Advantages and disadvantages are compared to conventional ion beam implantation and physical vapor deposition for PBII and PBIID, respectively, followed by a summary of the physics of sheath dynamics, plasma and pulse specifications, plasma diagnostics, and process modelling. The review moves on to technology considerations for plasma sources and process reactors. PBII surface modification and PBIID coatings are applied in a wide range of situations. They include the by-now traditional tribological applications of reducing wear and corrosion through the formation of hard, tough, smooth, low-friction and chemically inert phases and coatings, e.g. for engine components. PBII has become viable for the formation of shallow junctions and other applications in microelectronics. More recently, the rapidly growing field of biomaterial synthesis makes used

of PBII&D to produce surgical implants, bio- and blood-compatible surfaces and coatings, etc. With limitations, also non-conducting materials such as plastic sheets can be treated. The major interest in PBII processing originates from its flexibility in ion energy (from a few eV up to about 100 keV), and the capability to efficiently treat, or deposit on, large areas, and (within limits) to process non-flat, three-dimensional workpieces, including forming and modifying metastable phases and nanostructures.

We use the acronym PBII&D when referring to both implantation and deposition, while PBIID implies that deposition is part of the process.

I. INTRODUCTION

Among various ion source concepts reviewed in this IEEE Special Issue, plasma-based ion implantation (PBII) and deposition (PBIID) are truly special techniques because the conventional separation of ion source and target does not apply. In contrast to conventional ion implantation, the target is part of the beam-forming system. Yet, PBII&D represents a group of techniques in which ion beams are generated and used. We use the acronym "PBII&D" when generally referring to both ion implantation and deposition, while "PBIID" implies that deposition is an integral part of the treatment process.

A conventional ion source is comprised of a plasma generator and means for ion extraction and acceleration. Usually, the type of discharge in the plasma generator appears in the name of the ion source, e.g., radio frequency (RF) ion source, electron cyclotron resonance (ECR) ion source), etc. Ion extraction is typically done either through a single hole (Pierce) system or via multi-aperture, gridded extraction [1-3].

Ion beam systems are characterized by having a preferred direction, the direction of ion beam propagation. As a consequence, ion beam treatment, like ion implantation, is a line-of-sight process, which is well-suited for planar substrates like wafers, but impractical for treatment of three-dimensional objects because complicated substrate motion would be required.

Plasma immersion ion implantation and deposition was originally developed as a revolutionary non-line-of-sight process by incorporating a three dimensionally shaped target (substrate) in the ion acceleration scheme itself, rather than utilizing conventional ion extraction. The to-be-treated object was immersed in the plasma, and by biasing it, it became part of an ion source in a more general sense. Ion acceleration is occurs in a dynamic, self-adjusting sheath that forms around the biased target surface.

Plasma based ion implantation and deposition is known by a variety of names, acronyms, and trademarks, including, but not limited to the following: Plasma Source Ion Implantation (PSII), Plasma Immersion Ion Implantation (PIII or PI^3), Plasma Ion Implantation (PII or PI^2), Plasma Ion Plating (PIP), Plasma Immersion Ion Implantation and Deposition (PIIID), Metal Plasma Immersion Ion Implantation and Deposition (MePIIID), IonClad, Plasma Doping (PLAD), Plasma Ion Immersion Processing (PIIP). Some of these names are synonymous; others emphasize a certain aspect such as the presence of metal ions. More recently, the term Plasma-Based Ion Implantation and Deposition (PBII&D) has gained popularity, perhaps because this is the newly adopted name of the series of international workshops.

In this review, a brief introduction to the physical background and history is given, followed by considerations to more recent developments in technology and applications.

II. CHRONOLOGY OF PLASMA-BASED ION IMPLANTATION (PBII) AND ITS DEVELOPMENT TO A HYBRID TECHNIQUE WITH DEPOSITION (PBIID)

Before the physics of PBII and PBIID is explained in some detail, a look at the historical development is deserved. The physical roots of plasma based ion implantation can be traced back several decades, and in particular to simulation work in the 1960s by Widner and co-workers [4] who investigated the generation of ion acoustic waves in plasmas by applying negative voltage pulses to electrode plates. Another body of work was ion implantation research by Adler and co-workers [5] at Mission Research in the early 1980s. They used metal ions from a pulsed metal plasma source and pulsed-biased the substrate holder up to –80 kV, achieving ion implantation without the use of ion extraction in an ion source. The historically important impetus came with the work of Conrad and co-workers [6] at the University of Wisconsin in

1986, when the PBII principle was clearly spelled out and applied to ion treatment of three-dimensional components. Conrad and his group made major contributions to the physics of the high voltage sheath [7] and materials modification using the PSII principle [8, 9] (initially, the acronym PSII was preferred). They stimulated research at several laboratories throughout the world [10-17], which eventually lead to the start of the PBII-workshop series in 1994 [18].

From an application point of view, two major research directions emerged in the late 1980s and early 1990s. One was the improvement of wear and corrosion behavior of metal surfaces, which was mainly accomplished by formation of nitride phases on and near the surface of metal parts treated with nitrogen-PBII [6, 9, 19, 20]. PBII was thought as a technique between traditional high temperature nitriding and nitrogen ion implantation, to be further discussed below. The other research direction was for large area doping of semiconductors wafers and patterned structures, such as trenches [12, 13, 21-23].

The depth associated with ion implantation is relatively shallow (typically 100 nm or less), and treatment depth can be greatly enhanced by diffusion at elevated temperature. In the early 1990s, a new idea was pursued, namely combining implantation with deposition, such as to create almost any desirable elemental composition profile ("pseudo-implantation." [24]). A preferred "condensable" plasma was found in cathodic-arc generated plasma [25] because such plasma is characterized by a very high degree of ionization and the presence of multiply charged ions [26, 27], thus application of substrate bias is very efficient. Cathodic arcs are also known as vacuum arcs [28] as long as the process gas can be neglected. PBII with cathodic arcs became known as Metal Plasma Immersion Ion Implantation and Deposition (MePIIID) [29, 30] and under other names such as arc ion plating (AIP) [31]. Condensable plasmas can also be generated by other means, both of physical and chemical nature. For example, the process may

use sputtered material, especially when measures are taken to at least partially ionize the sputtered atoms [32-34]. Another example of having deposition involved is when the processing gas is a precursor gas whose radicals can condense and form a film. The most popular example is the deposition of (hydrogenated) diamond-like carbon made from hydrocarbon gas plasmas [35, 36].

The PBII field acknowledged the development towards hybrid processes with deposition by explicitly including 'D' for deposition in the acronym PBII&**D**. More information on the early and intermediate history of the field has been published elsewhere [37, 38], and much information can be found in the publications of the series of PBII (now PBII&D) workshops.

III. PHYSICS OF PLASMA-BASED ION IMPLANTATION

A. Principle of PBII: advantages and limitations

In the PBII technique, substrates are immersed directly in the plasma and biased negatively with high voltage pulses. The plasma conformably surrounds the substrate, its whole surface is implanted at the same time (non-uniformities at small feature size are discussed later). PBII eliminates the intermediate stages of beam extraction, focusing, scanning, and substrate or wafer manipulation.

The PBII technique has many advantages over conventional implantation, such as high ion current density and relatively short processing time (e.g. minutes), high dose rates (e.g. 10^{14} cm^{-2} s^{-1}), wide ion energy range (up to about 100 keV), large implant areas (100s of cm^2), 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) The PBII concept does not allow for ion-mass separation:

All ions at the plasma sheath edge are accelerated and implanted, regardless of ion mass and charge state. In the case of molecular gases, a mixture of molecular and atomic ions is utilized, which necessarily implies at least two peaks in the energy (per mass) distribution. (II) Even for atomic gases, the ion energy distribution is not mono-energetic, it depends gas pressure and bias pulse shape. (III) The production of secondary electrons under ion impact and their acceleration in the sheath leads to loads of the pulse modulator, making the process less economical and additionally cause undesirable x-rays when the sheath voltage exceeds about 20 kV; the issue becomes intolerable when the voltage approaches the 100 kV range. (IV) Biasing of dielectric objects is not possible, and the therefore treatment of insulators is limited to thin sheets or requires special set-ups with meshes.

Despite these disadvantages, PBII appears particularly attractive for certain processing steps in automotive, semiconductor, display, and biomedical industries.

B. Plasma sheath dynamics

When a rectangular high voltage negative 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, which has already been extensively studied for different geometries, planar, cylindrical, or spherical, in the case of non-collisional sheaths [4, 7, 11, 39-41] and collisional sheaths [42], is now well understood.

According to physical timescales, three different phases can be distinguished [43]. Suppose a bias voltage is supplied instantaneously, electrons are repelled on the timescale of the inverse electron plasma frequency,

$$\omega_{pe}^{-1} = \left(\varepsilon_0 m_e / n_e e^2 \right)^{1/2}, \tag{1}$$

exposing a matrix of ions, which are too massive (inertia) to respond: an "ion matrix sheath" is formed. In Eq.(1), the symbols have their usual meaning, ε_0 is the permittivity of free space, n_e and m_e are the electron density and mass. On the slower timescale of the inverse ion plasma frequency,

$$\omega_{pi}^{-1} = \left(\varepsilon_0 m_i / n_i \left(\overline{Q} e \right)^2 \right)^{1/2}, \tag{2}$$

the ions in the matrix sheath are accelerated towards the substrate and the ion current density reaches a sharp maximum, before decreasing (cf. Fig. 1). In Eq.(2), the index i refer to ions, and $\overline{Q}$ is the mean ion charges state number, which is unity for most but not all plasmas. In the initial transitional phase, the energy distribution of ions depends on their initial position in the ion matrix sheath. Plasma ions arriving at the sheath edge (that is, the boundary between sheath and plasma) are accelerated by the sheath's field and therefore "extracted" from the plasma. The sheath edge moves away from the biased surface, i.e., the sheath thickness increases.

Third, on a longer time scale, typically tens of ω_{pi}^{-1}, the sheath and the current density evolve toward a steady-state configuration. Experimental data (Fig. 2) were found to be in very good agreement with the theoretical evolution shown in Fig. 1. The duration of negative pulses is usually much longer than ω_{pi}^{-1}, therefore we can generally consider that the steady-state sheath thickness is given by the steady-state Child-Langmuir law, i.e.,

$$g = \frac{2^{5/2} \varepsilon_0 V_0^{3/4}}{3 \exp(-1/4) e^{1/4} n_e^{1/2} (kT_e)^{1/4}} \approx \lambda_{De} \left(\frac{eV_0}{kT_e} \right)^{3/4} \tag{3}$$

where V_0 is the negative potential of the substrate during the pulse (as a first approximation, the plasma potential can be assumed equal to the ground potential), T_e is the electron temperature, k

is the Boltzmann constant, and λ_{De} the electron Debye length. As shown in Eq.(3), 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. This is illustrated in Fig. 3. For example, considering a typical plasma with $n_e \approx 10^{10}$ cm^{-3} and $kT_e \approx 1$ eV, we find that the sheath thickness exceeds 40 cm as the voltage approaches $V_0 = 100$ kV. This extreme case has of course implications for the size and design of a high voltage PBII reactor. Though, most processing is done with much lower voltages, and the sheath thickness in not that critical unless substrates with three-dimensional features are being treated.

C. Plasma specifications

A first specification concerns the size of the plasma itself. When operating in a low energy range (bias is much less than 10 kV), the sheath thickness remains small with respect to the substrate and reactor dimensions, so that PBII processing in this range can be performed in any conventional plasma reactor. In contrast, when operating with bias of a few tens of kV, the plasma dimensions must be larger to avoid depletion of the plasma "reservoir" between the substrate and the vessel walls. The characteristic size of the plasma must exceed the Child-Langmuir sheath thickness, Eq.(3).

The second plasma specification concerns the energy distribution function of the ions (IEDF) being implanted. For most implantation applications, the desirable energy of implanted ions is predetermined, e.g. computed to achieve a desirable range of depth, and thus control of the energy distribution function is necessary. Ion implantation using PBII is never monoenergetic but this desirable feature can be best approximated by requiring that ions transit the sheath without collisions. In other words, the ion mean free path, λ_{in}, must be larger than the sheath

thickness, *g*. Otherwise, ion-neutral collisions in the sheath (elastic collisions and inelastic collisions, such as charge-exchange collisions) will significantly spread the distribution and reduce the mean ion energy well below the expected value. Additionally, the angular distribution with be broadened, which can be beneficial in some cases as for the treatment of sidewalls of trenches.

If we approximate the ion-neutral collision cross-section σ_{in} as being independent of the ion energy, the threshold condition $\lambda_{in} = g$ can be expressed in terms of gas pressure *p* according to

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

where T_0 is the temperature of neutrals (which could be as low as room temperature, $T_0 = 300$ K). The numerical evaluation of the transitional gas pressure as a function of bias voltage is shown in Fig. 4. For example, at the very high voltage $V_0 = 100$ kV, a collisionless ion sheath would require a pressure p < 10^{-4} Torr (1 Torr = 133 Pa), demonstrating that PBII in the high-energy range requires large plasma volumes at very low pressures. Here, the difficulty lies mainly in achieving plasma ignition below 10^{-4} Torr. In order to illustrate this challenge, we must recall that the mean free path for ionisation of 50-eV electrons is 11.5 m in argon at 10^{-4} Torr, and 115 m at 10^{-5} Torr.

III. TECHNOLOGY FOR PBII&D

A. Plasma technology

The beginnings of plasma-based ion implantation were characterized by a competition towards high voltages, and consequently towards large-size equipment. The high voltage "race"

exposed several practical difficulties such as producing large-volume uniform plasmas and excessive "plasma consumption" at low pressure. Indeed, a decrease in plasma density for large-volume conditions induces a correlating increase in sheath thickness, thus requiring even larger plasma dimensions. Efforts to increase the plasma density can be done and they produce a decrease of sheath thickness proportional to the inverse of the square root of the plasma density, cf. Eq.(3). This, however, causes an increase of the electric field at the substrate surface proportional to the square root of the plasma density [44], hence a much higher risks of arcing [45, 46].

The 1990s were characterized by the desire to scale PBII facilities to higher voltages and sizes [47-55]. Characteristic achievements are summarized in Table I, indicating that the performance of these high-voltage facilities involved compromises between reactor dimensions, operating pressure range, and plasma density. Plasmas were produced by DC hot cathode (filaments) or magnetron discharges, by RF discharges sustained at 13.56 MHz, or by ECR (electron cyclotron resonance) discharges at 2.45 GHz. However, besides contamination, the lifetime of filaments in reactive gas plasmas (oxygen, halogens) is too short for intense plasma production, hence the interest of RF or microwave excitation. In order to operate in the very low pressure range, these reactors utilize magnetic field confinement by applying either axial magnetic fields (coils) or multipolar magnetic fields (permanent magnets).

In fact, the pulse voltages compiled in Table I generally corresponds to the nominal performance of the pulse generator implemented in connection with the substrate holder. However, the PBII performance reported was often much lower due to other limitations such as the maximum peak current available, limited plasma dimensions, or arcing. For example, the facility described in reference [55], Fig. 5, utilizing DECR plasma and a pulse shape as shown in

Fig. 6, cannot operate above 70 kV because the plasma dimensions of 60 cm in diameter and 70 cm in height were too small. Actually, this facility was routinely operated up to only 50 kV. This example demonstrates the difficulty to realize processing in the 100 kV range, which appears to constitute a practical upper limit for the PBII concept.

In the low energy range, typically in the 10 kV range and below, PBII processing can be performed in any kind of plasma reactor. In other words, the choice of the plasma technology depends much more of the process to be performed than of the specifics (pulse duration etc.) of PBII substrate biasing. In particular, pulsed discharges, low-pressure or medium pressure plasmas can be used together with PBII as well as with PBIID processing. For example, pulsed discharges are used when the presence of plasma between high voltage pulses is undesirable, and medium pressure plasmas are preferred when collisional sheaths are required and secondary electrons are to be used for plasma enhancement.

B. Reactor considerations

The main design considerations for a PBII reactor include: the type of plasma generator, size, number, and throughput of substrates, voltages involved, and gas supply and distribution, pumping, substrate *in-situ* pre-treatment, substrate heating, motion, ports for *in-situ* plasma diagnostics and materials characterization. Compared to other plasma processing chambers, PBII chambers need to be of sufficient size and equipped with high-voltage feedthroughs and various shielding. The chamber size is determined by the requirement that sufficient plasma need to be present when the sheath reaches its maximum distance from the substrate surface [56]. When batch processing of many substrates is considered, substrates needs to be separated such as to avoid sheath overlap, otherwise non-uniform treatment will occur.

Shielding of feedthroughs is required; designs have been developed that prevent discharges at feedthroughs and the contamination from condensable plasmas, vapors, or sputtered material. Shielding is also used to protect chamber walls and other vacuum components. Furthermore, when the applied voltage exceeds 25 kV, protection from x-rays must be considered. Many of these issues are discussed in the handbook [37].

For high voltages and low-density plasma, the sheath can attain appreciable thickness. To limit the expansion of the sheath, a grid can be positioned such as to divide the volume in a plasma reservoir and sheath volume [57]. In some sense, introduction of a grid is a step to reconstruct a broad-beam ion source inside the chamber, with the grid and sample being parts of the extraction system.

While in this approach the grid can be grounded, a similar approach has previously been proposed by to address PBII of thick insulators [58, 59]. In the latter case, the grid is biased, not the substrate, and the sheath expands from the grid while the usual PBII theory applies.

Compared to ion-implantation-only chambers, PBIID chambers must deal with condensation of material on all components, hence application of shields is critical. If the condensing film is conducting, special precautions are needed to protect (hide) feedthroughs and insulator standoffs. In the other extreme, when the films are insulating, new problems may arise due to coatings on electrodes, which electrically "disappear." In reactive sputter deposition, this is well known as the "disappearing anode" problem. The voltages in PBIID do usually not exceed of a few kV, hence X-ray shielding is not needed.

C. *Pulse generator requirements*

The pulse generator is a central component in PBII processing since it has to deliver very high instantaneous power, to present rise and fall times within a microsecond and, finally, to manage possible sudden short circuits (arcing) in the load.

The specifications for the pulse generators in PBII processing directly follow from the sheath dynamics described above. Firstly, the pulse generator must be able to provide enough current at the beginning of bias pulse to produce high voltage at initially low impedance. In addition, as the sheath thickness (with a geometrical factor for non planar substrates) and secondary electron yield increase with increasing pulse voltage, the required maximum peak current also increases. Consequently, when the pulse generator cannot provide enough current, the rise time of the pulse voltage becomes large and may even approach the entire pulse duration, hence the ion energy distribution of the ions can become very broad [44].

The second specification, related again to the control of the ion energy distribution function (IEDF), also results from the sheath dynamics. To achieve tight energy control, it is necessary to apply pulses with rise and fall times of the order of ω_{pi}^{-1} *and* a duration time τ much larger than ω_{pi}^{-1}. In this way, the time during which the ion energy distribution is not monoenergetic is restricted to a minimum and thus much shorter than the total pulse duration τ. Since ω_{pi}^{-1} is typically of the order of 1 µs in the low density plasmas required for PBII, rise and fall times less than 1 µs and pulse durations more than a few 10 µs are relevant in most cases. Then, at a given plasma density, the dose per pulse is controlled by the pulse duration τ, while the dose rate is controlled by the product of τ and pulse repetition rate f. The final (incident) dose is then proportional to the total duration of the PBII process (the retained dose is limited by sputtering of previously implanted ions [60]).

Another important requirement is to control any reverse positive voltage, in particular at the end of the pulse. While a very brief reversal at lower voltage is sometime beneficial, for example to compensate charging of insulator surfaces, one generally wants to avoid reversal in most cases because ion sputtering of reactor walls could cause contamination of the substrate. Finally, additional requirements for the pulse generator, in particular in terms of reliability and safety are also important: the generator must be protected against short-circuits in the load (arcing) and stored energy should be kept as low as possible.

D. Pulse generator technology

The most commonly used high voltage pulse generators described in the literature combine a high voltage supply and/or energy storage element and a high voltage switch [50, 61, 62]. A typical system includes a positive DC high voltage supply (often, a few tens of kV and a few mA) connected to a capacitor (tens of nF or more) through a charging resistor (100 to 200 kΩ).

Vacuum ("hard") tubes are still popular in the voltage range of several kV because the can handle pulse duration 100 μs or more, with a repetition rate of up to one or two kHz, hence they can operate at high duty cycle and pulse frequency. The positive electrode of the capacitor is switched to ground through the tetrode by the tube's grid control, bringing the target (substrate) to negative potential. The target bias voltage and current during implantation can be monitored with a voltage divider and a current transformer. However, vacuum tubes have a limited current capability, generally of the order of 10 A [40, 49, 51-53, 63-65], a value corresponding to the maximum current emitted by thermionic cathodes.

Therefore, other kinds of high voltage switches have been used such as gas-filled tubes (thyratrons, crossatrons) [48, 66], spark-gaps [67], beam X switches [47, 68], or high-voltage high-current transistor switches [65, 69, 70].

These high voltage switches can be used in pulse modulators to either directly switch the pulse on and off, or they can be used with special pulse-shaping circuits such as pulse-forming-networks (PFNs) [67, 71-73]. Over the last decade, a number of PBII-specific pulse generators were developed for industrial applications ranging 10 to 100 kV and 0.1 to 10 kA, see reviews [62, 74]; a number of devices utilize transistor switches and pulse transformers [75-77].

In the range of about 1 kV, typically used in PBIID, numerous unipolar and bipolar pulsers are commercially available. They make use of advancements in high-power semiconductors such as IGBTs (insulated gate bipolar transistors) which can switch hundreds of amperes and hundreds of volts at frequencies up 100 kHz.

IV. PLASMA DIAGNOSTICS AND SURFACE CHARACTERIZATION DURING PBII PROCESSING

A. Probe measurements of plasma and sheath dynamics

A popular approach the measuring plasma and sheath in PBII is to position a small probe in a well-defined distance from the surface of the biased substrate. One may use the probe as a conventional Langmuir probe for the plasma but one should expect a typical probe characteristic only for the case that the probe is actually immersed in the plasma. At low plasma densities and high bias voltages, the sheath can be thick enough that the probe is inside the sheath and not in the plasma. In this case, the electron density will vanish and the ion density will be reduced due to ion acceleration by the sheath' electric field. This suggests utilizing positive probe bias only,

hence the probe becomes a sheath edge detector, showing electron current for thin sheath (probe in plasma) or negligible current (probe in sheath) [78]. The technique can be used to explore the time-dependent sheath behavior not only for planar geometry but also for three-dimensional objects [79]. While sheath edge detection is straight forward, one should be reminded that "translation" of a probe signal to quantitative plasma or sheath parameters is not trivial. This is due to the disturbance caused by the probe and by the complicated nature of charge particle trajectories in the probe's sheath [80], which is especially true if a magnetic field is present.

B. Optical diagnostics of sheath dynamics

The advantage of optical diagnostics is that the plasma and sheath region is not disturbed by the measuring instrument (like a probe). In emission spectroscopy, the light from excited atoms and ions is collected and evaluated by a range of standard methods. As a first step, emitted spectral lines can be identified, giving clues on the presence and concentration of elements. It should be pointed out that the intensity of emitted light is generally not proportional to the concentration of the emitting atom because the excitation conditions (electron temperature) vary spatially and in time. Provided the sheath is sufficiently thick, it can be often directly observed. Because electrons are repelled from the sheath, no excitations can occur in the sheath, and the sheath appears dark. Of course, the sheath edge is not identical with the edge of the dark zone, if observable, because atoms or ions excited in the plasma can drift into the sheath before emitting a photon. At relatively low voltages (< 1 kV), the sheath may be too thin to be optically observed.

C. Ion velocity distribution function measurements

The final velocities with which ions impact the surface of the biased substrate are determined by the acceleration in the sheath and the presence or absence of collisions. The ion velocities in a plasma are not really relevant because they are much smaller than the velocity gained in the sheath. (Though, ion velocities in the plasma matter as they affect the ion current supplied by the plasma). For collisionless high voltage sheaths one simply considers $E_{kin} = QeV_{sheath}$, where Q is the ion charge state number and V_{sheath} is the sheath voltage. The determination of the final ion velocity is therefore usually related to charge state distribution, often $Q=1$, the presence of molecules (if applicable), and the determination of the actual sheath voltage. The latter is time-dependent, and therefore the energy distribution of ions is time dependent. The sheath voltage can be determined by recording the substrate potential and the plasma potential. The exact determination of the plasma potential is difficult, e.g., one could use emitting probes. For most practical situations in PBII, one approximates the plasma potential with the potential of the chamber (ground).

In the case of molecular ions, the same acceleration physics applies but one should consider that a molecule would dissociate upon impact. For example, a N_2^+ ion in a 10 kV sheath would gained 10 keV and it would dissociate upon impact on the surface; effectively supplying two nitrogen atoms with 5 keV each.

D. Measurements of ion current, implanted dose, and coating thickness

A conventional way of measuring ion current is measuring the total current of the biased substrate using a shunt or inductive current monitor (like Pearson or Rogowski coil). Since $I_{substrate} = I_{ion} + I_{SE} = I_{ion}(1 + \gamma_{SE})$ one has to make reasonable assumptions on the contribution of secondary electrons. The problem with this approach is that the yield of secondary electrons,

γ_{SE}, depends on the kind of ions, ion energy upon impact, substrate material, and surface conditions. For many PBIID conditions, $\gamma_{SE} > 1$, and hence there is can be a large error in the ion current measurement, which directly affects the determination of dose of implanted ions (PBII), or film thickness (PBIID). Measurements of the yield γ_{SE} for PBII conditions can be found for helium [81], neon and argon [82], nitrogen [83], and several metal ions [84].

Due to the difficulties associated with secondary electrons, dose measurements have to be verified *ex-situ* using conventional materials characterizations techniques [85], such as Rutherford-backscattering (RBS) and secondary ion mass spectrometry (SIMS).

For coatings (PBIID), a range of *in-situ* techniques can be used such as *in-situ* ellipsometry. Provided the high-voltage bias is appropriately dealt with, a quartz-crystal microbalance can be incorporated next to the substrate. In all cases, *ex-situ* verification is advisable, for example by profilometry.

V. APPLICATIONS OF PLASMA-BASED ION IMPLANTATION (WITHOUT DEPOSITION)

A. Reduction of wear and corrosion, applications in metallurgy

For gear and machinery, improving component lifetime is on ongoing field of research and development. A traditional approach is to modify the surface by introducing hard and corrosion resistance phases to the surface region, often precipitates of nitrides. While high-temperature nitriding is a low cost, traditional approach, PBII was developed as high tech alternative with the goal to improve quality, reduce process temperature and processing time. Much work focused on improvement of components made from stainless steel [86-99], tool steel [6, 19, 45, 100-109], tungsten carbide [110], nickel alloys [6, 111], chromium [112], pure

aluminum [113, 114] and titanium and aluminum alloys [20, 49, 115-121]. Möller and co-workers [122] describe PBII of nitrogen as "favorable boundary conditions for the efficiency of diffusive surface treatment." The kinetic energy of ions is only needed to penetrate the surface layer of contamination or similar barrier, while the actual nitriding step is dominated by diffusion. The PBII process delivers energy to the substrate, and this "side effect" is considerable that it can be used to limit the pulse repetition frequency, as done by a temperature-controlled feedback loop [63, 94, 117]. Although PBII nitriding is effective and has been proven to be superior for selected applications, it will not replace main-stream nitriding because of its relatively high cost.

B. Biomaterials and carbon-based materials

High elastic modulus, fatigue behavior and yield strength make metals interesting for prostheses. A number of metals are considered biocompatible, among them austenitic stainless steel (e.g. AISI 316L), tantalum, niobium, cobalt chrome nickel alloys, titanium and titanium alloys. Mändl and co-workers [123] used oxygen PBII for Ti and titanium alloys to form a rutile surface layer on small rods, which were implanted into rat femurs to evaluate biocompatibility and osseointegration. Oxygen PBII with parameters 0.3 Pa O_2, plasma formed by ECR microwave discharge, substrate biased with -30 kV pulses, 15 μs per pulse, 10^6 pulses, resulted in enhanced biocompatibility and osseointegration for pure Ti and to some degree improvements were found for NiTi alloy SM495. PBII treatment of anodized titanium and other materials did not result in improvement.

Some polymers are among preferred bio-compatible materials due to their resistance to corrosion, high fracture toughness, ease of molding and machining, density comparable to tissue.

Plasma and ion beam modification of polymer surfaces have been done to obtain desirable properties for interaction with cells and body fluids.

Han and co-workers [124] realized that oxygen treatment is widely used to hydrophilize polymer surfaces, and thus PBII processing should lend itself to an effective approach using oxygen plasma and pulsed bias of the sample holder. They found that oxygen implantation (5 kV, 10 μs pulses, 500 Hz, 5 min) was effective for all samples of polystyrene, polyethylene, poly(ethylene terephthalate), poly(vinylchloride), poly(ethylene naphthalene), polycarbonate, and silicone rubber. Contact angles down to 2º were observed. McKenzie and co-workers [125] demonstrated the change hydrophobicity and electrical conductivity of poly(aryl ether ether ketone) (PEEK) . Hydrogen, oxygen, and argon were used as process gases. The voltage (15 μs pulses, 10 kV) was applied to the substrate holder with 2-4 mm thick, 15 mm diameter substrates. Oxygen treatment produced a distinctly different modification, as shown by attenuated total reflection infrared absorption spectroscopy and directly observed by the decrease of contact angle to nearly zero. The depth and duration of the treatment determined the time required to recover the original hydrophobic character (contact angle 78º).

C. Plasma doping

It is well know that ion implantation can be used to change physical properties of a material by implantation of interstitial or substitutional elements. This is the case, for example, for the doping of silicon with P, B or As. As conventional implanters are not adapted to very low ion energies, implantation of doping elements via PBII processing with a collisional sheath is becoming a useful tool for shallow implantation. Plasma doping (or PLAD) thus constitutes, by

far, the most important application of PBII in microelectronics [10, 21, 23, 126-134], along with the production of SOI (silicon on insulator) wafers with the smart-cut process [135-138].

D. *Changing phases and their electrical and optical properties*

It is also possible to create new materials, including metastable phases. The physical properties of such new phases can be quite different from the properties of the initial materials (Table I). For example, implantation of carbon in Si produces SiC [139] whose band gap is much higher than the gap of silicon. Implantation of nitrogen in aluminium produces aluminium nitride [140], which is a dielectric material whereas aluminium is metallic. Implantation of nitrogen or oxygen in Si [139, 141] produces Si_3N_4 and SiO_2, respectively, which are dielectric materials whereas Si is a semiconductor. Similarly, the synthesis of the MgB_2 phase by boron implantation in magnesium produces a superconducting material whereas Mg is metallic.

Such transitions of electric properties can be favourably used in order to elaborate nanostructures and electronic or optoelectronic components. Transformation of magnetic properties of thin films can also be obtained via PBII techniques. This is the case of Ni films, which do not present any significant magnetic property after nitrogen implantation [142]. In contrast, the implantation of manganese films with nitrogen confers magnetic properties to the implanted layer [143].

The possibility of modifying the composition and physical nature of surface layers, and changing drastically their physical properties over several orders of magnitude, makes PBII technology very attractive for the elaboration of innovative materials, including metastable materials, and the realization of micro- or nanostructures [143].

E. Modification of polymer surfaces

The objective of this section is to show, from results available in the literature, the feasibility and interest of ion implantation of polymers using the PBII technique, but also to point out its limitations and discuss plasma specifications required to achieve control of the implantation process. Since the invention of the PBII technique, about 20 articles have been published on PBII processing of polymers [48, 124, 144-159].

The main topics concern surface modifications [144, 155-158], and in particular mechanical properties [48, 145, 147, 148, 154], wetting properties [124, 146, 151-153, 155, 157] and PBII processing of insulating materials [150, 151, 158]. One publication deals with protective treatments against oxidative environments, and a recent one demonstrates its interest for the fabrication of micro-electrical mechanical systems, or MEMS [159].

The first and most immediate application was the improvement of mechanical surface properties of polymers [48, 145, 147, 148, 154] such as hardness, wear life, and tribological properties (low friction and low wear rate). In particular, the enhanced mechanical properties of ultra-high molecular weight polyethylene (UHMWPE) after PBII was attributed to ion-bombardment-induced cross-linking [148, 154], hence surface hardening.

The second and major application concerns the improvement of either wetting [124, 146, 151-153, 155, 157] or hydrophobic [124] properties of polymers. Generally speaking, plasma- and PBII processing both lead to spectacular modifications of the wetting properties of polymers, but most studies have demonstrated that ion bombardment energy is the key parameter for stability after treatment or, in other words, for the durability of the treatment. As an example, Fig. 5 shows the time evolution of water contact angle after PBII processing of polyethylene in oxygen [151]. It was noted that hydrophobic recovery with time strongly varies when increasing

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the pulse voltage from 0 to 5 kV, but does not vary significantly above 5 kV. The generally accepted mechanisms are that improved wettability is due to the formation of oxygen-containing hydrophilic functional groups, and that the high-energy ion bombardment produces deeper cross-linking of polymer chains, so that the modified layers are more resistant to hydrophobic recovery with time.

Many of the above-noted studies are devoted to surface modifications induced by PBII processing, such as cross-linking, chain scission, creation of functional groups, and their relationship with the surface properties obtained after treatment. The resulting surface modifications in terms of mechanical, chemical and electrical properties can also be applied locally, for example with the help of a mask [159]. Thus, it seems feasible to apply PBII processing of polymers to the fabrication of MEMS.

Finally, a few experimental studies report PBII processing of electrical insulating materials, including polymers [150, 151, 158]. Clearly, the surface charging and potential drop across the substrates reduce the performance of PBII processes, on account of limited implantation depth, spreading of the ion energy distribution, and arcing. Besides decreasing t and n_e in order to reduce surface charging and time-dependent potential drop [150, 151], two other different techniques have been proposed to overcome these drawbacks. The first one, so-called "mesh-assisted" PBII, utilizes a conducting grid placed several mm above the substrate, which is pulse-biased at negative voltages [48]. The second involves depositing a very thin sacrificial conductive surface layer on the polymer, which is used to apply the pulsed bias voltage. Thus, the ions from the plasma are implanted through the conductive film into the polymer [158].

VI. APPLICATIONS OF PLASMA-BASED ION IMPLANTATION AND DEPOSITION

A. Diamond-like carbon (ta-C and a-C:H)

Ion implantation has limited processing depth, and therefore adding coatings to the portfolio of surface modification greatly enhanced the applicability of plasma immersion processing, now PBII&**D**. Typical classes of coatings materials include metals, transition metal nitrides, oxides, and various forms of diamond-like carbon.

Diamond-like carbon (DLC) materials are of great interested to application where high hardness chemical inertness are required, and where components are not subject to very high temperature (several hundred ºC). Diamond-like carbon can be deposited by various methods, and among them are several PBIID-type techniques.

Specifically, in one group of techniques, graphite is used as feedstock material. Graphite can be efficiently ionized by high-power pulsed lasers (laser ablation) or by a cathodic arc discharge, the latter can be pulsed or operating in DC mode. Provided that the energy of condensing carbon ions is in the range of 100 eV per carbon atom, which can be obtained by applying bias, ta-C (tetrahedral amorphous carbon) can be synthesized. Ta-C is the hydrogen-free, sp^3-rich and most diamond-like form of diamond-like carbon materials [160, 161]. Energetic condensation of highly ionized plasmas can be classified as physical vapor deposition (PVD) technique.

The second group of techniques uses carbon-containing gases, such as methane, acetylene, toluene, or mixtures thereof, and sometimes noble gases are added as to obtain Penning mixtures. Because hydrogen is present in these gases, the resulting films are composed of hydrogenated diamond-like carbon, also known as a-C:H. If not specified otherwise, the term diamond-like carbon conventionally refers to a-C:H materials or to all kinds of carbon materials rich in sp^3 bonds. The techniques for a-C:H are characterized by relative simplicity, high

deposition rate, and having the capability to coat three-dimensional components with the carbon form the gas phase. Carbon plasma may be produced by external power source (like RF or microwave plasma), or the energetic secondary electrons of the PBIID process can be used to generate the plasma. In the latter case, the pressure is relatively high and plasma generation and substrate biasing are directly coupled. One may consider PBIID processing of a-C:H as form of CVD (chemical vapor deposition).

While many techniques require a Ti or Si interlayer for enhanced adhesion, PBIID can lead to well adherent films by creating a graded interface with the substrate material. This has been demonstrated for DLC on Mg, Al, Si, Ti, Cr, Ni, W, and brass [36]. Of great interest is the application of diamond-like carbon on aluminum alloys because it would allow the user to have light-weight high-strengths components with low coefficient of friction and high corrosion resistance, which is particularly desirable in the automotive industry [162]. To obtain this goal, gradient layers between substrate and coating must be created, an idea discussed more than a decade ago [25], yet still a main topic of development [121]. Liao and coworkers [163] compared PBII-made a-C:H films (0.8 Pa of C_2H_2, 45 μs pulses, 18 kV) with films produced by RF plasmas (300 W, Ar/CH_4=13:7, DC bias 200 V), finding superior quality for the PBII films in terms of tribological performance. Earlier work by Lee, He and others [35, 164] used RF power and low bias voltage of –150 V, finding best tribological performance for low gas pressure (down to 0.04 Pa) and low C_2H_2/Ar ratio. The same group also investigated the optical properties of PBII a-C:H films on poly(methylmethacrylate) (PMMA), silicon, and glass [165], finding an optical gap greater than 1.9 eV, high transmittance in the visible, and a relatively low refractive index of 1.87. Metal-doped a-C:H coatings have a high application potential in fluid power transmission systems and in dry friction couples [166]. DLC films are of special interest

to numerus biomedial applications, because the material is carbon-based, chemically inert, and the wettability can be changed by ion and plasma methods. For example, PBIID-modified DLC showed changes in bacteria repellence [167]. Diamond-like carbon (DLC) is also considered for use in blood contacting devices [168].

B. Coatings for space applications

One emerging application is to create tailored surface for harsh environments. For example, PBIID can be used to synthesize a radiation protective coatings on polymers. Iskanderova and co-workers originally used ion implantation for this purpose [169] and later found that PBIID was elegant solution [170]. The group of Tan and co-workers investigated the use of Kapton for space application where protection of polymers from harmful radiation is required. Among the approaches explored, the best performance was obtained when an aluminum vacuum arc was used to create a thin, well adherent later on Kapton substrate [171].

C. Stress reduction and preferred orientation in nitrides

A rapidly increasing body of work is dedicated to stress control and establishing preferred orientation of PBIID produced films. The early work of Brown and co-workers indicated that well-adherent films can be obtained when using high voltage pulses are used in the deposition process [25, 29]. Furthermore it was recognized that the early recognized that the "diamondlikeness" of diamond-like films depend on the energy, and hence carbon-carbon multilayers can be produced (see previous section). In the search for methods to reduce the intrinsic stress, high-voltage biasing was found to be more than just a tool for interface tailoring,

rather, it can be used to significantly reduce stress and even to establish preferred orientation in the case of polycrystalline films.

In the case of TiN, still a popular coating in many tribological applications, a reduction of stress by over 50% has been shown [172]. Due to its golden color, TiN has also decorative functions and therefore remains popular despite better tribological performance of the greyish TiAlN. TiAlN has higher oxidation resistance and a lower coefficient of friction than TiN, which makes it a preferred modern coating on cutting tools and other tribological applications [173, 174]. Figure 7 shows that high voltage pulsing in the PBIID process reduces intrinsic stress from about GPa (no pulsing) to less than 2 GPa for both TiN [172] and TiAlN [175]. Qualitatively, this can be attributed to thermal spikes that anneal the material on a nanoscale [176, 177]. Recall that the ion acceleration in the sheath depends on the ion charge state, and that Ti and Al have charge states up to 3+ ([178]), and therefore multi-keV ions are present in the process. Most of the stress reduction occurs for bias pulses of about 1-2 kV. The effects of nanoscale thermal spikes can be displayed as a function of voltage (ion energy), as shown in Fig. 7, and a similar curve shape can be obtained when stress reduction is plotted as a function of the (voltage x pulse frequency) or (voltage x duty cycle). Besides stress reduction, nanoscale annealing also promotes alignment of grains, resulting in preferred orientation. In the case of TiAlN, {200} planes were found to be parallel to the surface of the film. Employing density functional theory, preferred orientation can be explained by minimization of the system's energy taking surface energy and bulk strain energy into account [175, 179].

The same tendencies have also been observed in the case of AlN. The intrinsic stress depends on the (pulse voltage) x (pulse frequency) product, and the crystallites exhibit hexagonal microstructure with $\langle 0001 \rangle$ direction in the plane of the film of low (voltage x frequency)

product, changing to ⟨0001⟩ direction normal to the plane of the film at high (voltage x

frequency) product [180].

VII. OTHER SPECIFIC APPLICATIONS

A. Treatment of insulating substrates

More than a decade ago, Emmert [181] presented a model for plasma immersion

treatment of relatively thin insulators placed on pulsed biased substrate holders. According to

Emmert's model, the bias voltage is divided between voltage drop in the sheath and the voltage

drop in the insulator, the latter related to built-up of surface charge. As long as the surface

charge is allowed to be compensated, either by letting the high-voltage sheath sufficiently

collapse, or by forced voltage reversal, insulator treatment is possible and can indeed be

effective, as previously mentioned when considering polymer surface modification for

biomedical applications [124, 125, 167].

Modification of electrical and tribological properties are sought for MEMS (micro-

electro-mechanical systems) and other devices. The goal of the work by Tonosaki and

coworkers [182] was to improve the hardness of amorphous poly-olefin (APO). They used a

filtered cathodic arc as a carbon ion source and supplied bipolar pulses of 10 kV with 5 μs.

Nanoindentation revealed increase of surface Young's modulus from 1.8 GPa to 25 GPa.

In a fundamental study on possibilities and limitations of PBII treatment of insulators,

Lacoste and co-workers [151] varied plasma density, pulse duration, and sample thickness and

permittivity. Not surprisingly, severe limitations in terms of actual implantation energy was

found, especially when considering long pulses and thick (mm) insulating substrates.

B. *Treatment of complex structures and inner surfaces*

An advantage generally put forward to justify the interest of the PBII technique is the possibility to uniformly implant 3-D workpieces of complex shape. Indeed, when immersed in plasma, the substrates are entirely surrounded by the ion sheath, so that mechanical manipulation is not necessary. However, even in perfectly uniform plasmas, treatment of three-dimensional objects with complex shape will be non-uniform, especially when the object has small features. This problem has been extensively studied and the results obtained by simulation are in good agreement with experiments. In particular, the effects resulting from usual geometrical shapes (edges, holes, trenches, corners) are now well identified and understood [51, 183-198].

As a general rule, the condition to achieve conformal PBII processing on a complex surface is that the plasma *as well as* the ion sheath must follow the surface topography of the substrate during the high voltage pulse. This condition is of course obtained when the sheath thickness is much smaller than the characteristic size of surface features (curvature radius, hole diameter, trench width). Considering Fig. 3, such a condition implies that conformal PBII processing is possible only with macroscopic features in the cm and greater length scale, depending on to the pulse voltage. However, many experimental results also demonstrate the possibility of achieving almost conformal PBII processing under various process and shape conditions.

Conformal PBII processing can effectively be achieved or improved in various ways which can be summarized as follows:

i) Conformal treatment of three-dimensional substrates is promoted when substrates have *regular, convex shapes*. In this case, the above general condition on the sheath thickness can be relaxed.

ii) The operating conditions are in the transition regime from non-collisional to *collisional sheath*. The angular distribution of ions in the sheath is strongly broadened by the presence of collisions. In this way, improvement of the treatment uniformity can be expected, especially in the case of concave shapes, provided the ion mean free path λ_{in} is on the order of or shorter than the characteristic size of the surface features. On the other hand, the energy distribution function of ions is broadened and the mean energy reduced, as previously discussed.

iii) Using a *long processing time* or high incident dose: in order to reach an asymptotic implantation profile given by the retained dose. It is now well established, theoretically [60] and experimentally [199], that a PBII process generally leads to an asymptotic process with time (incident dose). This phenomenon is the result of the equilibrium between at least two competing effects. A steady-state profile is reached when the dose rate of the implanted element becomes equal to its sputtering rate. In case of reactive gases (N_2, O_2) are involved, gas desorption and etching can also play a role in reaching the final stoichiometry (nitrides, oxides). Therefore, by using a rather long processing time, surface parts with quite different exposures to the ion flux may exhibit very close final profiles;

iv) A combination of the previously discussed PBII processing conditions. An example is provided by the implantation of boron (B) in high aspect ratio, sub-micron trenches etched on a silicon wafer immersed in a BF_3 plasma ([10, 127], cf. also section on plasma doping). The conformal B implantation probably resulted from of multiple competing effects: implantation of boron on the trench bottom and on side-walls, sputtering of the trench bottom and re-deposition on side-walls, ion-induced etching of the trench bottom, etching of the side-walls. It also certainly resulted from the collisional character of the ion sheath by broadening the angular distribution of BF_x^+ ions before entering the trenches. Nevertheless, this complex example

demonstrates the possibility to obtain conformal PBII processing even with extreme surface topographies.

Concerning the treatment of inner surfaces, e.g. cavities or tubes, the problem is totally different since the difficulty essentially lies in the production of the plasma and in the possibility to pulse bias negatively the inner surface with respect to the plasma potential. This is generally achieved by introducing within the cavity an auxiliary electrode [200, 201].

VIII. FUTURE PROSPECTS AND TRENDS

Until the mid 1990s, the size and number of substrates was increased and the pulsed high voltage reached the 100 kV level [37]. At this point, fundamental physical and economical limitations became clear. They are primarily associated with the large yield of secondary electrons leading to a host of disadvantages. First, the pulse modulator must be able to handle a total current which is dominated by secondary electrons rather than ions, leading to great technical challenges and uneconomically high cost. Additional cost and inconvenience arise from the need to install appropriate shielding against x-rays which are generated when high-energy electrons impact the chamber wall or other components. Therefore, most modern developments of PBII and PBIID deal with much lower voltages, often only a few kV or even less, where pulse modulation is affordable. Most modern applications are therefore not a new way of doing conventional ion implantation, instead, PBII and PBIID have enabled new, often large-area processing in emerging fields, such as novel surface modification of bio-materials, deposition of thin films with controlled (reduced) stress, and synthesis of nanostructured thin films, to name a few. In the near future, important breakthroughs in PBII and PBII&D could result from in-situ process control and development of new plasma technologies such as multi-

dipolar plasmas [202], which can offer extended operating conditions (pressure range from less than 10^{-2} Pa to a few Pa and plasma density from 10^9 to 10^{12} cm^{-3}), as well as a total flexibility in terms of design allowing plasma-assisted chemical vapor deposition (PACVD) and/or plasma-assisted physical vapor deposition (PAPVD) in combination with plasma-based ion implantation.

Acknowledgements

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FIGURE CAPTIONS

Fig. 1. Theoretical evolution of the reduced ion current density J with reduced time τ (the time unit is the inverse ion plasma frequency ω_{pi}^{-1}) when applying a negative step voltage on a planar substrate. The contributions from ion matrix ($\tau \leq 2.7$) and sheath expansion ($\tau \geq 3.0$) are indicated; (from [11]).

Fig. 2. Experimental variation of the current density as a function of time when applying a negative step voltage on a substrate. The units are expressed in terms of reduced units for comparison with Fig. 1. The peak current is much smaller, probably due to a too long rise time of the rectangular pulse.

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

Fig. 4. Transition between collisional and non-collisional sheaths as estimated by Eq.(4), assuming an argon plasma with $n_e = 10^{10}$ cm^{-3}, $kT_e = 1$ eV, $\sigma_{in} = 6 \times 10^{-15}$ cm^2, and $T_0 = 300$ K.

Fig. 5. Typical voltage and current waveforms obtained with a 1 mTorr nitrogen plasma using a 100 kV – 100 A pulse transformer. The surface of the stainless steel substrate is 300 cm^2.

Fig. 6. Schematic design of a PBII facility using a DECR plasma excitation: (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 (from [55])

Fig. 7. Reduction of intrinsic stress of TiN and TiAlN coatings obtained by pulsing high voltage bias in the PBIID process (data from [172, 175]). Each pulse was 20 µs with a pulse repetition frequency of 500 pulses per second (hence 1% duty cycle).
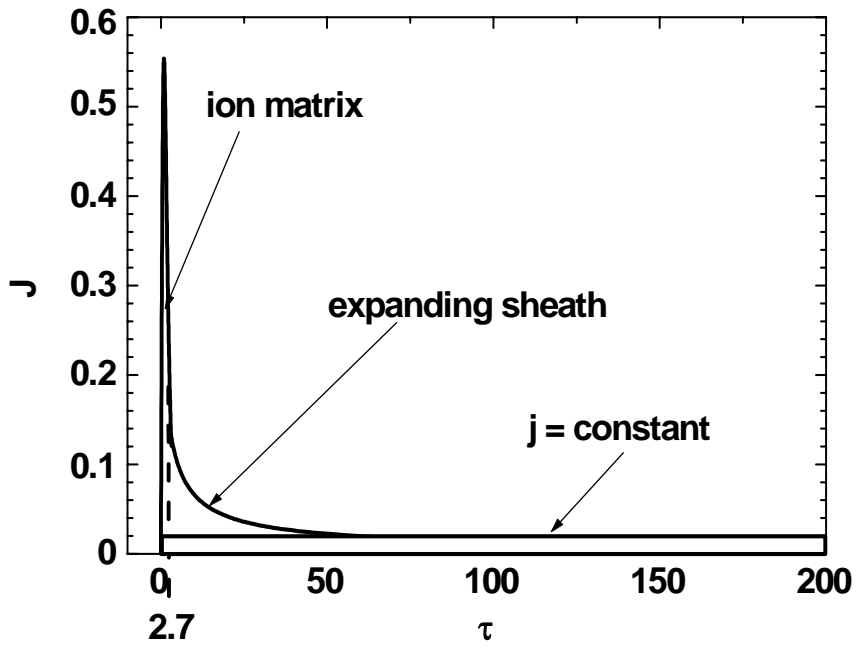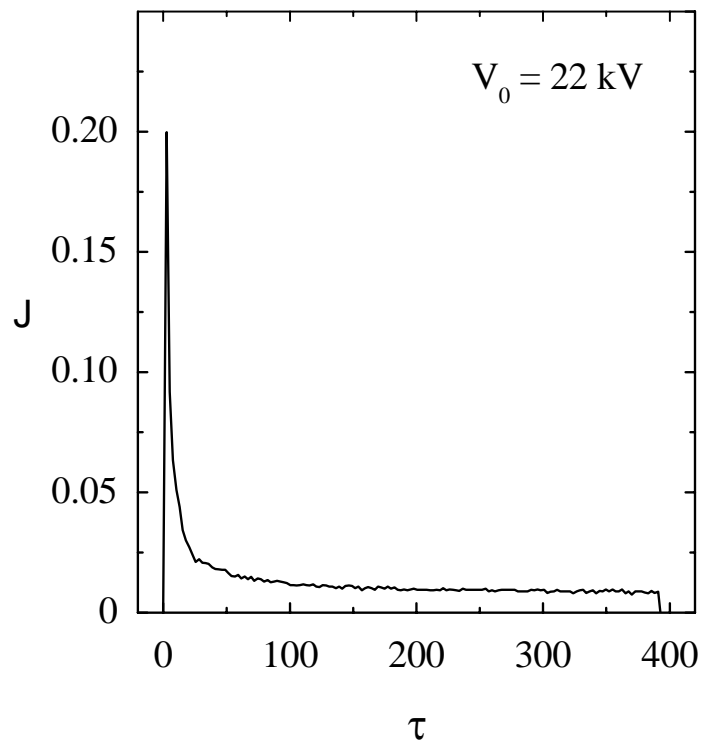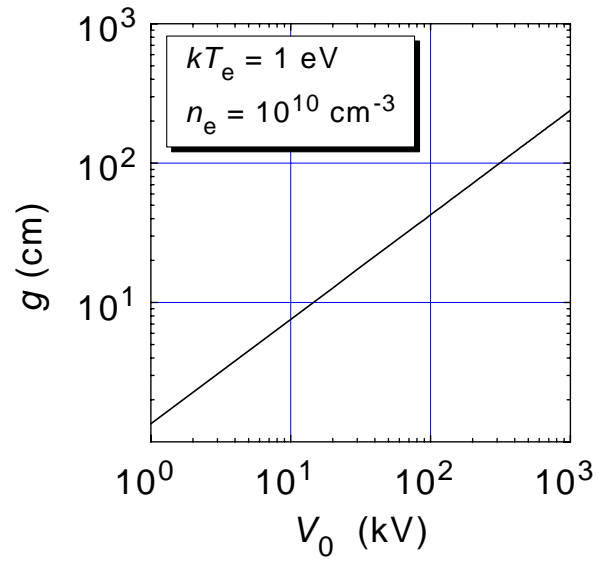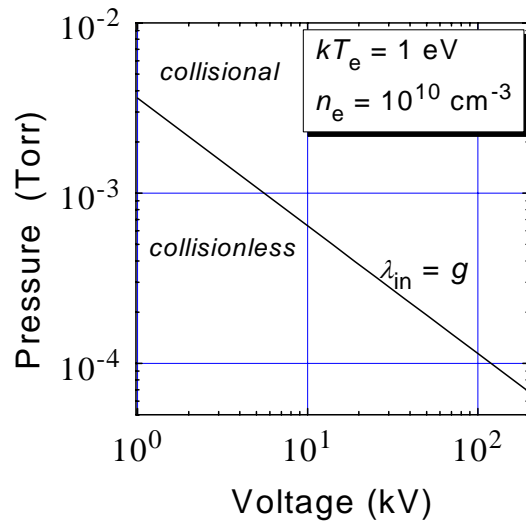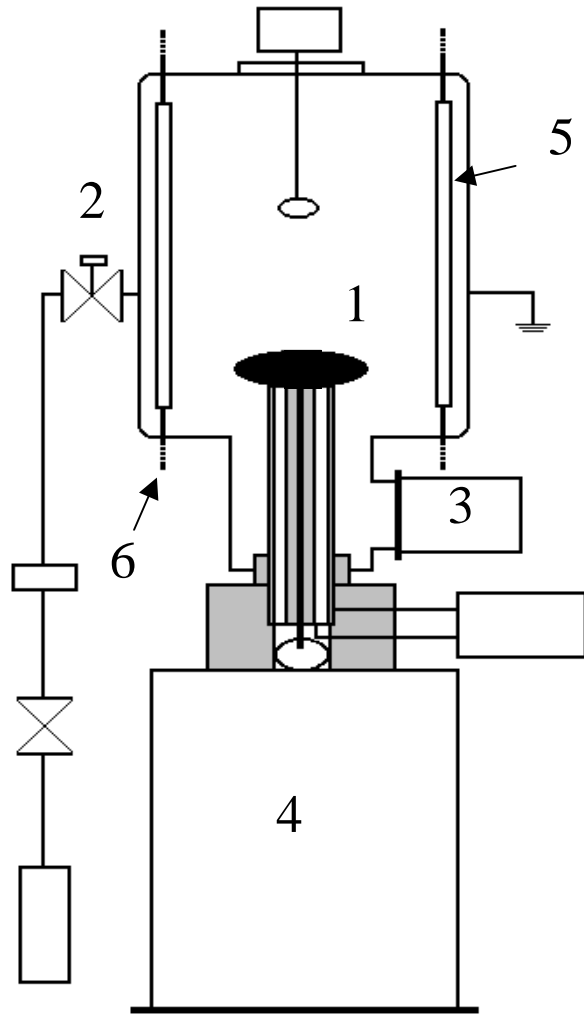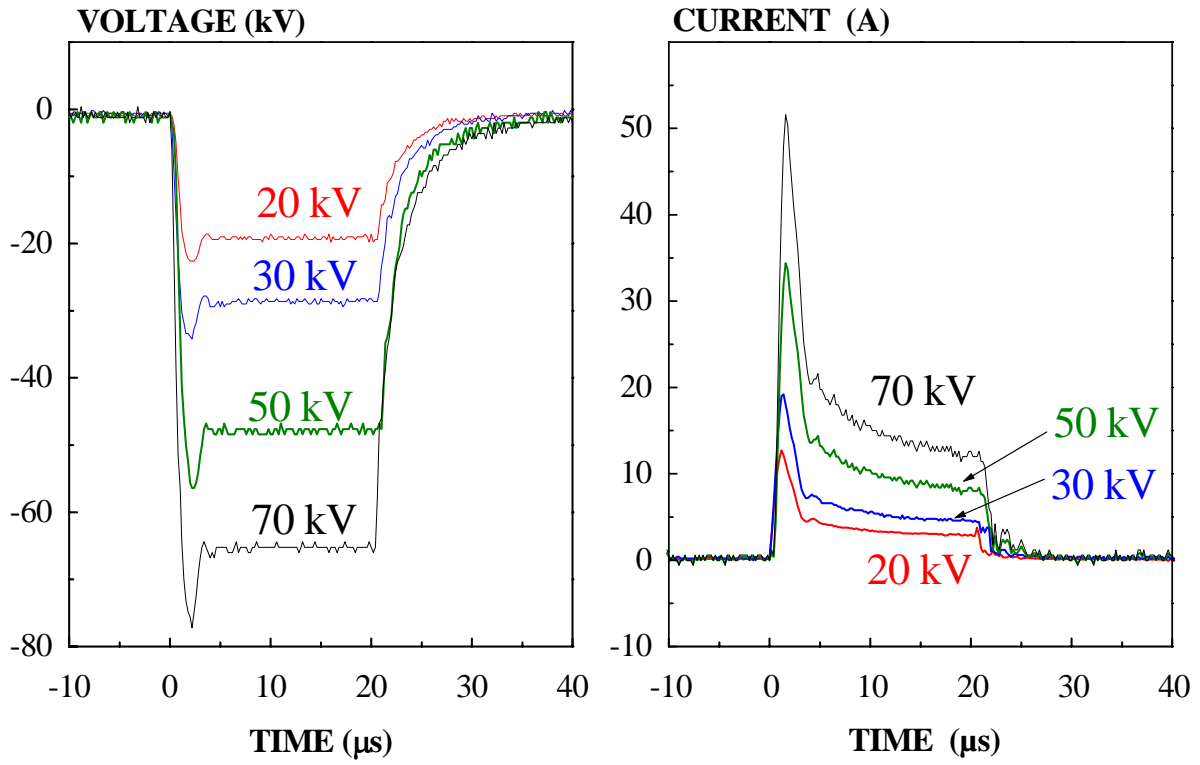
Figure 1

Figure 2

Figure 3
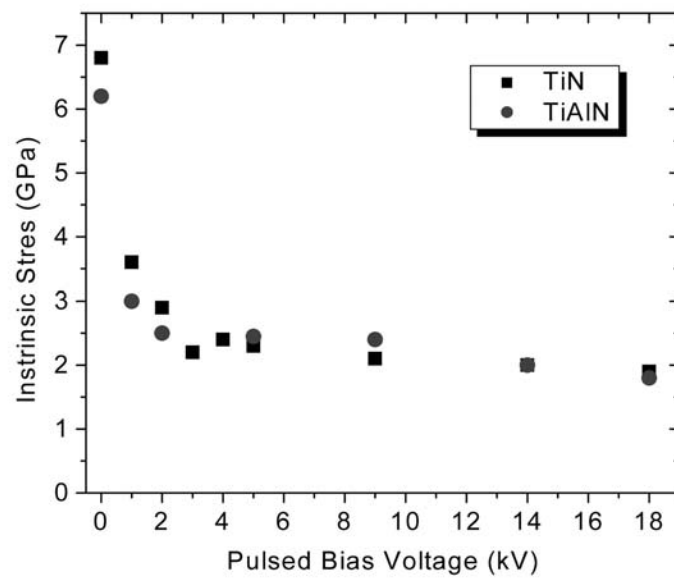
Figure 4

Fig. 5

Fig. 6

Fig. 7

TABLES AND TABLE CAPTIONS

Table I. Examples of modification of layer properties or phase transition obtained via plasma-based ion implantation.

	Starting material	**Implanted element**	*Result*
Mechanical modifications	Steel TiAl6V4 Aluminium	N, C, O, Cr	wear increase friction decrease hardness increase
Electrical transitions	Al (metallic)	N	AlN (dielectric)
	Si (semiconductor)	P, B	Si-n or Si-p (resistivity)
	Si (semiconductor)	N, O	Si_3N_4, SiO_2
	Mg (metallic)	B	MgB_2 (superconductor)
Magnetic transitions	Ni (ferromagnetic)	N	Ni_3N (non-magnetic)
	Mn (antiferromagnetic)	N	Mn_4N (ferromagnetic)

Table II. Main characteristics of high voltage PBII facilities.

Research Center	Plasma production mode	Pulse voltage (kV)	Plasma volume (liters)	Plasma density (cm^{-3})	Pressure range (mbar)	Reference
LANL (USA)	RF (13.56 MHz)	120	8100	5×10^8	3×10^{-4}	[47]
Hughes R. L. (USA)	Filaments	100	2700	10^9 - 10^{10}	2×10^{-5} to 10^{-3}	[48]
Univ. Wisconsin at Madison (USA)	RF (13.56 MHz)	50	1000	2×10^8	6×10^{-4}	[49]
SWIP (PR China)	RF (15 MHz)	100	200	10^8 - 10^{10}	2×10^{-5} to 5×10^{-4}	[52]
FRZ Rossendorf (Germany)	ECR (2.45 GHz)	100	100	6×10^9	2×10^{-3}	[50]
Bosch GmbH (Germany)	Magnetron	50	250	-	-	[53]
ANSTO (Australia)	RF (13.56 MHz)	50	840	4×10^9	10^{-3}	[54]
CNRS (France)	DECR (2.45 GHz)	100	200	5×10^{10}	5×10^{-4} to 2×10^{-3}	[55]