From Plasma Immersion Ion Implantation to Deposition:

A Historical Perspective on Principles and Trends

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Abstract

Plasma immersion techniques of surface modification are known under a myriad of names. The family of techniques reaches from pure plasma ion implantation, to ion implantation and deposition hybrid modes, to modes that are essentially plasma film deposition with substrate bias. In the most general sense, all plasma immersion techniques have in common that the surface of a substrate (target) is exposed to plasma and that relatively high substrate bias is applied. The bias is usually pulsed. In this review, the roots of immersion techniques are explored, some going back to the 1800s, followed by a discussion of the groundbreaking works of Adler and Conrad in the 1980s. In the 1990s, plasma immersion techniques matured in theoretical understanding, scaling, and the range of applications. First commercial facilities are now operational. Various immersion concepts are compiled and explained in this review. While gas (often nitrogen) ion implantation dominated the early years, film-forming immersion techniques and semiconductor processing gained importance. In the 1980s and 1990s we have seen exponential growth of the field but signs of slowdown are clear since1998. Nevertheless, plasma immersion techniques have found, and will continue to have, an important place among surface modification techniques.

Keywords: Plasma Immersion Ion Implantation and Deposition, Review.

1. Introduction

Plasma immersion techniques of surface modification are known under a myriad of names, including, but not limited to, 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), Plasma-Based Ion Implantation (PBII). Following the convention of a recent Handbook [1], the acronym PIII&D is generically used for the whole family of plasma immersion processes (including film-forming techniques), while PIII is used when referring to processes without film formation.

The family of techniques covers indeed the range from pure plasma ion implantation, to implantation-deposition hybrid modes, to modes that represent plasma film deposition with substrate bias. In this review, the common ground of plasma immersion techniques is described first, followed by a description of individual applications, ideas, and concepts that lead to the development of immersion technique "family members."

2. The common ground of plasma immersion techniques

In the most general sense, all plasma immersion techniques have in common that the surface of a substrate (or "target") is exposed to, or immersed in, a plasma and that a relatively high substrate bias voltage is applied. The substrate bias is usually pulsed

- to avoid arcing on the substrate,
- to limit the sheath size when operating with very high voltages (> 10 kV) and low pressure plasmas

- to allow the near-substrate region to be "refilled" with ions during the bias-off time
- and also to have additional degrees of freedom such as pulse length and duty cycle for the design of treatment processes.

Because the basics of immersion technique have been described many times (e.g., [1, 2]), only a very brief summary needs to be given here. When a high negative high voltage is applied to a conducting substrate (also referred to as sample, target, workpiece, ect.) immersed in a plasma, the plasma electrons are repelled from the near-substrate region in a time scale of the inverse plasma electron frequency, $\omega_{pl,e}^{-1} = \left(\varepsilon_0 \, m_e / e^2 \, n_e\right)^{1/2}$. At this time scale, ions are still at their original location due to their larger inertia, forming the ion matrix sheath. On the longer time scale of the inverse ion plasma frequency, $\omega_{pl,i}^{-1} = \left(\varepsilon_0 \, m_i / e^2 \, n_i\right)^{1/2}$, ions are accelerated to the negatively biased substrate. They impact the surface with an energy that depends on their initial position within the sheath. Only ions that traveled the whole sheath thickness without collisions have a kinetic energy equal to the sheath voltage times their charge state. Usually, the voltage pulse applied to the substrate has slow rise and fall time (slow relatively to the ion travel time), thus ions have less energy at the beginning and end of each pulse. PIII&D is never an ideally mono-energetic process. The sheath expands due to motion of ions. For very long bias pulses, the sheath may become stationary if the ion motion in the plasma can supply the space-charge-limited current as determined by Child's law. These details and refinements for various situations such as other-than-plane geometry, collisional sheath, supersonic plasmas, are discussed in the literature, e.g. [3-5].

3. Historical roots

The process of energetic ion treatment of surfaces may be traced back to a time when energetic ions were produced for the first time. Electrical discharges in exhausted tubes were intensely studies in the second half of the 19th century, that is even before the atomic nature of matter was generally accepted. In 1886, Eugen Goldstein [6] performed experiments at the University of Berlin in which he pierced holes ("canals") in the cathode of high-voltage glow discharge tubes (Fig. 1). He observed a "not yet investigated form of radiation". He found glowing beams in the residual gas caused by "Kanalstrahlen" (canal rays), as he called them, coming through the canals pierced in the cathode. In some sense, Goldstein constructed the first ion beam extraction system using the cathode sheath.

Major steps to the understanding what we now call plasma and ion beams have been done with the discovery of the electron by Joseph John ("J.J.") Thomson (1897), the atomic nucleus by Ernest Rutherford (1911), and the model of the atom with transitions of bound electrons between discrete excited states (Niels Bohr 1913).

Even before plasma and beams were understood, ion-matter interaction was investigated at the beginning of the nuclear age. In 1900, when investigating alpha particles (i.e., helium ions of high kinetic energy), Madame Curie [7] observed that "alpha rays are material particles which are susceptible to the loss of their velocity as they traverse matter." In a general sense, using very energetic ions from radioactive sources, Rutherford and his students Hans Geiger and Ernest Marsden performed ion implantation as early as 1911. Important contributions to the understanding of the interaction of ions with solids were done in the first half of the 20th century, eventually leading to the **L**indhard, **S**charff, **S**chiott (LSS) model of 1963. The LLS model provided predictions for the projected ion range and straggling. With the introduction of Monte Carlo computer simulation, fairly accurate calculations of implantation profiles could be done.

Computational efficiency was improved by the introduction of a universal interaction potential by **Z**iegler, **B**iersack and **L**ittmark [8] in the early 1980s. The ZBL model is the theoretical basis for the Monte Carlo Code **TRIM** (**T**ransport and **R**ange of **I**ons in **M**atter) which has become a standard in the ion implantation and PIII community.

So far, the historical roots of the production of very energetic ions and their interaction with solids were considered. Energetic film deposition has increasingly gained importance among the plasma immersion techniques. Therefore, we will need to briefly touch also the roots of deposition techniques.

Deposition by "cathodic disintegration" in gas discharge tubes had been reported as early as in the middle of the 19th century (William Robert Grove, 1852; Michael Faraday, 1854; and Julius Plücker, 1858). Great progress was made with the improvement of vacuum technology, e.g. by Johann Heinrich Wilhelm Geissler (platinum seal, Geissler tube 1855) and the invention of the Rühmkorff induction coil by Heinrich Daniel Rühmkorff in 1851. Today we would describe a Rühmkorff induction coil as an iron-core high-voltage pulse transformer. In 1876, Arthur Wright used these devices to make thin films from numerous cathode materials [9]. Although Wright did not show any picture in his paper and was sparse in describing the electrical circuit parameters (a polite understatement), his set-up must have been similar to what is shown in Figure 2. Because the current must have been small, his discharge was most likely a pulse glow discharge.

Thomas Alpha Edison was the first who used and patented cathodic arc plasma coating [10]. Edison's patent story is interesting because it marks the beginning of the ongoing discussion of pulsed versus DC plasma processing. In light of Wright's pulsed work, the patent examiner forced Edison to limit his claims to a continuous arc [11]. Ironically, the power load of a continuous arc plasma led to damage of the original wax phonograms Edison tried to duplicate.

Eventually, Edison used therefore a sputtering technique for phonogram duplication. Thermal evaporation and sputtering became the dominant physical vapor deposition (PVD) techniques of the 20th century.

There are too many inventions and developments in the 20th century to even mention them here. To conclude this section, it should be pointed out, in analogy to the above historical discussion of ion implantation, that *dynamic* Monte Carlo simulation codes can be used to calculate deposition profiles in analogy implantation profiles. Dynamic versions of the TRIM code update the substrate or target composition by incorporating the arriving ions. Dynamic codes such as T-DYN [12] or TRIDYN [13] can be used for both implantation and deposition processes.

4. PIII&D emerges

As part of their plasma physics studies, Melvin Widner and coworkers calculated the generation of ion-acoustic waves at a negatively pulsed plate [14]. They obtained the time dependent ion flux and ion energy on the plate, which turned out to be the beginning of PIII theory, as recognized 15 years later by John Conrad and coworkers.

In the early 1980s at Mission Research Corporation, Richard Adler and coworkers developed a metal ion implanter that was based on short-pulse vacuum arcs with synchronized negative high-voltage pulses applied to a substrate holder [15]. A direct line-of sight between the plasma-producing cathode and the to-be-implanted substrate was intentionally blocked by the anode. Carbon and titanium ion implantation was demonstrated. In some sense, this was the first plasma immersion experiment.

Conrad and his group realized that ion implantation by high-voltage biasing is not limited to metal ions but represents a alternative way for a wide range of gas ion implantation with the

potential to be a truly three-dimensional process [16-18]. Nitrogen incorporation in stainless steel or aluminum alloys improves their wear and corrosion properties. Conrad and co-workers introduced nitrogen-PIII as an alternative to both conventional beamline ion implantation and plasma nitriding using elevated workpiece temperatures. The 1986/87 work of Conrad and his group at the University of Wisconsin is generally considered as the "birth" of PIII, or PSII as they called it.

As pointed out by John Conrad in the introductory chapter of [1], it may be too difficult and perhaps unjust to some research groups to describe all following PIII&D work from a historical perspective. Instead, I will now switch to a presentation format that emphasis various plasma immersion applications, ideas, and concepts leading to "family members" of plasma immersion techniques. The following collection is by no means complete or represents a systematic analysis. It should simply serve as a proof for the broad range of currently used or developed immersion techniques, and for the vitality of the field. The focus is here on immersion concepts while neglecting the different ways and advances of plasma production and operation of pulse modulators.

5. Ideas and concepts associated with the family of plasma immersion techniques

Concept 1. Nitriding by immersion implantation of nitrogen ions

Due to its importance, let us consider the plasma immersion incorporation of nitrogen in stainless steel, steel, chrome-plated steel, aluminum, and aluminum alloys as concept 1. Conrad and coworkers [16, 17] combined nitrogen plasma production with negative high-voltage, repetitive pulse biasing of the substrate (target[*]). In the original concept of PSII (as they called it),

[*] I try to avoid the term "target" because it very differently used in the ion implantation and sputter deposition community.

the ion energy was intended to be as high as possible to maximize the thickness of the modified surface layer. Greater depth than the projected implantation range is obtained by diffusion, an effect than can be well-combined with PIII [19]. As mentioned above, nitrogen incorporation lead to beneficial effects for wear properties and corrosion protection. Many papers have been published dealing with the physical understanding and optimization of the process, and improvement of materials properties. Most of these results are summarized in chapter 11 of [1] and here we review only a few recent points.

Wolfhard Möller and coworkers [20] studied the role of the oxide surface layer on the nitriding process of austenitic stainless steel. Using controlled conditions in terms of oxygen partial pressure in ultra-high vacuum (UHV) environment and in-situ elastic recoil detection (ERD) analysis, they prooved that the surface oxide acts as a barrier for nitrogen diffusion. It was shown that the oxide surface layer is dynamic and results from the balance of sputtering and re-oxidation.

From the same group, Reinhard Günzel and coworkers [21] compared the effectiveness of PIII and glow discharge plasma nitriding (GDPN) of stainless steel. They confirmed that GDPN with pure nitrogen is ineffective because the ion energy at the relatively high process pressures of 500 Pa is only 50 eV, thus too small to penetrate the oxygen surface layer. In contrast, PSII with a bias voltage of -700 V gives nitrogen ions enough energy to pass the surface layer. Nitrogen incorporation is greatly enhanced for both GDPN and PSII process if a nitrogen-hydrogen mixture is used. Hydrogen removes the surface oxide chemically and thus the flux of nitrogen radicals from the plasma can contribute to the nitriding process. In another work [22], 50 keV boron implanted austenitic stainless steel was treated by nitrogen PIII. It was shown that a thick layer of expanded austenite is formed with excellent wear behavior but compromised corrosion resistance.

Blawert and coworkers [23] investigated expanded austenite obtained by PIII with nitrogen and methane. Improved wear and corrosion resistance was demonstrated. The nitrogen-PIII samples performed better in terms of wear resistance while the carbon-implanted materials should be preferred for applications where corrosion resistance is important.

Uglow and coworkers [24] found complicated phase transitions that followed nitrogen and carbon immersion implantation into AISI M2 steel with consequences for the ion diffusion processes.

Concept 2. Metal plasma immersion ion implantation (without deposition)

As mentioned before, Adler and Picraux [15] introduced repetitively pulsed high-voltage bias for carbon and titanium ion implantation. Both metal arc plasma and bias voltage were pulsed. By synchronizing these pulses, they demonstrated pure metal ion implantation. Blake Wood and coworkers [25] used the same concept to implant erbium into various substrates.

The concept was extended by Chung Chan's group at Northeastern University, Boston. They used DC-biased substrates (as opposed to pulsed) and avoided unwanted arcing of the substrate by rapidly pulsing the vacuum arc discharge. Aluminum [26] and antimony [27] ion implantation into silicon was demonstrated.

Concept 3. Metal plasma immersion ion implantation and deposition (MePIIID) in vacuum mode

Ian Brown and co-workers [28, 29] modified Adler's experiment by operating the pulsed vacuum arc longer than the pulsed substrate bias, thereby shifting the process from a pure ion implantation technique to a hybrid ion implantation and film deposition technique. In their original experiments, each arc pulse was synchronized with one bias pulse. This concept was

made more efficient by using longer arc pulses (milliseconds instead of microseconds) combined with a burst of many bias pulses for each arc pulse [30]. In principle, this technique could be performed in CW mode (DC plasma and sequence of bias pulses) if the pulser equipment can supply the necessary average power and if the substrate temperature can be kept in the desired range despite the high power load.

The concept can be used to make high-quality thin metal films provided arc-generated macroparticles are removed by magnetic filtering (for filtering, see review [31]). Othon Monteiro optimized pulse bias conditions and plasma flow conditions to demonstrate not only plane films but the filling of trenches with copper and the deposition of nm-size tantalum barrier layers in trenches [32].

Tetrahedral amorphous carbon (ta-C) films, i.e. one kind of diamondlike carbon films, can be obtained using this concept (see, e.g., [33, 34]). Using unusually high pulsed bias pulses of up to 20 keV, very thick (4.5 μm) films can be made that have properties like glassy carbon [35].

Concept 4. Metal plasma immersion ion implantation and deposition (MePIIID) with reactive gases

For the concepts 2 and 3, fully ionized metal plasmas were generated by cathodic vacuum arcs. Films deposited this way consist of cathode material. If a reactive gas is introduced, and the cathode material has a propensity to chemically react with this gas, compound films can be deposited [29, 36, 37]. Films made this way are usually dense, smooth, and under compressive stress. If more than one cathode material is used, compound alloy films can be made [38].

Concept 5. Trench doping using collisional PIII sheath

Already in the late 1980s, the concept of high-energy implantation of gaseous ions was extended to a process of lower bias voltage and energy that is suitable for doping of trenches of semiconductors [39, 40]. Because the sheath dimension (millimeters or centimeters) is much larger than the dimension of the trenches (micrometer or less), ions can reach the sidewall of trenches only by collisions. By optimizing bias voltage and gas pressure, conformal doping was demonstrated [41].

Concept 6. Silicon-on insulator (SOI) fabrication and microcavity engineering by gas ion immersion implantation

Gas plasma immersion ion implantation can lead to gas segregation in the region of peak concentration, leading to the formation of microcavities when the substrate is annealed. For an ion-cut process of silicon wafers, hydrogen is well suited for this process, leading to a manufacturing process of integrated circuit-grade SOI wafers [42]. A first commercial PIII system for 200 mm wafers operating in the Protonic Mode™ is now in operation [43]. Hydrogen and helium generated microcavities can be used for impurity gettering [44]. Collins and coworkers [45] formed helium bubbles of about 2 nm diameter in titanium and titanium alloys using a PIII process at -20 kV and -40 kV with possible applications in catalysis, for medical implants, and selective solar absorbers.

Concept 7. PIII as a technique to fabricate p/n junctions

Already in the late 1980s, it has been shown that boron-containing gases such as BF_3 can be used to fabricate p/n junctions [46]. With the continuously shrinking size of integrated circuits, ultrashallow junctions need to be fabricated which is difficult for conventional beamline

implanters due to the low current at low ion energy. PIII is a promising alternative although one need to realize that PIII does not have the feature of mass selection. The junction depth versus PIII-bias and other details have been discussed recently [44, 47, 48].

Concept 8. PIII as ion beam assistance method to thin film deposition

Broad ion beams of relatively low ion energy (~1 keV or even less) can be used for ion-beam-assisted deposition (IBAD) of thin films. The film-forming material is usually provided by magnetron sputtering although other physical vapor sources such as electron beam evaporators are possible too. The assisting ions are usually argon (reactive gases are discussed in concept 9). The ion beam source can be replaced by extracting ions directly from the plasma via the immersion concept [49]. The difference to concept 3 is that the film-assisting ions do not contribute to film growth.

Concept 9. PIII in reactive physical vapor deposition (PVD) of thin films

If concept 8 is generalized to reactive gases, e.g. by using argon-nitrogen gas mixture when a nitride film is being made, gas ions become incorporated into the growing film. However, in contrast to the film forming metal plasmas of vacuum arcs, as discussed in concepts 3 and 4, a separate vapor source of metal is needed such as a magnetron. Such a hybrid PVD-PIII system was proposed by Ensinger [50]. Schoser and coworkers [51] tested the concept for TiN coatings. In yet another variation, Ensinger and coworkers [52] used the high-voltage pulser for driving the sputter target inside a tube in order to obtain protective coatings on the inner side of a cylinder.

Concept 10. PIII with chemical vapor deposition (CVD) of thin films: Plasma Immersion Ion Processing (PIIP)

As discussed until here, film formation by immersion techniques required a physical vapor source, either in the neutral vapor phase (evaporation, sputtering), or in the plasma phase (cathodic arc and similar plasmas). However, there is the possibility that the processing gas decomposes thereby suppling film-forming species, a process known as "pulsed-DC plasma-enhanced CVD," e.g. for the deposition of TiN from $TiCl_4$ + N_2 (or NH_3) gas mixtures. A research group at Los Alamos National Laboratory has pioneered the PIII approach to plasma-enhanced CVD using high voltage for both plasma generation and bias. They dubbed the concept "Plasma Immersion Ion Processing" (PIIP). The principle can be applied to a wide range of CVD films, and was intensely investigated for (hydrogenated) diamondlike carbon films synthesized from hydrocarbon precursor gases, both experimentally [53, 54] and theoretically [55]. Mike Nastasi and coworkers [56] demonstrated hard boron carbide and chrome-carbi-oxide coatings as protective coatings for aluminum die casting. Baba and Hatada [57] used acetylene and added nitrogen and titanium tetraisopropoxide to obtain diamondlike carbon films doped with nitrogen and titanium oxide. Anatase photocatalytic TiO_2 was synthesized by the same authors in a similar PIII-CVD method [58]. Other experiments involving microwave plasmas of metallorganic precursors are also under way in Japan [59].

Concept 11. Low-energy PIII as a substrate preparation and etching method

Plasma and low-energy ion beam etching of substrates is standard in the semiconductor and other industries. For instance, carbon can be removed with oxygen ions and oxide films can be removed with hydrogen ions. The advantage of PIII is that due to the many free process

parameters, the cleaning process can be optimized for the specific application via amplitude, pulse length, duty cycle, and the choice of gas and its pressure. In order to avoid material damage and increased surface roughness, the voltage for surface preparation applications should be low.

Concept 12. Formation of compound layers by gas-PIII in metals and semiconductors

Instead of depositing a compound layer on a workpiece, such layer can be formed if the workpiece is made of a suitable metal and the reactive gas ions are provide by the PIII process. If the base metal can be elevated to temperatures that allow the implanted ions to diffuse, the compound layer can be thicker than the projected range of the ions. This concept is very similar to the original PSII (concept 1) but aims at the formation of a stoichiometric compound phase. Using this concept, Wolfgang Ensinger and coworkers [60] formed rutile TiO_2 and α-TiO on Ti and Ti6Al4V. The compound films are used to improve the biocompatibility of these materials for medical implants. Mändl and coworkers [61] did also form rutile TiO_2. They focussed on the oxygen diffusion profile at temperatures greater than 400°C.

In a study of nitrogen diffusion in stainless and aluminum, Möller and coworkers [62] found a substantial difference between these materials. While nitrogen motion in stainless steel can be described as diffusion in the presence of chromium traps (see concept 1), a stoichiometric AlN layer forms in the case of aluminum, facilitated by the diffusion of aluminum atoms to the surface from the underlying bulk.

Nitrogen-PIII has also been used to form a compound layer on a semiconductor. Paul Chu and coworkers [63] used a GaAs substrate to form a highly saturated nitrogen-doped GaAs layer of about 40 nm thickness. A strained, GaN-containing surface layer is obtained after rapid thermal

annealing. It is believed that this layer is suitable for epitaxial growth of high-quality GaN, a material used for blue laser diodes and other applications.

Ueda and coworkers [64] found evidence for the formation of SiO_2 and Si_3N_4 formed by PIII of nitrogen into silicon wafers. The as-implanted layers were highly stressed.

Concept 13. Pulsing not only the substrate but also the plasma potential

Provided ions travel through the sheath without collisions, their energy is directly proportional to the sheath voltage. The sheath voltage is the potential difference between the substrate surface and the potential at the sheath edge which equals approximately the plasma potential (a difference of a few eV can be neglected). In practically all cases, the plasma potential is close to ground because the plasma is enclosed by the process chamber which is grounded for safety reasons. The sheath voltage could be enhanced if not only the substrate is negatively biased but the plasma positively biased. This would require to have a plasma enclosure that is electrically insulated from ground. The plasma-producing discharge may be pulsed to positive high voltage; preliminary experiments using a modified Marx generator scheme were promising [30].

Concept 14 Increasing the ion energy by utilizing multiply charged ions

In most PIII&D processes, singly charged ions are used. Some discharge processes and plasma sources can provide multiply charged ions thus offer the possibility to increase the ion energy. This energy is given by $E_i = Q\,V_s$ if collisions and the initial ion energy in the plasma can be neglected, where Q is the ion charge state, and V_s is the sheath voltage. Examples of plasmas with multiply charged ions are some ECR plasma sources, laser ablation plasma sources, and vacuum arc plasma sources. For the latter, recent measurements [65] have confirmed that ion

charge states are significantly higher at the beginning of each arc pulse – a very interesting fact for systems that use rapidly pulsed vacuum arcs.

Concept 15. Plasma immersion treatment of insulators

With some restrictions, the principles of PIII&D can be applied to the treatment of insulating substrates, for instance polymer sheets. Because the bias cannot be applied to the substrate itself, it is applied to the substrate holder with the idea that most of the voltage drop between the holder and plasma will occur in the sheath between the polymer and the plasma. Properties of the insulator such as the wettability [66, 67] and oxidation resistance [68] have been modified. Tonosaki and coworkers [69] used cathodic arc carbon plasma and pulsed biasing to enhance the surface Young modulus of amorphous poly-olefin plastic from 1.8 GPa to 25 GPa.

6. Brief discussion of the energetic relation between ion implantation and deposition

Film formation with energetic particles will lead to densification of the film. For "low-energy" implantation, the projected range of ions can be as small as a few monolayers. This process is called subplantation. Subplantation is well investigated as the key growth process for the various forms of diamondlike carbon (e.g. ta-C and a-C:H). It is known that ion energy of about 100 eV leads to the densest films that, in the case of carbon, exhibit the highest sp^3 content and associated highest hardness, compressive stress, largest optical bandgap, and lowest surface roughness. While carbon is a very special material due its various hybridization states, many findings apply to a broader class of materials.

While deposition is considered energetic if the film-forming particles have an average energy of ~ 100 eV, even higher energy leads to a significant increase of sputtering. Depending

on the material, the self-sputtering rate becomes unity when the energy is 300-1100 eV [70, 71]. That means, in the average, for each ion arriving at the substrate, an atom is removed from the surface by sputtering. In this sense ~ 500 eV could be considered as the transition energy from deposition processes to an implantation processes without film formation. However, in PIII&D processes, bias is usually applied in a pulsed mode, and thus film formation may occur at much higher bias voltage provided the bias duty cycle is low and/or the flux of film-forming neutral particles is dominant.

7. Issues and limitations

(1) A severe limitation of PIII&D for high energies is the generation of secondary electrons. For all practical means, PIII&D is limited to bias voltages less than -100 kV. Even in the -10 kV region, most power of the bias pulser is invested in secondary electrons because the coefficient of secondary electron emission can be greater than one [72, 73]. If the voltage exceeds about -30 kV, secondary electrons generate hazardous X-rays requiring shielding which adds to the process cost. Attempts have been made to circumvent the generation of secondary electrons or their acceleration in the sheath [74] but it seems to be clear that PIII&D techniques are practical in the lower voltage range only.

(2) Although PIII was initially hailed as a three-dimensional alternative to beamline ion implantation, conformal ion implantation is only obtained if the sheath thickness is much smaller than the features of the three-dimensional workpiece (with the exception of a collisional PIII, see concept 5). Substantial deviation from uniform treatment was found for conditions where the feature size if of the same order of magnitude than the sheath size [75]. Volz and coworkers

illustrated this by investigating the thickness-dependent color of oxide films [76], and Mändl and coworkers [77] studied scaling effects.

(3) Cathodic vacuum arc plasmas are characterized by a high flow velocity of order 10^4 m/s [78]. Although vacuum arc plasmas are fully ionized and therefore exceptionally well suited to be combined with immersion techniques, treatment of three-dimensional workpieces requires either workpiece motion or a multitude of cathodic arc plasma sources.

(4) PIII nitriding of metals does have advantages, as pointed out in the “Concept 1” section, however it is not cost-efficient compared to conventional plasma nitriding at elevated temperatures when nitrogen-hydrogen gas mixtures can be used. PIII nitriding should be preferred if the workpiece material has a strict limitation of allowable process temperature or use of hydrogen.

(5) PIII&D processes are not mono-energetic as discussed in detail by various researchers [47, 79]. This feature may or may not be tolerable depending on the desired process. If the plasma contains only ions of one mass and one charge state, the process can be conducted in a way that a dominant energy exists provided the bias pulse shape is essentially rectangular.

(6) PIII&D processes do not involve mass selection and can therefore not compete with beamline implantation where very high species purity is guaranteed. This limits the applicability of PIII&D for some semiconductor processes but the feature can be tolerated in some semiconductor applications such as ion-cut with hydrogen.

(7) PIII&D processes are usually limited to conducting substrates although insulating workpieces can be treated with certain geometry and plasma constrains, see concept15.

8. Outlook: Prospects and trends

- Plasma immersion techniques matured in the 1990s in theoretical understanding, scaling, and range of applications. First commercial facilities are now operational, e.g. at Silicon Genesis [43] and Empire Chrome [80]. In the 1980s and 1990s we have seen exponential growth of the field but signs of a slowdown appeared about 1998 as illustrated by the annual number of publications (Fig. 3). Nevertheless, plasma immersion techniques have found many applications, including the improvement of wear and corrosion resistance of stainless steel and aluminum alloys, smart-cut process of semiconductor wafers, shallow junction formation of semiconductors, assistance of film deposition for mechanical, optical, biomedical, and other applications.
- PIII&D research activities were initiated in the United States and spread to Europe, Australia and Asia. Based on the funding level of current and near-future PIII&D research, one can see a shift of activities to some European but mainly to Asian countries.
- While gas (often nitrogen) ion implantation dominated the early years, film-forming immersion techniques and semiconductor processing gained importance. There are reason to believe that this trend will continue because PIII&D is perfectly suited for processes that need to be energetic (subplantation and implantation range) but limited to relatively low energy compared to conventional beamline ion implantation. Both film formation and semiconductor processing have this requirement. Practical PIII&D applications are likely to be limited to voltages less than -50 kV.
- Although PIII&D techniques have their own limitations in terms of processing three-dimensional workpieces, treatment of trenches and holes is principally possible, and more research and applications can be expected in this area.
- In-situ monitoring of the PIII&D process will become increasingly important. While it is standard in nitriding applications, for example, to monitor the workpiece temperature and control

the process accordingly, in-situ monitoring of film growth and quality is not yet always due to the high cost associated.

- Hardware components of PIII&D systems have evolved and becoming more readily available. For instance, large area and three-dimensional treatment with DECR (distributed electron cyclotron resonance) plasma sources has extended the range of possibilities [81]. Better and more affordable pulse modulators are available from several commercial vendors. It can be expected that this trend will continue.
- Because PIII&D processing of films has many degrees of freedom, process parameters may be found leading to superior film quality. Conformal coating and filling of sub-micrometer trenches by MePIIID has been shown. Other examples can be anticipated, for instance PIII&D films for the production of MEMS (microelectromechanical systems), bio-medical implants, and optical structures for the communications industry.
- With the development, accessibility and affordability of modern PCs, simulation of PIII&D processes should become standard even if many particles are involved. New codes will evolve and modern techniques such as Molecular Dynamics can be applied to obtain deeper understanding for example of nucleation and energetic film growth processes. PIII&D is often a truly three-dimensional process, and models have to be developed that account for all dimensions.

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Figure Captions

Fig. 1 Goldstein's tubes for the observation of "canal rays" behind the tube's cathode, 1886.

Fig. 2 Reconstruction of Wright's experiments (1876) using a primary element (E), a mercury current interrupter (q), a Rühmkorff induction coil (A), and an exhausted glass tube with metal electrodes (M); from a German text book 1902.

Fig. 3. Scientific PIII&D publications published per year: A search of the INSPEC database was conducted for (Plasma Immersion Ion Implantation) OR (Plasma Source Ion Implantation) OR (Plasma Immersion Ion Processing) OR (Plasma Based Ion Implantation). Cross checks were performed to eliminate double counts. The number for 2001 was extrapolated based on the publications for the period January-June.

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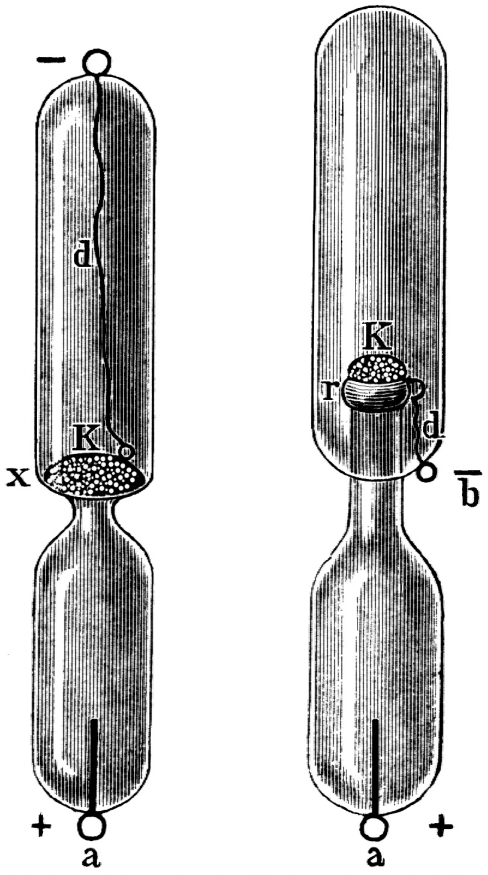

Fig. 1

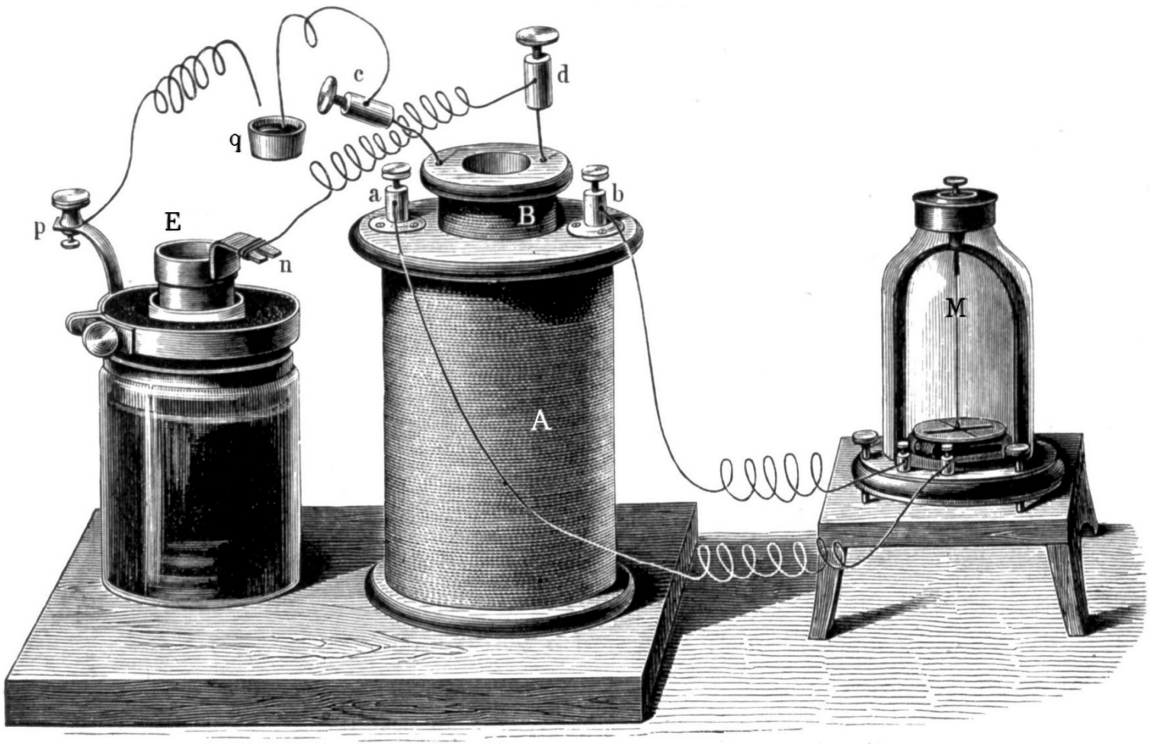

Fig. 2

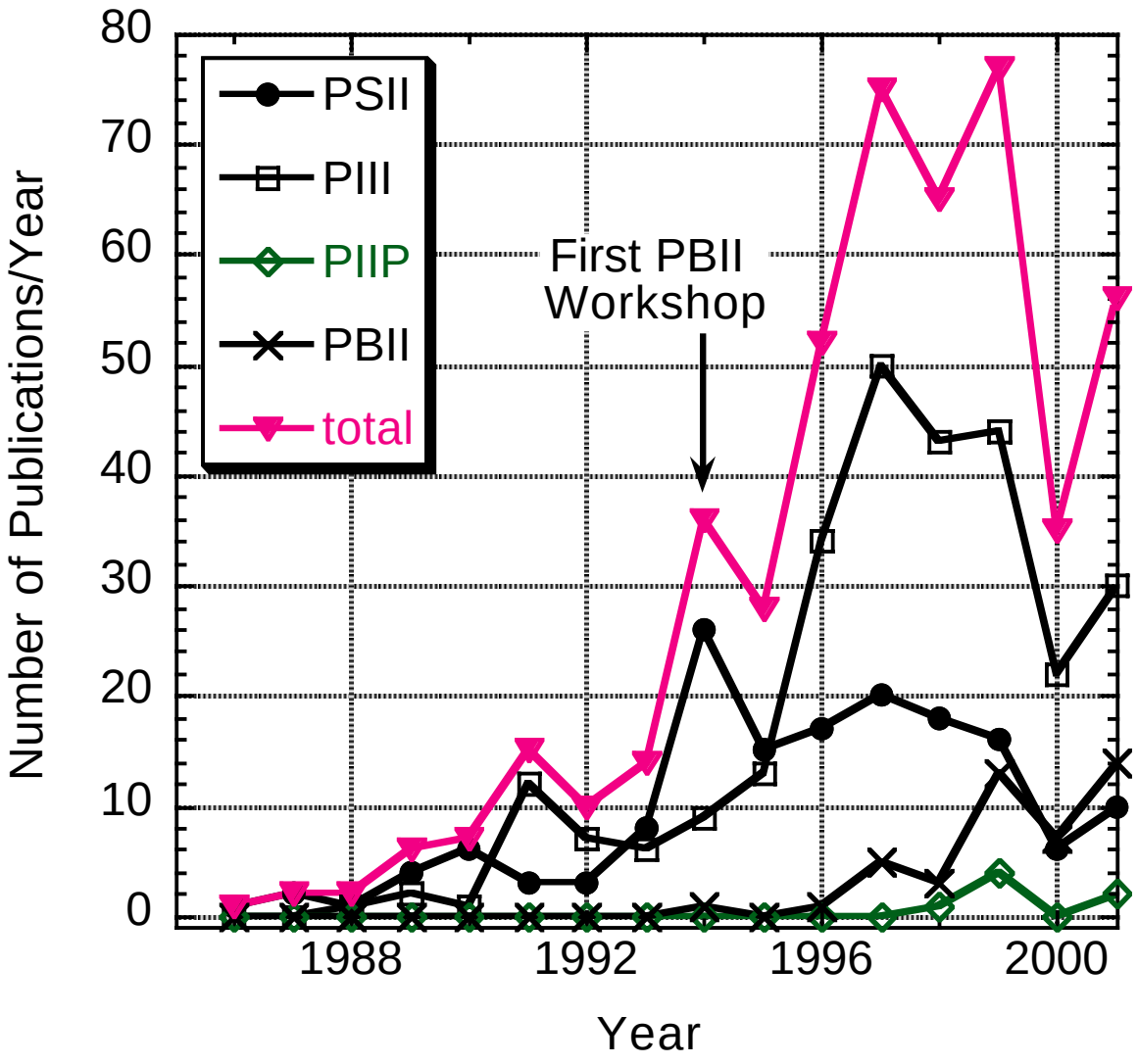
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Fig. 3