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Introduction

This monograph aims to introduce the basic concepts and applications of plasma nanoscience, a rapidly emerging multidisciplinary research area at the forefront of, the physics of plasmas and gas discharges; nanoscience and nanotechnology; astrophysics; materials science and engineering; surface science and structural chemistry [4], and to show the importance of plasma environments in nanoscale processes spanning from astrophysics to plasma-aided nanofabrication in the laboratory.

Plasma nanoscience is a multidisciplinary topic which involves knowledge, methods and approaches from a broad range of disciplines, ranging from stellar astrophysics and astro-nucleosynthesis through “traditional” nanoscience and nanotechnology, materials science, the physics and chemistry of plasmas and gas discharges, to various engineering, health-related and socio-economic and business subjects. At one extreme, a variety of nanoscale solid objects are produced in the plasmas of stellar environments, while at the other, plasma nanofabrication has had a marked impact on capital investment, economy, trade and other aspects of our lives [5]. As a consequence, one can find reports on plasma applications in nanoscience and nanotechnology in a wide range of publications; from electronic archives to Science, Nature, not to mention numerous monographs and edited books (see, e.g., References [1, 4, 6–8, 21, 22] and references therein).

We will begin this chapter by introducing the main concepts and issues of plasma nanoscience in Section 1.1, followed by a discussion of various reasons why a self-organized nanoworld should be created in a low-temperature plasma environment (Section 1.2). Section 1.3 explains how nature’s nanofab works in generating cosmic dust and discusses the issues related to nanotechnology research directions. In Section 1.4 we introduce the concept of deterministic nanofabrication and briefly discuss some of the most important aims and approaches of plasma nanoscience. Section 1.5 explains the structure of the monograph and gives advice to the reader.

Plasma Nanoscience: Basic Concepts and Applications of Deterministic Nanofabrication
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1.1
Main Concepts and Issues

By “a plasma” one usually implies a fully- or partially-ionized gas with many unique properties attributable to long-range electromagnetic interactions between charged particles, interactions which do not occur in neutral gases. The plasma is usually composed of electrons and two other categories of species, termed “ions” and “neutrals” depending on their charging state. The intrinsic property of the plasma is to preserve its overall charge neutrality, that is, that the combined number of all negatively-charged species is equal to that of all positively-charged species. Species that belong to the “ion” and “neutral” categories are identical except for the presence of positive or negative charges in the case of “ions”. Relevant species can range from individual atoms, molecules, monomers and radicals to chain and aromatic polymers and macromolecules, atomic and molecular clusters, small grains and nanocrystallites and even particle agglomerates and mesoparticles. Amazingly, all these objects can be charge neutral or otherwise charged positively or negatively. The electric charge of such particles varies from a single electron charge for most positive and negative ions to hundreds and even thousands of electron charges for solid nanosized clusters and micron-sized grains.

It is common knowledge that more than 99% of the visible matter in the universe finds itself in the plasma state. Therefore, plasma plays a prominent role in a variety of processes that take place over spatial scales as large as galaxy-scale turbulence, which can be of the order of tens of light years, and as small as atomic collisions and interactions, the latter occurring at distances comparable to the sizes of individual atoms (ca. 0.1 nm). Here we focus on the relatively narrow spatial range, namely ca. 10^{-10}–10^{-5} m, which covers atomic processes and most of the existing microscopic structures. The main attention here will be the assembly of nanoscale objects from sub-nanometer-sized atomic (and also other) building units (BUs) in plasma environments and the discussion of the role of the plasma environment in such processes [23].

The concept of building units is central to plasma nanoscience and is used throughout this monograph to denote all microscopic matter that can be gainfully used to create nanoscale objects. Depending on the specific situation BUs can vary from the most fundamental atoms to macromolecules, nanoclusters, nanoparticles, nanocrystallites and even nanoparticle aggregates [4]. There are numerous examples of plasma-grown nanoscale objects, for example, ultra-small solid dust particles in stellar environments, interstellar gas, cometary tails, the upper layers of the earth’s atmosphere, industrial materials processing reactors, electrostatic precipitators and laboratory plasma devices [24–28]. Additionally there are a number of higher-complexity nanoassemblies of different dimensionality, such as quantum dots (0D), nanotubes, nanoneedles, nanorods, nanowires (1D), nanowalls, nanowells, nanoribbons (2D), bulk nanocrystals, nanocones, nanopyramids, nanoparticles and other nanostructures of complex shapes (3D) synthesized by using laboratory plasma-aided nanofabrication [4,21,22,29–31].

It is noteworthy that in the existing literature most of the above mentioned nanoscaled objects are often termed "nanoparticles" . In turn, the "nanoparticles" are also commonly, and arguably well-justifiably, referred to as the building blocks of nanotechnology. To avoid confusion and emphasize that the nanoassemblies are also built using the smallest bits of matter we use the notion of building units rather than building blocks. And since one of the main aims of this work is to advocate the deterministic approach for plasma-based nanofabrication, we try wherever possible to be more specific when referring to individual nanoassemblies. Nonetheless, in cases where the shape and internal structure are not important we also use the term "nanoparticle". Wherever unconventional terminology is used it is explained at the beginning of the relevant section.

It is interesting to note that carbon nanotubes, arguably the cutting edge research topic at the moment (at least judging by recent citation reports), were first synthesized using arc discharge plasmas [3]. However, the existing approaches for fabrication of exotic nanostructures and functional nanofilms in plasmas still remain process-specific and suffer from cost-inefficient "trial and error" practices. This is mostly due to the fact that the ability to control – in the plasma – the generation, transport, deposition and structural incorporation of the BUs of such films and structures still remains elusive. On the other hand, the idea of deterministic plasma-based nanofabrication is treated with a bit of a caution due to the fact that plasma is inherently unstable and is thus quite difficult to control as controlling tools may introduce fresh instabilities. Recently, advanced non-linear dynamic techniques suited for instability control in low-pressure cold plasmas through chaos control mechanisms have been developed [32]; however, most of the existing plasma nanotools still have relatively weak control capacities at the microscopic level. To this end our basic understanding of intimately interlinked elementary processes in the ionized gas phase and on solid surfaces during the plasma-based nanoassembly needs to be substantially improved [23].

This is one of the main issues plasma nanoscience deals with. In this monograph we discuss a broad range of problems related to the assembly of nanoscaled objects in various plasma environments ranging from stellar envelopes in astrophysics to nanofabrication facilities in research laboratories and commercial nanofabs of the near future. Further, we will elucidate the naturally occuring self-assembly of nanometre-sized particles in the universe and how to approach the problem of deterministic synthesis of exotic nanoassemblies in laboratory plasmas.

We will also address the important issue of how to challenge one of the previously intractable problems of *deterministic* plasma-based nanofabrication, namely the ability to create nanosized objects with the required composition, structure and properties for their envisaged applications. This level of determinism is based on the relation between the macroscopic process parameters and the eventual function and performance of the nano-object in question and can be termed macroscopic determinism.

On the other hand, from the viewpoint of fundamental science, the required level of determinism can be achieved by properly creating, manipulating and arranging elementary building units into nanoscale assemblies in a way that will eventually determine the highly unusual properties of such nano-objects. This is in essence the method for creating exotic, unusual forms of matter by arranging "the atoms one by one the way we want them" envisioned by R. Feynman in his speech "There is plenty of room at the bottom" at the Annual Meeting of the Americal Physical Society on 29 December 1959 [2]. This is exactly what we are aiming to discuss in this book, with the specific focus on the arrangement of atomic building units in various ionized gas environments of plasma discharges.

As will be seen from the following discussion, microscopic determinism can be achieved via bridging macroscopic and microscopic processes that are characterized by spatial scales that differ by nine orders of magnitude! Indeed, typical dimensions of plasma nanofabrication facilities (ca. 0.5 m) are more than a billion times larger than the sizes (ca. 0.1 nm) of adsorbed atoms (adatoms) that self-assemble into intricate nanoassemblies and nanopatterns on solid surfaces.

One possibility [4] is to manipulate the plasma-generated species in the plasma sheath that separates the plasma and solid surfaces and to control self-organization of nanostructure building units on plasma-exposed surfaces and their insertion into nanoassemblies (NAs). By nanoassemblies, we will hereinafter refer to any solid object with at least one dimension larger than approximately 1 nm. Nanoassembly can also mean the process of arrangement of subnanometer-sized building units into structures with at least one dimension exceeding approximately 1 nm. This concept involves appropriate preparation of building units and the actual synthesis of the NA and is illustrated in Figure 1.1. If

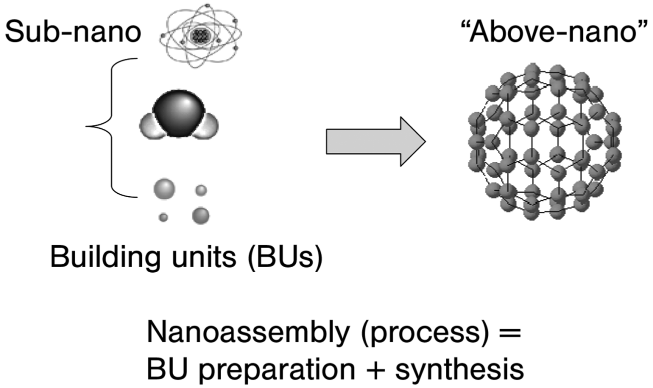


Figure 1.1 Basic concept of nanoassembly.

appropriate, the process of nanoassembly can also involve removal or exchange of bits of matter.

The word "approximately" was added deliberately to this definition even though our commonsense suggests 1 nm as the most obvious lower size limit of nanoassemblies. However if we are dealing with a nanocluster of 0.5 nm diameter, it would be more accurate to consider it as a "sub-nanoassembly" (since it is constructed from more elementary building units) or as a building unit of larger nanostructures and nanoassemblies. Additionally, the diameters of surface-bound single-walled carbon nanotubes (SWCNTs), the most common nanostructures, which were always considered to exceed 1 nm, have in the last few years shrunk to approximately 0.6–0.7 nm. Does this mean that such ultra-thin SWCNTs with lengths well in the micrometer range should be excluded from the list of common nanoassemblies? Of course not! Instead, the lower limit for at least one size of nanoassemblies should be flexible and not necessarily be a fixed value of 1 nm. For example, to include micron-long and 0.7 nm thin SWCNTs in the list of nanoassemblies this lower limit should be reduced to below 0.7 nm. This might spark a discussion on the smallest diameter a single-walled nanotube can have yet having a length of excess of 1 μm. This is one of the as yet open questions in nanoscience; it will be addressed in the carbon nanotube-related section of this monograph.

By "nanofabrication" [5] one usually means the combination of a nanoassembly process and a suitable process environment; for example, synthesis of 1.5 nm-sized SiC quantum dots on a silicon surface in a thermally non-equilibrium low-temperature plasma of a $SiH_4 + CH_4$ gas mixture. However, common usage suggests that fabrication ultimately means producing some commercially marketable goods (otherwise this might be just a sophisticated academic exercise to satisfy scientific curiosity!). Therefore, at the very least, the above combination *nanoassembly* + *process environment* has to be complemented by one more component: *function* (ultimately related to the envisaged applications) to warrant serious consideration as *nanofabrication*. In simple terms, nanofabrication implies production of functionalities, elements, materials, and ultimately, coatings and devices (using just these examples for simplicity) that contain nanoscale features (e.g., size, nanostructure, nanopores) or have been made by using nanostructures or nanoassemblies as building blocks. Thus, synthesis of a carbon nanoneedle-like (at least potentially operational) microemitter mounted in a nanosized electron emitter cell or ordered arrays of luminescent quantum dots on stepped terraces on Si(111) surfaces are viable examples of nanofabrication.

Therefore, the ability to optimize the process environment and parameters to produce (at least potentially) the required function(s) of the nano-objects and show unique and unusual (intrinsic to the nanoscale only) properties is what differentiates between a simple process of nanoassembly (which often proceeds via self-assembly) and nanofabrication.

Plasma nanoscience is often understood as a bridge between plasma physics and surface science. Currently, there are enormous problems with the compatibility of *in situ* plasma diagnostics and surface science characterization techniques. Thererefore, researchers have to rely on quite separate experimental studies of the plasma processes and (in most cases *ex situ*) nanostructure characterization. On the other hand, there is a vital demand for reliable physical models and numerical simulations that could bridge the "unbridgeable" gap between gas-phases and surface processes separated in space by nine orders of magnitude.

In the following, we will discuss some advantages of using plasmas to generate, process and transport a variety of building units and then using them to synthesize nano-scale objects and, moreover, control "uncontrollable" atomic-level self-organization processes on plasma-exposed solid surfaces. We will also introduce basic concepts of plasma nanoscience and overview the ongoing reserach efforts aimed at achieving the ultimate goal of plasma-based deterministic synthesis of various nanostructures and elements of nanodevices. Finally, we will show that plasma nanoscience is a broad multidimensional notion that covers all situations in the universe and terrestrial laboratories wherein the nanoassembly process sketched in Figure 1.1 occurs in an ionized gas environment rather than merely the surface science of plasma-exposed surfaces.

1.2

Self-Organized Nanoworld, Commonsense Science of the Small and Socio-Economic Push

In the previous section we have mentioned self-organization and self-assembly as very useful and effective tools for nanoassembly. Both terms are crucial for nanoscience and nanotechnology and there exist plenty of definitions (see, e.g., Introduction to Nanotechnology [6]). However, such definitions generally do not reflect the overwhelming variety of different situations where self-organization processes play a role. Here we will only give working definitions to both of the terms; these definitions, although accurate in general, will mostly be related to those nanoassembly processes in ionized gas environments of our interest here.

Before giving the definitions we need to introduce the appropriate environment where self-organization and self-assembly take place. In this regard it will be prudent to introduce a broad term, "nanoworld", which will be used to denote various ensembles of nanoassemblies, with patterns or ordered arrays of individual nanostructures on solid surfaces as a typical example. This nanoworld is exposed to the plasma as shown in Figure 1.2. It is important to note that the nanoworld can have dimensions much larger than the sizes of individual nanoassemblies that compose it. In the example shown in Figure 1.2, the nanoworld on a plasma-exposed solid surface is made of small (1–20 nm in size) nanoislands, which can occupy large surface areas comparable to those of silicon wafers presently used by microelectronic industry.

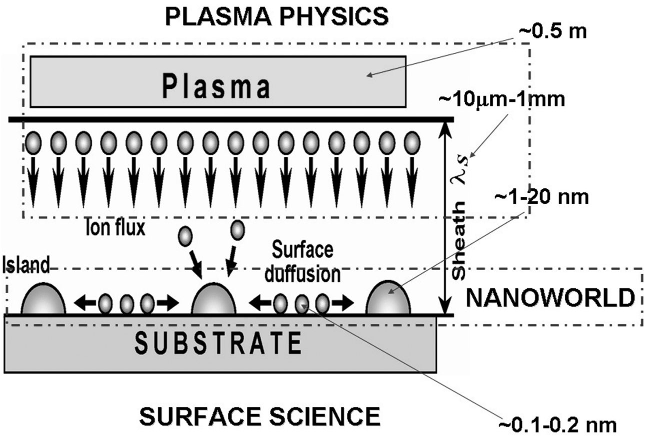


Figure 1.2 Nanoworld exposed to a plasma. Typical sizes of the plasma sources, transition layer (sheath) between the plasma and solid surface are shown.

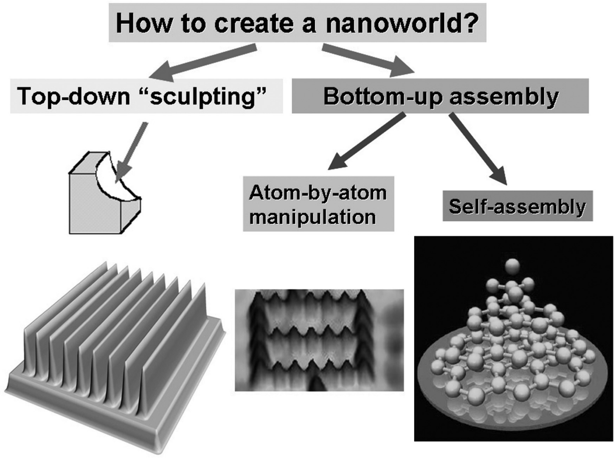


Figure 1.3 Two fundamental approaches of modern nanotechnology. Bottom-up approach has two basic possibilities: either atom-by-atom manipulation (nanomanipulation) or self-assembly.

In some cases the nanoworld can be limited to a single nanoassembly, this is the case for a single nanocluster levitated in a gas. It is also possible that the nanoworld can have macroscopic dimensions in all three dimensions yet having nanoscaled features. Dense arrays of micrometer-long single-walled carbon nanotubes with an average thickness of approximately 1 nm and bulk films with nanocrystalline or nanoporous features are especially good examples.

Some readers might find the introduction of this new term a bit artificial. The main reason we have introduced the nanoworld as a special term is the need to have the most generic notion that would be appropriate for virtually all objects that have any feature with at least one size ranging from sub-nanometers to the upper limit of approximately a few hundred nanometers. This generalization allows us to treat surface-bound dense SWCNT forests, ordered arrays of quantum dots, nanolayers and heterostructures, nanoporous and nanocrystalline films, films with nanoscale inclusions (e.g., nanocrystalline or simply cluster-sized defects), nanometer-sized trenches, vias and interconnects in nanoelectronic circuitry, complex assemblies such as nanoelectromechanical systems (NEMS), nanophotonic functionalities, as well as freestanding (e.g., gas borne) nanoassemblies from the same principles.

Once we have reached a convention on what the nanoworld is, the most obvious next step would be to identify plausible ways to create it. The two basic approaches of nanoscience are sketched in Figure 1.3. In the first, the "top-down" approach, smaller objects are carved from larger ones as sketched on the left side in this figure. For example, one can use energetic ion beams or reactive radicals to reduce the size of an initially micrometer-sized crystal to the nanometer range using the effects of physical sputtering and reactive chemical etching, respectively. The "top-down" approach based on masks, pattern transfer and reactive chemical etching is widely used in microelectronic manufacturing to fabricate patterns of two-dimensional trenches in silicon wafers or ordered arrays of high-aspect-ratio cylinders for two-dimensional photonic crystals. In this case reactive species etch holes through a mask placed on top of a bulk substrate; nanostructures are formed after a sufficient amount of matter has been removed from the bulk material.

It is worth noting that this technique requires pattern transfer and delineation, which is commonly achieved using microlithography approaches, which are based on micropattern transfer through natural templates or artificially created masks. Porous alumina with hexagonal nanopore arrays is perhaps the best example of natural templates used for creating ordered arrays of metal (e.g., nickel-based) catalyst nanoparticles required for carbon nanotube synthesis. This is also an example of a templated top-down nanofabrication approach, even though bits of matter are added to the substrate through the mask rather than removed. Artificial masks can be prepared, for example, by steering focused ion or laser beams about a solid surface; these beams can be used to drill small holes in thin and soft materials.

From the above arguments it becomes clear that "top-down" nanofabrication approaches critically depend on the ability to remove or add bits of matter along pre-delineated patterns. In simple terms, the resolution of this process strongly depends on the characteristics (hole patterns and sizes) of the masks involved in nanofabrication. Therefore, the smaller the nanostructures which are targeted, the smaller should be the mask holes. For example, using porous anodized alumina one can produce masks with tuneable pores of diameter ca. 10–500 nm, heights up to 6 μm, and nanopore densities of up to 10^{11} cm^{-2} (minimum spacing between the pore centres of ca. 30 nm), arranged in fine hexagonal arrays [33,34]. These holes can be used to fabricate, for example via a hot-filament evaporation process, hexagonal arrays of metal catalyst islands of sizes about the same as the sizes of the template nanopores. These catalyst islands can in turn be used to synthesize carbon nanotubes and related structures with diameters almost the same as the nanopores, which is 10–500 nm as mentioned above. Unfortunately, the sizes of nanopores in such templates are usually very non-uniform with the size dispersion reaching 100% and even more! This means that the carbon nanotubes will also be very non-uniform in size, and moreover, must be separated by at least 30 nm, the minimum inter-nanopore spacing.

However, what can be done as regards ultra-thin single-walled carbon nanotubes which require metal catalyst nanoislands as small as 0.6–0.7 nm in diameter? Moreover, how does one position such nanoislands very close to each other (inter-island spacing $\sim$ island diameter)? How should one design and create such a mask with holes so small and dense that they would be suitable for condensation of metal atoms? This size range is apparently far too small for the "top-down" nanofabrication despite very impressive recent advances in nanolithography [35] and more sophisticated nanopattern transfer techniques such as nanopanthography [36]. Generally speaking, "top-down" nanofabrication already experiences substantial problems in the sub-100 nm range [5]. Therefore, the global economic and technological demand for continued reduction in feature sizes in microelectronic devices (which as of mid-2007 are approximately in the 60–70 nm range in width and as thin as a few atomic layers) will inevitably move the top-down approach to the sidelines of industrial nanofabrication.

So, is there any other approach that can outperform and potentially replace the commonly used top-down nanofabrication techniques? If we consider the ultra-small metal (e.g., nickel) nanoislands required for the synthesis of single-walled carbon nanotubes, how many atoms do they contain? Such semi-spherical islands are generally constructed from approximately 15-25 atoms.

In such cases involving small number of atoms, would it not be wise to consider manipulating and stacking them one by one, the way Feynman suggested in his visionary speech? Yes, indeed for such a small number of atoms one could use another procedure, the "bottom-up" nanomanipulation approach, sketched in the middle of Figure 1.3. There are numerous reports on using nanomanipulators to displace and then reposition individual atoms into atomic chains or structures similar to the commonly known "atomic coral" [6]. At present, suitably adjusted scanning tunnelling and atomic force microscopes (STM and AFM, respectively) are extensively used for this purpose. By varying the amplitude, duration and sequence of voltage pulses applied between the tip of the microscope and the sample surface, one can induce electric charge on, or polarize otherwise charge-neutral atoms. In this way one can lift, move, replace, or otherwise manipulate individual atoms. Interestingly, this process involves ionization – the most important physical process that leads to the creation of a plasma! However, in nanomanipulation one ionizes only a very small number of atoms, which cannot qualify as a plasma. Nevertheless, it is worth noting that ionization is used not only in plasma-based nanotools!

We should also stress that the nanomanipulation technique is exactly what Richard Feynman meant by stating “atom by atom, the way we want them”. In other words, to create a 50-atom nickel cluster on a silicon surface (or, for example, a Ge/Si quantum dot of a similar size), a nanomanipulator device (e.g., STM) should repeat the

ionize/polarize → *lift/remove* → *move* → *stack*

sequence at least 50 times (if everything works well) for each island. Aiming to achieve any reasonable Si surface coverage by SWCNTs, one would be looking at creating something in the order of ca. 10^{12} (or even more!) nanoislands per square centimeter. This enormous number of nickel clusters would thus require approximately 5×10^{13} atoms to be ionized/polarized, lifted, moved, and then stacked *individually*! If every move takes only 1 s, then the whole process of synthesizing the required array of nickel nanoislands would take approximately 10 million years!

But what if the atoms do not want to be stacked where they are moved by the nanomanipulator arm? What if the position they are put into is not suitable or is unstable? Will the atoms remain firmly stacked in this place or would they prefer to move further? These are just a few questions that need to be considered before committing time, resources and effort to this arguably very precise and sophisticated technique, which is commonly accepted as the best nanotool to manipulate very small numbers of individual atoms.

The most obvious and nature-inspired answer is just to do nothing and let the atoms do what they want, in other words, self-assemble into nano-objects of nature’s choice. One of the most powerful of nature’s tools in this regard is the fundamental energy minimization principle

$$\mathcal{E}_{\mathrm{NA}} = \mathcal{E}_{\mathrm{NA}}^{\mathrm{min}} < \Sigma \mathcal{E}_a$$

which states that the ensemble of atomic building units should self-assemble to ensure that the resulting nanoassembly will have a total energy $\mathcal{E}_{\mathrm{NA}}$ less than the combined energy of individual building units $\Sigma \mathcal{E}_a$. Moreover, the assembly process will proceed along the minimum-total-energy pathway, which means that $\mathcal{E}_{\mathrm{NA}}$ will have the minimum possible value $\mathcal{E}_{\mathrm{NA}}^{\mathrm{min}}$ under equilibrium conditions.

From this point of view, the ultimate crux of nanoscience is to create unusual arrangements of atoms by whatever means, be it “top-down” nanofabrication, nanomanipulation, or self-assembly. To illustrate this concept, let us assume that there is some structure with a “regular” (reference) atomic structure and we want to create a similar structure but with another arrangement of atoms, using one of the basic approaches of the nanoscience. It is noteworthy that "regular", nature-inspired structures are the simplest, the most stable and satisfy the minimum energy principle under equilibrium conditions.

Therefore, our commonsense would suggest that nature's approach is actually nothing else but the line of the least resistance. Indeed, the nature-preferred equilibrium conditions are normal for every particular environment; such conditions include room temperatures ($T = 20\,^{\circ}C$) and gas pressure of 1 atm ($= 760\,mm$ mercury). Quite similar normal conditions exist elsewhere, outside the earth; moreover, such conditions are the most appropriate for the normal (line of the least resistance!) course of events and are chosen by the "lazy" yet "astute" nature.

For example, under normal terrestrial conditions, graphite is the most abundant and stable form (allotrope) of carbon. Carbon atoms are arranged in flat graphene sheets with a periodic hexagonal atomic network. Bulk graphite is made of parallel stacks of graphene sheets separated by a small interlayer spacing. Interestingly, the strength of atomic bonds between different graphene sheets appears lower compared with the inter-atomic bonds within each two-dimensional sheet. This is the reason why it is so easy to remove these sheets one by one, which is the way conventional pencils work! We can consider this atomic arrangement as a regular reference structure.

It is worth recalling at this juncture that creating exotic nanoassemblies implies applying some additional effort to create and use unusual, non-equilibrium conditions to rearrange the atoms in a different way than in the reference structure. Let us consider what that means in the context of carbon nanomaterials. If high pressures are applied and some other conditions are met, by using exactly the same carbon atoms one can synthesize diamond, a very different carbon material. This new material has a quite different crystalline lattice made of pyramid-like unit shells. These shells are interlinked three-dimensionally; this is why it is no longer possible to scrape off atomic carbon layers one by one as was possible in the case of graphite. It goes without saying that pure diamond and a range of diamond-like carbon (DLC) materials exhibit very different physical and chemical properties compared to graphite. We reiterate that diamond is usually synthesized under non-equilibrium conditions, such as high pressures, and once synthesized, remains stable at normal conditions. Even more non-equilibrium conditions are used to synthesize a very special diamond-like material – nanocrystalline diamond. More importantly, these non-equilibrium conditions are found in thermally non-equilibrium low-temperature plasma, a common environment for the synthesis of ultrananocrystalline diamond – a nanoworld made of ultra-small (ca. 1–3 nm in size) sp^3-hybridized (diamond-like) carbon [37,38].

Under different non-equilibrium synthesis conditions, which include relatively high temperatures and extrusion of carbon atoms through metal (e.g., nickel) catalyst nanoparticles, one can assemble carbon nanotubes. The same carbon atoms are now arranged in a similar graphene sheet but rolled into a graphitic tubule. Carbon nanotubes are also stable and also meet the energy minimum principle but under *modified* process conditions. Furthermore, their properties appear to be very different from the "regular" graphitic structure. Carbon nanotubes synthesized under non-equilibrium conditions (such as arc discharge plasmas in Iijima's pioneering experiments [3]) also remain stable under normal conditions and can be used for a variety of purposes including hydrogen storage, reinforced ceramic and polymer composites, electron field emission and wire-like interconnects in nanodevices to mention a just few.

Generalizing the above examples, we can state that nanoscience and nanotechnology aim at *using specific, non-equilibrium process conditions to create unusual and otherwise non-existing ultra-small nano-objects*! An important point to keep in mind is that these nano-objects must remain stable once returned to normal conditions.

Let us now return to the discussion of the possibilities offered by self-assembly and try to relate that to non-equilibrium process conditions. To begin with, let us pose a simple question: from the self-assembly perspective, what should one expect from a randomly chosen ensemble of atomic building units? Using the arguments we have already developed, it becomes clear that if the BUs are left without any external action and under equilibrium conditions, the BUs will simply self-assemble into the froms nature and the energy minimum principles prescribes under the given (in this case normal) conditions! Therefore, if one wants to create an exotic yet stable nano-object via self-assembly, suitable non-equilibrium conditions are required. In this case one can reasonably expect that self-assembly will proceed quite differently and will result in an exotic arrangement of atoms, otherwise non-existent under the equilibrium conditions. It is very important to stress that altering the process environment is perhaps the only way to control self-assembly, since the BUs are left without any external action and are not manipulated externally by any nanomanipulator arm!

We hope that the reader has become convinced that self-assembly can be effectively controlled by the nanofabrication environment. And with that we have just inadvertently revealed the fundamental concept of *guided self-assembly*, which is central to the entire nanoscience!

In this regard, it would be instructive to note that the ionized gas (plasma) environments of our interest here in most cases offer strongly non-equilibrium conditions. Capitalizing only on this point, we are now in a very good position to state a priori that low-temperature plasmas are excellent process environments for nanofabrication. For more background on why such plasmas can be regarded as a versatile nanofabrication tool please see [4]. These reasons will be discussed throughout this monograph and supported by relevant experimental and theoretical/computational results. More importantly, from the following consideration it will become clear that low-temperature plasmas have a number of effective (electric charge and field-related) tuning knobs to guide this self-assembly.

Moreover, as will be clarified in Section 1.3, nature creates non-equilibrium conditions (simply by adding a weakly ionized gas component) deliberately (or in other words, deterministically) to create a sufficient amount of solid dust particles in stellar environments. The ionization degree, one of the most important parameters of weakly ionized plasmas, turns out to be a very effective control of the formation of self-assembled nanoparticles.

Let us now complete the introduction of the main concepts used in this monograph and more specifically, in the context of plasma nanoscience. In this context, by self-assembly, we will imply a "bottom-up" process of arrangement of building units into subnanometer and nanometer-sized objects without any external action. In a sense, the nanoassemblies build themselves on plasma-exposed surfaces.

It is noteworthy that the terms self-assembly and self-organization are often used interchangeably in the literature; moreover, both terms are also frequently related to the formation of structured patterns such as quantum dot arrays. In this monograph we will try to avoid this ambiguity by using self-organization as a more global and generic term related to the nanoworld rather than an individual nanostructure. More specifically, self-organization phenomena considered in this monograph will also include the evolution of structural, size and positional order in nanoassembly patterns on solid surfaces from essentially non-uniform patterns, which cannot be merely attributed to self-assembly of individual nanostructures. In the following we will use the term "self-organized nanoworld", which encompasses any nanoscale objects that are formed exclusively via self-assembly and self-organization processes.

We hope that we have made our terminology and contextual issues more transparent to the reader. It should be emphasized, however, that many of the terms, although used commonly, do not have conventional definitions and their meaning may vary from one context to another. For example, many literature sources separate nanofabrication and self-assembly and attribute top-down and nanomanipulation processes to the nanofabrication. However, we believe that there is no good reason whatsoever why nanofabrication should not include a self-assembly step. Moreover, it is extremely important to note that to include self-assembly as a commercially viable nanofabrication approach, one should learn how to control it and so create exactly what is required. Thus, we have just arrived at the new, important notion of controlled (ultimately deterministic) self-assembly (and more globally, self-organization) – something which is still remains elusive despite the enormous efforts of a large number of universities, research and development institutions and industrial laboratories worldwide! However, if the level of understanding of how self-assembly works is poor (as it presently is!), nanofabrication and self-assembly are indeed quite separate issues and this is reflected in the existing terminology.

After this seemingly long discussion of basic terms and relevant issues, we will now try to answer one of the central questions of plasma nanoscience:

why should the nanoworld be self-organized and created in a plasma?

To answer the first part of this question let us consider a strong socio-economic push for miniaturization and nanotechnology. In the mid-1960s the introduction of computer and IT technologies transformed virtually every sector (manufacturing industry, transport, agriculture, finance, trades, government, defence, etc.) of our society and revolutionized the way we live. Many economists refer to this as the computer and communications revolution of the mid-1960s. Computer-based technologies received a rapid boost, which after a certain period of time slowed down and reached saturation in the mid-1990s. This behavior is commonly referred to as the "S-curve of technology".

We are currently entering the Information Age, when everyone (including developing countries) will (hopefully!) have a wireless broadband access to global information networks, and all information can be retrieved and processed almost instantly using palmtop computers with the capabilities of powerful present-day workstations. This is just one impression of what the Information Age can bring to society and how it can dramatically change our lives. In fact, the actual possibilities of what new technologies will be able to do (e.g., store and process) with enormous amounts of information go beyond our imagination.

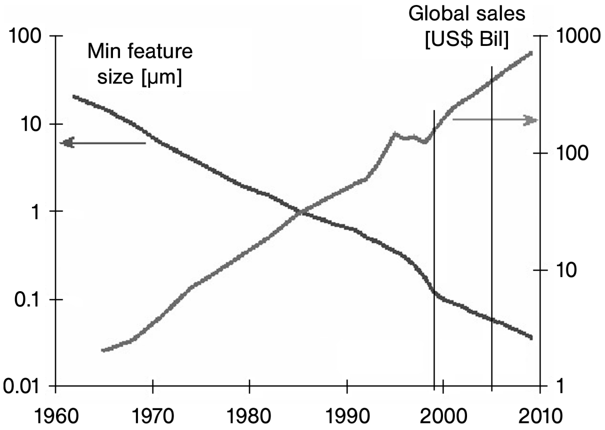


Figure 1.4 Minimum feature sizes of integrated circuitry and global sales of semiconductor microelectronic products (after [39]).

These new Information Age technologies require more powerful and faster computers in ever greater numbers. This results in a rapidly growing demand for better, faster computers and eventually in an exponential increase of the global market for computer-related products.

At this stage it would be instructive to recall that the main component of any computer is its motherboard which includes a central processing unit (CPU) and random access memory (RAM) on a semiconductor chip platform. Thus, to satisfy the demands of the Information Age, computer CPUs should work much faster and RAMs store a lot more information without any substantial increase in the microchip surface area. This in turn has led to an *exponential* increase of the total annual market (TAM) of semiconductor-based microelectronic products from only a couple of billion $US in the mid-1960 to more than $US 500 Billion in 2005 [39]. As can be seen from Figure 1.4, this amount is set to rise further to $US 1 trillion in 2010 and has excellent prospects of reaching $US 1.5 trillion in the foreseeable future.

However, careful size-cost-function-demand calculations show this can only become possible if the cost per electronic function falls at a rate of at least 18% per year to drop below 1 microcent per transistor within the next few years. To sustain this significant cost reduction while maintaining the cost of one square centimeter of a silicon wafer in the few $US range, the feature sizes (which determine the number of field effect transistors (FETs) and ultimately the number of logic operations a computer can perform per second) should reduce in size as shown in Figure 1.4. As can be seen from Figure 1.4, to reach $US 1 trillion in sales (thus, satisfy

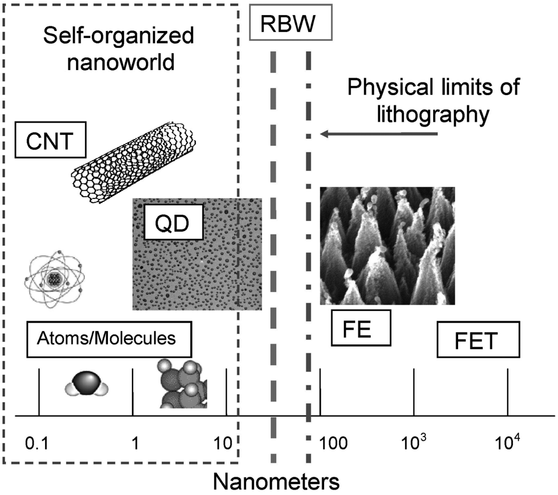


Figure 1.5 Self-organized nanoworld, physical limits of lithography, and red brick wall (RBW) of semiconductor technology. CNT = carbon nanotube; QD = quantum dot; FE = field emitter; FET = field effect transistor.

the demand of the Information Age), the feature sizes must be reduced to at least 20–30 nm by 2010–2012.

Therefore, there is a very strong socio-economic push to develop semiconductor features with sizes in the 20–30 nm range and below. If we have a look at the typical sizes of most common building units and nanoassemblies depicted in Figure 1.5 we will immediately notice that these sizes are comparable with those of carbon nanotubes and semiconductor quantum dots. Moreover, upon reduction of the nanostructure sizes to approximately 10 nm (which is of the order of the exciton's Bohr radius for some common semiconductors) quantum confinement effects begin to manifest. These effects lead to unique electronic properties of low-dimensional nanostructures not available in bulk materials. Therefore, the "true" nanoworld begins at spatial scales of approximately 10 nm as shown in Figure 1.5.

Another feature of Figure 1.5 is that it shows the present-day limits of lithographic tools (dash-dotted line) and also the ultimate physical limits the top-down nanofabrication approaches can achieve in the foreseeable future. A set of these ultimate physical limits is often referred to as the red brick wall (RBW) of semiconductor technology. Even the 20–30 nm features the semiconductor market demands to be achieved by the year 2010–2012 find themselves on the other, "nanoworld's", side of the RBW. Therefore, the strong socio-economic push forces one to develop means to fabricate 20–30 nm and smaller features and eventually “barge” into the “true” nanoworld with outstanding electron confinement capabilities.

It needs to be added at this stage that there is another group of breakthrough technologies with a rapidly expanding multi-billon dollar market that also demand substantially reduced sizes of nanoscale objects. As the reader may have guessed we are talking about biotechnology, which is becoming increasingly reliant on sophisticated nanotechnology products. The examples are numerous, for instance, quantum dot-based luminescent biomarkers, nanoparticle-based drug delivery systems, biocompatible and bioactive nanofilms and various biosensors on nanostructured film platforms. Synergy of nanostructured materials and biology gave rise to a rapidly emerging field of bionanotechnology. It is commonly accepted nowadays that the transition to the new industrial age will be marked by a synergetic triangle formed by information and communications technology (ICT), biotechnology and nanotechnology [39].

To be a bit more specific, let us concentrate on the link between the ICT and nanotechnology and consider how to challenge the problem of ultra-small size range of the “true” nanoworld. Some may say that this is easier said than done. Indeed, by which means are we supposed to achieve this? Since the required size range is on the other side of the RBW, the top-down nanofabrication approaches may not be applicable anymore. The other remaining choices are thus nanomanipulation and self-assembly (Figure 1.3). However, due to the extremely large number of atoms that make even a tiny interlayer in a single metal-on-semiconductor field effect transistor (MOSFET), the nanomanipulation approach should be immediately taken off the list.

Therefore, we are left with the only one option:

“True” nanoworld is self-organized and we must “barge” into it to satisfy the socio-economic push for better, faster, cheaper computers!

Now the question is, what does this have to do with plasma and plasma nanoscience in particular? To answer this seemingly non-trivial question one should note that computer microchips are commonly produced in semiconductor fabs equipped with sophisticated plasma microfabrication facilities. In fact, the semiconductor industry widely uses inductively coupled RF plasma devices as sources of low-temperature thermally non-equilibrium plasmas. A representative plasma source of this type is shown in Figure 1.6.

The examples of plasma-based processes used in semiconductor microfabrication are numerous: reactive highly-anisotropic and highly-

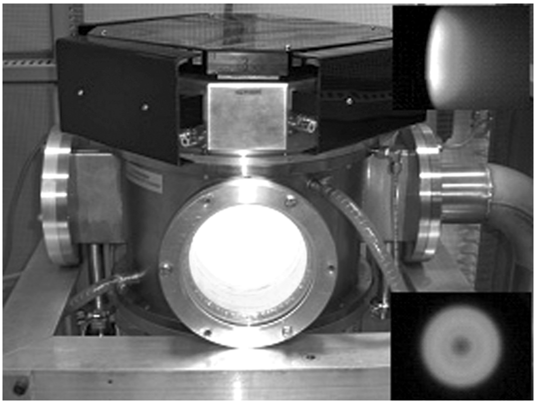


Figure 1.6 A source of high-density, highly-uniform inductively coupled RF (∼460 kHz) plasmas. Plasma sources of this type are widely adopted in semiconductor industry as a benchmark plasma reactor. Almost 50% of process steps in USLI micromanufacturing use low-temperature, thermally non-equilibrium plasmas. The insets show plasma glows around the magnetron sputtering targets which serve as sources of solid precursors. Photo courtesy of the Plasma Sources and Applications Center, NTU, Singapore.

selective chemical etching is used to fabricate deep high-aspect-ratio trenches in semiconductor wafers; plasma enhanced chemical vapor deposition is used to deposit ultra-thin (with the thickness approaching a few atomic layers) interconnect and copper diffusion barrier layers as well as surface activation and passivation; electric-field guided ion fluxes in the plasma-assisted physical vapor deposition (commonly known as i-PVD) are used for metallization of deep semiconductor features where neutral species cannot penetrate, just to mention a few practical applications. For a detailed coverage of the most important aspects of applications of plasma-based processes in microelectronics the reader should refer elsewhere [40]. Here we should stress that the total cost of plasma facilities used by the semiconductor industry worldwide is enormous and is clearly in the multi-billion range.

It is now a good time to move to the next step and pose another important question: is it possible to create a self-organized nanoworld made of nanoassemblies smaller than 10 nm in a typical plasma environment as currently used in semiconductor microfabrication? So far plasma-based nanotools, although extremely successful in the syntheis of carbon nanotubes and related structures, have not shown particularly impressive results in nanoassembly of low-dimensional semiconductor structures, which are of utmost importance for the creation of nanodevices based on quantum confinement effects. The reasons for this will be analyzed elsewhere in this monograph by using the arguments of balancing the demand and supply of plasma-generated building units. This is perhaps the most likely reason why sophisticated and extermely expensive nanotools such as molecular beam epitaxy (MBE), where one can precisely control incoming fluxes of neutral species, have shown a clearly better performance compared with the plasma nanotools.

Therefore, one might be tempted to start replacing plasma microfabrication facilities with non-plasma-based nanofabrication tools to enable production of "self-organized" computer microchips as soon as possible and no later than in 2012. However, the cost of such a replacement of entire microchip production lines may be completely unsustainable, taken that the yearly demand will be well above $US 1 trillion at that time. And one should also not forget about possible disruptions of computer production cycles, which may cost many billions of dollars.

But why is this radical change needed? To allow the use of tools which can create those self-organized nanoworlds so badly needed to satisfy the demand of the Information Age for better, faster, smarter and cheaper computers! And these tools need to replace the existing multibillion dollar pool of plasma facilities currently used by the semiconductor industry worldwide.

However, before committing such enormous resources and efforts one should make absolutely sure that it is not possible to create the self-organized nanoworld with the existing production lines, which, as we emphasize, are at present largely plasma-based. Indeed, why replace the existing production lines without first trying to create self-organized nanoworlds in the existing plasma-based microfabrication facilities!

Therefore, we have arrived, again inadvertently, at the conclusion that if we want to avoid huge losses because of major disruptions in the microchip (actually, nanochip!) production we need to learn

how to create a self-organized nanoworld in a plasma

and, moreover, in a *deterministic fashion*. Amazingly, this is what plasma nanoscience is all about!

From the above it becomes perfectly clear that there is a very strong socio-economic push to further develop plasma-based nanofabrication approaches and techniques and make them versatile nanotools of the new industrial age dominated by a synergy of information and computer technology, biotechnology and nanotechnology. Without a successful synergy of the three breakthrough technologies the S-curve of technology may not rise quickly enough and the age of transitions may stretch to quite a number of years, thus significantly delaying the much expected new industrial revolution.

What is even more amazing is that nature also encourages one to more widely use plasma-based environments for deterministic nanoassembly. In the following section we will discuss how nature's mastery works in the self-assembly of nanometre-sized particles in the universe. We will also comment on the nanotechnology research directions of the U.S. Nanotechnology Initiative.

1.3
Nature's Plasma Nanofab and Nanotechnology Research Directions

Let us now discuss how exactly nature uses plasma environments to create nano-sized objects. As we have already mentioned above, plasmas constitute more than 99% of the visible matter in the universe. The most striking example of how nature creates solid nanoscale objects from atomic building units is condensation and nucleation of cosmic dust in stellar environments. This process involves structural transformation from atomic (less than 1 nm in size) to nanocluster/nucleate stage (exceeding 1 nm) and, according to the convention we introduced in the previous section, qualifies as a nanoassembly process. In the following we will briefly discuss how the plasma nanofab works in the universe-based nanoassembly of dust grains and comment on the unique and specific roles of the plasma environment [23]. An astrophysical setting where cosmic dust nucleation takes place is sketched in Figure 1.7.

It is a common knowledge that in the universe most of the visible matter exists as a fully- or partially-ionized gas composed of subnanometre-sized particles such as atoms, molecules, radicals and ions. Therefore, synthesis of any bits of matter with sizes exceeding 1 nm (such as interstellar solid dust and other particles of increased complexity) necessarily involves the nanoassembly stage!

First of all, we note that this "above-nanometer" matter is solid and therefore cannot be made of hydrogen or helium atoms. Therefore, something should be done to create atoms of stable solid elements, which will be suitable for nanoassembly purposes. What is remarkable is that hydrogen is far more abundant in the universe than any heavier element such as helium, lithium, beryllium or carbon. Therefore, any heavier elements should be created by nuclear fusion of hydrogen nuclei. Nuclear fusion requires extra-high temperatures of the order of tens of million (or even more, depending on the required energy release) degrees to get the fusing atoms close enough for nuclear forces to come into play. Such high temperatures also serve the purpose of stripping interacting atoms of their electrons to eliminate atomic repulsion at distances com-

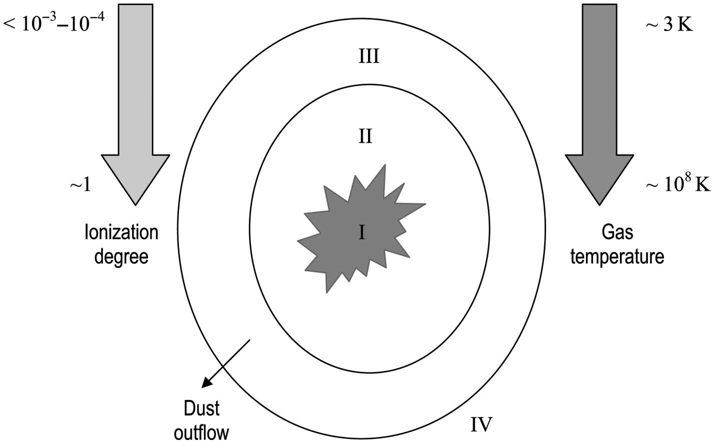


Figure 1.7 Schematic of nature's nanofab [23].
I – star; II – area of nanoparticle nucleation; III – area of further dust growth and expulsion; IV – interstellar space.

parable with the radii of electron orbits (or more precisely, with the sizes of electron clouds as accepted in quantum mechanics). In other words, the gaseous environment should be hot enough to find itself in a hot and fully ionized (plasma) state. Such conditions are met in the interiors of stars. For example, temperatures inside the sun can be as high as 15 million degrees. Nuclear fusion reactions in hot and fully ionized plasmas result in release of enormous amounts of energy and as such sustain the entire existence of the stars and very possible, the universe.

However, here we are not interested in the energy generation processes and refer the interested reader to relevant astrophysical and nuclear fusion literature. What we emphasize is that stellar nucleosynthesis proceeds via chains of nuclear fusion reactions which start from the most elementary fusion of two protons into deuterium (heavy hydrogen) and eventually result in the formation of a large number of elements that are present in stellar environments.

Having a quick look at the Periodic Table of Elements, one would immediately work out that carbon would probably be the best candidate to serve as a building unit of solid nanoscale matter. What is the shortest and most effective way to create carbon using nuclear fusion and starting from protons and neutrons, the elementary building blocks of subatomic matter? One of the possibilities is to combine protons and neutrons into an alpha particle ^4_2He, and then fuse three such particles to form a carbon atom $^{12}_{6}\text{C}$. These reactions can be accompanied by the creation of other particles such as neutrons, positrons, and neutrinos and also by the release of substantial amounts of energy. The actual reaction chains, particles and amounts of energy involved depend on the mass of the star. For example, for stars comparable with the sun the nucleosynthesis processes proceed along a quite different scenario than in heavy (e.g., red giant) stars.

Therefore, the first building units (carbon atoms) suitable for the nanoassembly of solid matter can be generated in fully ionized plasmas of hot star interiors (denoted I in Figure 1.7) as a result of nuclear fusion reactions involving three alpha particles, such as the following "triple-alpha" reaction

$$^{4}\mathrm{He} +^{4}\mathrm{He} \rightarrow^{8}\mathrm{Be}\,;$$

$$^{8}\mathrm{Be} +^{4}\mathrm{He} \rightarrow^{12}\mathrm{C} + 7.367\,\mathrm{MeV}$$

which results in the synthesis of atomic carbon ^{12}C. Interestingly, this element is more effectively synthesized in the interiors of large stars evolved to the red giant and later stages. In fact, red giant stars are commonly recognized as primary sites of carbon synthesis in the universe [41].

New elements created as a result of nucleosynthesis are then carried away in stellar outflows to the star envelopes and then to the interstellar space. Therefore, carbon (and also other species synthesized in hot star interiors via nuclear fusion) condense and nucleate in the relatively cold and partially ionized plasmas of star environments. This happens in the area of primary nucleation denoted II in Figure 1.7. As a result, basic nanoassemblies such as critical clusters are formed [24]. A quite similar process is also possible in planetary atmospheres.

Thus, nature's "nano-mastery" proceeds in three stages. First, building units are generated via nucleosynthesis in hot fusion plasmas of star interiors. This is followed by expulsion of the as-created atomic building units in stellar outflows (in other words, they are delivered where they are required for nanoassembly). Finally, during the third stage the BUs condense into larger assemblies, this time in a much cooler and less dense low-temperature plasma environment. Thus, the whole process can be split into creation, delivery and assembly stages. Let us bookmark this point and compare it later with the building unit-based "cause and effect" nanofabrication approach, which we will introduce in Chapter 2 and commend throughout this monograph.

More observant readers should have already noticed that for some reason nature has chosen cold and weakly ionized plasma as the most suitable environment for the most elementary nanoassembly! Exploring alternative possibilities for nanoassembly in astrophysical environments, we should immediately exclude atom-by-atom nanomanipulation. Indeed, where are nanomanipulator arms (e.g., STM tip) in the universe that could ionize/polarize and move atoms from one place to another? Top-down "sculpting" is, in principle, possible; for example, nonthermal sputtering of amorphous carbon grains can reshape them. However, such processes have very low reaction rates under typical conditions of stellar environments. Therefore, self-assembly remains the only realistic choice.

One can thus write the basic formula that governs the operation of nature's nanofab:

$$\textit{Nature's mastery} = \textit{self-assembly of building units} + \textit{plasma.}$$

As was mentioned in the original article [23], this statement might spark philosophic arguments on the appropriateness of the terminology used. For instance, there are numerous examples of natural self-assembly of biological objects on earth, which do not require plasma as a nanoassembly environment. Thus, one possible alternative term for the phenomenon depicted in Figure 1.7 would be the "universe's nanofab", with a multidimensional notion of the "nature's nanofab" attributed to all natural nanoassembly processes in the universe, in space and on earth. However, some other philosophers would offer counter-arguments based on the fact that earth itself takes its origin from cosmic dust created earlier in the "universe's" nanofab! Moreover, as we have mentioned in the preface, there is a possibility that the most basic building blocks of life were created in atmospheric gas discharges under primordial earth conditions. These and all other philosophical issues of the relevance of the nanoscale processes in the universe and on the earth to the awe of creation are outside the scope of this monograph.

The basic solid nanoassemblies mentioned above may grow further through other mechanisms, such as collection of atoms/ions from the adjacent plasma, and eventually form dust matter [28]. The area where the dust formation process proceeds by this method, is denoted III in Figure 1.7. The dust matter may be expelled into interstellar space, denoted IV in Figure 1.7. More importantly, the dust expulsion may serve a specific purpose, such as synthesis (via reactions on solid surfaces of dust grains) of molecular hydrogen H_2, much needed to maintain a proper chemical balance of the universe [25]. This and similar mechanisms lead to the appearance of various (mostly in simple nanoparticle forms) nanoassemblies in low-density partially ionized interstellar and interplanetary plasmas. To transport such nanoassemblies where they are actually needed (for example, to deliver atomic and molecular carbon for the synthesis of the solar system [42]), nature's nano-factory uses various "conveyor belts" such as high-velocity dust streams or comets [23,42,43]. We will return to the issues related to cosmic dust creation and its role in the universe later in this book.

A straightforward conclusion from the above arguments is that if the laboratory-based nanotechnology aims to be truly nature-inspired, it should ideally be plasma-based. Moreover, as we have already mentioned, the laboratory-based plasma-aided nanoassembly follows the same sequence of steps as the universe-based model, namely, generation of building units in the plasma environment and their transport and assembly into nano-objects [4]. Unfortunately, despite remarkable progress in the plasma-assisted synthesis of nanomaterials and functional nanostructures, the current use of the plasma-based techniques in nanotechnology is still quite limited, and mostly used for the synthesis of relatively simple nanoparticles, nanometer-thick functional coatings, nanocrystalline films and post-processing of nanostructures. Even though each of these are in most cases state-of-the-art on their own, none of them really deal with plasma-controlled self-assembly, the most effective driving force of self-organized nanoworld discussed in the previous section.

At this stage the reader might ask about the actual role of the plasma in nucleation of nanometer-sized nanoclusters and dust particles in the astrophysical situation depicted in Figure 1.7. In other words, why does the nucleation not happen either inside the stars (Area I) or in the interstellar space (Area IV)? The answer to the first part of the question is obvious: star interiors are suitable for generating the first solid atoms as a result of nuclear fusion reactions, but are way too hot for their nucleation. On the other hand, at the periphery of stellar gas envelopes and in the interstellar space (zones III and IV in Figure 1.7) the atom density is too low for the efficient nucleation. It is remarkable that dust nucleation actually takes place in the areas where the gas density is still reasonably high, the temperature is low and a weakly-ionized plasma is present (Area II in Figure 1.7).

It has been suggested that the nano-sized protoparticles appear as a result of ion-induced nucleation, which significantly increases the rates of generation of new solid grains [24]. Amazingly, a very similar conclusion was also made for laser ablation plasmas with the parameters different by many orders of magnitude [44]. Therefore, nature's nanofab actually uses plasma to increase the efficiency of the dust growth process and make it faster. And this sparks some extra optimism to pursue the plasma nanoscience research even further!

Unfortunately, despite all the apparent advantages and existing experience of the nature's nanofab, plasma-based nanoassembly routes have not been highlighted in the Nanotechnology Research Directions of the US Nanotechnology Initiative [45]. This provokes a reasonable question: since our major nanoscience and nanotechnology programs did not adequately follow nature's plasma nanofab mastery (which, as we have seen from the above discussion, explicitly prescribes one to use cold and weakly-ionized plasmas in nanoassembly processes), how did it affect the overall progress in the "nano-area"? Some might even consider this as one of the major reasons for the significant delays of the much expected industrial revolution that would lead us to the "IC-Nano-Bio"-Age.

However, extra care should be taken when assessing what plasma nanotools can and what they cannot do [23]. Let us recall one of the earlier remarks that the basic nature's nanofab formula usually leads to relatively simple, mostly nanoparticle-like nanoassemblies. Such nanoscale objects feature the minimum possible energy, are most stable, and hence, are the easiest to synthesize under equilibrium conditions. If a more complex nanostructure is targeted, some additional effort is required, such as using masks, catalysts, delineated patterns, and so on, which are not readily available in nature's nanofab. Thus, the basic formula should be complemented by the "minimum effort" principle. In this particular "ugly" nanoparticle-making process nature is indeed quite "lazy"! However, nature did spend some effort to ionize the background gas, which effectively leads to higher rates of "ugly" nanoparticle production. Here we stress that if the synthesis of more "beautiful" nanostructures is a goal, then more complex, non-equilibrium processes should be used.

Let us now recall that the main aim of modern nanotechnology is to create *complex* and unusual nano-objects such as quantum dots or nanowires and arrange them into intricate arrays and/or integrating into nanodevices. The relative simplicity of the nanostructures fabricated in nature's plasma nanofab is a possible reason for the common belief that other (e.g., chemical, lithographic, template-directed assembly, etc.) ways to create complex nanostructures and their nanopatterns had a better appeal for their inclusion and better highlighting in the Nanotechnology Research Directions [23,45].

This leads to another couple of concerns. The first and the most obvious is the level of competitive advantage of plasma-based nanoscale processes, techniques and facilities over the most commonly used non-plasma-based ones? Indeed, can plasma nanotools and processes compete with leading atomic-precision techniques and ensure a better quality of the resulting nanoassemblies and a higher process efficiency? Such high-precision, non-plasma-based routes include, but are not limited to, atom-by-atom nanomanipulation (e.g., by using the tip of a scanning tunneling microscope, STM), metal-organic vapor phase epitaxy (MOVPE), atomic layer deposition (ALD) and various modifications of molecular beam epitaxy (MBE) [23].

The future of plasma-based nanotools will critically depend on how realistic the prospects are of them winning this competition. If such prospects are not so optimistic, then it is very likely that plasma-based nanotools and processes will remain in the sidelines of modern nanoscience and nanotechnology and perform only certain steps (even though the number of such steps can be quite large) in nanomanufacturing, in a similar way to how plasma is currently used in microelectronics.

Shall we settle for this, or is there a better, more prominent role for plasma nanotools and approaches? Resolution (and, hopefully, positive) of this vital dilemma is one of the main aims of plasma nanoscience. Research endeavors in this area focus, in particular, on competitive advantages and disadvantages of using plasma-based tools and processes as compared with the leading and most established nanofabrication techniques [23].

At the momment it looks like the only way to resolve the "plasma-or-no-plasma" dilemma is to carry out a detailed investigation into how exactly the majority of nanoscale synthesis processes work. As has already been highlighted above, such processes rely in most cases on guided or controlled self-organization (building units into nanostructures, nanostructures into ordered patterns, etc.) in a specific nanofabrication environment.

Because of the extreme importance of the issue, let us briefly summarize what we have already learned form the previous sections. First, the role of self-assembly processes becomes even more prominent as the sizes of nanoassemblies shrink. Indeed, when the sizes of typical nanostructures become smaller than the presently achievable feature sizes of lithorgaphic patterns and nano-templates, self-assembly becomes the only possible way to control the formation of nanostructures and their self-organization into ordered patterns, the fundamental processes that lead to the formation of the self-organized nanoworld. This is particularly important for nanofabrication of ordered arrays of tiny ($<\sim 10\,\mathrm{nm}$) quantum dots (QDs) or ultra-thin and high-aspect-ratio single-walled carbon nanotubes, which have been successfully fabricated by non-plasma synthesis techniques, such as MBE, MOVPE or CVD.

Therefore, the discussion about the suitability of plasma nanotools for the next-generation of nanofabrication is at the level of their ability to guide self-assembly of building units on solid surfaces, and eventually to create a self-organized nanoworld of "beautiful" (and ultimately properly functioning and useful in applications) nano-assemblies. If the plasma-based methods of controlling self-assembly of building units and nanostructure growth turn out to be competitive in terms of quality, cost efficiency, economic viability and investment risk assessment, plasma nanotools will have a bright future. The anticipated rapid expansion of the nanotooling market, which is expected to exceed $US 1.2 billion in 2008 [46] and is set to rise even further beyond that, makes us quite optimistic in this regard.

Having said that, one should use plasma-based tools and approaches to create a self-organized nanoworld, we should now try to specify how exactly to approach that in a highly-controlled, ultimately deterministic, fashion. Another important aspect is to properly identify the research area of plasma nanoscience and the main issues it deals with. These issues are clarified in the following section.

1.4
Deterministic Nanofabrication and Plasma Nanoscience

Previously, it has been stressed that the uniqueness of any plasma-based nanofabrication environment is the presence of a highly unusual layer of uncompensated space charge that separates the charge-neutral plasma bulk and a nanostructured solid surface. Referring to Figure 1.2, one sees that the typical dimensions of plasma nanofabrication facilities (ca. 0.5 m) differ by at least nine orders of magnitude from the sizes of the atomic building units (ca. 0.1 nm). In this section we will discuss how to challenge one of the previously intractable problems of bridging this nine order of magnitude spatial gap and systematically approach the problem of deterministic plasma-aided nanofabrication. As was suggested earlier [4], one of the possibilities is to manipulate the plasma-generated species in the plasma sheath that separates the plasma and solid surfaces and to control self-assembly of building units into nanostructures on plasma-exposed surfaces or their direct incorporation into growing nanoassemblies.

Owing to enormous problems with the compatibility of *in situ* plasma diagnostics and surface science characterization techniques, researchers have to rely on quite separate experimental studies of the plasma processes and (in most cases *ex situ*) nanostructure characterization. However, there is a vital demand for reliable physical models and numerical simulations that could bridge the "unbridgeable" gap between gas-phases and surface processes separated in space by nine orders of magnitude and generate recipes that can be used in nanofabrication process development.

From the previous section, it becomes clear that plasma-based environments are beneficial for creating solid particles. If such particles can have nanometer dimensions, they can be termed nanoparticles and as such become suitable as building blocks of nanotechnology. Here, by nanoparticles we mean solid grains in a purely crystalline or amorphous phase or a mixture thereof. This is why there is such a large, and continuously increasing, number of reports on nanoparticle synthesis in various plasmas, ranging from low-pressure glow discharges to atmospheric-pressure arc discharges and "submerged" discharges in water. Considering the importance of nanoparticles, which feature large surface-to-volume ratios (which in turn increases their surface reactivity and makes them particularly attractive for applications in chemical catalysis), relevant processes are already state-of-the-art on their own. For a comprehensive review of nanoparticle synthesis in thermally non-equilibrium and thermal low-temperature plasmas the reader can be referred elsewhere [5]. By using plasmas it becomes possible to significantly increase the concentrations and reactivity of assembling species, which eventually gives rise to very high nanoparticle production rates. Moreover, high gas temperatures in thermal plasma discharges are very favorable for the effective and rapid crystallization of solid particles in the ionized gas phase. Highly-crystalline and perfectly shaped nanoparticles can also be synthesized in thermally non-equilibrium plasmas, see for example [47,48].

At this point it would be worthwhile to shed a reasonable doubt on the applicablity of low-temperature plasmas for the fabrication of more delicate individual nanoassemblies of higher complexity and differing dimensionality. A few examples of such more complex nanoscale objects are zero-dimensional (0D) quantum dots (QDs) and tiny nanopores, one-dimensional (1D) nanorods, nanowires, nanohelixes, nanosprings, nanoneedles, two-dimensional (2D) nanowells and nanowall-like structures, periodic heterostructures and superlattices as well as three-dimensional (3D) nanostructures of complex shapes (e.g., pyramids, cones, multifaceted crystals, etc.). Moreover, are low-temperature plasmas appropriate for the fabrication of more complex assemblies of individual nanostructures, such as spatially-ordered patterns and arrays, mixed-dimensionality assemblies (a multilayered 2D heterostructure with zero-dimensional nanodot inclusions is a good example of such an assembly), interlinked networks of nanostructures arranged in ordered nanoarrays and eventually integrated nanodevices? What is even more important, all these nanoscale objects ranging from individual nanostructures to nanodevices should be fabricated at the minimum cost and maximum efficiency, which necessarily demands a substantially reduced number of experimental trials. We also recall that the way of creating such objects should ideally be through controlled self-organization on plasma-exposed surfaces.

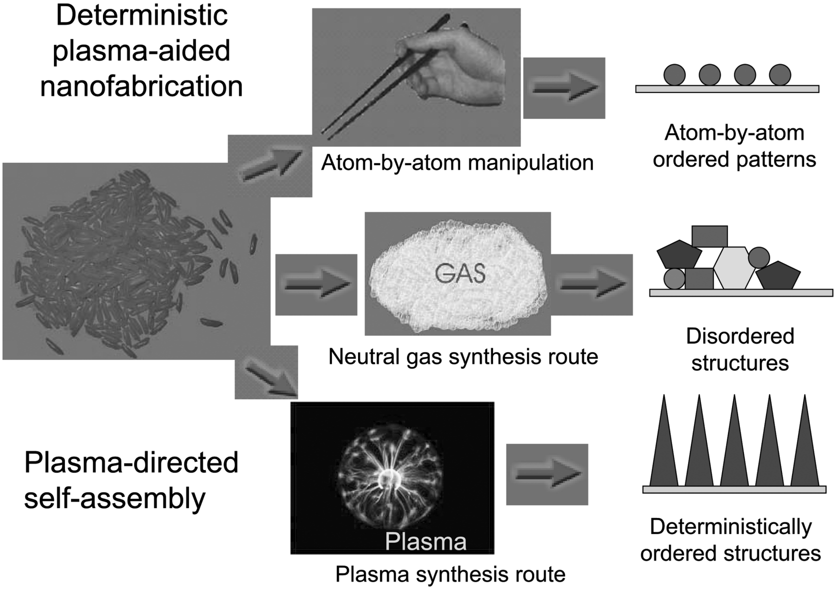
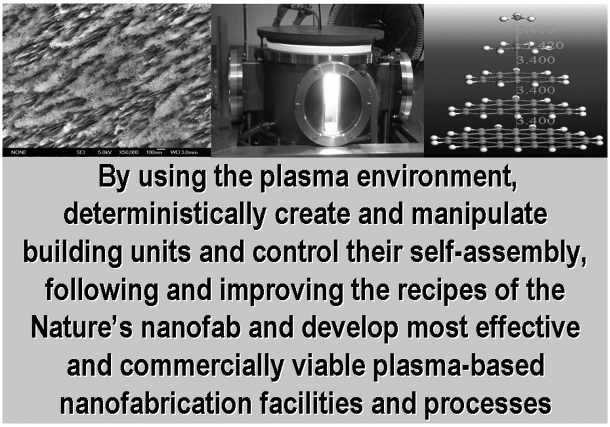


Figure 1.8 Deterministic concept of plasma nanoscience [23].

This leads to the need of pursuing a more efficient, deterministic approach, which is central to plasma nanoscience and is sketched in Figure 1.8. Generally speaking, full determinism means the ability to reach the targets (e.g., the shape, size, ordering and other parameters of the nanoassemblies concerned) using the absolute minumum number of experimental trials. In fact, Figure 1.8 illustrates one of the major aims of plasma nanoscience. It shows a process wherein self-organization of a "handful" of building units (for simplicity visualized here as rice grains) in a plasma environment results in a much more efficient (compared to the extremely time-consuming atom-by-atom nanomanipulation) and better-quality (compared to a neutral gas route) nano-sized product [23]. Identifying such processes and elaborating specific conditions when such a clear advantage of using plasma-based tools, approaches and techniques can be achieved is one of the major thrusts of plasma nanoscience.

Figure 1.9 summarizes the main aim of plasma nanoscience, which in other words is to generate suitable species and in some way control their self-organization in a suitable ionized gas environment. This needs to be done in a highly-controlled, ultimately deterministic fashion. To do this, nature's recipes (e.g., how to create solid nanoparticles in weakly ionized plasmas) should be rigorously followed, modified and optimized to achieve the required determinism not only in nanoscience research



By using the plasma environment, deterministically create and manipulate building units and control their self-assembly, following and improving the recipes of the Nature's nanofab and develop most effective and commercially viable plasma-based nanofabrication facilities and processes

Figure 1.9 Main aim of plasma nanoscience.

but also eventually in industrial nanomanufacturing, which as we have discussed in the previous section, will be based on the plasma-created self-organized nanoworld.

Therefore, the

> *Plasma Nanoscience is a multidisciplinary research area which aims at elucidating specific roles and purposes of the plasma environment in assembling nano-objects in natural, laboratory and technological situations and find ways to bring this plasma-based assembly to the deterministic level in nanofabrication.*

Some of the most commonly asked questions in this research area are: "should plasma be used?", "if so, why?" "what sort of plasmas to use?", "how exactly to use it?", and "what competitive advantages over non-plasma-based routes can one gain?". These scientific enquiries are expected to be directly related to a specific pre-determined goal, such as a nanoassembly with the desired characteristics.

Plasma nanoscience is intimately linked to the physics of plasmas and gas discharges, interdisciplinary nanoscience, surface science, astrophysics, solid state physics, materials science and engineering, structural chemistry, microelectronic engineering and photonics and some other areas [23]. These links naturally come about owing to the intrinsic ability of low-temperature plasmas to generate all sorts of building units ranging from atoms and ions to nanoclusters and nanocystallites as depicted in Figure 1.10. The processes of building unit generation, transport and self-assembly or incorporation into growing nanoassemblies, accompanied by a suitable surface preparation (Figure 1.10) by other plasma-generated

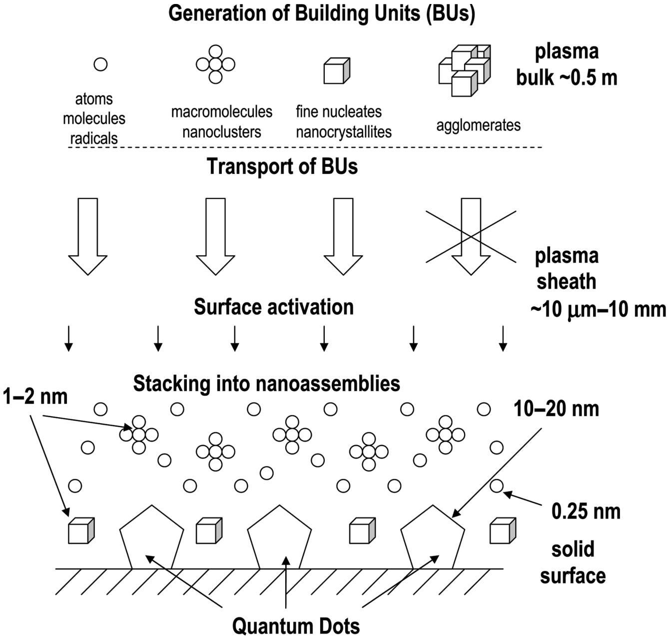


Figure 1.10 Schematics of a typical plasma-aided nanofabrication environment [23].

species (termed "working units" in this monograph) is what necessarily requires input from the above mentioned research areas.

As we have already mentioned above, in a typical plasma environment for nanoscale synthesis and processing (shown in Figure 1.10) the plasma bulk and the nanoworld are separated by the plasma sheath. A typical size for the plasma bulk area can be taken approximately as the typical dimensions of conventional plasma reactors, for example ca. 0.5 m for the integrated plasma-aided nanofabrication facility (IPANF) used in nanofabrication experiments within our research network [49,50]. On the other hand, the width λ_s of the charge non-neutral area (plasma sheath) in the vicinity of the surface critically depends on the plasma (e.g., electron density and temperature) and process (e.g., DC substrate bias) parameters. Nonetheless, λ_s typically ranges from ca. 10 μm to 10 mm as can be seen in Figure 1.10.

It is instructive to note that the ionized gas within the plasma sheath contains uncompensated positive charge. In this case the quasi-neutrality condition ($n_e = n_i$, where n_e and n_i are the number densities of electrons and ions, respectively), the most essential requirement for a plasma to exist, does not hold. Hence, the plasma sheath is no longer charge neutral and cannot be termed plasma in its usual sense.

We can now make a very important conclusion:

Plasma is separated from surface nanoassemblies by several orders of magnitude.

In other words, the plasma bulk ends several orders of magnitude before one can even "touch" nanoscale objects on a solid surface! In the example depicted in Figure 1.10, a representative size of quantum dots is in the range from a few to a couple of tens of nanometers. Here we recall that the nanodots most desired for the self-organized nanoworld should have the size less than 10 nm. Comparing this size with the typical dimensions of plasma sheaths (ca. 10 μm to 10 mm), one can immediately notice a huge difference of 3 to 6 orders of magnitude.

This interesting finding immediately prompts the curious reader to ask a very reasonable question: *Since the plasma does not directly "touch" the nanostructures like a common neutral gas, then what is its actual role in the nanoassembly process?*

Let us briefly clarify this issue. If a plasma is partially ionized, it contains two components, namely the ionized (electrons and ions) and neutral (all neutrals) gas components. The above conclusion about the multi-order of magnitude separation applies to the ionized component only. Therefore, the actual contact of the environment with the surface nanoassemblies in fact critically depends on the ionization degree of the plasma

$$\xi_i = \Sigma n^+ / \Sigma n_{\text{tot}}, \tag{1.1}$$

where n^+ is the combined number density of all positively charged species ($n^+ = n^-$ in quasineutral plasmas) and $n_{\text{tot}} = n^+ + n_n$ is the total (combined) number density of neutral and positively charged species. If $n^+ < n_n$, we have partially ionized plasmas, most common to laboratory- and universe-based synthesis of nanoscale objects. In cases where $n^+ \ll n_n$, the plasma is commonly termed weakly ionized. Equation (1.1) is also valid in case of fully ionized plasmas ($n_n = 0$) and yields $\xi_i = 1$.

Let us now consider the issue of the contact between a plasma-based environment and a solid surface in more detail. The two components of the plasma contact the surface in their own ways. The neutrals are not affected by electric fields in the plasma sheath area and deposit on the surface via random thermal motion. In a two-dimensional geometry sketched in Figure 1.2, the flux of neutral species impinging on the surface can be written as

$$j_n = \frac{1}{4} n_n V_{Tn},$$

where V_{Tn} is the thermal speed of neutrals. On the other hand, positively charged ions are accelerated by the electric field and, if ion-ion and ion-neutral collisions are not very frequent, are driven towards the surface. Even though the concentration of ions is usually less than that of the neutrals, the ion flux

$$j_i = n_i V_i$$

can in many cases exceed the neutral flux j_n. This can happen because ions can be easily accelerated to velocities V_i, which can be much larger than V_{Tn}. Therefore, even though the ions may be much less abundant than the neutrals, they can still arrive on the surface in larger amounts. Moreover, the energies of the ions impinging on the surface are usually very different from neutrals; this can cause very different effects discussed elsewhere in this monograph.

Therefore, if the plasma is weakly ionized ($\xi_i \ll 1$, which is the case in many low-temperature gas discharges), the neutral component of the plasma "touches" the surface nanostructures in almost the same way as in thermal, non-plasma-based chemical vapor deposition. However, the ions and the surface charges interfere with this process and eventually make the nanoassembly process quite different. It is amazing that the ionized gas species which in many cases constitute an overwhelming minority, can make a dramatic difference at virtually every growth step of nanostructures. In a sense, this effect is "remote"; intuitively, it is mostly related to electric fields, electric charges, and ionized atoms/radicals not otherwise available in neutral gas environments.

If the ionization degree is of the order of unity (which can be the case in various i-PVD schemes), then the surface is mostly exposed to intense ion fluxes rather than the neutral fluxes. In this case the ion- and charge-related effects lead to the creation of a very unique nanofabrication environment, impossible in any neutral gas-based routes.

As we can see from these very basic arguments, the presence of ionized species, uncompensated space charge, charges on solid surfaces and nanostructures and electric fields can make a dramatic difference in a very large number of processes that involve nanoassembly synthesis and processing. Most importantly, this difference can be quite substantial even if the fraction of ions among all atomic/radical species in the gas is very small!

Plasma nanoscience aims to shed some light on this issue and quantify the related effects. As was proposed earlier [4], this important issue can be approached systematically by following the sequence of events that occur when plasma-generated species cross the near-surface sheath area and self-assemble on (charged) plasma-exposed solid surfaces or incorporate into already existing nanoassemblies. Let us now turn our attention to the "plasma-building unit" nanofabrication approach that involves a range of specific working units as a primary cause of the growth of nanoassemblies ("effect") [4] and describes the above mentioned events. This approach will be considered in detail in Chapter 2 of this monograph. We emphasize that fully deterministic synthesis can only be achieved by following the cause and effect sequences involved in any particular nanoassembly process. In addition to the already introduced concept of building units, the "cause and effect" approach uses another notion of working units (WUs) to reflect the fact that some of the plasma-generated species (BUs) work as a primary building material for the nanoassemblies whereas others serve different purposes such as surface activation or passivation, reactive chemical etching, physical sputtering, and so on and for simplicity are referred to as WUs.

It is noteworthy that while building units are being transported to the surface nanoassemblies from the plasma bulk through the plasma sheath, the solid surface is being suitably prepared (by specific working units, e.g., argon ions or reactive radicals) to accommodate the deposited building units. Depending on the specific requirements, these working units can activate or passivate surface dangling bonds, alter the surface temperature, modify surface morphology via chemical etching or physical sputtering processes and perform some other functions. The last step discussed in the original publication [4] was to appropriately control the fluxes and energy of building units that tend to stack into nano-patterns being assembled.

However, as it turns out, in many cases this is just the beginning of the surface stage of the story. Indeed, it is extremely important where and how exactly the building units land onto the nanostructured surface. Depending on prevailing surface morphology and temperature, as well as the energy and incidence angle of impinging species, there can be an overwhelming variety of different possibilities.

Let us briefly consider some of these possibilities and begin with low-energy species that land on surface areas unoccupied by nanoassemblies. Such species are usually adsorbed at the surface and show the ability to migrate from one site to another. The notion used for such species is formed by adding the prefix "ad-" to their names. For example, the term adatom means an adsorbed atom, adradical denotes an adsorbed radical, and so on. In most cases it is implicitly assumed that any electric charge the species may have had in the gas phase is completely dissipated/neutralized upon adsoption on the surface. In neutral gas-based chemical vapor deposition and related processes the surfaces are charge neutral. However, this is not so obvious for plasma-based routes. Indeed, surface charges and/or currents make interaction of the incoming species with the substrate quite different. In some cases plasma-generated ions can retain their electric charge (or at least remain charged) upon deposition and therefore become adions. Another possibility is that plasma-generated neutral species become polarized either upon a close approach or chemisorption to the (possibly charged) nanostructured surface. In this case, microscopic electric fields in the vicinity of the substrate can substantially redistribute the polarized species about the surface as compared to the purely thermal chemical deposition case.

For simplicity, we will deal mostly with low-energy neutral adatoms. Migration of such adatoms is primarily controlled by the substrate temperature and material, morphology, chemical structure and other properties of the solid surface. Phenomenologically, these properties are reflected by the diffusion activation energy, which is usually calculated using atomistic simulation approaches, such as the density functional theory.

Upon migration from one surface site to another, adatoms can collide with other adatoms or surface features (such as defects, dislocations, bunched terraces, etc.) and form small clusters which in turn can serve as seed nuclei for nanoassemblies being created. It is imperative to note that adatoms migrate to where it is most energetically favorable for them to move. For example, consider a crystal with a few different facets; all these facets (numbered using superscript i) have quite different diffusion activation energies ε^i_{da}. Therefore, adatoms will prefer to move towards a facet with the lowest ε^i_{da}. Indeed, it saves a great deal energy to hop to a site where less energy is required to enable surface diffusion.

Adatoms can also leave the surface by desorbing and/or evaporating back to the bulk of the gas phase or join the two-dimensional vapor which remains in the immediate vicinity of the surface. Eventually, adsorbed species can find a suitable surface site to form chemical bonds with the surface atoms; this process excludes them from any further migration about the surface. Interactions between the plasma-generated species and the surface also include chemical etching which happens, for example, when highly reactive working units extract volatile species from the solid surface. We emphasize that the exact scenario ultimately depends on the relative chemical reactivity and affinity (which reflects elemental compatibility from the energetic point of view) of the building units and the host surface.

Using plasmas for nanofabrication has another indisputably attractive feature; this feature is related to the possibility of ion acceleration to relatively high energies and using highly energetic ions in surface modification and processing. If the ion energy upon landing is high, some sort of surface damage is inevitable. Physical sputtering is perhaps the simplest effect caused by energetic species; more complex phenomena may include ion subplantation as well as more substantial structural transformations in the material exposed to such fluxes. It is amazing that high-energy species can also do useful things when they crash onto the surface. Substantially improved crystallinity and structural transformations of amorphous materials to the crystalline state under the action of reasonably enertgetic ions is one salient example of this effect. We reiterate that this option is unique to ionized gas environments and in most cases involves appropriate substrate biasing.

From the above simple considerations, it becomes clear that using plasma environments in nanofabrication or surface processing does make a substantial difference as compared to the neutral gas processes. On the other hand, it is commonly understood that the plasma is a more complex environment than an equivalent neutral gas. The main evidence of a

higher complexity of the plasma environment is in the presence of the ionized component

otherwise non-existent in charge neutral gases. Moreover, the presence of even a small fraction of ionized component and associated electric fields dramatically improves the plasmas ability to generate the entire range of building and working units in atomic, molecular, cluster and other forms [4].

Therefore, for the purpose of deterministic nanoassembly it is crucial to selectively generate and manipulate the required BUs and WUs. It goes without saying that different nanoassemblies and nanofabrication processes require very specific control strategies; some of them may be appropriate for one sort of plasma-generated species and completely ineffective for another. Therefore, which recipes should one use to fabricate the desired nanoassembly in a plasma?

Apparently this question has no general answer, with the number of possible solutions exceeding the number of presently known nanoassemblies. It was therefore proposed that the problem of choice of the appropriate building units (to be generated in the plasma) can be based on the "cause and effect" logic sequence:

precursor → building unit(s) → nanoassembly,

which also requires a feedback/optimization procedure, which will be discussed in detail in Chapter 2. The above choice should be supported by the existing knowledge from other areas. For example, sophisticated surface science experiments or atomistic simulations can shed some light on what species are most suitable for each particular purpose.

Otherwise, an infinite sequence of trials (these trials can for example be aimed at generating larger densities of specific precursors) can go to nowhere due to a huge number of abundant species (including highly-reactive ones) and polymerization, clustering, and nucleation scenarios in a plasma. Therefore, research efforts in the plasma nanoscience area are usually based on assumptions on the specific building units that are needed for the desired plasma-synthesized nanostructured materials.

Without trying to provide exhaustive recipes for the appropriate choice of building and associated working units (this in fact deserves to appear in the near future as the Encyclopedia of nano-assemblies and their building units), one can state that the relevant choice should be motivated by the structural considerations of the nanoassemblies being created. At this stage, it would be reasonable to appeal to the established theories of growth kinetics of specific nano-sized objects.

For example, in the assembly of open-ended carbon nanotubes (with a simple chiral structure) or ultrananocrystalline diamond, one can use reactive dimers C_2, which can appropriately insert into carbon atomic networks on reconstructed surfaces. Other details of the building unit-based "cause and effect" approach of the plasma nanoscience will be discussed in Chapter 2 (see also the original article [4]).

As was mentioned above, stacking or incorporation of plasma-generated building units into a developing nanoassembly can proceed via two major routes. The first route involves landing of the plasma-generated building units onto open surface areas followed by their surface migration from the deposition site to the nanoassembly site. The other pathway for the BUs to stack into the nanopattern being synthesized is via their direct incorporation from the low-temperature plasma [51,52]. From Figure 1.10 one can clearly notice a huge (up to nine orders of magnitude!) difference between the spatial scales of the area where the building units are generated (ca. 0.5 m, which is a typical dimension of plasma reactors), the nanoassembly sites (ca. 5–20 nm, which is a typical size of quantum dots), and atomic/ionic/radical building units themselves (ca. 0.1–0.25 nm).

Therefore, in an attempt to achieve a fully deterministic plasma-based synthesis of surface-bound nanoassemblies, one needs to "bridge" the spatial gap of nine orders of magnitude to be able to generate, manipulate, and insert the building units into the nanoassemblies being grown. And all this needs to be done in a highly-controlled (ultimately deterministic) fashion enabling one to reduce the number of experimental trials and errors to the absolute minimum.

Figure 1.11 shows the sequence of events involved in the process of bridging the processes occuring in the plasma bulk and on solid surfaces;

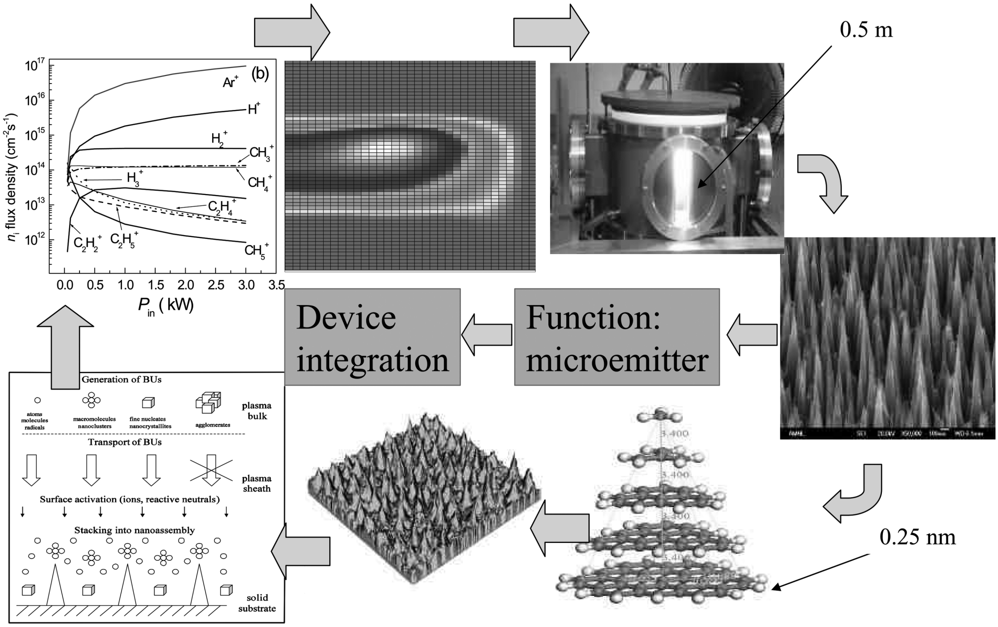


Figure 1.11 Bridging the macroworld of plasma reactors to atomic arrangement in nanoassemblies [23]. An example of carbon nanotip microemitter structures is shown.

some of these processes are characterized by spatial scales that differ by up to nine orders of magnitude and even more [23]. Let us describe the sequence of research steps involved in such a synthesis. First and foremost, one should be very clear on exactly what nanostructure is required, what are its sizes, shape, structural properties, and so on. In the example considered, high-aspect-ratio (sharp) conical nanotip-like nanocrystalline structures are of interest.

The first step in this direction is to figure out possible chemically stable atomic structures with the required shape and aspect ratio [23]. This can be achieved by using the *ab initio* atomistic density functional theory (DFT) simulation of downscaled (to within the acceptable number of atoms the most advanced computations can handle; at present this is a couple of hundred atoms) carbon nanotips [50]. One such atomistic structure of a downscaled carbon nanotip is shown in the bottom right side of Figure 1.11. Using energy minimization principles, one can work out stable configurations of the nanoassemblies concerned. In particular, it turns out that single-crystalline carbon nanotips are most stable if their lateral surfaces are terminated by hydrogen atoms as can be seen in Figure 1.11. Using these results, it is possible to work out specific aspect (height to radius) ratios, which the nanostructures may have.

We stress that such atomistic simulations do not describe the process of synthesis of the nanoscale objects concerned. However, they can specify the numbers of atoms located in the bulk or on the surface of the nanoassemblies. These data can then be used in the modeling of controlled and site-specific delivery of building units. Once this is done, it is possible to proceed with the modeling of the actual growth process which involves the two main routes of building unit incorporation into the nanotips being grown. As has already been mentioned above, this can be done via BU diffusion about the surface or their direct insertion upon deposition onto nanostructure surfaces. The next thumbnail figure in Figure 1.11 shows a three-dimensional microscopic topology of ion fluxes distributed about an ordered two-dimensional pattern of carbon nanotips [51].

Having estimated the rates of arrival of different species to specific nanoassembly sites on nanostructured surfaces, it is possible to formulate the process conditions for the optimized delivery of the plasma-generated building units to where they are actually needed. The fluxes of ionic species are most effectively controlled by the parameters of the plasma sheath, such as the potential drop across it. Moving backwards from the desired characteristics of nanostructures, one can elaborate the parameters of the plasma sheath (shown in the next thumbnail figure in the bottom left corner of Figure 1.11), such as the value of the DC substrate bias. It is prudent to mention here that the electric field magnitude, sheath width and the energy of the plasma ions significantly affect the surface temperature, which in turn dramatically influences the nanostructure growth. For example, additional heating and activation of the surface of nickel-catalyzed silicon substrates by intense ion fluxes turns out to be a decisive factor in low-temperature synthesis of carbon nanotubes and related structures.

Meanwhile, the fluxes of the building units are intimately linked to the plasma parameters, such as the electron temperature, number density of electrons/ions, neutral gas temperature, species composition and some others. This logic link is reflected by the next thumbnail figure in Figure 1.11 which shows a representative composition of thermally non-equilibrium plasmas sustained in a mixture of argon, hydrogen and methane gases. In the same figure, the dependence of the surface flux of cationic species on the input power applied to sustain the discharge is also shown [53].

The next logical step in this direction is to use the information on the composition, number densities, energies and fluxes of the required building units as input conditions in two-dimensional fluid modeling of the species and energy balance in the plasma discharge. Such modeling can generate detailed spatial maps of the densities/temperatures/energies of the most important charged and neutral species inside the plasma reactor. A typical two-dimensional distribution of neutral radical species in the integrated plasma aided nanofabrication facility (IPANF) [49] is shown in the next thumbnail figure in the middle of the top row in Figure 1.11 [54].

In the above, we have mapped the way from the atomistic carbon nanotip structure on the bottom right in Figure 1.11 (which, in fact, is much smaller than the actual carbon nanotip microemitter structure) to the spatial profiles of the main plasma-generated species in a macroscopic (with ca. 0.5 m dimensions) plasma reactor (the third figure from the left in the top row in Figure 1.11) used in nanofabrication of the carbon nanotip microemitter structures in question [49,50,55]. The numerical results mentioned so far can be used to optimize the parameters of trial laboratory experiments and eventually commercial nanofabrication processes [23].

This parameter optimization can be implemented through experimental verification of numerical results on spatial distributions of neutral and ionized atomic and radical plasma species in the plasma reactor concerned. Relevant experimental approaches can include Langmuir probe (LP), optical emission spectroscopy (OES) and a range of mass spectrometry diagnostic techniques. Application of these plasma diagnostic techniques to monitoring various plasma-based nanoassembly processes is discussed in detail in a recent monograph [1]. For example, one can match the experimentally measured and computed values of the electron number density by placing the probe tip at various spatial points and adjusting the gas pressure, gas flow rates and the RF input power. If the densities of negatively charged species other than electrons (e.g., anions or dust grains) are low, the electron and ion number densities will be approximately the same. The value of the substrate temperatures can be estimated by considering several factors that include external heating sources, heat conduction of the substrate material and the gas ambient, radiative losses, as well as the intensities of the plasma ion fluxes onto the surface. The calculated/measured changes of the surface temperature due to the ion bombardment may allow one to quantify the effect of the plasma environment on the deterministic nanoassembly process being developed. In the case of the ordered patterns of vertically aligned carbon nanotips shown in the thumbnail scanning electron micrograph on the far right in Figure 1.11, the relations between the computed and experimental values of the ion/radical densities and fluxes have been used to substantially reduce the number of experimental trials [49,50,55].

The outcomes of nanostructure synthesis are commonly investigated by using a range of analytical tools of materials science and surface

Figure 1.12 A Field Emission Scanning Electron Microscope, a common high-resolution tool for surface analysis. Photo courtesy of the Plasma Sources and Applications Center of Nanyang Technological University, Singapore.

science such as scanning electron microscopy (SEM) (a field-emission scanning electron microscope is shown in Figure 1.12), atomic force microscopy (AFM), scanning tunnelling microscopy (STM), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, low-energy electron diffraction (LEED), low-energy electron microscopy (LEEM), X-ray photoelectron spectroscopy (XPS), X-ray diffractometry (XRD), secondary ion mass spectrometry (SIMS), secondary neutral mass spectrometry (SNMS) as well as several other techniques.

At the end of the relatively long chain of processes (with every one of them occurring at quite different temporal and spatial scales) depicted in Figure 1.11 one should expect an array of shaped and structured carbon nanotip microemitters arranged in ordered spatial arrays. If the quality of the final product meets the expectations, it is possible to proceed with testing the nanoassemblies for their performance in microemitter devices. After such tests are completed and if the results are encouraging, one can move on to the final process step, namely, nanodevice integration. Thus, the arrays of crystalline nanotips need to be properly integrated into microemitter devices. From the practical perspective this step can be implemented by the growth of the carbon nanotip arrays directly in the specified device locations. In this case, low-gas-temperature conditions of gas discharges are extremely useful for direct *in situ* processing of nanoelectronic features with interlayers and interconnects, which can melt very easily because of their ultra-small thickness (down to ca. 1 nm and even thinner).

However, as was mentioned in the original article [23], if the quality of the nanostructures does not meet the required standards, the entire process or some of its cycles need to be repeated and new, even better optimized, process parameters should be used. In this way the process stages and parameters can be optimized within any segment of the nine-order of magnitude "bridge" in Figure 1.11 until the desired outcome is achieved [56]. Some would argue that this is often easier said than done in practical applications because of the huge number of processes in the ionized gas phase and on the surface. However, such practical difficulties can be overcome by studying a lumped effect of any change in a single process parameter, one-by-one, in order of their decreasing importance (e.g., the surface temperature first, then the substrate bias, the working gas composition, the input power, and so on) [23].

To conclude this section, we emphasize that the process milestones of Figure 1.11 quite accurately reflect the main essence of research endeavors in the plasma nanoscience area. Finally, practical implementation of this approach (which is applicable to virtually any nanoassembly and can be used to deterministically create the nanoworld we want) requires well-coordinated and concerted experimental, theoretical and numerical simulation efforts; each of these efforts can focus on processes that occur at specific spatial scales.

1.5
Structure of the Monograph and Advice to the Reader

Let us now make it more clear which specific material one should expect in this monograph. Structurally, the monograph consists of this introductory chapter (Chapter 1), 7 main chapters, a concluding Chapter 9, and two Appendices A and B.

In the introductory Chapter 1, we have already introduced the main aims, notions and concepts of plasma nanoscience. It has also been stressed that the most viable direction for the future development of nanoelectronics, as well as the nanoscale materials synthesis and processing should be based on plasma-guided self-organization of ultra-small nanoassemblies, creation of their ordered and interlinked networks and eventually fully functional nanodevices. The plasma-based approach to creating nanoparticle matter is common in nature's nanofab, which relies heavily on the plasma environment to substantially increase the nucleation rates of cosmic dust which is in turn essential for maintaining the chemical balance in the universe. We have also introduced the determinism, one of the most important concepts of the nanoscience and have discussed a conceptual pathway to achieve it through bridging, via a chain of various plasma-assisted processes, a spatial gap of up to nine orders of magnitude between the sizes of the plasma reactors and atomic building units.

In Chapter 2, we will introduce the concept of plasma-based nanoscale assembly based on the "plasma-building unit" approach. This approach considers plasma-generated building units as a "cause" and the desired nanoassemblies (or a specific nanoworld made of such NAs). A range of important issues related to salient features of low-temperature plasma environments (such as the plasma sheath) is also discussed. We also specify how the plasma environment can affect some elementary processes on solid surfaces. In Chapter 2, the reader can find an answer to what exactly makes low-temperature plasmas a versatile nanofabrication tool of the nano-age.

Chapter 3 explains how the "plasma-building unit" approach introduced in Chapter 2 may be used in the nanofabrication of a range of nanofilms and low-dimensional nanostructures made of most common semiconducting and carbon-based materials. The details of the sophisticated numerical and computational approaches that can be used to bridge the spatial gap of up to nine orders of magnitude (see Figure 1.11) are introduced. This practical computational framework is used in different sections of this monograph.

In Chapters 4 and 5 we continue the study of specific plasma-based effects within the "plasma-building unit" approach. The main focus of this approach is to generate appropriate building and working units. For this reason the whole Chapter 4 is devoted to the consideration of different possibilities for generating the required species in low-temperature plasmas. The plasmas considered also include reactive plasmas, where it is possible to create a broad range of reactive radical species and also nanoclusters and nanoparticles. The main focus of Chapter 4 is on thermally non-equilibrium low-temperature plasmas of silane- and hydrocarbon-based gas mixtures. However, examples of plasma-assisted nanoparticle nucleation and growth in different environments (such as in very low-density stellar ouflows and very high-density pulsed laser ablation of solid targets) are also introduced and discussed.

Chapter 5 focuses on various aspects of the delivery of a range of plasma-generated building units to the nanoassembly sites on solid surfaces. In particular, it describes a way to control microscopic ion fluxes with subnanometer precision and deposit ions onto specified areas on nanostructured surfaces. Electric fields sustained in the plasma sheath and created by surface nanostructures turn out to be powerful control tools. By properly using a combination of forces representative of plasma environments, one can effectively manipulate the plasma-grown nanoparticles in the plasma sheath area and in this way control their deposition onto selected areas on nanostructured surfaces.

In Chapter 6, written jointly with I. Levchenko, we discuss the basic ideas and approaches of surface science of plasma-exposed surfaces. The main accent here is placed on the explanation of highly unusual features the elementary processes acquire owing to the presence of electric charges, ion fluxes and other plasma attributes. The material in this chapter is centered around the demonstration of the possibility of formation of self-organized arrays of size- and position-uniform arrays of quantum dots on solid surfaces facing the plasma environment. Practical ways to implement a range of other requirements that are essential for the eventual applications of such nanodot arrays in nanodevices are also discussed. In this chapter, the reader will also find a range of plasma-specific effects on nanoscale self-organization on solid surfaces.

Chapter 7 is devoted to a specific class of nanoscale objects that show a strong ability to focus ion fluxes. The examples of such objects include single- and multiwalled nanotubes, nanotips, nanoneedles, nanocones, nanorods and some other one-dimensional nanostructures. The plasma and, in particular, ion fluxes exert a significant effect on the growth of such nanostructures and make it very different compared to similar neutral gas-based processes. The examples of advantages offered by the plasma-based fabrication routes considered in Chapter 7 are higher growth rates, better size and positional uniformity of nanostructure arrays, vertical alignment, controlled reshaping and several others. One of the most exciting examples introduced in Chapter 7 deals with the unique possibility of using plasma-controlled self-organization to synthesize uniform arrays of carbon nanocones from essentially non-uniform nickel catalyst nanoislanded films.

Examples of using various plasma-generated building and working units in nanoscale applications are shown in Chapter 8. In the first example, it is shown that a suitable variation of the plasma and sheath parameters can enable electric field-related control of ion-assisted post-processing of arrays of nanotubes and nanorods with different densities. It is demonstrated that ion- and plasma-assisted processes offer a great deal of advantages (compared to the neutral gas routes) in terms of charged species penetration into the areas inaccessible by the neutral species. In another example, we demonstrate the possibility of synthesizing ordered arrays of gold nanodots using nanoporous template-assisted ionized physical vapor deposition (i-PVD). Reactive plasmas can also be used to generate building units on solid surfaces as is the case in the synthesis of metal oxide nanostructures such as nanopyramids and nanowires. Nanocluster building units can be successfully used to synthesize nanostructured titanium dioxide films with excellent biocompatible properties. In particular, by capitalizing on size-dependent properties of such nanoclusters one can control the relative presence of rutile and anatase phases in the film.

The monograph concludes in Chapter 9 with a brief summary of current issues of the plasma-aided nanofabrication and an outlook for future directions in this exciting research area. In particular, Chapter 9 further elaborates on the issues of determinism and complexity, summarizes some of the most salient benefits and advantages in nanoscale assembly offered by the plasma-based processes and approaches, as well as providing a concise outlook for the future developments in the area.

Despite a very large number of relevant works cited in this monograph we did not aim to provide an exhaustive coverage of the current status of the major research efforts in the area of plasma-based nanoscience and nanotechnology. Such was clearly impossible to implement given the limited size of this work, and even more importantly, because of extremely limited time budget of the author. Nonetheless, Chapter 9 contains a link to Appendix B, which briefly outlines a large number of other reasons why nanoscale synthesis and processing should be ultimately plasma-based.

As we have stressed in the preface, this monograph is primarily based on personal research experience of the author and refelects his personal views on a range of relevant issues. Most of the results discussed in this work have been published in high-impact international research journals. These results have been put in the context of the "plasma-building unit" approach advocated by the author in his earlier publication [4]. This makes this work a little specialized and more suitable for researchers, academics, engineers and postgraduate students. However, tertiary college and school teachers and undergraduate students may also be interested to understand how the advocated generic nanofabrication approach works in a large number of applications. Moreover, anyone interested in general science is encouraged to browse this work to see how intricate phenomena in very complex systems can be eventually explained using commonsense approaches supplemented by solid scientific findings. This is why the level of presentation varies from a very simple, commonsense-based to highly-technical with multiple formulas and graphs. Moreover, a large number of visualizations and illustrations should make the basic concepts and ideas of this monograph easily understood by a broad audience with a very limited specialist knowledge. Above all, this monograph can also serve as a textbook or a reference manual for third-year undergraduate, Honours and postgraduate courses.

Readers are also highly recommended to familiarize themselves with the contents of the sister monograph “Plasma-aided nanofabrication: from plasma sources to nanoassembly” [1] which gives a number of essential practical hints on how to appropriately choose the plasma and develop processes and facilities suitable for the envisaged nanoscale applications. Of particular importance, especially for broad audience, is the introductory section [1] which explains what is a plasma, what are the most important, from the nanofabrication perspective, issues in nanoscience and nanotechnology and how to choose the right plasma type with certain features for the envisaged nanoscale applications. The lists of references in these two monographs are complementary and should be appended to each other. However, even this will not cover the whole range, and exponentially increasing, number of publications related to applications of low-temperature plasmas at nanoscales. To convince yourself and to observe what is happening in the area, the reader is strongly encouraged to do the subject search “nano and plasma” using any major research database such as the ISI Web of Science or Scopus.

Finally, all the best with the reading (which is expected to be enjoyable and relatively easy yet not effortless) and feel free to ask any questions!