PI asma Immersion Ion Impl antation (PIII) Process - Physics AND Technol ogy

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Abstract

Plasma Immersion Ion Implantation (PIII) is a versatile process technology with its vast applications in materials engineering and microelectronics processing. This paper reviews first, a brief historical aspect of conventional ion implantation and Plasma Immersion ion implantation, followed by their comparison. Then the basic mechanism of a PIII technique and the physics of sheath dynamics developed in such a system is discussed together with necessary plasma specifications in a PIII process. Finally the main components of a PIII system, the existing trends and future prospects of this promising process technique are discussed.

Keywords: Plasma immersion ion implantation, conventional ion implantation, ion matrix sheath, Child-law sheath, ion plasma frequency, pulse generator system.

1. Introduction

Gordon E. Moore predicted the swift growth of Integrated Circuit (IC) technology way back in 1965. Moore's Law, as it is commonly known, states, "*The complexity for minimum component costs has increased at a rate of roughly a factor of two per year.Certainly over the short term this rate can be expected to continue if not to increase*" [1]. By 1975, this pace slowed down slightly, and the device density was approximately doubled in every 18 months [2] and this is the current definition of Moore's Law, being depicted in Fig. 1.



Fig. 1 Growth rate of number of transistors per chip [Ref. 2].

The packing of more and more devices in the same chip area has resulted in products with better performance, more functionality and new capabilities at very low cost. To achieve these predictions of Moore's Law further into the future, researchers are continuously working on advanced technologies. On examining International Technology Roadmap for Semiconductors (ITRS), it is observed that ion-implantation techniques play a key role in the field of microelectronics.

1.1 Historical Milestones

Before understanding the basic significance of Plasma Immersion Ion Implantation, it is necessary to consider the early history of Conventional Ion Implantation (CII) technique. As historical perspective, the first ion implanter was a helium based implanter, constructed and operated in 1911 at Cavendish Laboratory in Cambridge by Ernest Rutherford and his students [3]. In 1949, Shockley filed for a patent, "*Semiconductor Translating Device*" describing the p-n junction fabrication using ion implantation [4]. In 1954, he filed another patent, "*Forming of Semiconductor Devices by Ionic Bombardment*" giving fundamental description for ion implantation equipment [5]. Between 1960 and 1976, the industry of commercial equipment manufacturing of ion implanters became firmly established. In 1976, Varian Associates developed the model DF-4, the first in-line, wafer to wafer, high-throughput (about 200 wafers per hour) ion implanter and by the end of 1978, it became the most widely used commercial ion implantation system in the world [6,7].

Initially, the development of ion implantation technology was utilized to dope semiconductor materials for the IC industries [8]. Then in mid-seventies, these high energy ion beams were also used to enhance the surface properties of metals [9], where implantation of nitrogen or carbon into steel and other alloys resulted in increased wear and corrosion resistance with enhanced surface properties.

CII is a line-of-sight technique where the nonplaner objects need target manipulation in order to implant the desired/all sides of the target that adds complexity to the system and at times cost prohibitive and in many cases even the size of target is required to be reduced for achieving uniform implantation of the target. This target manipulation further aggravates by the requirement of heat sink arrangement during implantation [10]. Furthermore, CII is a '*serial*' technique where low beam currents lead to high costs for high-dose applications.

Consequently, to meet with the requirements of a '*parallel*' treatment that would act simultaneously on large size samples and of the applicability to 3D samples, a noval technique was envisioned in early 1980's, at Mission Research Corporation by Richard Adler et. al., where a metal ion implanter, based on short-pulse vacuum arcs with negative high voltage pulses (\cong -80 KV) biased to a target holder was proposed [11,12]. Here successful implantation of carbon and titanium ions was experimented without ion extraction mechanism which is now assumed to be the basic principle of PIII technique. Later in 1986-87, John R. Conrad and Castagna at the University of Wisconsin-Madison devised a 3-D ion implantation equipment named Plasma Source Ion Implantation (PSII) as an alternative to the conventional ion immersion implantation which is considered as the birth of PIII [13]. Here Conrad et. al. combined nitrogen plasma production and the target being biased with negative high voltage repetitive pulses [14-16]. To maximize the thickness of modified surface layer, the ion energy was kept as high as possible that leads to beneficial effects for wear properties and corrosion protection. Thereafter tremendous research work has been carried out in understanding the physics and optimization of

PIII process. Today, PIII is a subject of research in over 120 laboratories worldwide on account of its various tribological applications, viz., for strengthening metal, glass, plastic, polymer and ceramic components. This process technique is also helpful in altering the chemical and physical characteristics of surface of a material to produce high strength, lightweight, corrosion resistant components at a much lesser cost. Subsequently, this processing technique was pioneered by B. Mizuno et. al. [17,18] and P.K.Chu et. al. [19,20] for semiconductor applications and was named as Plasma Immersion Ion Implantation and Deposition (PIII&D), commonly known as Plasma Immersion Ion Implantation (PIII) processing technique. Since then this fledgling technique is getting popular among technologists and researchers each year for its numerous applications.

1.2 Conventional Ion Implantation (CII) Verses Plasma Immersion Ion Implantation (PIII)

Conventional Ion Implantation (CII), commonly known as ion implantation technique is a process for injecting ions of any element into any solid material, resulting in desirable modification in its chemical, optical and mechanical properties. For semiconductor applications, it is extensively used for selectively doping silicon wafers in precise control and for depth profiles of specific impurities.

In a general ion implantation system, shown in Fig. 2, atoms of desired species are ionised to form plasma of ions and are then allowed to pass through an orifice to a high vacuum region. Here these ions are first accelerated by an electric field and the desired ion species are then extracted according to the mass by a magnetised type mass analyser. A set of extraction grids helps in focusing these rays of ions to form a collimated beam. This fine beam passes through a beam steering system, which first accelerates the ions to a desired energy and then deflects it across the target to uniformly implant the ions into the target by an electrostatic scanning mechanism. For a non-planar target, a manipulator stage is required to rotate the target to implant it from all sides for which sophisticated computer-controlled system is also provided. This target manipulator stage further needs heat sink provision at the target to limit the rise in temperature during implantation.



Fig 2 Conventional ion implantation system.

The CII technique is a sophisticated line-of-sight process where a sample can be doped at room temperature, free from any contaminants and with wide variety of dopants in the range of 10^{15} to 10^{21} m⁻² in the energy range from few hundred KeV to MeV. This technique can even be carried out for depositing controlled amount of a charge species in a specific region of a sample. Despite these unique features, CII is an expensive and complex tool for surface modification and

semiconductor applications. The mechanisms like, mass separation, beam extraction, focusing, transport, scanning, acceleration, etc., enhances the complexity to the system and, therefore, a small size sample can only be conveniently implanted. In addition, CII is also limited by the retained dose problem [21,22] that occurs on account of the angle of incidence of the beam (Fig. 3.a) which causes undesired excessive sputtering. To circumvent this problem, masking fixtures are mounted on the target, thereby, introducing more complexity and cost to the system (Fig. 3.b). Usually, sputtering of mask also contributes the contamination to the target.

In case of PIII process, the target is directly immersed in a chamber of plasma of ion species to be implanted and is biased with a pulse of high negative potential of the order of KV with respect to the ground potential of chamber walls. The applied negative potential drifts the electrons away from the target to form a positive ions sheath around the target. With time, the positive ions present in the sheath are being dragged towards the target due to its negative potential and get implanted onto the target surface from all sides (Fig. 3.c). Thus PIII, being a non-line-of-sight technique, completely eliminates the complicated and sophisticated mechanisms of CII and proves to be a comparatively simple and cost competitive process technology.



Fig. 3 Retained dose issues for Conventional ion implantation vs. PIII.

Some of the advantages of PIII can be summarized as:

- 1. Less Hazardous: System is relatively easy to operate and maintain.
- 2. *Economical*: Capital investment and running cost are substantially less.
- 3. *Less Time Consuming*: Process time is independent of sample size and its surface area.
- 4. Flexible: Any shape, size and weight of sample can be processed.
- 5. *Versatile*: Multiple processes can be carried out like implantation, deposition, etching, etc., and not just semiconductor or metals, even insulating samples can be treated.
- 6. *High Throughput*: Number of samples can be processed at the same time.
- 7. *Uniformity*: The sample surface can be implanted ensuring uniform dose rate with good conformity.
- 8. *Implantation Flux*: As high as 10^{20} m⁻²s⁻¹.
- 9. Implantation energy varies from 1 KeV to 300 KeV.

- 10. *No charging*: Charge build-up in insulating samples is readily alleviated by secondary electrons indigenous to the plasma.
- 11. Low-temperature process.
- 12. Implantation of multiple species with multiple charges is possible in the same system.

Although all these unique features establish PIII as a promising technique, it has also few drawbacks:

- 1. As no mass separation is possible, there are always chances of implantation of undesired impurities present in the plasma into the target, in addition to the desired dopants.
- 2. Secondary electrons limit the efficiency and generate x-rays.
- 3. Accurate in situ dose monitoring is tough.
- 4. Implant energy distribution is inhomogeneous.

2. Basic Mechanism of a PIII System

The schematic diagram of a PIII [13, 21] with its main building blocks is shown in Fig. 4. It consists, a vacuum chamber, a plasma generation system, working gas supply, a high voltage pulse modulator and a target stage.



Fig. 4 Plasma immersion ion implantation.

A pulse generator with varying pulse durations is used to provide a negative bias (ranging from 1 to 300KV) to the target. The lower ranges of pulse potentials (5 to 10KV) are used for semiconductor applications, viz., shallow junctions fabrication, trench doping, etching and contamination study, etc., while higher values of pulse potentials ranging –50KV to 300KV are generally used for metallurgical applications. Some of the semiconductor structures (SOI/SPIMOX) use relatively high voltages (30 to 60KV). The magnitude of this bias voltage is usually limited by the limitations of pulse modulator and the process related constraints.

Other basic accessories like, Langmuir probe to measure plasma density and electron temperature, ionization gauge to measure neutral density during implantation, IR pyrometer to monitor target temperature during implantation, etc., are also parts of a PIII system.

To implant the ions in a PIII system [23-25], the target to be treated is placed on an isolated and properly insulated target stage in the vacuum chamber. Plasma of ions of desired species, to be implanted on to the target is generated and a series of negative high voltage pulses, with respect to the chamber walls are applied to the target.

2.1 Plasma Sheath Dynamics

The basic physics of plasma sheaths under steady state conditions can be described by assuming a plasma, consisting of electrons, ions, neutral atoms and molecules, confined between two grounded absorbing walls, separated by a distance l, as depicted in Fig. 5.a. Since plasma is usually quasineutral, i.e., the densities of positive ions and electrons are same $(n_i=n_e)$, the net charge density will be zero [26-29] and so will be the electric potential and the field. As we know that the electron temperature is larger than ion temperature, especially at low-pressure discharges and the electron is lighter than the ion, the electron thermal velocity becomes very large (100 times) than ion thermal velocity.



Fig. 5 Plasma sheath formation under steady state: (a) initial charge densities and potential (b) charge densities, electric field and potential variation after sheath formation.

Therefore, high mobile electrons are not confined within the plasma and are lost to the grounded chamber walls, resulting in the formation of positive charge sheaths at the wall edges (Fig. 5.b) with net charge density as positive ($:: n_i > n_e$). This leads to a varying potential profile, i.e., positive within the plasma, reducing to zero near the walls. This non-neutral potential region interfaced between plasma and the chamber walls is known as *sheath* [30,31].

The sheath potential further acts as a force for the confinement of electrons and ions by reflecting the electrons towards the plasma and accelerating the sheath ions towards the wall edges. At the interface of plasma and sheath dynamics, it is required that the mean ion velocity at the plasma-sheath edge should be given as equal to Bohm (ion-sound) velocity, $u_B = (eT_e/M)^{1/2}$, where e and M are the charge and mass of ion, respectively and T_e is the electron temperature in volts [32].

In a PIII process, which is an intrinsically pulsed process, transient characteristics of sheaths are considered. The time evolution of plasma sheath for one pulse can be described if we consider that the planar target to be implanted is directly immersed in a uniform plasma as shown in Fig. 6.a. It is assumed that a high-voltage negative pulse with an instantaneous rise-time of pulse voltage at time t=0 is applied to the substrate. Due to the field developed across the sheath, electrons with lighter mass respond first. In a very short time (\approx few nano seconds), the electrons near the target surface are driven away on a time scale of inverse electron plasma frequency, $\omega_{pe}^{-1} = (\epsilon_0 m_e/n_e e^2)^{1/2}$. As a result, ions being heavier in mass are exposed and an electron-depleted sheath of uniform ion density develops around the substrate, which is known as ion-matrix sheath (Fig. 6.b).



Fig. 6 Time evolution of plasma sheath during PIII pulse: (a) uniform plasma (b) ion-matrix sheath (c) expanding sheath (d) expanded sheath.

Subsequently, on a time scale (\approx few micro seconds) of the order of inverse ion plasma frequency, $\omega_{pi}^{-1} = (\epsilon_0 m_i/n_i e^2)^{1/2}$, ions within sheath are accelerated across the sheath by the electric field so developed and are ultimately driven into the surface of the substrate. As the ions are implanted, charge imbalance drifts more electrons away from the substrate, thereby uncovering more ions from the plasma, resulting in an expansion in sheath thickness (Fig. 6.c). After several transit times (\approx several µs), steady-state ion current flow is established across the sheath, principally governed by the Child-Langmuir equation. This expansion in sheath thickness is commonly known as dynamic sheath or Child-law sheath [14, 16] as depicted in Fig. 6.d that contributes the major part of implantation of ions [33]. For example, in the case of Helium plasma with an ion density of $10^{16} m^{-2}$, when the target is applied -10KV potential, ion-matrix sheath thickness is around 0.01m and the Child-law sheath varies with time upto a value of around 0.08m for pulse duration of 10µs. The dynamic sheath evolution has been studied by various researchers through analytical models and numerical simulation models in various regimes.

2.1 Plasma Specifications:

A major concern in PIII Process is the plasma size that must be much larger than the sheath thickness in order to avoid total depletion of plasma ions between substrate and the plasma walls. Thus the characteristic size of plasma must exceed the Child-Law sheath thickness.

Another main concern is the mean ion penetration depth for which it is necessary to control the energy distribution function of the ions being implanted. To obtain optimum energy, it is desirable to control the actual ion energy distribution function at the impact by controlling the ion charge state, sheath voltage and pulse shape [34]. This can be best approximated when ions traverse the sheath without collision i.e. when ion mean free path (λ_i) is greater than sheath thickness.

In case of multi-species plasmas, different ions reach the target with distinct velocities and are, therefore, get implanted with distinct projected depths. Thus a perfect control of velocity distribution function of ions at substrate surface, low pressure plasmas would be preferable so as to exploit the total capabilities of the voltage pulse supplier.

Lastly, denser the plasma, shorter is the sheath thickness and larger would be the ion current densities which may cause arching in the sheath and so causing increased substrate heating [35,36].

3. PIII PROCESSING SYSTEM

A PIII system comprising three basic components, i.e., a processing chamber, a plasma generation mechanism and a pulse modulator is shown in Fig. 7.



Fig. 7 Basic components of a PIII processing chamber.

3.1 PIII Processing Chamber

The design of a PIII processing chamber is usually decided by the type of applications to be performed in it. In terms of chamber size, implantation voltage and processing power, a chamber used in tribological treatments will be different from the one used in semiconductor applications. The chamber size and type of applications are correlated, as the samples treated in

tribological treatments are usually bigger in size. It is seen that the average chamber size for surface modification applications ($\cong 1m^3$) is about 20 times larger then that utilized in semiconductor processing ($\cong 0.05 \text{m}^3$) [37, 38]. For a particular application, an optimum chamber size X_{CT} can be defined as: $X_{CT} \ge X_{SH} + X_{TT} + X_{FD} + 0.3m$, where X_{SH} is the net sheath expansion at the completion of negative pulse, X_{TT} is the thickness of target to be implanted ($\cong 0.001$ m for Si wafers), X_{FD} is the dimensions of fixtures provided for electrical insulation purposes in the chamber. An empirical value of 0.3m, for any application, is added as plasma dimension, recommended for any plasma reservoir that can regenerate the plasma at the end of every pulse. As an example, if we again consider the case of He plasma with ion density 10^{16} m⁻² and pulse voltage with -10KV applied for duration of potential 10 μ s, the value of X_{SH} is $\approx 0.08m$ that corresponds to a chamber of $5.12 \times 10^{-4} \text{m}^3$ in volume with square shape. The chamber shape can be rectangular, square, cylindrical or bell type, and can be mounted either horizontally or vertically. It can have an access for loading/unloading of samples at any of its faces. The materials for such processing chambers can be aluminium, stainless steel or carbon steel. Similarly, higher implantation voltages and processing power are needed in tribological applications. The average implantation voltage for semiconductor processing is about 10 times and processing power is over 100 times lower than the surface modification applications.

3.2 Plasma Generation System

Plasma, generally called the fourth state of matter, is a collection of free charged particles moving in random directions and on the average is electrically neutral but highly conductive. The plasma is generated by an electric discharge for which various forms have been developed like, hot filament discharge, radio frequency discharge, microwave discharge, etc. To employ a specific type of discharge, various kinds of plasma generation systems/plasma sources have been developed [39] and applied to Plasma Immersion Ion Implantation and Deposition (PIII&D). Plasma can be produced either remotely from the target or by using the target as one of the electrodes. Some of the commonly used plasma generation systems are discussed below:

a) Thermionic Discharge

This simple system is based on electron emission from a hot cathode, which generates the plasma by ionization of the background gas. These cathodes made-up of refractory metals (Tungsten, Tantalum, Molybdenum) are inserted in the vacuum chamber through insulated feed-throughs and are biased with a negative floating power-supply (< 200V) with respect to the vacuum chamber walls that is kept at ground potential [40]. These thermionic cathodes generate plasma of 10^{15} to 10^{18} m⁻³ ion density by providing a discharge current ranging from ten to hundreds of amperes. The plasma in thermionic discharges is confined magnetically by providing an array of permanent magnets to the chamber walls. Some of the limitations of thermionic emitters are:

- Cathode material itself causes the contamination to the target.
- Due to evaporation and sputtering, cathodes have finite lifetime.
- Hot cathode material sometimes reacts with the source gas.

b) Pulsed Glow Discharge

If only relatively low ion energy is required, plasma formation and substrate bias can be done by a pulsed power supply. It is a straightforward technique where high voltage pulses are used for the generation as well as acceleration of ions in a PIII chamber [41, 42]. It can be produced from any shape and size of electrode using any gas and for the treatment of any size of surfaces. The conducting target acts as cathode thus eliminating the drawbacks associated with thermionic discharge. A few disadvantages of pulsed glow discharge are:

- Not a versatile technique.
- Always a limitation for pulse repetition rate, maximum pressure and ion current density.
- At higher pressures, for a given voltage, the ions may not have optimum energy.

c) RF Plasma Discharge

In RF plasma discharge, the electric power is either capacitively or inductively coupled into the plasma and is widely used to generate macroscopically stationary gas plasma.

i) Capacitively Coupled Type

This is extensively used in PIII systems because of its simplicity, low-pressure operation, uniformity and relatively low equipment cost. Here, no magnetic confinement is required and the plasma can be generated even at a gas pressure of $\cong 0.1$ mTorr. A typical capacitively coupled plasma discharge system, suggested by Rank et. al. [43], is shown in Fig. 8. Such a plasma has very good properties to treat polymer surfaces.



Fig. 8 Capacitively coupled RF plasma discharge system.

Most of the RF generators operate at a frequency 13.56MHz [44]. Since most RF generators have an output impedance of 50 Ω , matching network is added for maximum power transfer to the plasma load. Any conductor placed in the plasma can behave as RF antenna. Relatively higher plasma densities of 10^{14} to 10^{16} m⁻³ can be achieved at a moderate power of \cong 1KW [45]. To enhance plasma density and associated deposition or etch rates, frequencies higher than 13.56 are employed, e.g. Rudiger et. al. suggested a source operating at 81.36 MHz, to be used with silane for the deposition of microcrystalline silicon films [46].

ii) Inductively Coupled Type

This class of plasma source is used for the production of higher plasma densities and for the conformal surface treatment of samples, over a wider range of pressures. In this a conducting coil to which RF power is supplied surrounds a dielectric chamber. This induces an electric field that helps in ionising the gas inside the chamber and sustains a discharge without any need of magnetic field. For semiconductor applications and most PIII&D processes, this is a well-suited technique. Different shapes of inductively coupled RF Plasma are available [47] depending on the specific application area. Planar inductively coupled RF Plasma (Fig. 9) is appropriate for semiconductor etching applications.



Fig. 9 Planar type inductively coupled RF plasma discharge system.

The plasma density of low-pressure RF discharge ranges from 10^{16} to 10^{18} m⁻³. Wu and Lieberman [48] developed inductively coupled large area (71 c.m. x 61 c.m.) plasma source driven by a 13.56 MHz travelling wave. Park et. al. [49] suggested a 2x2 array of inductively coupled plasma (ICP) sources, each having its own planar, circular antenna and quartz window and thus achieved oxygen plasma for uniformly processing glass plates of flat panel fabrication.

d) Microwave Plasma Discharge

Microwave power is very efficient in generating plasma and chemically active species. Also for large plasma volumes, microwave plasma discharge are used in which the plasma is generated either in resonant or non-resonant modes. Generally, Electron Cyclotron Resonance (ECR) and Microwave Multipolar Bucket (MMB) types are used in PIII applications [50] due to their high ion density, low ion energy and low impurity levels. Fig. 10 shows the basic schematic of MMB plasma source [51]. The multipolar magnetic field helps in the confinement of plasma and also in trapping the fast electrons in the lobes produced by the alternating magnetic polarity. The microwave source includes a magnetron to supply microwave power (\cong 1KW) at a frequency of 2.45GHz and a three-stub tuner for impedance matching of magnetron and plasma load.



Fig. 10 Microwave multipolar bucket (MMB) plasma system.

Some of the main features of microwave plasma discharge are:-

- High plasma densities can be achieved.
- The cost of power generation is low especially when magnetrons at a frequency of 2.45GHz are used.
- Less noisy and more stable at microwave frequencies.
- Behave as efficient ion sources when the degree of ionization is low ($\leq 10^{-4}$).
- Finer control of ion bombardment energy.

3.3 Pulse Modulator

In a usual PIII processing system, pulse modulator is the third important component that supplies a high voltage negative pulse to the target for implantation of ions. Although a high negative DC voltage can also be applied to the target for implantation, but is avoided due to the arching on the surface of the target. Also there will be deficiency of ions in the plasma due to implantation and on longer time scale the plasma will collapse with the walls of processing chamber due to the expansion of sheath thickness during implantation. Therefore, to recover regeneration of fresh ions and to avoid the collapse of plasma, the voltage to the target is applied in pulsed manner. In this way the plasma is recovered during the interval of consecutive pulses. To achieve pulses of desired voltage, current, pulse width, and repetition rate, a pulse generator usually consists of a high voltage supply, an energy storage system usually a capacitor that holds the energy to supply to the load per pulse without any snags, high voltage switches to monitor the ON/OFF intervals of pulse to minimize the rise and fall times, and pulse transformers to supply an output pulse to the load [52,53]. The basic criterion for selecting an appropriate pulse modulator is to provide a pulse with minimum rise and fall times in voltage as compared to the pulse length so that maximum number of ions should accelerate with full bias voltage while implanting the target surface [54].

As a pulse generator system, it includes a positive DC high voltage supply (10's of KV and few mA) connected to a capacitor (10's of nF or more) through a charging resistor (100-200 K Ω).

The vacuum tubes are still popular as they can handle pulse durations of 100 μ s or more, and can operate at high pulse frequency and duty cycle. Since vacuum tubes have a limited current capability (\cong 10A) [55-57], high voltage switches like thyratrons [58], spark gaps [59] or high voltage high-current transistor switches are employed [54,60]. These high voltage switches directly switch the pulse ON/OFF. Over the last one and half decade, a number of PIII-specific pulse generators have been developed for industrial applications, ranging 10-100KV and 0.1 to 10KA [61].

4. Technology Business and Future Trends

PIII has been utilized for a variety of material surface modification and semiconductor surface engineering applications. Although there are many promising applications of PIII process technique that have been experimented by various researchers as scientific research at laboratory level but has yet to be fully established in vast fields of industrial production. PIII has to compete with other well established process techniques which have been developed through last many decades, such as conventional ion immersion implantation for semiconductor applications and plasma nitriding for tribological applications. In comparison with these techniques, PIII allows us to realize many new and much improved surface properties at a much lower production cost with high throughput.

PIII has been observed as an appropriate tool for surface modifications and metallurgical applications on account of its potential of overcoming the line-of-sight processing limitations, thereby producing a high dose of ions in a conformal, simple, fast, efficient and cost effective manner. PIII has been experimented in the improvement of hardness, wear and corrosion resistant surface layers thus facilitating various tools and industrial components like bearings, rivets, bolts, screws, of prolonged lifetime (\cong 70 times); improvement in electrochemical and cycling properties of batteries; modification of insulating surfaces like polymers, glasses, ceramics, etc.; hard hydrogenated diamondlike carbon (DLC) coatings on large plates for embossing and decorative materials [62,63], etc.

In the field of semiconductor electronics, PIII has been successfully implemented in the fabrication of ultra-shallow p+/n junctions, conformal doping of trench sidewall in deep trenchbased dynamic RAMs, precise control over gate oxide thickness for memory and logic transistors, formation of Silicon on Insulators (SOI) substrates, poly-silicon thin film transistors (TFTs) for flat-panel displays, thin film growth, fabrication of low dielectric constant materials for ULSI multilevel interconnects [64,65], etc.

Another recent application area of PIII is the biomaterial development where improvement in biocompatibility of artificial materials is utilized in medical transplants such as artificial heart valves, artificial teeth; enhancing the blood clotting time; enhancement of hemocompatibility; which could be a great boon to the animals and human beings in near future [66, 67].

Therefore, it has been observed that PIII is a burgeoning process technology having wider applications in surface treatments of any type of materials and in the development of novel device structures of the order of nano-scale, suiting ULSI applications.

On an international scenario, PIII is a thorough dynamic area of research. To explore the new possibilities in the area of PIII, a number of Governments, Universities, individual organizations and Central and National laboratories, throughout the world are getting established. Michael Dudzik, Director, Environmental Research Institute of Michigan (ERIM) International's Automotive quoted, "*This cost-effective technology could have a multi-billiondollar impact on the auto industry alone.*" According to industry statistics, extending the life of manufacturing tools and dies could save the domestic auto industry more than \$5 billion annually and will thus be able to substitute lightweight and durable engines, saving another \$500 million annually. It appears that commercialization of this technology is well on its way. The firms like, Silicon Genesis [68] and Empire Hard Chrome Inc. [69] has already started selling PSII treated parts in batch quantities. Likewise PVI has focused on applying diamond-like coatings to tribological and electronic equipment. Diversified Technologies Inc. has also started manufacturing the high-power electronics required for PIII process.

PIII research activities were earlier initiated in United States and then spread to Europe, Australia and Asia. The Australian Nuclear Science and Technology Organization (ANSTO), which is also involved in PIII equipment business has topped the A\$1 million mark in 2002 by selling its equipment to research laboratories in the UK, Germany, Hungary, Thailand and Singapore as well as to universities within Australia. Even Japan is not behind and has planned to spend over \$200 million to catch up and surpass the U.S. The PIII facility in Hong Kong, set-up in 1995 with an allocation of HK\$ 1.6 Million from RGC Central Allocation Funding, is one of the most advanced in the world and has attracted research collaboration from academic institutions and corporations worldwide. Meanwhile, Boeing is on the way to develop durable, high-quality, corrosion resistant aircraft components with PSII. "All these applications are just the tip of the iceberg," says ATP Project Manager Jack Boudreax.

From theoretical point of view, various theoretical research groups, viz., Plasma Immersion Ion Implantation Simulation Group [70] at University of Erlangen (Germany), Plasma Doping Users Group [71] at City University of Hong-Kong, etc., are working on the lines to develop an optimum simulation code for a PIII system. The Plasma Theory and Simulation Group (PTSG) at University of California (USA) is the first group to achieve some success in producing a basic code for a plasma device. In early 90's, J.P. Verboncoeur et. al. [72] came up with an object oriented style programs in standard C language for 1-D and 2D bounded plasma system, named PDP1 and PDP2, respectively. These Windows driven code were drawn for a planar-bounded plasma system and were designed on basis of Monte Carlo scheme to model the collisions of electron- and ion-neutral particles. In the models, particle-in-cell technique [73,74] was implemented to solve the particle and field parameters self-consistently. In order to compare the analytical results of various plasma processes especially PIII processes, many researchers used PDP1/PDP2 in their research work [75-77]. Currently, PDP1 and PDP2 have been replaced with XPDP1 and XPDP2 with better performance and more capabilities. XPDP1 and XPDP2 are X-Windows versions running on UNIX workstations with X-Windows [78] and PC's with X-Windows emulator and are helpful in simulating a PIII process under varying constraints, provided one is having basic training of running this code and the facilities of X-Windows running on PC's or UNIX workstations. Through these codes, one can observe the difference in profiles of ion energy and angular distribution at the target by varying the pressure of neutral gas.

Although research and application potentials of PIII are expected to grow more, some of the areas yet to gain interest in near future are:

• Combining Plasma Immersion Ion Implantation and Deposition (PIII&D) and filmformation techniques to achieve get much deeper depths.

- PIII&D treatments inside very low dimensional structures like, holes, pipes, cavities, etc.
- To develop PIII&D for nano-scale device structures and varying and controlling the doping depths..
- Suppression of secondary electrons to maximize the processing voltage.
- To develop the pulsers with improved performance and at affordable cost.
- Process automation to monitor the dose rates, leading to superior films quality.
- Production of MEMS (Micro-electro-mechanical System).
- Developing optical structures for communication industry.

• Developing simulation and analytical models for 3D regime to get to know a thorough theoretical understanding of the process.

• Improve in-situ monitoring of high quality film growth.

In India, Facilitation Centre for Industrial Plasma Technologies (FCIPT), set up in 1997 at the Institute for Plasma Research (Gandhinagar), is the nodal institute for PIII processing. This centre is established to exploit the advanced plasma processing technologies like PIII, for material processing and environmental remediation to meet the needs of industrial applications. The author is also involved in exploring the theoretical aspect of PIII process for the last more than a decade.

5. Conclusions

Plasma Immersion Ion Implantation is a potential alternative that circumvents the limitations of conventional ion implantation, such as the requirements of low ion beam current, complicated target handling, non-uniform implantation profile and ion beam scanning complexity for implantation of three-dimensional targets. On account of the maturity and its simplicity, it is believed that the PIII process technology will find many more applications in the surface modification and semiconductor industry. Reliable and non-expensive equipment is still one of the key issues.

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