

APPLICATION OF PLASMA IN DIFFERENT BRANCHES OF INDUSTRIES

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Abstract: plasmas underlie numerous important technological applications and devices as well as our understanding of much of the universe around us. Plasma processing technologies are of vital importance to several of the largest manufacturing industries in the world. Foremost among these industries is the electronics industry, in which plasma-based processes are indispensable for the manufacture of very large-scale integrated microelectronic circuits. Plasma processing of materials is also a critical technology in, for example, the aerospace, automotive, steel, biomedical, and toxic waste management industries. Most recently, plasma processing technology has been utilized increasingly in the emerging technologies of diamond film and superconducting film growth. The dominant role of plasma-treated surfaces in key industrial sectors, such as microelectronics, is well known, and plasmas, certainly experimentally and, in places, industrially, are being used to modify a huge range of material surfaces, including plastics, polymers and resins, paper and board, metals, ceramics and in organics, and biomaterials. The objective of this work is to give a comprehensive description and review of the science and technology related to plasmas, with particular emphasis on their potential use in the textile industry.

1. Introduction

Plasma

A gas is normally an electric insulator. However, when a sufficiently large voltage is applied across a gap containing a gas or gas mixture, it will break- down and conduct electricity. The reason is that the electrically neutral atoms or molecules of the gas have been ionized, i.e. split into negatively charged electrons and positively charged ions. The nature of the breakdown and the voltage at which this occurs varies with the gas species, gas pressure, gas flow rate, the materials and the nature, geometry and separation of the surfaces across which the voltage is sustained, the separation distance of the electrodes, the nature of the high voltage supply (e.g. dc, ac, radiofrequency or microwave) and the actual electrical circuitry. The resulting ionized gas is often called a discharge or plasma. The interactions of the electrically charged particles with each other, with the neutral gas and with contact surfaces produce the unique physical and chemical properties of the plasma environment. This environment is distinct from that found in solids, liquids or gases; hence plasmas are sometimes called the fourth state of matter. Plasma is defined as a collection of positive and negative charges which act collectively. This implies that not only do the charges exert coulomb forces on each other but also that these forces are as important as, and dominate over, externally applied forces and effects due to collisions between themselves and any neutral gas present. In other words, the 'self- generated' electric fields play an essential role in how the particles move. A major consequence of this collective behavior is the ability of the plasma to screen out local density perturbations and to create a sheath region between the plasma and contact surfaces. Not all ionized gases or discharges can be classified as plasmas; certain criteria must be meeting before an ionized gas will exhibit the phenomena associated with plasma's collective behavior.

Since their introduction in the 1960s, the main industrial applications of plasmas have been in the micro-electronics industries. In the 1980s their uses broadened to include many other surface treatments, especially in the fields of metals and polymers. The dominant role of plasma- treated surfaces in key industrial sectors, such as microelectronics, is well known, and plasmas, certainly experimentally and, in places, industrially, are being used to modify a

huge range of material surfaces, including plastics, polymers and resins, paper and board, metals, ceramics and inorganic, and biomaterials. Properties enhanced include wettability, adhesion, biocompatibility, protection and anti-wear, sterilization, and chemical affinity or inertness. The prospects of very good technical and economical results, as experienced in the microelectronics industry, are stimulating efforts world-wide to apply plasma processing more widely[1, 2].

2. Plasma reactors

Different types of power supply to generate the plasma are:

Low-frequency (LF, 50–450 kHz)

Radio-frequency (RF, 13.56 or 27.12 MHz)

Microwave (MW, 915 MHz or 2.45 GHz)

The power required ranges from 10 to 5000 watts, depending on the size of the reactor and the desired treatment[1].

3. Types of plasma

3.1.Low-pressure plasmas

Low-pressure plasmas are a highly mature technology developed for the microelectronics industry.

A vacuum vessel is pumped down to a pressure in the range of 10^{-2} to 10^{-3} mbar with the use of high vacuum pumps. The gas which is then introduced in the vessel is ionized with the help of a high frequency generator. The advantage of the low-pressure plasma method is that it is a well-controlled and reproducible technique.

3.2-Atmospheric pressure plasmas

The most common forms of atmospheric pressure plasmas are described below.

3.2.1 Corona treatment

Corona discharge is characterized by bright filaments extending from a sharp, high-voltage electrode towards the substrate. Corona treatment is the longest established and most widely used plasma process; it has the advantage of operating at atmospheric pressure, the reagent gas usually being the ambient air. Essentially, the corona plasma type is too weak. Corona systems also rely upon very small interelectrode spacing (~ 1 mm) and accurate web positioning, which are incompatible with 'thick' materials and rapid, uniform treatment.

3.2.2 Dielectric barrier discharge (Silent discharge)

The dielectric barrier discharge is a broad class of plasma source that has an insulating (dielectric) cover over one or both of the electrodes and operates with high voltage power ranging from low frequency AC to 100 kHz.

These results in a non-thermal plasma and a multitude of random, numerous arcs form between the electrodes. However, these microdischarges are non-uniform and have potential to cause uneven treatment.

3.2.3Glow discharge

Glow discharge is characterized as a uniform, homogeneous and stable discharge usually generated in helium or argon (and some in nitrogen).

This is done, for example, by applying radio frequency voltage across two parallel-plate electrodes. Atmospheric Pressure Glow Discharge (APGD) offers an alternative homogeneous

cold-plasma source, which has many of the benefits of the vacuum, cold-plasma method, while operating at atmospheric pressure.

3.2.4 Atmospheric pressure plasma jet (APPJ)

This non-thermal, atmospheric pressure, glow discharge plasma produced in continuously flowing gases [1].

4. Applications of plasmas

Plasmas find well-established use in industrial applications (e.g. for surface modification, lasers, lighting, etc.), but they are also gaining more interest in the field of life sciences, related to environmental issues and biomedical applications. From a scientific point of view, the plasma yields a transformation of either (i) particles, (ii) momentum or (iii) energy. Indeed, particles, momentum or energy can be considered as input in the plasma, whereas the output is again either particle (with changed chemical composition), momentum (e.g. acceleration, beaming) or energy (e.g. heat, light). Keeping this in mind, the following subdivision of applications could be made.

1. Transformation of particles, i.e. plasma chemistry, either at the surface (surface modification, such as etching, deposition, etc.) or in the plasma itself (e.g. powder formation, ozone generation, environmental applications);
2. Transformation of momentum, i.e. plasma beaming, such as for lasers, plasma thrusters, rocket propulsion;
3. Transformation of energy, e.g. creation of light, such as in lamps, plasma displays or lasers. In the following, we will describe some of the most widespread applications in more detail.

4.1 Plasma-Surface modifications

Surface modification by gas discharge plasmas plays a crucial role in the microelectronics industry. For the microfabrication of an integrated circuit (IC), one-third of the hundreds of fabrication steps are typically plasma based. A few examples are:

- Argon or oxygen discharges to sputter-deposit aluminum, tungsten or high temperature superconducting films;
- Oxygen discharges to grow SiO₂ films on silicon;
- SiH₂Cl₂/NH₃ and Si(OC₂H₅)₄/O₂ discharges for the plasma-enhanced chemical vapor deposition of Si₃N₄ and SiO₂ films, respectively;
- BF₃ discharges to implant dopant (B) atoms into silicon;
- CF₄/Cl₂/O₂ discharges to selectively remove silicon films;
- O₂ discharges to remove photo resist or polymer films.

These types of steps (i.e. deposit or grow, dope or modify, etch or remove) are repeated again and again in the manufacture of a modern integrated circuit. They are the equivalent, on mm-scale size, of cm-sized manufacturing using metal and components, bolts and solder, and drill press and lathe[3]

4.2 Plasma –polymers

Plasma, the fourth state of matter, is an ionized gas with an essentially equal density of positive and negative charges. Plasma, which is spatially neutral, has free electrons and positive ions comprising most negative and positive species. Well-known plasmas are the solar corona, lightning, flames, and fluorescent lights. Owing to the constituent species' high reactivity, plasma treatments may be used for cleaning or chemically modifying surfaces. For

these reasons, plasma treatment should have significant benefits for adhesive systems by minimizing contamination and imparting favorable chemical moieties at the surface. It is well known that surface treatment of plastic surfaces generates polar functional groups. Often, surface analysis techniques, such as electron spectroscopy for chemical analysis (ESCA) are used to quantify the chemistry changes at the surface. Atmospheric plasma treatment for improved bonding is desirable as surface chemistry can be tuned to achieve functionalities that are conducive to various adhesive cure chemistries.

In particular, it is believed that the increase in surface energy is especially beneficial. Traditionally, plasmas have been generated using high temperatures and in a low-pressure environment. Recent advances have permitted plasmas to be generated at ambient temperatures and atmospheric pressure. Helium is used as a carrier gas, based on its inert nature and high thermal conductivity. Adding oxygen at low levels yields plasma that oxidizes both surface groups and contaminants. Other gases can be used in conjunction with the helium carrier to produce additional effects, such as surface reduction or surface functionalization. Atmospheric plasma unit is a source of atoms and radicals that are carefully selected for surface treatment, cleaning, etching, or depositing thin coatings. One of the most attractive features of this technology is its effectiveness at low temperatures without the need for reduced pressure (vacuum).

There has been a large amount of work in the new field of atmospheric plasma treatment. Much of the work has focused on increasing the wettability of materials.

Plasma treatment of low-surface-energy polymers (polyethylene and polystyrene) has been shown to increase the surface energy and improve the wetting characteristics. This wetting improvement leads to a concurrent, significant improvement in adhesion to these polymer surfaces, allowing bonding with adhesives that cannot be used with these polymers without surface treatment. The changes in surface energy and the increases in adhesion are primarily due to the chemical changes at the surface induced by exposure to the plasma[4].

Epoxy resins have been widely employed as impregnating materials, adhesives, and advanced composite matrices in aerospace and electronic industries, due to their electrical insulation, low density, high elastic modulus, strong bond ability, and convenient manufacturing process. Additionally, epoxy resins have also been used for cryogenic applications, such as superconducting magnet impregnation, cryogenic valve, and cryogenic tank. However, epoxy resin has a large coefficient of thermal expansion (CTE) and relatively low thermal conductivity. When the operational temperature is decreased to cryogenic temperature, the internal stress and microcrack will arise from the volumetric shrinkage due to the large CTE. Therefore, preparing new epoxy resins with reduced or controlled thermal expansion property would be of practical interest and always be desired for cryogenic applications. In order to attain a target CTE, one approach is to tailor the chemical and network structures of epoxy resins, but it is not so effective due to the essential properties of polymer. The other approach is to introduce inorganic filler particle and (or) short fibers with low CTE into the epoxy resin matrix. In order to further reduce the CTE of epoxy resin, a new approach is related to develop a controllable-CTE epoxy resin composite by employing negative thermal expansion (NTE) material, which expands on cooling, as a component of the composite. It is well known that the strong interface between the nanoparticles and polymer matrix is essential to transfer load from the matrix to the nanoparticles.

Therefore, for excellent properties, the surface modification or functionalization of particles has to be achieved. Plasma polymerization is a novel and effective method for surface functionalization of nanoparticles. The main principle of the plasma polymerization is that the

ionized and excited monomer molecules created by the electrical field bombard and react on the surface of the substrate. After the plasma polymerization, a thin polymer film is deposited on the surfaces of nanoparticles.

Huang et al. studied to obtain epoxy resin composites with controlled thermal expansion properties and thermal conductivities as well as producing a strong interface between the filler and polymer matrix by means of plasma treatment and obtained epoxy-matrix composite with low CTE, high thermal stability, and high thermal conductivity [5].

The interaction between the very active chemical species (and photons) presents in the plasma gas and a substrate is the basis of all industrial applications of the above technologies. As a consequence of the very complex and non-equilibrium nature of cold plasmas, a multiplicity of very different phenomena can occur, depending on the nature of the gas and the operating conditions. Here, our attention will be limited to polymeric materials.

- **Cleaning or etching:** For such a phenomenon to occur, 'inert' gases (Ar, He, etc.), nitrogen or oxygen plasmas are typically used. The bombardment of the substrate with the plasma species causes the breakdown of covalent bonds. As a consequence, detachment of low molecular weight species (ablation) takes place. In this way, contaminants or even thin layers of the substrate are removed, producing extremely 'clean' surfaces, modifications in the surface area, or controlled reduction of weight of the exposed substrate.
- **Activation:** Interaction with plasma may induce the formation of active sites on the polymer surface (radicals or other active groups, such as hydroxyl, carboxyl, carbonyl, amine groups), which can give rise to chemical reactions, not typical of the untreated material, with substances brought in contact with the material after plasma processing.
- **Grafting:** Radical species present in the plasma may be directly grafted onto the polymer surface.
- **Polymerization:** by using specific molecules, a process known as plasma-enhanced chemical vapor deposition (PECVD) may occur. These molecules, activated in the plasma, may react with themselves forming a polymer directly on the surface of the substrate. Depending on the different experimental conditions, chemically unique, nanometric polymeric coatings are obtained and chemical, permeation, adhesion and other properties of the starting material can be dramatically modified. All these phenomena are limited to the most external layer of the substrate. Normally, the effects do not involve layers deeper than 10–100 nm. However, it must be noticed also that ultraviolet (UV) or vacuum ultraviolet (VUV) radiation (with wavelength <200 nm) is an important component of plasma. VUV radiation can give rise to a variety of photochemical interactions with the substrate, such as bond breakage and formation of free radicals, reaching inner layers (>10 nm) depending on the absorption coefficient of the substrate [1].

4.3 Plasma –Textile

In the textile field, significant research work has been going on since the early 1980s in many laboratories across the world dealing with low-pressure plasma treatments of a variety of fibrous materials showing very promising results regarding the improvements in various functional properties in plasma-treated textiles. A variety of commercial low-pressure plasma machines, mostly in prototype form, have been offered for batch/in-line processing of textiles for more than 15 years. In recent times, some companies have also started to offer commercial systems for atmospheric-pressure plasma processing of textiles, both in-line and on-line. Despite all the significant benefits demonstrated in the laboratory and industrial prototypes, plasma processing on an industrial scale has been slow to make an impact in the textile industry. This may be due to factors such as important gaps in the relevant applied

research, slow development of suitable industrial plasma systems, late focus on developing in-line atmospheric pressure plasma systems and less public transparency regarding the successes and failures of industrial trials. The coupling of electromagnetic power into a process gas volume generates the plasma medium comprising a dynamic mix of ions, electrons, neutrons, photons, free radicals, metastable excited species and molecular and polymeric fragments, the system overall being at room temperature. These species move under electromagnetic fields, diffusion gradients, etc. on the textilesubstrates placed in or passed through the plasma. This enables a variety of generic surface processes including surface activation by bond breaking to create reactive sites, grafting of chemical moieties and functional groups, material volatilisation and removal (etching), dissociation of surface contaminants/layers (cleaning/ scouring) and deposition of conformal coatings. In all these processes a highly surface specific region of the material ($<1000 \text{ \AA}$) is given new, desirable properties without negatively affecting the bulk properties of the constituent fibers.

Plasmas are acknowledged to be uniquely effective surface engineering tools due to:

- Their unparalleled physical, chemical and thermal range, allowing the tailoring of surface properties to extraordinary precision.
- Their low temperature, thus avoiding sample destruction.
- Their non-equilibrium nature, offering new material and new research areas.
- Their dry, environmentally friendly nature.

The textile and clothing industries in Europe, North America and some other developed countries are facing some big challenges today, largely because of the globalization process. Therefore, the shift to high- functional, added value and technical textiles is deemed to be essential for their sustainable growth. The growing environmental and energy-saving concerns will also lead to the gradual replacement of many traditional wet chemistry-based textile processing, using large amounts of water, energy and effluents, by various forms of low-liquor and dry-finishing processes. Plasma technology, when developed at a commercially viable level, has strong potential to offer in an attractive way achievement of new functionalities in textiles. In recent years, considerable efforts have been made by many plasma technology suppliers to develop both low-pressure and atmospheric-pressure based plasma machinery and processes designed for industrial treatment of textiles and nonwovens to impart a broad range of functionalities [1].

When this plasma is applied to the substrate, the free electrons or other metastable particles, upon collision with the substrate, break the chemical bonds creating free radicals on the polymer surface. Atmospheric pressure plasma techniques are gaining more popularity due to the ease of incorporating them in textile finishing operations. Low temperature plasma (LTP) has been used industrially for the treatment of metal and polymer materials. Inorganic plasma gases such as oxygen can produce etching ablation effect on the treated substrate surface. Plasma is a surface treatment, environmentally friendly, cost efficient, uniform, and applicable to many materials with keeping the bulk properties of the substrate [6].

Cold plasma treatment is found to improve adhesion between fiber and matrix. As a type of environmentally friendly physical surface modification technology, plasma treatment is a simple process without any pollution. This technique appears to be original in compare to many chemical treatments as it modifies the surface of the fibers without affecting the bulk properties and the duration times of treatment are also short. Two major types of reactions possible with cold plasma are (1) surface modification of polymer and (2) polymerizations of the monomers in the plasmas [7].

Textile materials are increasingly used in various industries. In these applications, the surfaces of textile materials play a key role, because a range of performance properties depends on surface characteristics. As with many other types of materials, the surface properties of textiles can be readily altered by the treatment of the materials with gas plasma, without impairment of their bulk mechanical properties.

In recent years, surface modification of textile materials by plasma treatment has opened up new possibilities in this field. It has been increasingly used in the etching, deposition, or other modifications of solid surfaces including various forms of textile materials to improve surface properties.

Gas plasma treatment can have profound effects on the properties of textile materials. Different gas plasma treatments have different effects on the surfaces of textiles. Plasma treatments provide great potential for the modification and functionalization of textile materials. Plasma-based techniques offer such advantages as:

- Plasma treatment is applicable to different materials and various forms.
- Plasma treatment can result in such changes as morphology, chemical, tribological, electrical, optical, and biological properties.
- Plasma treatment is an environmental friendly technique [8].

Hundreds of articles have been written on these subjects and a very large number of patents have been granted in the field of plasma treatment of fibres, polymers fabrics, nonwovens, coated fabrics, filter media, composites, etc. for enhancing their functions and performance. This survey has pointed out the potential use of plasma treatments of fibres, yarns and fabrics for the following types of functionalisation:

- Anti-felting/shrink-resistance of woollen fabrics.
- Hydrophilic enhancement for improving wetting and dyeing.
- Hydrophilic enhancement for improving adhesive bonding.
- Hydrophobic enhancement of water and oil-repellent textiles.
- Facilitating the removal of sizing agents.
- Removing the surface hairiness in yarn.
- Scouring of cotton, viscose, polyester and nylon fabrics.
- Anti-bacterial fabrics by deposition of silver particles in the presence of plasma.
- Room-temperature sterilization of medical textiles.
- Improved adhesion between textiles and rubber.
- Plasma-treated fabrics with high hydrophilic stability when stored in alkaline media.
- Graft plasma polymerization for producing fabrics with laundry-durable oleophobic, hydrophobic and stain-resistant finishes.
- Atmospheric plasma-based graft polymerization of textiles and nonwovens having different surface functional properties on the face and back side of the fabric.
- A fabric which is coated with sizing agent inactive to plasma on one side and on the other side left as hydrophobic or hydrophilic after size removal, the resultant fabric having different functionality on its two sides.
- Flame-retardant coating using monomer vapour (halogen and/or phosphorus) in combination with nitrogen and/or silicone.
- Silicone coating of air-bag fabrics using crosslinked silicone (polyorganosiloxanes).
- Scouring of cotton, rayon, polyester fabrics using a non-polymerisable gas (nitrogen, argon, ammonia, helium), followed by wet treatment for removing the impurities.
- Prevention of readily-occurring colour variation in textiles.

- Durable antistatic properties using PU-resin and plasma processing.
- Shrink resistance of animal hair textiles using urethane-based resin and plasma processing.
- Electro-conductivity of textile yarns by surface plasma deposition [1].

4.4 Plasma – Biomedical and Health

Surgical equipment, dental instruments and long-term implants are intended to penetrate the human body and, therefore, are coming in direct contact with the patient's first immune defense system. According to the existing guidelines, all these devices have to be sterilized and decontaminated, to prevent any kind of infection or inflammation. This is especially true for the cases of reused instruments, like endoscopes, bone-saw blades, neurosurgical or vascular tools, whose insufficient cleanliness has been reported to cause post-surgical problems.

The nature of the possible contamination is very diverse and ranges from the presence of living microorganisms (e.g. Gram-positive *Staphylococcus aureus*) to various biomolecules. Compared to conventional sterilization and decontamination methods, non-equilibrium plasma discharges offer fundamental advantages – they can be operated at low temperatures suitable for the treatment of heat-sensitive materials and since they are usually sustained in non-toxic gases like hydrogen, oxygen, nitrogen, argon or air, their operation is harmless both for the operator and the environment. For these reasons, plasma-based sterilization and decontamination techniques have attracted increased attention in recent years, as illustrated by the number of publications devoted to this topic.

Hasiwaet al found that the human whole-blood incubation test is a sensitive method to detect residues of immune stimulating components directly on the surface by an indirect test, without the problem of preparing eluates and related losses on the surface. Furthermore, they found that the low-pressure microwave discharge plasma is an appropriate method to eliminate various immune stimulating components relatively quickly, under low temperature conditions preventing treated substrates from the heat-induced modifications and without the necessity of using toxic compounds. Gram-positive stimuli, which are gaining more and more importance, could be removed as well with a very fast removal rate. Also zymosan, a monocyte and macrophage stimulus was removable to a major extent [9].

Synthetic and natural materials have been used in the medical area for the design of implants or other supporting materials (e.g. vascular grafts, artificial hearts, intraocular lenses, joints, mammary prostheses, sutures) for utilization of extracorporeal therapeutics and other supporting devices (e.g. hemodialysis, hemoperfusion, blood oxygenation, intravenous lines, needle catheters, blood-bags), for controlled release systems (e.g. trans-dermal drug delivery patches, microspheres, microcapsules for targeted drug-delivery devices for different routes of administration), and for clinical diagnostic assays (mainly as carriers and supporting materials).

When any material is used in contact with body fluids, it should be compatible with the biological environment without adversely affecting the biological constituents of the entire living organism.

Polyurethanes are among the best choices for biomedical applications because of their desired mechanical properties due to their segmented polymeric character, their availability in a wide range of physical properties and their excellent blood and tissue compatibility. These materials played an important role in the development of many medical devices ranging from catheters to total artificial hearts.

Surface modification methods in order to improve the hemocompatibility include chemical treatment such as surface oxidation, fluorination, introduction of reactive groups, surface grafting, glow plasma discharge, etc. Plasma contains free electrons, radicals, excited atoms and neutral particles and constant bombardment of the polyurethane surfaces with these active particles alters the surface chemistry breaking some bonds of the surface molecules and forming new ones.

Hasircie and Aksoy concluded that polyurethanes are the most widely used materials in the design and production of bloodcontacting devices because of their inherent non-thrombogenic properties. Although it is accepted as such, intense research continues to modify the surfaces and increase bio and blood compatibilities of polyurethanes. The most important point is the medical purity of the materials and the research mentioned here covers the synthesis of polyurethanes in medical purity without the addition of any solvent or ingredient. On the other hand, the surface is very effective in triggering cell adhesion or blood coagulation and therefore modifications may be needed to improve these properties. One very effective method used in surface modification is glow-discharge plasma application. Plasma changes the chemistry of the surface, and therefore affects protein adsorption and cell attachment on the surfaces. It was observed that plasma application causes an increase in cell adhesion when they were brought into contact with blood. Further modifications with heparin immobilization caused a significant decrease in cell adhesion. Heparin immobilization on the surface is a very efficient method to prevent thrombi formation for cardiovascular systems. On the other hand, for tissue engineering purposes where cell attachments are required, oxygen plasma modification can be considered as an effective technique [10].

Tamaki et al studied to develop a contamination-free porous titanium scaffold by a plasma-activated sintering within an originally developed TiN-coated graphite mold.

A long segmental bone defects repair is one of the challenging problems in orthopedic surgery. Although allogenic bone grafts are a current major option, this technique is associated with problems of significant failure rates, poor mechanical properties, and immunological rejection. Porous materials are of significant importance for bone tissue engineering applications because of the good biological fixation to surrounding tissue through bone tissue. Porous titanium and titanium alloys have been investigated as they provide favorable mechanical properties with an elastic modulus closed to that of natural bone under a load bearing condition. Surface characteristics of porous titanium are important determinants in its scaffold properties since the surface condition of titanium has been reported to play a critical role in bone formation associated with superior osteoblast adhesion and subsequent cell behaviors. The plasma-activated sintering is a rapid sintering method associated with self-heating phenomena within the powder. This is capable of sintering metal or ceramic powders rapidly to its full density at a relatively lower temperature compared to the conventional furnace sintering methods. The carbon graphite mold has been employed in the plasma-activated sintering due to its electro conductive property and thermo stability. The direct heating of graphite mold and the large spark pulse current provide a very high thermal efficiency

In conclusion, the TiN-coated carbon graphite mold is a new method for processing a contamination-free porous titanium sheet. This modified titanium sheet is expected to be a new tissue engineering material in orthopedic bone repair [11].

Plasma sputtered, native surface of nickel–titanium insures a good biocompatibility of the alloy.

Plasma sputtering is a promising, easy, and cost-effective technology used to modify the surface of nickel–titanium for biomedical applications [12, 13].

4.5 Plasma –Laser

Lasers are used as cutting instruments for metals in order to make very narrow cuts which would be impossible with conventional thermal cutting methods. If a jet of gas, which produces exothermic reaction, is so directed that it flows on to the region of a workpiece at which a laser beam is focused, not only is there an increase in the rate of cutting but the accuracy and the fineness of the cut are unaffected by the addition of gas stream, in spite of the fact that the cross-sectional area of the stream at the workpiece may differ by an order of magnitude from that of the laser beam. Substantial surface plasma occurs at a high oxygen pressure (172.5 kPa) and for a 1.5 mm thick work-piece. This plasma causes an increase in erosion of the surface due to thermal effects. This is also true for 34.5 kPa oxygen gas pressure. In this case the surface plasma may partially block the incident laser beam, resulting in less energy from the laser beam reaching the surface. This plasma then expands to the surrounding atmosphere due to the pressure differential in the plasma. As a result more incident energy reaches the target, which in turn increases the mass removal rate from the surface, causing more surface plasma. This process occurs periodically. Also cutting quality improves when the surface plasma is small and transiently hot. However, the opposite is true when the surface plasma is substantial [14].

Gas discharges are also used for laser applications, more specifically as gas lasers. Several kinds of gas lasers exist, but they have one common characteristic, i.e. the mechanism of population inversion, necessary for laser action, always occurs via gas discharges. The gas, at reduced pressure, is contained within a glass discharge tube with mirrors at the ends of the tube. Anode and cathode can be placed at both ends of the tube.

Generally, three classes of gas lasers can be distinguished, depending on whether the lasing transition occurs between energy levels of atoms, ions or molecules.

4.5.1. Atomic lasers

4.5.1.1. He–Ne laser

The He–Ne laser is one of the most-used lasers. As predicted by the name, the active medium is a mixture of helium and neon in a typical ratio of 10:1. The He–Ne laser is used for optical alignment, by producing a visible line which can be used for positioning an object, for guidance of equipment in construction (aircrafts, ships), or for the alignment of other (e.g. IR) lasers, as well as for interferometry (e.g. in the Michelson interferometer). Other applications are in laser printers and optical disks.

4.5.1.2. Copper vapor laser

The copper vapor laser (CVL) is based on a glow discharge at high temperature (wall temperature typically 1400– 1500 °C). The CVL has found application in medicine (dermatology and oncology), as pumping sources for dye and Ti:sapphire lasers for tunable output, and for industrial materials processing.

4.5.2. Ion lasers

4.5.2.1. Argon ion laser

In conventional argon ion lasers, the active medium is the positive column region of a high current density argon glow discharge. The mechanism for laser activation typically occurs in two steps: (i) ionization of argon, and (ii) excitation of Ar^+

4.5.2.2. Metal-vapor ion lasers

The metal-vapor ion lasers (MVLs) are probably most similar to analytical glow discharges. They operate in a rare gas (mostly helium or neon), at a pressure of 100–1000 Pa. The metal vapor is traditionally introduced by thermal evaporation.

4.5.2.3. Recombination lasers

Finally, we would also like to mention here recombination lasers, in which the lasing transition can occur between energy levels of either atoms or ions. It is initiated by electron-ion recombination, which populates a highly excited atomic or ionic level.

4.5.3. Molecular lasers

4.5.3.1. CO₂ laser

The CO₂ laser operates in a low-pressure d.c. discharge, in a mixture of He, CO₂ and N₂. The laser transition occurs between vibrational energy levels of CO₂. The CO₂ laser is a very versatile laser. It is available with a wide range of output powers (continuous power typically tens of kW) and at technological applications (e.g. welding and cutting of steel, pattern cutting, laser fusion, etc), as well as for medical applications (e.g. as cutting tool for surgery).

4.5.3.2. N₂ laser

Unlike the CO₂ laser, the lasing transitions in the N₂ laser occur between electron energy levels of N₂, and consequently, they are in the UV range (at 337 nm). Because the lower laser level has a longer lifetime than the upper laser level, only short laser pulses are possible, before self-termination of the laser occurs.

4.5.3.3. Excimer lasers

An 'excimer' is an *excited dimer*. It is a diatomic molecule, which is stable in the excited level, but unstable in the ground state. A large number of excimer lasers exist, with output wavelengths between 120 and 500 nm. The XeF and KrF lasers are very efficient (up to 10–15%), and high powers can be obtained. This makes them particularly useful for the pumping of dye lasers.

4.5.3.4. Chemical lasers

Chemical energy can also be used to create population inversion, i.e. when the products of a chemical reaction are produced in an excited state. In most chemical lasers, the reaction products are formed in highly excited vibrational levels.

4.5.4. Ozone generation

Ozone (O₃) generation is also a typical application of DBDs or high pressure GDs. Ozone can be generated from oxygen, air or from other N₂/O₂ mixtures. The first step towards ozone formation in gas discharge is the dissociation of O₂ molecules by electron impact and by reactions with N atoms or excited N₂ molecules, if nitrogen is present. Ozone is then formed in a three-body reaction involving O and O₂.

The main applications are in water treatment and in pulp bleaching. Applications in organic synthesis include the ozonation of oleic acids and the production of hydroquinone, piperonal, certain hormones, antibiotics, vitamins, flavors and perfumes [3].

4.6 Plasma- Lamps

Several types of light sources are based on gas discharge plasmas. In the following, we will make a subdivision into conventional ‘electroded lamps’ and the more recent types of ‘electrodeless discharge lamps’. In both categories, low-pressure non-LTE lamps (e.g. fluorescence lamps) and high-pressure, thermal LTE-lamps (e.g. high-intensity discharge (HID) lamps) exist.

4.6.1. Electroded lamps

4.6.1.1. Electroded low-pressure lamps. Fluorescence lamps are electroded low-pressure non-LTE lamps, which operate in the positive column of d.c. glow discharges, in a mixture of a rare gas with mercury; the latter is present both in liquid and gaseous form.

4.6.1.2. Electroded high-pressure lamps. Electroded high-pressure lamps, also called HID (high intensity discharge) lamps, operate in the regime of an arc discharge. The pressure is typically a few atm. In contrast to low pressure light sources, which are far from LTE, HID lamps are close to LTE, with gas and electron temperatures typically approximately 6000 K at the cell axis and approximately 1000 K near the walls.

4.6.2. Electrodeless lamps

In conventional electroded discharge lamps, the energy is typically supplied as d.c. or low-frequency a.c. current, so that electrodes inside the tube are required to sustain the discharge. The presence of electrodes causes serious limitations to the lamp design.

4.6.2.1. Electrodeless low-pressure lamps. The most well-known, and the only commercial types of electrodeless low-pressure fluorescence lamps, are the *electrodeless ICP lamps*, where the energy is inductively coupled to the discharge plasma.

4.6.2.2. Electrodeless high-pressure lamps.

The only commercial electrodeless high-pressure, or HID lamp is a microwave HID resonant cavity lamp. The discharge tube is placed in a resonant cavity and microwave power is coupled to the discharge through this cavity. There was only one commercial lamp of this type used for general lighting purposes, i.e. the Fusion Lighting ‘Solar 1000’, which is, however, no longer commercially available [3].

4.7 Plasma displays

Until now the television (TV) market has been dominated by bulky cathode ray tube (CRT) displays. Yet, display researchers have always been looking for more elegant alternatives. Recently, two alternative display technologies have emerged that offer the possibility of large, lightweight, flatTV monitors. Both are based on small gas discharges: microdischarges. The most well-known is the plasma display panel (PDP) technology, using microdischarges to generate the light of the display. The other is the plasma addressed liquid crystal (PALC) technology, where microdischarges serve as electrical switches.

4.7.1. Plasma display panels (PDPs)

A plasma display panel (PDP) w150–153x consists of two glass plates placed at a distance of 100–200 mm from each other. The region between the plates is filled with a gas at a pressure of 0.6 atm. The plates are covered on the inner side with a large number of thin parallel electrodes, in such a way that the electrodes of one plate are placed perpendicular to the electrodes of the other plate. There are several reasons why plasma displays are attractive for flat panel TV-screens.

4.7.2. Plasma addressed liquid crystal (PALC) technology

Besides PDPs, plasma addressed liquid crystals (PALCs) are possible candidates as new types of TVs and monitors. The PALC technology is a variation of the LCD (liquid crystal display) technology, which is nowadays widely used, e.g. in laptops [3].

4.8 Plasma-- Aerospace

The use of surface plasma for aerospace applications is a relatively new, though rapidly expanding, field. Radio frequency glow discharges have been used for many years for microelectronics fabrication, ozone generation, pollution treatment, and surface modification. For aerospace applications, the classic parallel plate geometry can be effectively uncoiled so that plasma is generated over a surface. Such plasma actuators can be maintained in atmospheric pressure air and result in a direct momentum coupling into the neutral gas. Consequently, the devices are expected to prove useful for flow control applications.

The devices may have advantages over traditional actuators such as pneumatic or hydraulic devices, as they have power consumption of the order of 100 W/m with a typical response time of around 10 ms. AC plasma actuators have already produced promising results for lift enhancement and delaying separation on airfoils, reducing drag on flat plate boundary layers, controlling separation on low-pressure turbine blades, influencing the shedding frequency of circular cylinders, and controlling dynamic stall.

Surface plasma actuators have been used successfully in reducing the skin-friction drag of the turbulent boundary layer by up to 45 percent by creating a spanwise forcing at the wall, similar to spanwise wall oscillation or spanwise Lorentz forcing.

Authors (Jukes et al) have been used hot-wire anemometry, cold-wire anemometry, flow visualization, and thermal imagery to study the induced flow from a single symmetric plasma electrode in initially static air at atmospheric pressure.

The pulsed forcing of the plasma actuator creates a sequence of wall jets, which are similar to those resulting from a synthetic jet. In the initiation stages of the flow, the plasma creates a pair of vortices that are characteristically moving at 0.1 m/s and 25° to the surface. After initiation, the plasma drives a series of tangential jets with vortex roll-up in the outer region. The measured air temperature near the electrode sheet and the surface temperature agree well, showing that the gas temperature in the plasma region is around 4 °C above ambient. Consequently, the plasma transfers little heat to the ambient gas and the induced flow is not expected to be thermally driven. The plasma clearly acts as a gaseous pump which transfers electrical energy into direct momentum coupling of the air with a velocity magnitude of the order of 1 m/s for the excitation parameters [15].

4.9 Plasma – Micro-satellite application

Conventional thermal control materials (TCMs) used in satellites tend to deteriorate in the severe space environment, many times leading to unanticipated mission problems. New and better TCMs are constantly sought to reduce difficulties in satellite thermal design.

Micro-satellite technologies are the current trend in satellite development because they provide cost-effective solutions to a wide range of missions. When satellites get smaller in size, the thermal control becomes more important, in view of reduction in packaging space and thermal mass. Passive thermal control methods are commonly used for small satellites, because active methods require electric power, more hardware and space for installation.

For the passive thermal control method, reflective and radiative coatings are mostly applied on surfaces of different components. However, most of the coatings deteriorate in the harmful space environment. Most scientific and military satellites are launched to low earth orbit (LEO), which is generally in the range 300–1000 km. Satellites in the LEO environment are first subjected to irradiation of vacuum ultraviolet photons, ionizing electrons (keV), and protons (MeV). Additional damage is induced through hyperthermal oxidation by atomic oxygen (AO), hypervelocity impacts from micrometeoroid/ orbital debris and other hazards such as extreme temperature variations. The plasma spray technique consists of the injection of powders into a direct current plasma jet of temperature up to 10 000 K and velocity up to 200 m/s, in which they are melted and accelerated. The molten particles are sprayed onto a substrate to form splats, which rapidly solidify, eventually depositing a coating onto the substrate. Plasma sprayed ceramic coatings are widely used for corrosion, wear and heat protection of hot components in gas and steam turbines.

Li et al examined the possibility of using plasma-sprayed alumina (PSA) coating for thermal control of a satellite. Such PSA coatings have proved to be a good thermal barrier coating material for hot section components in aircraft engines. Panels of aluminum alloys, and so on which are commonly used for satellite applications, form a very compatible substrate for PSA coatings. Preliminary investigations reveal that the PSA coatings have good potential as a substitute to conventional TCMs for micro-satellite panels, including solar arrays [16].

4.10 Plasma – Nano powders

Because of the induction plasma characteristics (large volume, high energy density and high chemical reactivity), the radio frequency inductively coupled thermal plasma (RF-ICTP) synthesis process is one of the most efficient processes available for the synthesis of nanoparticles especially for ceramics. For this reason, many researchers have become involved in the investigation of the tailoring of produced nano-powders with specific properties, such as their degree of agglomeration and size distribution. Furthermore, for some applications and the associated process control and for modeling calibration, there is the need to access to the formation and growth history during the induction plasma synthesis process. To study nanoparticle size distribution, as produced under plasma conditions, a variety of approaches have been used for performing such measurements, including laser light scattering (LLS), particle mass spectrometry (PMS), direct sampling (DS) and the use of a plasma as a detection source. The LLS method has considerable appeal in this application because it is both non-intrusive and it provides information on the plasma flame without intervention in the chemical and physical processes present. However, the minimum nano-particle sizes detectable by conventional LLS are about 20 nm. Shiratani et al. have developed a polarization-sensitive laser light scattering method (PSLLS), with which they have successfully determined a range of particle sizes down to 10 nm. Whereas nano-particles with sizes less than 10 nm still remain undetectable.

Lu Jia and Francois Gitzhofer reported: A particle-sampling probe has been demonstrated to successfully collect gas borne nanopowders, produced by the RF-ICTP synthesis process for subsequent analysis. Compared to a reactor wall collection procedure, this technique has many advantages, these include a quick clean-up, a reduction in the risk of contamination a minimum disturbance to the plasma gas flow pattern and a fast and continuous withdrawal of the nano-powders from the desired internal plasma chamber position. This sample probe and the associated processes (obstruction, dilution, collection-quench, cleaning) enable a quick mapping of the nano powder induction plasma synthesis process. Grain sizes as measured by

TEM observations are small enough (4 nm) to demonstrate that the local quenching by helium gas is efficient. Numerical simulation of the plasma flow circulation near the sampling probe tip was conducted to study the influence of the probe tip geometry on the disturbance to the plasma gases motion. The result demonstrated that a probe tip, with an inclined angle of 45° , contributed to the reduction of the plasma flow disturbance. The effects of plasma power and chamber pressure on particle size were also investigated. It was found that the particle mean size increases with chamber pressure, due to longer residence times for coagulation taking place at higher chamber pressures. The mean size also increased with decreasing plasma power [17].

4.11 Plasma – Supercomputers

No less than 99.9% of the matter in the visible Universe (except for the dark matter distribution, which is visible through gravitational lensing) is in the plasma state, that is, in the state of ionized gases. The solar/stellar system is filled with plasmas ejected from the upper atmosphere of the Sun or stars. The stream of plasma is called the solar wind or stellar wind, which carries the magnetic field of the Sun or stars. Various phenomena, such as space storms or geomagnetic storms, are caused by interactions between the solar/stellar wind and a planetary intrinsic magnetic field. Thus, studies of space plasma are important to understand our Universe.

Since the density of space plasma is low, collisions between individual plasma particles are neglected. Then, the kinetic dynamics of such collisionless plasma are described by the first-principle Vlasov–Maxwell system equations. The Vlasov–Maxwell system equations are commonly used for studies of electron-scale processes in space plasma. For larger-scale processes, however, electron-scale processes can be sometimes neglected, and various approximations are applied to the Vlasov–Maxwell system equations. For investigating global structures of plasma, such as stellar or planetary magnetospheres, the magnetohydrodynamic (MHD) equations are used, in which full kinetics of plasma are neglected by taking the moments of the Vlasov equations. The Vlasov–Maxwell system equations and MHD equations are highly nonlinear and are very complex to solve by hand calculations.

Thus, computer simulations play an essential role in studies of space plasma. The numerical MHD code for space plasma has been optimized for vector-type supercomputers for a long time, because most supercomputers with vector processors reached high performance in the 1990s. These codes often have achieved a very high computational efficiency (the ratio of the effective performance to the theoretical performance).

However, almost 100% of the ‘top 500’ supercomputer systems in the world recently adopt the scalar-type processors, and more than 85% of systems consist of 64bit-x86 processor architecture. The other scalar-type computers are POWER and SPARC architectures.

The purpose of Fukazawa and Umeda study was to make performance tuning of MHD code for space plasma simulations on scalar-type massively parallel supercomputer systems [18, 19, 20].

Plasma (high-temperature ionized gas), consisting of mobile free electrons and positively charged ions, is one of the most complex forms of matter that we encounter.

Because of long-range nature forces between particles, plasma exhibits collective motions-modes in which the particles in large regions move coherently or in unison.

Computer modeling can treat many of the complex plasma problems of interest. Such modeling gives more detailed information that can be obtained experimentally, so that the important physical phenomena can be determined [21].

4.12 Plasma – Nuclear fuel

Timofeev have analyzed plasma methods for processing spent nuclear fuel. It is shown that, by ICR heating in a non uniform magnetic field, the energy of the heated ash ions can be increased substantially, while nuclear fuel ions can be kept cold. Two methods for extracting heated ash ions from a cold plasma flow are considered, specifically, that by increasing the ion gyro radius and that due to ion drift in a curved magnetic field. He found that the required degree of separation of ash and fuel ions can be achieved in systems with quite moderate parameters.

The ICR-based plasma method for processing spent nuclear fuel (SNF)—removal of nuclear ash (NA) — was discussed. This method has long been used to separate isotopes. However, the problems of isotope separation and SNF processing differ in some aspects. Thus, in separating the isotopes of a certain chemical element, only one of them is extracted. In contrast, SNF processing implies the extraction of a group of elements with a broad mass spectrum. The isotopes have almost equal masses, whereas the masses of ash nuclei differ substantially from those of fuel nuclei.

These factors necessitate that the ICR separation schemes be different. In order for the ICR separation of isotopes with nearly the same masses to be selective (i.e., for the cyclotron resonance lines of neighboring isotopes not to overlap), it is desirable to heat them by a monochromatic RF field in a sufficiently strong uniform magnetic field.

In those experiments, aimed at cleaning hydrogen plasma of heavy impurities, a plasma flow was passed through the region with a curved magnetic field. The plasma flow through the system was observed to be stable, in contrast to the view held at that time that it should escape toward the weaker magnetic field region.

An analysis of the simplified model of selective ICR heating and separation of ash ions shows that the parameters of a system for SNF processing can be rather moderate. These parameters can be significantly modified if an appreciable fraction of ^{238}U atoms in the plasma flow is doubly ionized.

However, since the flow is inclined with respect to the magnetic field, the charges will be accumulated near the ends of the flow: specifically, the positive charge will occur near the collector of ash ions, while the negative charge will be concentrated near the entrance to the separator. The positive charge should be rapidly carried by moving ions away to the chamber end, and the negative charge will likely be neutralized in the plasma source [22].

At the temperatures needed for the D-T[hydrogen-deuterium (D) and tritium (T)] reaction to occur, the D-T fuel is in the plasma state, comprising a mixture of charged particles (nuclei and electrons). In a reactor, there must be sufficient fuel present and the energy losses must be kept sufficiently low to ensure that more energy is released from the fusion reaction than is needed to heat the fuel and maintain the necessary temperature. The plasma nuclei can be contained by gravitational forces, as in the Sun, or by magnetic fields. For magnetic confinement, the effectiveness of the magnetic field in containing plasma and minimizing thermal losses can be measured by the time taken for the plasma to cool down after the source of heat is removed. This is called the energy confinement time and needs to be between one and two seconds in a reactor, although the plasma will be contained for

considerably longer. The power output depends on the amount (or density) of fuel present, which is only a few thousandths of a gram per cubic meter, but is sufficient to yield vast amounts of energy. Thus a fusion reactor must produce high-temperature plasmas of sufficient density that can be contained for long enough to generate a net output of power.

Keen and Watkins concluded that magnetic confinement of plasmas, using the tokamak concept, is the most advanced approach to controlled thermonuclear fusion [23].

4.13 Pulsed plasma thruster

Electric thrusters are very attractive for attitude control, north-south station keeping, and orbit transfer of spacecrafts and satellites, and their study is an important research topic in propulsion technology. Stationary plasma thruster (SPT) is of the Hall thruster type and has the following features: (a) offering an ideal specific impulse for deep space exploration and micro/small spacecraft and (b) high efficiency and security. However, the plasma plume of SPT contains many high energy particles, whose possible interactions with the spacecraft could induce contamination. In the case of Hall thrusters, there are three particular spacecraft integration issues: (a) the divergence angle of these devices is relative large, leading to the possibility of the direct impingement of high energy propellant ions onto the spacecraft surfaces, which may result in sputtering and degradation of material properties, (b) backflow impingement of ions caused by the formation of a charge-exchange (CEX) plasma, and (c) the high-energy ions created inside the thruster cause significant erosion of the walls of the acceleration channel and erosion residuals may transport out of the thruster and become deposited on the spacecraft surfaces. To effectively assess the contamination of the plasma plume and improve the performance of electric thrusters, greater efforts should be putting on finding more details of the plume. Experimentation and numerical simulation are two common research approaches. The former method usually needs much fund. However, it is difficult to obtain full information of plasma plume, though it is a veracious means and can acquire some valuable information that is necessary and helpful for numerical study. The latter method is proved to be adoptable, effective, and sometimes significant in many areas [24, 25, 26].

The plume characteristics of a pulsed plasma thruster (PPT) are considered necessary in the evaluation of plume/spacecraft interactions. Quian et al, has characterized the rarefied plasma plume of a laboratory PPT. First, a three-dimensional (3D) physical model with boundary conditions is presented. Then, the particle-in-cell and direct simulation Monte-Carlo hybrid methods are employed to study the flow field. The profiles of the plasma density and potential and their variations versus time are analyzed. Also, the computational results are compared with experiment data as well as with results from existing two-dimensional (2D) simulations.

The comparisons show that the computational model can predict the electron density of plume in both parallel and perpendicular planes. It is also shown that the 3D predictions are more accurate than those of the 2D model. Analysis of the plume backflow indicates that less than one thousandth of the mass that is released from the solid propellant enters the backflow region at the end of a pulse period.

The following conclusions are reached based on the research presented in this article.

1. The numerical model of this article is valid and the simulation results show good quantitative agreement with the measured data. Predictions of a 3D model are better than those of a 2D model, especially at the early stage of simulation.

2. The 3D simulation can better display the expansion of the neutral and ion components of plasmoid than the 2D simulation.
3. The estimation of plume backflow indicates that less than one thousandth propellant will move into the backflow region in a pulse period, i.e. the backflow mass of the PPT plume is very small. In addition, the efforts of this article are referable for further study of the PPT plume [27].

5. Conclusion

Different types of plasmas are used in a wide range of growing application fields. Surface modification (both in the semiconductor industry and for materials technology) is probably the most important application field. Plasma processes appear to have some distinct advantages compared to conventional (wet chemical) processes. A number of different plasma technologies are essential to different steps. The use of plasmas as lamps, more specifically fluorescent lamps, is probably the oldest application. Nowadays, new types of so-called electrode less lamps are being developed, their main advantage being a longer lifetime because damaging of the electrodes (e.g. by sputtering) is avoided. An application which attracts a lot of interest from a broader public is the use of low temperature plasmas for displays, to be developed as large and flat television screens, either directly as plasma display panels, or indirectly as plasma switches for liquid crystal displays. However, in order to become competitive with the conventional (cathode ray tube) TV technology, the luminous efficiency of plasma displays still has to be considerably increased, and their price has to be lowered. also, Gas plasma treatment can have profound effects on the properties of textile and polymeric materials.

Another application is in laser technology. Finally, we have also outlined some emerging applications of (mainly) high-pressure gas discharges for environmental and biomedical applications.

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