Plasma Immersed Ion Implantation (PIII) Process and its utility in the industry

Rushil Mital

Department of Energy Science and Engineering, IIT Delhi

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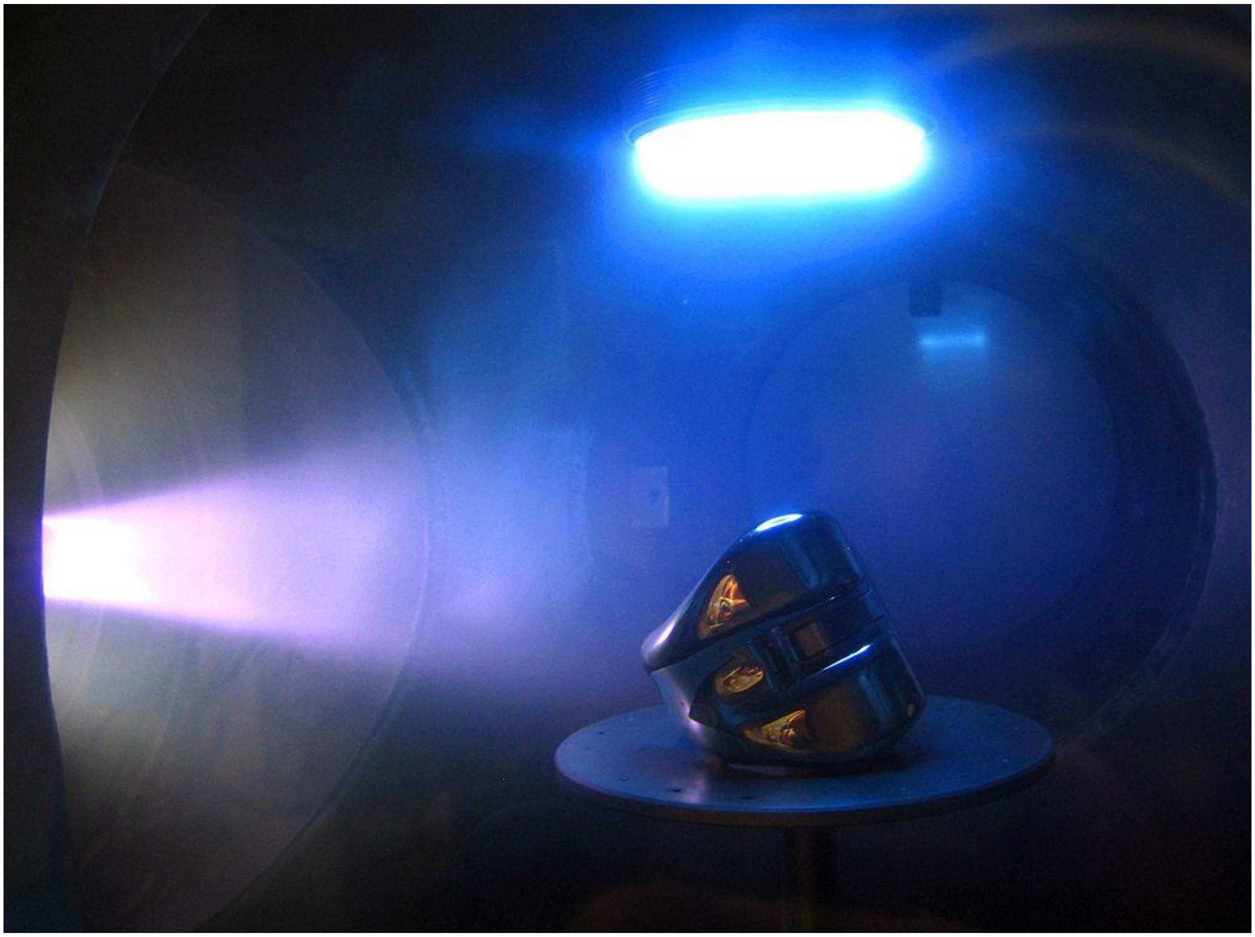
Rushil.Mital.es121@dese.iitd.ac.in

Introduction



Ion implantation is a process in which an energetic ion beam is injected into the surface of a solid material with the result that the atomic composition and structure of the near-surface region of the target material is changed, and thereby also the properties of the material surface are changed.

The process is routine in semiconductor device fabrication. Metallurgical implantation is an emerging technology; in this application, new surface alloys are created with improved resistance to wear, corrosion, and fatigue. Conventional ion implantation is carried out in a vacuum environment in which an ion source is used to create an intense beam of ions of the species to be implanted.

Today, PIII is a subject of research in over 120 laboratories worldwide due to its various tribological applications such as strengthening metal, glass, plastic, polymer, and ceramic components.

History- Conventional Ion Implantation Process

Conventional Ion Implantation (CII) is a line-of-sight technique that requires target manipulation for implanting all sides of the target, adding complexity and cost. It is a 'serial' technique with low beam currents, leading to high costs for high-dose applications. To address these issues, a novel technique was proposed in the early 1980s by Richard Adler et al. at Mission Research Corporation. This technique, based on short-pulse vacuum arcs with negative high voltage pulses biased to a target holder, allowed for successful implantation of carbon and titanium ions without an ion extraction mechanism.

Subsequently, at the University of Wisconsin-Madison, John R. Conrad and Castagna invented Plasma Source Ion Implantation (PSII), a three-dimensional ion implantation device that gave rise to Plasma Immersion Ion Implantation (PIII). This methodology integrated the generation of nitrogen plasma with the application of negative high-voltage repetitive pulses to bias the target. By maintaining the ion energy at its maximum level, the thickness of the modified surface layer was optimised, resulting in advantageous outcomes in terms of corrosion protection and abrasion properties.

Advantages and Drawbacks of PIII

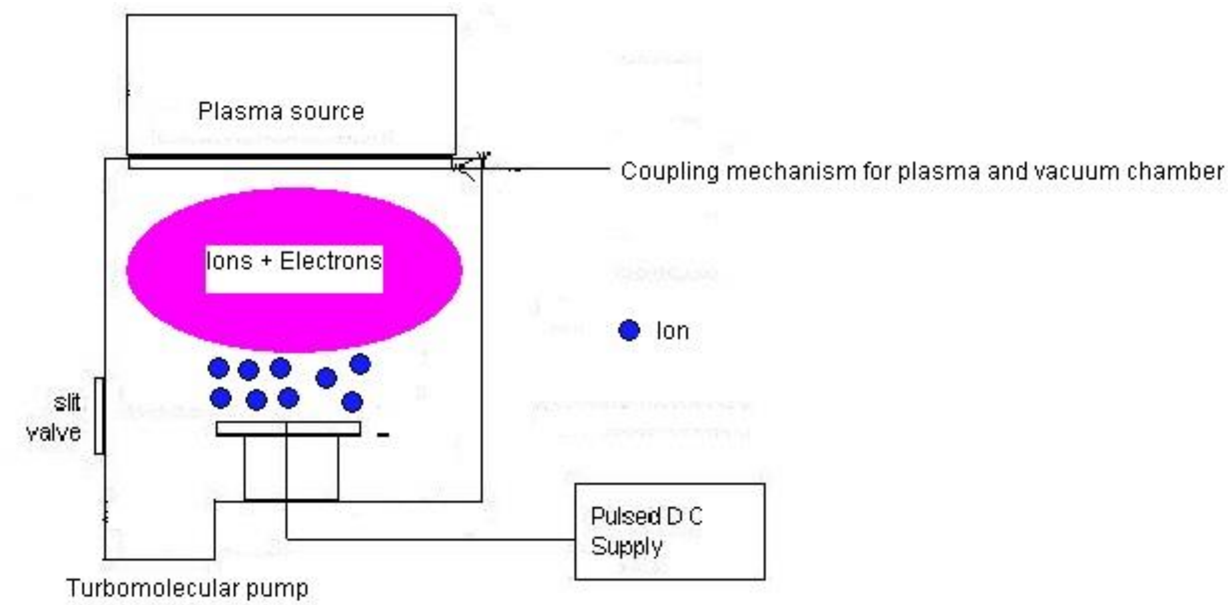
Some of the advantages of PIII can be summarized as:

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 semiconductors 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 also has 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 efficiency and generate x-rays.
3. Accurate in situ dose monitoring is tough.
4. Implant energy distribution is inhomogeneous.

Working and Construction of Diode Type Plasma Immersed Ion Implanter



In a conventional immersion type of PIII system, also called as the diode type configuration, the wafer is kept at a negative potential since the positively charged ions of the electropositive plasma are the ones who get extracted and implanted. The wafer sample to be treated is placed on a sample holder in a vacuum chamber. The sample holder is connected to a high voltage power supply and is electrically insulated from the chamber wall. By means of pumping and gas feed systems, an atmosphere of a working gas at a suitable pressure is created.

A pulse generator, capable of delivering variable pulse durations, is instrumental in supplying a negative bias to the target, spanning an extensive range from 1 to 300KV. The lower end of the pulse potential spectrum (5 to 10KV) finds widespread use in semiconductor applications, including the fabrication of shallow junctions, trench doping, etching processes, and contamination studies. On the contrary, the higher voltage ranges of -50KV to 300KV are primarily harnessed for metallurgical applications. Some specialized semiconductor structures, such as Silicon-on-Insulator (SOI) and SPIMOX, necessitate relatively elevated voltages, typically ranging between 30 to 60KV, to facilitate precise implantation processes. The extent of bias voltage is inherently constrained by the limitations of the pulse modulator and the specific requirements of the PIII process.In addition to the pulse generator, various essential accessories enhance the functionality of a PIII system. These include a Langmuir probe, employed for the measurement of plasma density and electron temperature, an ionization gauge, used to monitor neutral density throughout the implantation procedure, and an infrared pyrometer, which plays a crucial role in real-time monitoring of the target's temperature during the implantation process.

Collisional Sheath Model vs Collisionless Sheath Model for PIII Process

In the context of plasma processing, such as Plasma Immersion Ion Implantation (PIII), sheath models are used to describe the behavior of the plasma sheath that forms at the interface between the plasma and the material being treated. These sheaths play a crucial role in controlling the energy and flux of ions that bombard the material's surface. Two common models used to describe the sheath in PIII processes are the collisional sheath model and the collisionless sheath model.

1. Collisional Sheath Model:

- The collisional sheath model assumes that collisions between plasma particles (e.g., electrons and ions) and neutral background gas are frequent and significant.
- In this model, the sheath is characterized by a gradual transition of plasma properties, such as the electric potential and particle density, from the bulk plasma to the material surface.
- The collisional sheath model is often applied in situations where the gas pressure is relatively high, and collisions are significant. It is valid for low to moderate ion energies.

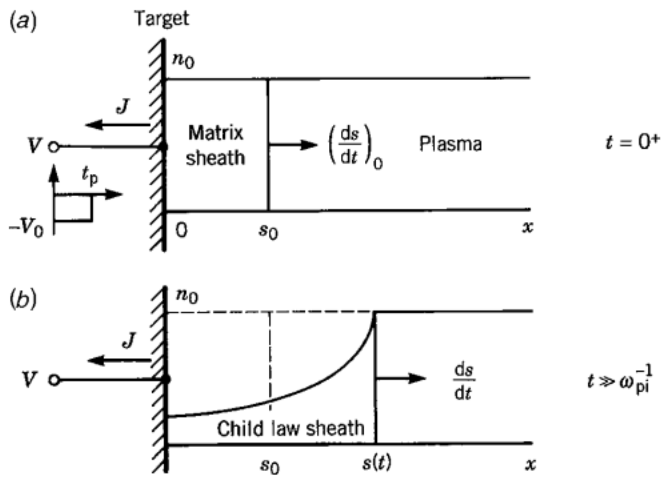
2. Collisionless Sheath Model:

- The collisionless sheath model, on the other hand, assumes that collisions between plasma particles and background gas are negligible. Instead, it focuses on the motion of ions and electrons in the absence of significant collisions.
- In the collisionless sheath model, the sheath is characterized by a more abrupt transition of plasma properties near the material surface, resulting in a thin and high-energy sheath region.
- This model is typically applied when the gas pressure is low, and ion energies are relatively high. In collisionless sheaths, the sheath thickness is often in the order of the Debye length, which is a measure of the screening length of electrostatic interactions in the plasma.

The choice between a collisional sheath model and a collisionless sheath model depends on the specific conditions of the PIII process. Factors that influence the choice include the gas pressure, the plasma density, and the energy of the ions being implanted. In some cases, a combination of both models may be used to capture the behavior of the sheath in different regions.

In the following section, we discuss the underlying physics regarding both, the collisionless sheath model as well as collisional sheath model.

Collisionless Sheath Model



After a short transient, the ion matrix sheath evolves into a Child law sheath with time-varying current density and sheath thickness. The Child law current density J_c for a voltage V_0 across a sheath of thickness s is given by:

$$J_c = \frac{4}{9}\epsilon_0\left(\frac{2e}{M}\right)^{1/2}\frac{V_0^{3/2}}{s^2}$$

where symbols have their usual meanings. Equating J_c to charge per unit time crossing the sheath boundary:

$$\frac{ds}{dt} = \frac{2}{9}\frac{s_0^2 u_0}{s^2} - u_B$$

We find the sheath velocity where s_0 is the matrix sheath thickness and u_0 is the characteristic ion velocity:

$$s_0 = \left(\frac{2\epsilon_0 V_0}{en_0}\right)^{1/2} \qquad u_0 = \left(\frac{2eV_0}{M}\right)^{1/2}$$

Integrating, we can find the steady-state Child law Sheath thickness:

$$\tanh^{-1}\left(\frac{s}{s_c}\right) - \frac{s}{s_c} = \frac{u_B t}{s_c} + \tanh^{-1}\left(\frac{s_0}{s_c}\right) - \frac{s_0}{s_c} \qquad s_c = s_0\left(\frac{2}{9}\frac{u_0}{u_B}\right)^{1/2}$$

Since $s_c >> s_0$ and assuming $s_c >> s$, we find by expanding and then substituting, the implanting current density:

$$\frac{s^3}{s_0^3} = \frac{2}{3}\omega_{pi}t + 1 \qquad J \equiv J_c = \frac{2}{9}\frac{en_0u_0}{(1+\frac{2}{3}\omega_{pi}t)^{2/3}}$$

The initial charge density in the matrix sheath is uniform thus the electric field varies linearly with x. Thus the ion motion, after performing a first order Taylor approximation on s will be:

$$\frac{d^2x}{dt^2} = \omega_{pi}^2(x - s_0) - \frac{2}{9}u_0\omega_{pi}^2 t$$

Integrating this equation, we find:

$$x - s_0 = (x_0 - s_0)\cosh\omega_{pi}t - \frac{2}{9}s_0 \sinh\omega_{pi}t + \frac{2}{9}u_0 t$$

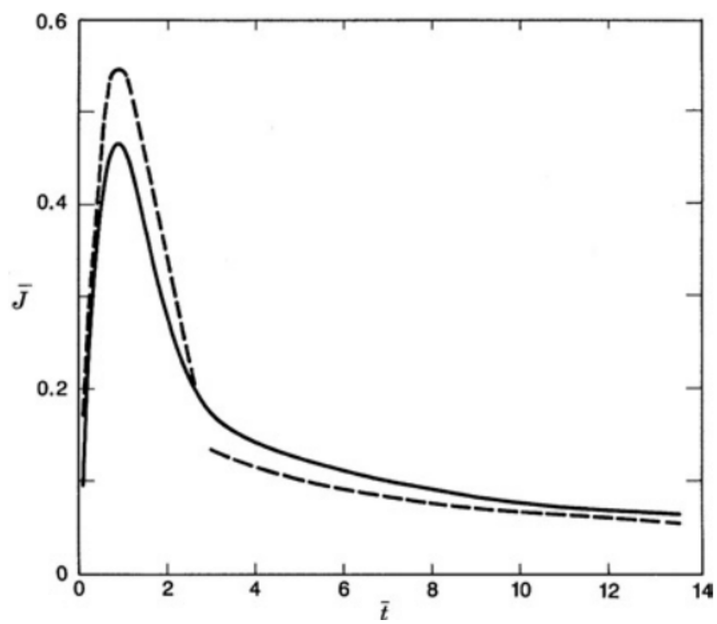
In the time interval between t and t+dt ions from the interval between x_0 and x_0+dx_0 are implanted. Differentiating x_0 with respect to t, we have

$$\frac{dx_0}{dt} = \frac{\omega_{pi}(s_0 - x_0)\sinh\omega_{pi}t + \frac{2}{9}u_0(\cosh\omega_{pi}t - 1)}{\cosh\omega_{pi}t}$$

We obtain the implantation current density as:

$$\bar{J} = \frac{\sinh\bar{t}}{\cosh^2\bar{t}} + \frac{2}{9}\frac{1 + \bar{t}\sinh\bar{t} - \cosh\bar{t}}{\cosh^2\bar{t}}$$

where $\bar{J} = J/(en_0u_0)$ is the normalized current density and $\bar{t} = \omega_{pi}t$



Collisional Sheath Model

Ion collisions within the sheath at high gas pressures lead to reduced implantation energies and finite width energy and angular distributions for ions that greatly affect their implantation over topography, that is, within trenches.
It is also assumed that the ion charge density n_s in the sheath is uniform in space but slowly varying in time, with $n_s(t) < n_0$, the bulk plasma density.
A uniform distribution is seen experimentally for similar sheaths, such as the cathode sheaths in dc glow discharges, and is also seen in PIC-MCC (Particle-In-Cell, Monte-Carlo-Collision) simulations of collisional PIII.
To determine the energy distribution of the bombarding ions, the Maxwell equation, is integrated from x=0 to position x to obtain the second equation mentioned below with the boundary condition of E=0 at x=s being used:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{en_\mathrm{s}}{\epsilon_0} \qquad E = \frac{en_\mathrm{s}}{\epsilon_0}(s - x)$$

Integrating again to determine the potential, we obtain the following:

$$\Phi = -\frac{en_\mathrm{s}}{2\epsilon_0}(s - x)^2$$

Letting $\Phi = -V_0$ at x=0 , we obtain the matrix sheath result:

$$n_\mathrm{s} = \frac{2\epsilon_0 V_0}{es^2}$$

The equation of motion of an ion starting from rest at $x=x_0$ after a charge transfer collision in the sheath, is:

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = \frac{eE}{M} = \frac{2eV_0}{Ms^2}(x - s)$$

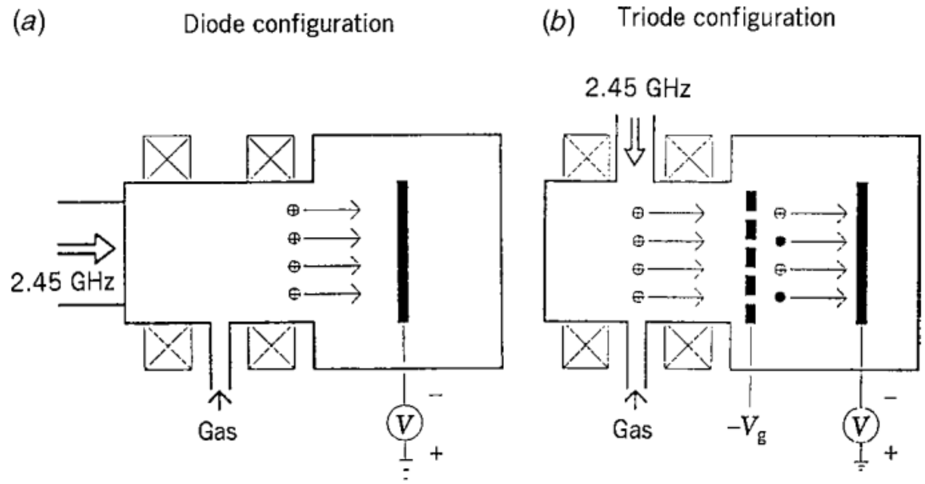
We can then determine the ion velocity at the target by:

$$u_\mathrm{t}^2 = \frac{u_0^2(2sx_0 - x_0^2)}{s^2}$$

After determining the distribution of ion flux by applying conservation of particles, we find the mean ion velocity near the target and the implantation current density to be:

$$\bar{u}_\mathrm{t} = \left(\frac{eV_0\pi\lambda_\mathrm{i}}{Ms}\right)^{1/2} \qquad J_\mathrm{t} = en_\mathrm{s}\bar{u}_\mathrm{t} = \epsilon_0\left(\frac{4\pi e\lambda_\mathrm{i}}{M}\right)^{1/2}\frac{V_0^{3/2}}{s^{5/2}}$$

Application to Semiconductor Processes



Two configurations of PIII using ECR sources are illustrated above a diode configuration and a triode configuration. The diode configuration uses gaseous sources like Ar, N_2, BF_3, H_2O and O_2 for ionization and implantation. It's suitable for doping applications and can operate as an ion-assisted chemical vapor deposition system when metal-containing gases are used.

The triode configuration adds another negatively biased target controlled by a separate power supply. Atoms from this target are sputtered into the plasma and some are ionized and implanted into the substrate. However, secondary electron emission from the target can be a serious x-ray hazard and leads to poor power efficiencies.

- PIII has been applied to several semiconductor processes like sub-100-nm p+/n junction formation, selective metal plating etc. For example, it's used for ultra shallow junction formation where silicon is preamorphized with a 4-kV SiF_4 PIII implantation prior to a 2-kV BF_3 PIII implantation. After annealing, an extremely shallow junction depth of 80 nm is obtained.
- In selective metal plating, PIII has been used for selective and planarized plating of copper interconnects using palladium seeding. A palladium sputtering target is immersed in the plasma and has an independently controlled negative bias to regulate the sputtering rate.
- PIII has also been used to conformally dope silicon trenches. High packing densities of devices on silicon substrates are achievable by making use of vertical sidewalls for active transistor channels and as charge storage elements such as trench capacitors.

Application to Metallurgical Processes

PIII can also be used for metallurgical surface modification to improve wear, hardness, and corrosion resistance. In this context, the process has been called plasma source ion implantation (PSII). PSII can easily be used to implant nonplanar targets, for example, tools and dies, with minimum shadowing and sputtering of the target. The latter can limit the retained dose of the implanted ion species. Ions have been implanted under batch processing conditions, with acceptable dose uniformities to the depths and concentrations required for surface modification, resulting in dramatic improvement in the life of manufacturing tools under actual industrial conditions.

- In a typical PSII process, the target is immersed in a nitrogen plasma of density $n_0 \sim 5 \times 10^9$ cm^{-3}.
- A series of 50-kV, 10-ms pulses at 100 kHz are applied to the target for minutes to hours. For these conditions the initial matrix sheath thickness is 3 cm, and the Child law sheath thickness is 24 cm, but the pulse width is short enough that the Child law sheath does not have time to fully form.
- Plasma is generated by a hot tungsten filament source, which is inserted into the chamber and biased at – (100 – 300) V. The filament emits electrons that are accelerated across the filament sheath into the plasma, where they subsequently ionize the background gas, which is typically at a pressure of 10^{-4} Torr. The dynamics of hot filament plasma sources are well understood. Multipole magnets are required on the surface of the implantation chamber to confine the primary electrons.

Future Areas of Research Related to the PIII Process

These are ways in which the PIII process can be further refined

- Combining Plasma Immersion Ion Implantation and Deposition (PIII&D) and film formation techniques to achieve much deeper 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 the 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.

Further applications include:

- Biomedical applications such as orthopedic implants to improve biocompatibility and increase longevity.
- Thin film deposition in microelectronics and optics industries
- Contamination control and cleaning of surfaces in semiconductor cleanrooms etc.
- Enviornmental applications such as water treatment and pollution control
- Nanoscale surface engineering to create nanostructures and nano-patterns on materials
- Miscellaneous applications in the field of Material Science and Energy Science.

Acknowledgements, Conclusions and Bibliography

I would like to extend my sincere gratitude to Professor Ramesh Narayan and Professor Satyanendra Kar for granting me the invaluable opportunity to delve into the world of plasma physics and write about the PIII process.

Plasma Immersion Ion Implantation presents a promising alternative to address the drawbacks associated with conventional ion implantation techniques, namely, the need for low ion beam currents, intricate target handling, non-uniform implantation profiles, and the complexity of scanning ion beams for three-dimensional targets. Given its well-established nature and straightforward operation, PIII technology is expected to find widespread applications in surface modification and the semiconductor industry. However, the challenge of developing reliable and cost-effective equipment remains a crucial consideration.

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