Application of Non-Eqilibrium Plasmas in Top-Down and Bottom-Up Nanotechnologies and Biomedicine

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Abstract – In this paper we discuss how a better understanding of thermal and mainly non-thermal plasmas provides basis for their application in a number or nanotechnologies. One should bear in mind that one may design unique properties of plasmas thus affecting very directly properties of the resulting nanostructures. A number of examples where plasmas contribute to production of nanomaterials, modification of surfaces and functionalization at nanoscales are given here. Plasmas are not a panacea but in nanotechnology their application may be the best strategy to convert production of individual structures to massively parallel production that may become a viable industrial technology.

I. What are Nanotechnologies, and how Plasmas fit there

A well known nursery rhyme tells a story about seven blind men (persons) who went to India to "see" an elephant. Unable to see the big picture they had to resort to feel different sections of a large elephant's body by their hands. Not surprisingly their reports of what elephant really is, differed greatly. At first sight (no pun intended) one may fail to see justification for using an elephant as a paradigm for anything related to the nanoscience and nanotechnology. But having in mind the famous Faynman's quote about "a lot of room at the bottom" with our limited ability to grasp the detail and at the same time the big picture, the parallel becomes obvious. We mainly feel the details with our diagnostics but we cannot easily find a continuous method of observation with enough depth of focus to give us the very high resolution that is needed for singular structures while giving the developments over a wide range. We often feel like one of those blind men, blinded both by our ability to measure some details and failure to see the connections. Now add to the picture the funding agency and you get each blind man (person) defending his (her) "view" so vigorously often disregarding even ridiculing other possible "viewpoints".

At the same time the funding for the nanoscience/ nanotechnologies has been very similar to the feeding (funding) frenzy of sharks, i.e. a significant amount of resources is given to a starved population of large and until recently successful predators. In that respect plasmas are often overlooked and have to defend their right to be a part of the nanotechnology buzzword domain. In order to justify this we need to define nanotechnologies as opposed to the nanoscience. While the later deals with objects that have nanometer dimensions one could claim that a large part of science falls into this category. On the other hand the former (nanotechnology) is more difficult to pin down and we could here define it here as technologies required to manipulate objects of nanometer sizes in order to achieve the desired functionality both at this and much larger scales. In that respect plasmas are often used for nanotechnologies and nanoscience as well as they offer a number of techniques to grow, separate and manipulate and study objects of the order of few nanometers.

While we justify the importance of plasmas against other "blind men" we may end up being one of them by assigning plasma more importance than it really deserves. Nevertheless we cannot overemphasize the wide range of possible applications and how plasmas match either directly or indirectly (thin film deposition, beams, light sources, cleaning, functionalization, …).

Recently we have prepared a much more detailed review of numerous applications of plasmas in nanotechnologies [1], a specialized book on plasmas for production of integrated circuits [2] which is certainly the most widely used and economically successful nanotechnology. There is also a wide range of reviews and specialized papers dealing with plasmas in nanotechnologies [3]-[5] from other sources. In this paper we present how plasmas may be designed to achieve certain goals and give some examples of their relevance to nanotechnology.

II. Top-Down versus Bottom-Up Technologies

Top down technologies take a bulk piece of material and change its structure, shape and functionality so that nanostructures and nanodevices are developed. Another possible approach to define it is that one may follow the existing and well proven technologies and to allow them to achieve further miniaturization through research. Its best known version is the technology designed to produce

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integrated circuits which involves: thin film deposition, ion implantation, photolithography, plasma cleaning, plasma etching, plasma ashing and few more. While plasma is often mentioned here it is also present in almost every step of the technology from implantation to light sources for lithography.

This approach is best realized by following the path set out by Moore's law (more than 40 years ago) and by the roadmaps outlined by the microelectronic (now already nanoelectronic) industry. The top down approach in industry is at the moment at 65 nm - 45 nm production while 32 nm and 22 nm technologies are being developed. Having in mind the inertia of the industry mostly stemming from the large existing investments and reduced risk with a proven technology it is hard to see that standard technology will be replaced before the year 2040.

The bottom-up approach (which is currently in the domain from 1 nm to 10 nm) is based on using the best of our abilities and facilities to produce some structures with extremely small dimensions from even smaller building blocks, even at the level of single atoms. While that approach is based on the most advanced devices and abilities of mankind those more often than not manage to produce only individual functional nano-structures. An even more difficult step will be to transfer this into industrially applicable and economically viable technology. For example, in integrated circuits one needs billions of individual transistors all properly manufactured and connected to give the circuit its functionality. While amazingly promising individual devices have been identified and manufactured, like fullerenes, Si nano-crystals, and many more the design of the technological process that could produce integrated device is still far from development although one could see that in many cases plasmas could be involved in a hybrid mix of the two approaches. The critical research in this approach will not be only in achieving a basic result but also in providing the technology for its practical implementation.

III. Plasma Sources for Nanotechnologies

Ionized gases are gases with free charged particles. The definition encompasses very weakly ionized gases that are also known as "swarms" of charged particles (ensembles of independently moving charged particles driven by external field and collisions with the unperturbed molecules of the background gas), gas discharges (where charged particle densities may become sufficient to affect the distribution of the external electric field) and plasmas. As the charged particle density increases, properties of the ionized gas change dramatically.

Plasmas may be categorized by a number of different criteria. They can be collisional or non-collisional although here collisions only refer to encounters with the background gas atoms or molecules. Plasmas may be in equilibrium or non-equilibrium. The former are also the so called thermal as all species may have temperatures that are similar. At the same time the non-equilibrium plasmas are often associated with terms low temperature plasmas or even cold plasmas as gas particles may be at room temperature, slightly higher or even lower, while ions are not much warmer either. At the same time electrons may have effectively millions of degrees ($T_e>>T_i=T_g$).

Plasmas may be highly or weakly ionized. The former favours thermal while the later favours non-equilibrium plasmas. This is due to strong Coulomb coupling between electrons and ions which allows significant transfer of momentum through long distance interactions.

Thermal plasmas are usually more productive as all particles participate in inducing the initial dissociation that open all further channels or reactions and surface interactions. On the other hand heating of gas and eventually surfaces of the vessel is excessive and such system is hardly useful for treatment of organic materials, living tissues or complex multi-component systems such as integrated circuits. Nevertheless, such staple nano-items as the fullerenes [6], were discovered in an arc (thermal) plasmas.

In non-equilibrium plasmas one uses the great mass ratio between electrons and background gas molecules to decouple transfer of energy in elastic collisions of electrons with gas molecules [2]. Thus electrons may gain high energy from the electric field without subsequent transfer of kinetic energy to ions and molecular particles. Under the non-equilibrium conditions under discussion, the temperature of electrons, and even ions, are not well defined, and energy distribution may be quite complex and different from a Maxwellian distribution. Electrons provide ionization and dissociation as well as excitation of gas particles and thus initiate and sustain the plasma. As mentioned earlier gas molecules and ions have low energies, thus allowing plasmas to treat thermally unstable materials including polymers, organic materials, even the living matter.

One of the essential differences between equilibrium (thermal) and non-equilibrium (low temperature) plasmas is in the fact that in the latter case individual collisional processes may change the electron energy distribution function (EEDF) considerably [2] allowing design of desired properties of plasmas by controlling mixtures, flow rates and power input. Thermal plasmas, on the other hand are almost insensitive to the species of the buffer gas and mixture composition.

Non-equilibrium plasmas open various possibilities that are already being used or considered in nanotechnologies. They allow creating structures which would be unattainable under thermal (equilibrium conditions). One such example is anisotropic plasma etching [7] which was discovered in mid 70s and was explained a few years later [8].

The anisotropic etching is enabled by the combined effects of production of high density of chemically active species and acceleration in the sheath of the plasma which is generated by the region close to electrode that is depleted of electrons due to their higher mobility. As a result, ions get accelerated at the right angle to the surface hitting it with considerable energy and breaking numerous bonds that fall prey to the adsorbed chemically reactive molecules generated in the bulk of the plasma.

Thermal plasmas would produce undercutting as wide as the depth of the trench leading to an isotropic etch. Non-equilibrium plasmas may produce a number of structures that may not be found in thermal growth and some of those will be mentioned in the section on nano-materials.

A. *Plasma Sources for low pressures*

Non-equilibrium plasmas are easily produced at low pressures (around 1 Torr) and under those conditions one may achieve large volumes, great uniformity and easily controllable properties. The sources for such conditions may be dc, rf (capacitively and inductively coupled) or magnetically enhanced discharges [2].

The Capacitively Coupled Plasmas (CCPs) are mainly maintained by the input of energy to electrons from the moving sheath boundaries and by the effect of collisions on electron motion in rf field [2,9]. In addition, other effects may be contributing to the overall production of ionization such as double layer formation [10], while in the case of rare gas buffer gases; metastables may play a significant role in plasma maintenance [11].

Inductively coupled plasmas (ICPs) have also been used very much in recent times. Reduced losses lead to a higher density of charged particles and metastables [12]. ICPs allow special design of the coils that make it possible to achieve uniformity over large areas. ICPs operate in two modes capacitive (E) and inductive (H) [13].

B. *Plasma modeling*

Comprehensive tools for modelling plasmas while allowing for complex geometries have been developed. Those provide the basis for understanding and modifying the performance of plasma tools [14]-[17]. The basis of these models are the collisional data and transport properties and those are often in limited supply and difficult to interpret (e.g. [18]).

These modeling tools include the basic description of plasmas through either fluid equations coupled with calculated or measured swarm data or kinetic models. Models should include plasma surface interactions as those are the key to effects that are sought but also as some of the critical processes for maintenance of plasmas take place at surfaces. Those should include a wide range of data: reflection coefficients, accommodation coefficients, surface adsorption and desorption and related recombination coefficients, efficiency of inducing secondary electrons and other particles and etching and implantation rates for all relevant particles. One needs to follow kinetics of excited species, metastables and photons including their collisions with surfaces. When dust particles are present their properties need to be included in the model as well. Comprehensive plasma models need to be developed to deal with complex geometries of industrial and experimental plasma reactors and with external parameters such as temperatures, gas flow and loading and other issues. Finally the model should deal with the interior of the integrated circuit as it may be strongly affected by potentials that develop on surfaces due to charging and by high energy ions and photons penetrating the surface [19].

Development of plasma technologies for nano-manufacturing will open the need for the data for new gases that were not subject of main interest of plasma modeling community, even the return to some of the standard gases that have been a subject of much scientific interest in past but may require further improvement to meet the goals.

C. *Plasma Sources for atmospheric pressure*

At high pressures, sparks and arcs are easily produced which damage the surface of the treated material. This is fine for thermal plasma applications but in order to achieve non-equilibrium operation of plasma at elevated pressures one needs to limit the charged particle production. It can be achieved in very inhomogeneous fields (corona discharges), by spatial interruption of the field with an inserted dielectric (dielectric barrier discharges), by high frequency fields or localized microwave plasma production in a flow of rare gases mixing with the atmosphere or sometimes even in air. According to the Paschen law [20] the optimum gap for breakdown in most gases is at 1 Torr for 1 cm gaps. Non-equilibrium operation at atmospheric pressure may be thus achieved with gaps of the order of 100 μm or less. This would allow us to take advantage of all the properties of non-equilibrium plasmas although the nature of some parameters and processes may change at high pressure.

Apart from being thermally unstable some of the possible targets may not withstand vacuum very well, like most of the living organisms and thus require atmospheric pressure treatment. As discussed above one of the most promising techniques to achieve the goal of atmospheric pressure non-equilibrium plasmas are micro discharges.

D. *Micro discharges*

Micro-discharges have grown (again no pun intended) into one of the most interesting topics in plasma physics. Standard dimension/pressure discharges (1 cm-1 Torr) operate near the minimum of the Paschen curve (breakdown voltages vs. pressure times gap (pd)) where conditions for the so-called Townsend mechanism of breakdown are optimal while other modes of breakdown favouring transition to sparks- the streamers are unlikely. Adherence to the scaling laws supports the same breakdown mechanisms as for the standard discharges [22]-[24], any departure indicates a new mechanism. For example at small gaps field emission may become dominant source of secondary electrons and in that case breakdown voltage will decrease with decreasing gap (d) towards very small values, but this mechanism was found to be relevant only below 10 μm [25]. On the other hands numerous reports of a constant breakdown voltage across the left hand side of the Paschen curve are perhaps due to a long path breakdown and poorly determined gap [26]. Other scaling parameters include electric field to gas number density ratio (E/N), current density normalized by the electrode gap to the square (jd^2) and frequency times gas number density (ωN) for RF discharges.

Micro-discharges operate in a number of different geometries where parallel plate is perhaps the most difficult to achieve. The most frequently chosen geometry is that with a hollow cathode [27]. Applications are numerous including light sources [28] and analytical measurements in situ but promise are very good for localized treatment of surfaces within the realm of nanotechnologies.

The benefits from the studies of micro discharges may also be in understanding breakdown that may occur in integrated circuits, MEMS, hard disk drives and flat panel displays. The breakdown voltages under those small gaps may be of the order of a hundred volts which is considerably less than the breakdown for gaps of few millimetres or more. The Breakdown voltage may become the limiting factor in transferring energy to some small dimension electro mechanical applications.

E. *Plasma needle and atmospheric pressure jets*

High breakdown voltage of the standard mixture in the atmosphere (due to attachment to oxygen) leads to the conditions where streamers and sparks are generated. To reduce the breakdown voltage a flow of rare gas is used which mixes with the atmospheric gases in the discharge region allowing production of chemically active species. Apart from the large scale atmospheric pressure plasma jets (APPJ) smaller scale devices have been developed and named μ-APPJ [30] and plasma needles [31]-[33].

Plasma needles and some other micro discharges may be the area where nanotechnologies meet medicine and biology. Four important areas of application of plasmas in medicine and biology may be specified: 1) diagnostics, 2) drug delivery, 3) neutral prosthetics and tissue engineering and 4) minimally invasive surgery. Micro discharges may play an important role especially in tissue engineering and in minimally invasive surgery while opening room for spatially localized treatments that include sterilization even apoptosis. Our unpublished results indicate that efficient sterilization is even achieved for microorganisms which are suspended in liquid.

Plasma needle operates at atmospheric pressure and meets all the necessary conditions for treatment of organic materials and living tissues. It is desired that the plasma should be non-aggressive, local, with small penetration depth and, at the same time, it produces chemically active species at a low gas temperature.

In general plasmas may be regarded as sources of free radicals, charges with different energies and ability to affect surfaces and basis and support for numerous gas phase and surface chemical reactions. All plasmas may be tuned to some degree but non-equilibrium plasmas allow much more direct modification of critical properties such as electron energy distribution function or distribution of energies of ions hitting the surface. At the same time plasmas are quite complex and nonlinear requiring cutting edge scientific modelling to optimize reactors and industrial processes.

IV. Plasma Produced Nanomaterials

The term **Nanomaterials** has been used to cover [1]: nanostructured materials with imposed nanoscale topography; nanoparticles and nanocomposites where the nanoparticles are embedded in a matrix, often a polymer; nanocapsules; nanoporous materials e.g. membranes and scaffolds; nanofibres; fullerenes; nanowires; nanotubes particularly carbon; dendrimers; quantum dots and thin films (< 100nm thick).

A number of different techniques for synthesis have been used including: Self-assembly; Chemical Vapour Deposition (CVD); Chemical synthesis/solution methods (sol gel, colloidal chemistry); Gas-phase methods (flame pyrolysis, electro-explosion, laser ablation); Electrodeposition/electroplating; Spin coating; Spray coating; Physical Vapour Deposition (PVD) including plasma techniques such as magnetron sputtering; Plasma Enhanced CVD (PECVD).

In many applications the mere presence of the nanoparticles suffices for the application, such is the "oldest" nanotechnology the sun creams. However in specialized applications such as electronics that are driving the market and development it is the placement and connection of the nanostructures that gives the functionality to the ultimate product. Such products are of the highest potential value and possible markets include [1]: **Displays ($90B):** Field Emission Displays, LCD backlighting with carbon nanotubes (CNTs), Organic LEDs; **Photovoltaics ($50B):** Quantum dots (QD) for III-V solar cells; **Imaging ($10B):** CMOS imager with plasmonics, IR imager with III-V quantum dots; **Lighting ($6B):** LEDs with QD II-VI (ZnO) and high index III-V nanostructures, II-VI QD Organic LEDs; and many more.

A. Fullerens, nanotubes and graphene

One of the key events in the early development of nanotechnology was discovery of fullerenes. The applications of fullerenes include drug-delivery agents, fulleride-based superconductors and light-activated antimicrobial agents [1]. As mentioned before thermal plasmas are very efficient in producing a wide range of nanostructures starting with first discoveries of fullerenes and nano-tubes [34]-[36].

Individual nanotubes are grown as single-wall (SWNT) or with multiple concentric tubes (multi-wall MWNT) and quality parameters to be controlled are diameter, chirality, length and defects as well as incorporated impurities. Their applications range from transistors and interconnects for post CMOS IC technology, field emission displays, high surface area electrodes in biosensors to incorporation in nanocomposites and bulk gas storage or filter materials.

In addition to thermal (arc) plasmas, the synthesis routes have included laser ablation, chemical vapour deposition and PECVD. While arc and laser plasmas are used for bulk quantities of nanotubes the results suffer from high levels of metal and amorphous carbon impurities. As basic CVD is unable to produce high quality carbon nanotubes PECVD has been employed. Plasmas used in PECVD cover a wide range of pressures and frequencies. Both DC, RF (CCP –capacitively coupled plasma or ICP-inductively coupled plasma) [37]-[38]

Numerous issues are still open and worthy of scientific effort in relation to improvement of PECVD sources for CNT growth [1]. Those include the identification of the primary precursors and the role of other particles such as atomic hydrogen in the growth, what is the role of ions in the growth and how does it change with the ion energy, what is the mechanism of alignment and how is it influenced by the electric field, how to optimize the substrate bias, how to achieve uniform growth over large areas compatible with IC wafers, how to control chirality of fibres and how to produce SWCNTs by PECVD [37].

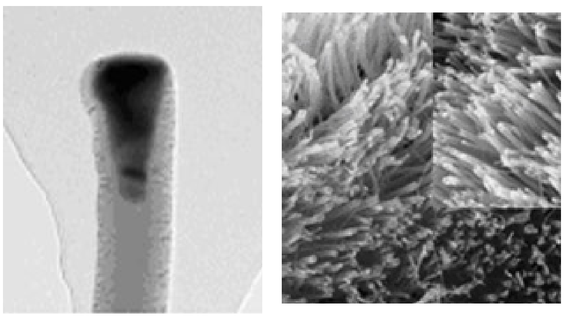

Fig. 1 a) TEM image of a carbon nanotube with metal catalyst nano-particle embedded in tip (left) and b) after plasma purification treatment (in nitrogen) where the metal has been removed (right) [1].

Growth of nanotubes proceeds from plasma sputter-deposited metal nanoparticles (see Fig. 3a). These often receive separate plasma pre-treatment to enhance nanoparticle uniformity For all nanotube synthesis methods, post purification is required to remove the metallic remains of the catalyst. Also unwanted amorphous carbon phases have to be removed. Plasma treatment may improve upon the standard wet techniques to remove impurities show considerable promise in this respect using ECR nitrogen plasmas (Fig. 1b).

Plasma is often used in order to achieve functionalization of nanotubes from increasing damage and cross linking to achieving particular functionality of a particular sensor. Nitrogen and oxidative functionalisations have been achieved in a number of different plasmas [39].

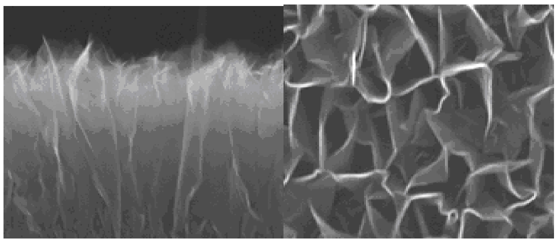

Fig. 2. Graphene nanowalls grown by M. Hori and colleagues using plasma enhanced CVD: end on (left) and side on (right) view [41].

Plasmas are also often used in the growth of graphene sheaths and nanowalls grown on surfaces consisting of graphene. Single grapheme sheaths were generated in atmospheric pressure microwave plasma [40] while Hiramatsu et al have grown graphene like wall structures as seen in Fig 2 in PECVD.

B. *Thin film nanomaterials*

Thin film processing is a standard technique nowadays but the films that are being made fall into nanomaterials category when their function depends on thicknesses below 100nm. In general, controlling is required of the three key parameters of the surface chemical composition, thickness and topography. Here the use of plasma based tools is common. Particularly interesting and still requiring a large degree of research are biocompatible films.

C. *Growth of nano-crystals, dust particles in the gas phase and growth of nanostructures on surfaces*

Non-equilibrium plasmas allow growth of structures that could not be created in the thermal equilibrium. The effects that help create these special structures include: charging, local heating, directionality of ions and their high energies and many more. Charging favours formation of monocrystals rather than agglomeration. Special active particle losses to the walls and also opens a possibility of self-organization of particles in the gas. Negative particles form a sheath, together with other energetic particles in plasma allow localized heating of particle surfaces that is sufficient to produce crystals with covalent bonds. At the same time surrounding gas is at the room temperature [42],[43]. Perhaps the best known example is that of cubic nanocrystals of Si that have been grown in plasma and shown to have remarkable properties and are considered as excellent transistors or active media for solar panels [41].

Pyramidal growth on surfaces is also unlikely under thermal growth conditions and in growing of pyramidal CdO nanostructures the reactive oxygen atom flux from the plasma was shown to be the determining factor [44]. Examples of nanostructures grown in plasmas are too numerous to be summarized here.

Over the past decade, extensive studies have been carried out on formation and behaviour of dust particles in non-equilibrium plasmas. Both dust particles and thin films of amorphous carbon having a cauliflower structure at the surface are readily created in rf plasmas in methane or acetylene [45]. Being charged those dust particles remain airborne and have amazingly narrow range of diameters directly proportional to the time spent in the plasma. When the particles grow beyond some weight they fall leaving a pristine plasma. The trapped particles may be controlled, moved, put-deposited onto the surfaces. One example of the particles deposited and then coated on the surface is shown in Fig. 3.

This may be just one of the techniques to produce nano-structured surfaces, for example for achieving hyper hydrophobic materials.

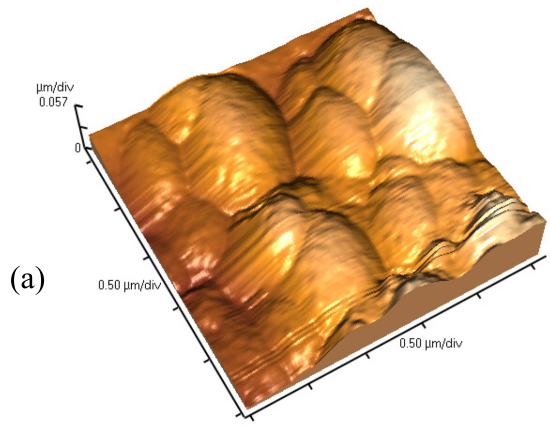

Fig. 3. Surface with dust particles incorporated into thin amorphous carbon film [1],[46].

V. Plasma Treatment of Surfaces

Ultimately, the plasma species interact with the walls and electrodes. Adsorbed species may react with the surface to form a product or desorb without or after a surface reaction. Volatile products will either be eliminated through pumping or may participate in the plasma chemistry. If the product is not volatile, it will contribute to the formation of a thin film at the surface. Ions, electrons and photons also interact with the surface.

The principal technology for integrated circuits is dependent on plasma interaction with exposed sections of the substrate. Positive ions are accelerated in the sheath and both high energy ions and the resulting very high energy neutrals contribute to modifications of the surface often aided by the adsorbed chemically active species. The removal of surface material is the key to top down plasma technology and the resulting surface is likely to show an increased roughness. On the other hand the roughness of the surface should not exceed 10% of the dimension of the structure and thus may prove to be a limitation for application of plasmas in nanotechnologies. It has been shown that very high energy fast neutrals that have been proposed to reduce the charging [47] provide etching that has a considerably smaller roughness as compared to the surfaces produced by ions [48].

Comprehensive (vertically integrated) plasma-surface-device models have achieved a high degree of reliability with the ability to treat complex systems and provide a realistic representation of surface processes [49]. The problems exclusively associated with nano-dimension of the structures in new technologies are numerous. The ability to deal with issues such as charging, control of pulsed two frequency plasmas [50] and also to predict profiles of structures seems to be essential for applying the same models to predict the properties and the development of nanostructures by bottom up and top down technologies.

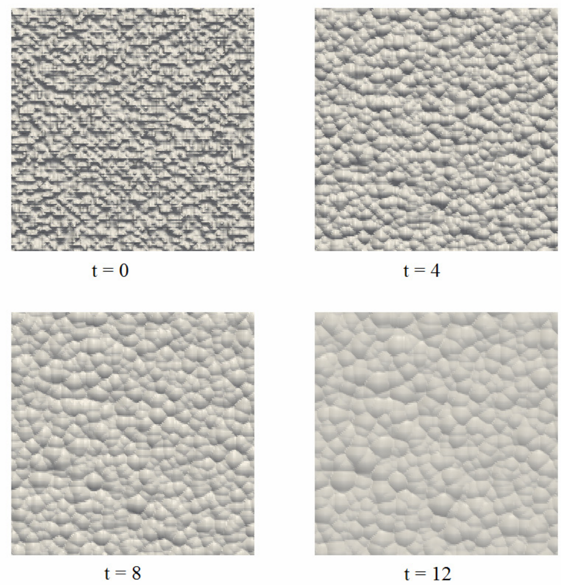

Fig. 4. Images of smoothing of a roughed substrate for several equidistant time intervals (in arb, units) during isotropic etch process.

When energetic ions enter into a solid, energy from the ions is transferred to the solid as the ions travel through it causing various kinds of modifications of the solid [42]. On the surface of a solid the energy transferred from the ions to the surface or near-surface atoms can cause sputtering of surface material. The evolution of surface topography during ion bombardment is governed by the interplay between the dynamics of surface roughening due to sputtering and smoothing due to material transport by surface diffusion. These competing processes are responsible for the creation of characteristic surface features like quasiperiodic ripples [51] and self-affine topographies [52]..

On the other hand, isotropic wet or plasma induced chemical etching of silicon can be a suitable process to construct structures with very smooth surfaces as can be seen in Fig 4. Smooth etching is also advantageous to produce surfaces that will be bonded together.

A completely different example of a surface treatment that gives new functionality to material and involves nanotechnology is given in Fig 5. When textile is treated by plasmas functionalized fibres allow much better adherence of polymers or nanoparticles that may be deposited. Here silver nanoparticles have been loaded onto a functionalized polypropylene surface [53] to achieve bactericidal properties.

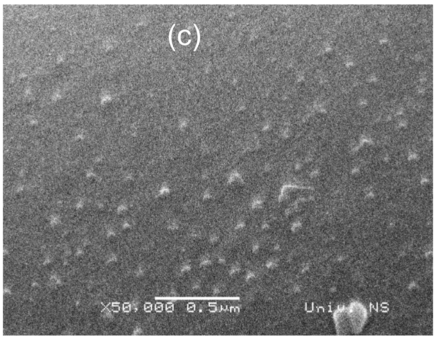

Fig. 5. SEM images of Poly Propylene fibre treated by air RF plasma and loaded with silver nanoparticles [1].

VI. Conclusion

What future holds for plasmas in nanotechnologies may be perhaps best seen in the roadmaps defined by the Japanese Society of Applied Physics (JSAP): http://www.jsap.or.jp/english/index.html. It may also be seen from the roadmaps for integrated circuits and projections for new technologies. With nanomaterials, once the current materials exploration phase has matured and priority exploitation paths determined, the process and equipment requirements can be more clearly defined. Only then it will become possible to design sources for precise ion energies or for selecting particular species with increasingly accurate control to meet the demands of nanotechnologies in an optimal fashion.

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