1
Introduction

For decades, low-temperature (frequently termed “cold”) plasmas have been extensively used in many industrial applications, just to mention a few: microstructuring of semiconductor wafers in microelectronic manufacturing; deposition of various coatings, protective, and other functional layers on solid surfaces; surface treatment, which includes hardening and modification of surfaces (e.g., metal tools such as drill bits, cutting blades), welding, drilling, cutting, and functionalization; chemical synthesis of ceramic and powder materials; toxic waste and flue exhaust management; all sorts of imaginable light sources from low-pressure bulb globes and commercial halogen lamps to high-intensity discharge lamps; plasma engines (ion thrusters) for the next-century adventures of space rocketeers; water purification, sterilization of medical instruments; energy converters, plasma antennas, satellite communication; various tools for isotope separation, materials characterization, detection of radioactive materials; gas lasers, and, of course, plasma TVs and large-panel displays, which have already found their place in our everyday’s lives.

Moreover, 99 % of all visible matter in the Universe finds itself in the plasma state. It is a common knowledge that stars are nothing else but light-emitting giant hot-plasma balls that generate enormous amounts of heat and electromagnetic radiation as a result of nuclear fusion reactions when lighter elements fuse together and release nuclear energy $\mathcal{E}$ according to the famous Einstein’s formula $\mathcal{E} = \Delta mc^2$, where Δm is the so-called defect of mass, which is a difference between the masses of the reacting species and products of the nuclear fusion reaction. After years of research and development, incredibly cheap electricity generated in nuclear fusion reactors is also becoming reality. Indeed, the International Thermonuclear Experimental Reactor (ITER) (probably the largest ever R&D project) will allow, for the first time, a positive energy gain in nuclear fusion reactions, will be commissioned and is just a couple of tens of years away from its international commercial operation.

Plasmas also play a prominent role in a variety of physical phenomena in the atmosphere and space. Bright atmospheric glows, solar wind, radio-emissions, bursty waves, shocks and other space phenomena owe their origin

Plasma-Aided Nanofabrication. Kostya (Ken) Ostrikov and Shuyan Xu

ISBN: 978-3-527-40633-3

to the plasma. Above all, does everybody know that a few-minute-long blackout in radio-communications during the re-entry of a space shuttle is also a plasma-related phenomenon?

The reader probably already understood that this monograph is about the plasma, which can be "cold" and "hot" and has so many natural occurrences and technological applications, absolutely impossible to cover in a single book. However, as the title suggests, it is also about nanofabrication and nanoassembly, which intuitively leads to a guess that this is something to do with nanotechnology. We intentionally avoided mentioning this very recent application in the first paragraph, which begins with "for decades"! This cutting-edge application emerged, first of all, because of continuing shrinkage of microelectronic features in sizes. The present-day ulra-large-scale-integration (ULSI) techhnology already deals with plasma-etching created features (e.g., trenches) as small as 90 nm and is gradually moving, according to the predictions of the International Technology Roadmap for Semiconductors (ITRS) [12] toward even smaller ones (∼40–50 nm). It is remarkable that almost a half of all process steps in the fabrication of semiconductor wafers and microchips involve plasma processing! Wafer processing in plasma reactors nowadays enables one to deposit stacks of barrier interlayers, with each of them being only a few to a few tens of nanometers thick.

On the other hand, Iijima's discovery of carbon nanotubes [13] was made from graphitic soot also synthesized in a plasma! Following this landmark work, a large variety of nanostructured films, nanoparticles, nanocrystals, individual nanostructures and their patterns and arrays have been successfully synthesized by using plasma-based tools and processes. One can thus think that the plasma indeed has something to do with carbon nanotubes and other nanostructures, the building blocks of nanotechnology.

However, a proper understanding of the relation between the plasma environment and fabrication of nanostructures is absolutely impossible without the knowledge of the main terms used, their basic properties, and typical examples of using plasmas for materials synthesis and processing at nanoscales. This is one of the main aims of this chapter. In the following, we will introduce the basic concepts and terminology (plasma, nanofabrication, etc.) used in this monograph, illustrate many uses of plasma-based processes in nanofabrication, analyze some of the most important issues in the development of suitable plasma tools and processes, and also explain the logic structure of this monograph.

1.1
What is a Plasma?

In this section we will introduce the most essential things the reader needs to know about the plasma. Owing to an incredibly large amount of knowledge accumulated to date about all sorts of plasmas and presented in a number of textbooks [14–17], we will focus only on the plasmas and their properties particularly suitable for materials synthesis and processing at nanoscales. None of the discussions in this chapter is exhaustive; our primary aim here is to provide the minimum amount of knowledge for comfortable reading of the remaining chapters of this monograph. Some of the basic concepts of nanotechnology and its relation with the low-temperature plasmas will be discussed later in this chapter. So, what is a plasma?

A plasma is generally understood as a fully or partially ionized gas. The ionization is a process involved in the creation of a positively charged ion from a neutral atom or a molecule. In this process, one or more electrons are stripped from the atom/molecule giving rise to a nett positive charge. The ionization process requires the atom/molecule to transit from the original, lower energy, to a higher energy, state and thus requires a certain amount of energy to be transferred to the atom/molecule. This transfer can occur via a number of channels, such as the impact of an incident electron (these kinds of processes are termed the electron impact processes), ion, or any other charged or neutral specie; energy transfer from a photon of a sufficient energy (this process is called photoionization); and external heating of the neutral gas (thermal ionization). Various and the many ways to ionize neutral gases are described elsewhere [18].

Laboratory plasmas are in most cases created and sustained in gas discharges in solid containers (e.g., vacuum chambers or discharge tubes). By a gas discharge one usually implies a process wherein a significant electric current appears in the originally neutral gas following its ionization [19, 20]. As was mentioned above, a large amount of external energy is required to ionize neutral gas atoms/molecules. The specific elementary mechanism of ionization in fact determines the most appropriate way to deliver the energy to the neutral gas. For example, intense laser beams can be used for photoionization and DC electric fields for acceleration of ionizing electrons that take part in electron impact processes. On the other hand, the actual amount of energy strongly depends on the operating gas pressure: generally speaking, the higher the pressure, the more molecules/atoms one needs to ionize, and hence the larger amount of energy is required to sustain the discharge.

At this point it would be prudent to read the title of this book again and notice the string “plasma sources” and ask what most essential parts a plasma source should have. First of all, there should be a vessel to contain the plasma. Secondly, there should be some means of delivering the energy required for the ionization of neutral species and sustaining the discharge. As follows from the above arguments, higher pressure operation would require more powerful means (e.g., more powerful DC or RF generators, lasers, etc.) of the ionization. Thus, operation of atmospheric-pressure plasma discharges normally implies larger power inputs to the neutral gas as compared to low-pressure (e.g., in the mTorr range) discharges.

This is one of the reasons why many laboratory plasmas are sustained at low pressures, when lower amount of input power is needed to sustain plasmas with comparable parameters. Thus, the costs of input power (and also of the power supply units) at low pressures are lower; however, the lower the pressure of the working gas, the more expensive is the vacuum pump system. This is the main tradeoff between the operation of plasmas at high (e.g., atmospheric) and low (e.g., mTorr pressure range) gas pressures. Thus, we arrive at the conclusion that a plasma source should have a vacuum system appropriate for the specific range of operating pressures; or, alternatively, not to have any vacuum system if the discharge is maintained at atmospheric pressures. The last essential thing of most of the existing commercial and laboratory plasma facilities is a gas handling system, which enables one to let working gases in the vacuum vessel and control the gas dosing, which is commonly done, e.g., by using special controllers of gas mass flows and partial pressures.

Of course, simplest gas discharges, such as a spark between two sharp electrodes in an open air, do not require all of the above components. The only thing needed in this case is a DC power supply and two electrodes. However, real present-day plasma fabrication facilities include not only all of the four essential components listed above but also a wide range of control, diagnostic and other auxiliary instrumentation. Some of this equipment will be described in relevant sections of this book.

From now, the reader might realize that a fully operational plasma source with all major components as well as with some "blows and whistles" is central to any plasma applications. Nonetheless, the question about what specific sort of plasmas one needs to use for applications in nanotechnology, still remains. We will discuss this issue, as well as some specific requirements for plasma sources suitable for nanoscale applications in more detail in Section 1.4.

Another important issue is to limit the number of possible options and to identify which sorts of plasma are worthwhile to use in general. For instance, would it be wise to use hot and fully ionized fusion plasmas with ion temperatures of excess of 100 million degrees? Our commonsense tells us: of course not! Such an environment is too hot for the assembly or processing of any solid substance. At such temperatures, not only the matter will melt and evaporate but will also most likely get stripped of some electrons and turns into the ionized gas (plasma) state. Apart from the synthesis of light-element nuclei from fusing nuclei of even lighter elements, no nanoscale processes are feasible in this environment.

One can thus conclude that a partially ionized low-temperature plasma is what really is needed for nanofabrication. The degree of ionization of the plasma

$$\xi_k = \Sigma_k n_i^k / n_0 \tag{1.1}$$

is defined as the combined fraction of all ionic species k among neutral gas atoms/molecules. Here, n_i^k and n_0 are the number densities of ionic species k and neutral species in the discharge, respectively. In hot nuclear fusion plasmas $\xi_k = 1$, whereas in cold processing plasmas ξ_k usually does not exceed 10^{-3}. Figure 1.1 shows sketches of fully and partially ionized plasmas.

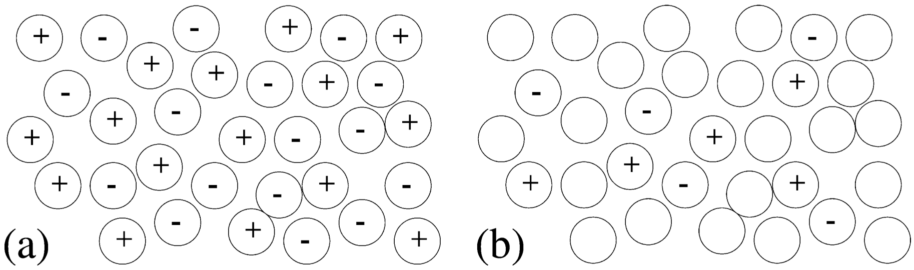

Fig. 1.1 Fully ionized plasmas (a) contain electrons and positive ions; partially ionized plasmas (b) contain electrons, ions, and neutral species.

We now arrive at the next obvious question: if the plasma needs to be cold, then how exactly cold should it be? Wait a minute! What exactly (plasma species) should be cold and how to define the plasma temperature? To this end, we note that partially ionized plasmas consist of at least three species (electrons, ions, and neutrals). Therefore, one needs to define three different temperatures for each of the three species: electron temperature T_e, ion temperature T_i, and temperature of neutrals T_n. Each of the temperatures T_j $(j = e, i, n)$ can be introduced as $T_j = 2/3\langle \mathcal{E}_k^j \rangle$ according to the kinetic theory of gases [14], where $\langle \mathcal{E}_k^j >$ is the kinetic energy of species j averaged over their energy distribution function. For comprehensive review of different energy distribution functions (e.g., Maxwellian, bi-Maxwellian, Druyvesteyn-like, etc.) the reader can be referred to Lieberman's and Liechtenberg's textbook on plasma discharges and materials processing [15].

However, we still have not answered the question about how low the temperatures of the plasma should be to be able to contribute to nanoassembly (this term will be properly defined in the next section) processes. Again, our commonsense tells us that a room-temperature gas would be the best option.

For the neutrals and ions this is perfectly fine and they can, e.g., participate in the nanoscale synthesis processes (e.g., nucleate) in their adatom/adion form. However, an equivalent electron energy of 300 K would be just 0.026 eV, which is much lower than what is needed for electron-impact ionization, one of the main mechanisms that sustains the plasma. We should note that in an ionized gas with an average electron energy of 0.026 eV there is always a small but nonnegligible population of higher energy electrons (frequently termed "electron tail" in the physics of gas discharges) with the energies 10–30 times higher than T_e (thus, ranging from 0.26 to 0.78 eV). However, even this energy is far below the ionization potentials of most of the gases, e.g., 15.6 eV for argon, 13.6 eV for hydrogen, etc. We thus arrive at an important conclusion that the electron temperature should at least be of the order of 1 eV ($\sim$11,600 K), to maintain the plasma with room-temperature ions!

Such plasmas are termed nonequilibrium ($T_e \gg T_i \sim T_n$) low-temperature plasmas; in fact, this is one of the two major types of low-temperature plasmas used in materials processing. One might ask a question: would it be right to keep terming the plasma a low-temperature one if the temperature of its ionic and neutral species is raised up to the level comparable with the electron one? The answer is definitely yes, if one notes that temperatures of $\sim$1 eV are still a few orders of magnitude lower than required for nuclear fusion. Plasmas with $T_i \sim T_n \sim T_e$, wherein each of the temperatures is of the order of or higher than $\sim$1 eV, are commonly termed equilibrium or thermal plasmas.

In reality, it is certainly easier said "increase temperatures of ions and neutrals" than done. For instance, how exactly can one implement a transition from nonequilibrium ($T_e \gg T_i \sim T_n$) to thermal ($T_i \sim T_n \sim T_e$) plasmas? From the viewpoint of turning knobs of commonly available plasma sources, what should be changed to achieve such a transition? As we have already learned, there are two main controls of the plasma with the same composition: the input power and the gas feedstock pressure. So, let us try to keep the pressure low and increase the input power aiming to heat the ions and neutrals. A higher input power will definitely result in stronger electron-impact ionization and larger densities of electrons n_e and ions n_i.

At this point it would be instructive to point out that the plasma is always *charge neutral*, which means that the total electric charge residing on positively charged species (e.g., positive ions or cationic radicals) is balanced by the negative charge of the electrons and negative ions (atoms/molecules with one or more electrons attached) or negatively charged solid grains. In the simplest but most common case of plasma experiments when all (or at least the overwhelming majority of them) positive ions are singly charged (i.e., their charge is $+1$) and there are no negative ions or solid particles, the number densities of the electrons and ions are the same $n_e = n_i$ and are commonly termed the plasma density n_p. If there are more than one ionic species and/or the species are charged with multiples of electron charges, then $n_e = \sum_k Z_i^k n_i^k$, where Z_i^k is the (positive) charge on ionic (and/or cationic) species k. In this case (as well as in most other cases) it is safe to determine the plasma density as that of the electrons. However, if there are negative ions and/or other (e.g., dust grains, nanoclusters or nanoparticles) species in the discharge, a more accurate convention as to how to define the plasma density is required.

Let us turn our attention back to what happens when an input power is increased in a low-pressure gas discharge. Common experimental observations suggest that the plasma density (here $n_p = n_e = n_i$) usually increases linearly with input power but the electron temperature does not. Therefore, even though the overall number of ionizing electrons increases, the main electron population does not become hotter and remains at almost the same temperature. Moreover, the temperatures of ions and neutrals do not increase either (at least significantly)! One can try to increase the input power again and again but in practice a substantial care should be taken not to eventually damage the power generator. This is just one of the examples when even most advanced technology ($\equiv$ powerful generator) cannot beat the physics! Indeed, why do not we observe a substantial increase of the neutral gas temperature when the input power is doubled or tripled? The basic reason is that when the pressure is low, the rates of collisions between the multiple species are not high enough to thermalize (i.e., bring to thermal equilibrium) all the species in the discharge.

Thus, we are basically left with no other option but to try to manipulate the operating gas pressure to generate a thermal (but still low-temperature) plasma. When the pressure increases, what would most likely happen is that the rates of collisions between the discharge species will become high enough to substantially increase the ion and neutral temperatures and bring the partially ionized plasma to thermal equilibrium ($T_e = T_i = T_n$). It would now be wise to pose one obvious question: since we are talking about plasma applications in nanotechnology, and already learned that hot plasmas are not suitable for this purpose, then which low-temperature plasma (nonequilibrium or thermal) one should give preference to? This not-so-simple question will be answered in Section 1.4.

So far, we have introduced the very basic concepts related to the plasma and should now approach the issues related to plasma uses in nanofabrication more closely. However, we still do not know what the nanofabrication or even the nanotechnology is; the main issues of nanoscience and nanotechnology will be introduced in Section 1.2. For now, we just stress (again by picking another word “nanoassembly” from the book’s title) that the plasma uses we are interested in will be primarily related to the synthesis of solid matter at nanoscales. Thus, the obvious question arises: our “cold” plasma should somewhere meet a solid, to contribute to some nanoscale growth on it.

In this regard, there could be two basic options: either some nanosized solid particles float in the plasma or some nanoscale objects are grown on a solid surface exposed to a plasma.

This is why it is essential to consider what actually happens when the plasma meets a solid surface. The most amazing thing is that when the plasma contacts a surface, a thin nonneutral layer of space charge, conventionally termed the plasma sheath, is formed. This phenomenon is intimately related to the plasma shielding (also called Debye shielding) of electric fields brought to the plasma by external objects and the notion of plasma confinement.

Figure 1.2 sketches some of the main physical phenomena that occur when a solid surface faces a plasma. Let us first consider what actually happens from the plasma confinement point of view. In nuclear fusion devices, hot plasmas are usually confined due to the balance between the magnetic pressure force (known in the physics of fusion plasmas as $\mathbf{j} \times \mathbf{B}$ force, where $\mathbf{j}$ is the current that flows through the plasma and $\mathbf{B}$ is the confining magnetic field) and kinetic pressure gradient force (this force is proportional to the gas density gradient). In low-temperature plasmas, it is common that the density of electrons and ions is higher in the central areas of the discharge chamber and decreases toward the surfaces of the vessel. However, very rarely such plasmas are confined by the magnetic fields. Then which force can counterbalance the kinetic pressure gradient force? The only viable possibility in this case would be to use an electric force. However, the plasma is always charge neutral, which means that no electric fields should exist in the plasma bulk area shown in Fig. 1.2. Thus, to create the electric field needed for the plasma

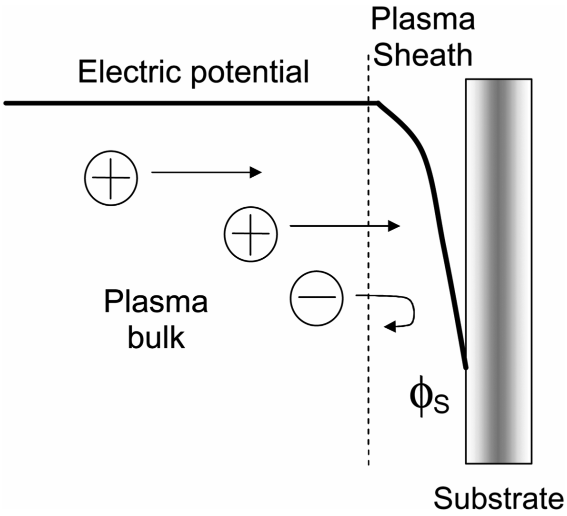

Fig. 1.2 Sketch of the near-substrate plasma area.

confinement, charge separation near the solid surface, is essential. Therefore, there is a need for a charge-nonneutral area (plasma sheath) in the vicinity of the surface.

At this point it would be wise to ask: how exactly the charge separation in the vicinity of the solid surface come about? Highly mobile plasma electrons reach the surface much faster than the ions and create a negative (with respect to the plasma bulk) electric potential on the surface, which repels the electrons and attract the ions as shown in Fig. 1.2. Let us consider the simplest case of a floating (disconnected from the chamber walls and the ground) substrate most widely covered in textbooks . As more electrons deposit on the surface, its potential further decreases, which results in a stronger ion flux to the surface and much reduced electron flux. When the surface potential reaches a certain value (called the floating wall potential), the ion and electron currents balance each other and the net current flowing through the substrate is zero. The electric field (directed from the plasma bulk toward the surface) thus arises and accelerates the positive ions toward the substrate. On the other hand, the electrons are repelled and their density in the plasma sheath is always less than that of the ions. This charge separation is the reason for the existence of the plasma-confining electric fields in low-temperature gas discharges.

However, as we have stressed above, overall charge neutrality of the plasma is equivalent to the nonexistence of electric fields (which, without external fields/actions can only appear as a result of charge separation) in the plasma bulk. We thus come to the obvious conclusion that the electric field should be confined in a relatively narrow area near the substrate. Moreover, the electron–ion separation should also take place in this area only. Hence, the electric potential should be nonuniform only in the vicinity of the solid surface as shown in Fig. 1.2.

We hope that our arguments have convinced the reader in the vital necessity of the plasma sheaths. However, some of the readers might still be curious how wide should the area of charge separation be and why is the sheath also commonly termed "Debye sheath." This is closely related to the unique ability of the plasma to shield any externally imposed electric fields; this phenomenon is called Debye shielding.

The essence of this phenomenon is that when a charged body is immersed in the plasma, a "coat" made of oppositely charged species shields the plasma bulk from this external electric field. In the case considered, a negatively charged surface is effectively screened from the plasma bulk by the "coat" mainly made of positively charged ions—the plasma sheath! If there were no thermal motions, this "coat" could be infinitely thin; in reality, it should have a finite thickness to accommodate for the effects of continuous ion recombination on the surface and mobile electrons that can still make it to the surface having overcome the potential barrier.

This finite thickness in the one-dimensional geometry of Fig. 1.2 can be quantified by using a balance of forces on an electron fluid element (here we do not consider the details of the plasma fluid theory and refer the interested reader to F. F. Chen's textbook [14])

$$-eE = \frac{k_B T_e}{n_e} \frac{\partial n_e}{\partial x} \tag{1.2}$$

and Poisson's equation

$$\frac{d^2\phi}{dx^2} = -\frac{e(n_i - n_e)}{\varepsilon_0} \tag{1.3}$$

where $\phi(x)$ is the electrostatic potential, x is the coordinate normal to the surface, n_i and n_e are the densities of the ions and electrons, respectively, and k_B and ε_0 are Boltzmann's constant and the dielectric constant of vacuum, respectively. The solution of Eq. (1.2) gives

$$n_e(x) = n_0 \exp\left(\frac{|e|\phi(x)}{k_B T_e}\right) \tag{1.4}$$

which is Boltzmann's relation for electrons, one of the most important relations in the plasma physics. Here, n_0 is the electron density in the plasma bulk in Fig. 1.2.

From Eq. (1.4) one can note that in the plasma sheath, where $\phi(x) < 0$ (potential in the plasma bulk is chosen as the zero reference potential), the electron density is less than that in the plasma bulk and, moreover, exponentially decreases toward the substrate. This is perfectly aligned with our earlier conclusions. It is important to note that Boltzmann's relation has a simple and transparent physical interpretation. Since the electrons are very light, then should the forces onto them not balance, they would indefinitely accelerate. Thus, an electron density gradient instantaneously sets up a charge separation with ions, which in turn results in a balancing electric field.

After substitution of expression (1.4) into Eq. (1.3) and expansion into Taylor's series in the area of an efficient electrostatic shielding ($e\phi(x) \ll k_B T_e$), one obtains

$$\phi(x) = \phi_0 \exp(-\frac{|x|}{\lambda_D}) \tag{1.5}$$

where ϕ_0 is the (negative) potential at the surface and

$$\lambda_D = \sqrt{\frac{\varepsilon_0 k_B T_e}{n_e e^2}} \tag{1.6}$$

is the Debye length. More careful calculations suggest that the width of the plasma sheath λ_s is typically a few Debye lengths, i.e.,

$$\lambda_s = \gamma_s \lambda_D \tag{1.7}$$

where γ_s is a numerical coefficient typically ranging between 1 and 5 for unbiased substrates [15]. We emphasize that beyond a few Debye lengths, the plasma shielding is quite effective and the negative potential due to the substrate surface is negligible as sketched in Fig. 1.2. If an external bias U_s (in most cases it is also negative) is applied to the substrate, the width of the plasma sheath increases, as suggested by the following formula [15]:

$$\lambda_s = \frac{\sqrt{3}}{2}\lambda_D \left(\frac{2U_s}{k_B T_e}\right)^{3/4} \tag{1.8}$$

which is valid when $T_e \ll U_s$.

At this stage the readers' curiosity would probably peak and prompts their mind to question the need of so quite a lengthy discussion of the plasma sheath and its parameters. Indeed, why do we need these details in a "nano"-book? The answer is simple: it is the ion fluxes and electric fields in the near-surface areas as well as the electric charges (and also currents) on the surface what makes plasma-exposed solid surfaces so different!

One of the key things that one needs to know to proceed with the plasma-assisted synthesis of nanostructures is the energy and flux of the ions impinging on the surface. Apparently, the ions enter the plasma sheath area with a certain velocity and then accelerate under the action of the electric field. Amazingly, this velocity is intimately related to the whole existence of the plasma sheath! More specifically, in the near-surface area sketched Fig. 1.2 the plasma ions enter the plasma sheath with the velocity equal to or larger than the Bohm velocity

$$v_i \geq V_B = \sqrt{\frac{k_B T_e}{m_i}} \tag{1.9}$$

where m_i is the ion mass. Equation (1.9) expresses the commonly known Bohm sheath criterion [15]. Thus, the kinetic energy the plasma ions have at the edge of the (unbiased) plasma sheath $|x| = \lambda_s$ is $\mathcal{E}_i^s = T_e/2$ and is expressed in terms of the *electron* temperature rather than the ion one. In low-temperature nonequilibrium plasmas with $T_e \gg T_i$ the ion velocity at the sheath edge can be substantially larger than the ion thermal velocity $V_{Ti} = (k_B T_i/m_i)^{1/2}$.

The ion velocity at any point x within the plasma sheath $v_i(x)$ can be calculated by using the ion energy conservation

$$\frac{1}{2}m_i v_i(x)^2 = \frac{1}{2}m_i v_{i0}^2 - e\phi(x) \tag{1.10}$$

and ion continuity

$$n_0 v_{i0} = n_i(x) v_i(x) \tag{1.11}$$

equations, where n_0 and v_{i0} are the ion number density and velocity at the sheath edge. Combining Eqs. (1.10) and (1.11), one obtains

$$n_i(x) = n_0 \left(1 - \frac{2e\phi(x)}{m_i v_{i0}^2} \right) \tag{1.12}$$

for the ion number density at any point within the plasma sheath. From Eq. (1.10), it follows that at the moment of impact at the nanostructured surface, the ion kinetic energy is approximately $T_e/2 + e\phi_s$. In the case of biased substrates ($\phi_s = U_s$), one usually has $T_e/2 \ll e\phi_s$ and it is quite accurate to assume that the ions are accelerated to the energy equal to the substrate bias. In this case the sheath width can be calculated by using Eq. (1.8). It is important to note, however, that the term $e\phi_s$ should also include contributions from micro- and nanoscaled morphology elements on the surface [21–24].

This is probably all of the most essential bits of knowledge the reader should have about low-temperature plasmas used in nanoscale applications. At this point we should map the most important issues of nanoscience and nanotechnology most relevant to this monograph.

1.2
Relevant Issues of Nanoscience and Nanotechnology

Presently, all high school children are probably aware that we live or at least entering the "nanoage" and that rapid advances in nanoscience and nanotechnology make their way into our everyday's lives. It is often said that the impact of nanotechnology over the next decade can be as significant as that of the commonly known groundbreaking inventions such as lasers, microchips, radio communications, and electricity. A number of countries have developed sophisticated, internetworked and well-coordinated national programs, with the most prominent one being the US National Nanotechnology Initiative, with almost US$1 billion spent in 2004 and additional US$3.7 billion allocated for 2005–2008 [25].

So, what is the nanoscience and nanotechnology in general? According to Richard Feynmann's vision given in his 1959 speech "There is plenty of room at the bottom" [26], the matter can be manipulated at atomic and molecular scales (just like Lego$^{\text{TM}}$ or Tetris building blocks in popular children games) to create exotic, unusual assemblies, structures, patterns, etc. Expressed in a simple form, the main idea of nanoscience is to arrange atomic building blocks in an unusual, otherwise nonexistent, way, create something (e.g., nanostructures or materials), which is extremely small (with sizes in the nanometer range) and have the properties very different from the objects with "normal," macroscopic sizes, as well as to explore and develop suitable means of controlled assembly at nanoscales. Put in Feynmann's words, the ultimate goal of nanoscience is to arrange atoms one by one, the way we want them, just like bricklayers arrange bricks and other building blocks into pillars, walls, and eventually into architectural masterpieces.

The nanotechnology would then be some set of recipes and nanotools, which on one hand emerges from nanoscience via the process of innovation and commercialization, and on the other hand, has an outstanding potential to create new and transform existing industries (virtually any, from construction and agriculture to microelectronics, aerospace and IT) and eventually significantly improve the living standards. According to the recent report of the National Nanotechnology Strategy Taskforce (NNST) "Options for a National Nanotechnology Strategy" [27], global sales of products incorporating emerging nanotechnologies in 2014 could total US$2.6 trillion, which is as much as ICT and ten times more than biotechnology revenues.

As a synergy of a range of platform technologies with the most advanced nanoscience knowledge, the nanotechnology can become an underlying technology within a number of industrial sectors (including but not limited to manufacturing, health care, energy, electronics, and communications) and is capable to provide environmentally sustainable and cost-efficient manufacturing processes, cleaner and efficient energy sources, new exotic materials and coatings with nanoscale structure and features (termed nanostructured materials or simply nanomaterials below), extra-small microchips with enormous data processing and storage capacity, new ways of targeted delivery of drugs to individual cells, and purified water, just to mention a few. According to the NNST, in Australia (the country with a relatively lower presence of the manufacturing industry sector as compared with the US, Japan, and EU) only the nanotechnology will be used in up to 15 % of products within the next 10 years.

We hope that the reader has already appreciated the main global aims and benefits of the nanoscience and nanotechnology and will not expand on this matter any further. A more comprehensive coverage of the nanotechnology-related topics is given elsewhere [28–30].

Let us now be a bit more specific on the main issues we will be looking at in this monograph and revisit the working definition we gave for the nanoscience. The first notion we come across is some "small" things. How exactly small should they be to qualify to be considered in nanoscience? There are no clear boundaries as to the sizes of the objects involved; with the only one requirement that the nano-objects should not be as small as atoms/molecules nor as large as macroscopic things. This implies that anything with the sizes exceeding 1 nm, which is approximately 4–7 times larger than the sizes of most common atoms and molecules (excluding macromolecular matter), does qualify as a nano-object.

It is a bit more difficult to estimate the upper limit for the "nanosize," in part because of not-so-clear interpretation of how to define macroscopic things precisely. Indeed, if we start combining atoms following Feynmann's recipes, we will soon find that the properties of these assemblies will be very different depending on the number of atoms involved, and hence, the object size. A single atom exhibits atomic properties (e.g., will have a clear structure of atomic energy levels). Two atoms will have a different chemical organization including a bond between them and as a result a quite different structure of energy levels. The electronic structure of a cluster made of a few atoms will certainly be even more different, with the main feature in the appearance of the energy bands, which are quite narrow in the case of a few-atom clusters and broaden as the number of atoms increases. It is quite straightforward to estimate the number of atoms that can make the smallest nano-object. For example, there are approximately 28 atoms in a silicon crystal with a volume of 1 nm^3.

As the object size increases further, their properties become even different and eventually start resembling those of bulk crystals when they become sufficiently large. It is commonly accepted that nanoparticles of a size of $\sim$1 nm feature properties no different from those of bulk materials. One more unusual thing that became reality owing to the recent advances in nanoscience is that the size dependence of electronic and other properties is much stronger when the nano-objects are real small. But exactly, how small? This is intimately related to the notion of electron (more precisely, the electron wave function keeping in mind the basics of the quantum mechanics) confinement, which turns out more efficient in the sub-10 nm size range. In low-dimensional semiconductor structures such as quantum dots, it is commonly accepted that the efficiency of the electron confinement is best when at least one of the sizes is less than the exciton's Bohr radius, which is also approximately equal to 10 nm.

The remarkable changes in the electronic structure lead to the prominent dependence of numerous properties of nanosized objects on their size. A "classic" example of such dependence is a dramatic change of gold spherical nanoparticles in color when their size is varied. Indeed, as the nanoparticle size is reduced from 30 down to 1 nm, their color changes from reddish-blue to orange and even become colorless [31]. On the other hand, when the gold particles are enlarged to the size of macroscopic crystals, their color reverts to the commonly expected yellowish golden. Therefore, the *size* does matter at nanoscales!

We emphasize that the above observation applies to spherical golden nanoparticles. In this case there is only one parameter that characterizes their size—obviously, the radius. On the other hand, ellipsoidal or cylindrical nanoparticles already have two different parameters that characterize their size. Let us take a nanocylinder as an example. The two parameters that determine its size are the length and the radius. If the length is much larger than the radius, the conditions for the electron confinement are much different along the cylinder axis and within parallel slice cut across the axis. However, since all the slices are identical, the electron confinement will be the same in every slice.

If we consider a cone, such slices will be larger near the cone's base and will be very small toward the cone's tip. Therefore, the electron confinement in the radial direction is more effective in the upper sections of the nanocone than near its base. But the most amazing thing is that there still only two parameters that characterize the nanocone's size and they are the same as in the case of the straight cylinder—the base radius and the height! So, what actually led to the remarkable change in the electron confinement? The answer is now obvious and it is the *shape*, which also means a lot at the nanoscales!

It goes without saying that it is also extremely important to make the nanoscale objects from suitable materials or any combination thereof. We thus work out another critical issue being the *elemental composition*. If it is a carbon nanotube or a carbon nanocrystal, then, apparently, they have to be made of carbon atoms and not any others. Then what is the difference between the nanotubes and the crystals if they are made of the same material? Of course, in their internal (also frequently referred to as the chemical) *structure*, which is yet another major issue in nanoscience and nanotechnology!

Let us turn our attention to Fig. 1.3, which shows two single-walled cylindrical carbon nanotubes. Structurally, they are hollow (there are no atoms inside) and are made of planar graphite (more precisely graphene) sheets wrapped in a specific way. Depending on the angle of wrapping up of the graphene sheet (which is made of a hexagonal network of carbon atoms), there are three possibilities of forming carbon nanotubes with the zigzag, armchair, or chiral structures. Put in a simple way, the main difference between these structures is in the way the hexagons with carbon atoms are tilted around the lateral surface of the nanotubes. There are other modifications of carbon nanotubes, with the two of them shown in Fig. 1.3. Panels (a) and (b) in Fig. 1.3 show sketches of a capped and open-ended (with no cap on top) single-walled nanotube, respectively. If a nanotube has more than one wall, it is called a multiwalled nanotube.

One remarkable structural feature of capped single-walled nanotubes in Fig. 1.3(a) is that all the atoms are intimately interlinked, with all their chemical bonds occupied by other carbon atoms. This is an example of a chemically pure structure, made of the same sort of atoms. For more details of the fascinating properties and applications of carbon nanotubes the reader can be referred to the landmark monograph [32].

Another nano-object with quite different structural properties is depicted in Fig. 1.4(a), where a nanocrystal with multiple unterminated dangling bonds

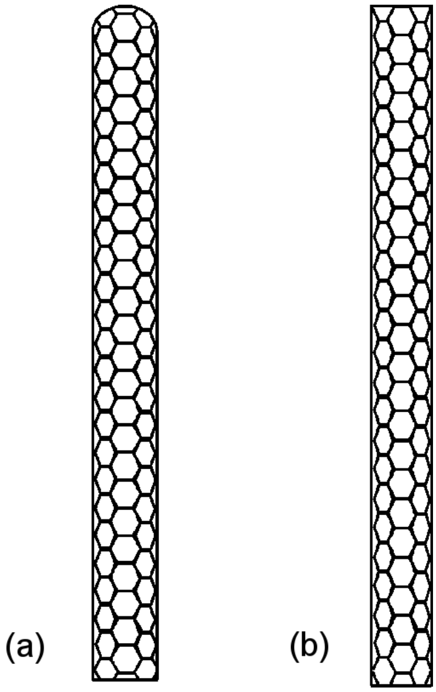

Fig. 1.3 Sketches of (a) capped and (b) open-ended single-walled carbon nanotubes.

is sketched. This structure has no internal voids and is fully filled with atoms of the same sort, which form an ordered three-dimensional crystalline lattice. This nano-object is also chemically pure; however, its multiple surface bonds can be easily terminated by highly reactive species such as atomic hydrogen (shown as black circles in Fig. 1.4(b)). Another nanocrystal in Fig. 1.4(b) is no longer chemically pure and is commonly known as a hydrogenated crystal X:H, where X denotes a chemical element.

For instance, if the silicon crystal is concerned, then Si:H would refer to a hydrogenated silicon nanocrystal. We note that amorphous nanoparticles can also be hydrogenated and denoted as *a*-Si:H nanoparticles. The structure sketched in Fig. 1.4(b) is an example of a nanostructure that lacks chemical purity. Thus, the *chemical purity* is yet another important issue to highlight.

It is relevant to note that if a nanoassembly is made of more than one sort of atoms, then there is one more essential requirement, which demands that the actual numbers of the atoms of all sorts are *stoichiometric*. In simple terms this means that the number of different atomic species is proportional to what should be according to the chemical formula of the material. For example, in SiC the numbers of silicon and carbon atoms are expected to be the same.

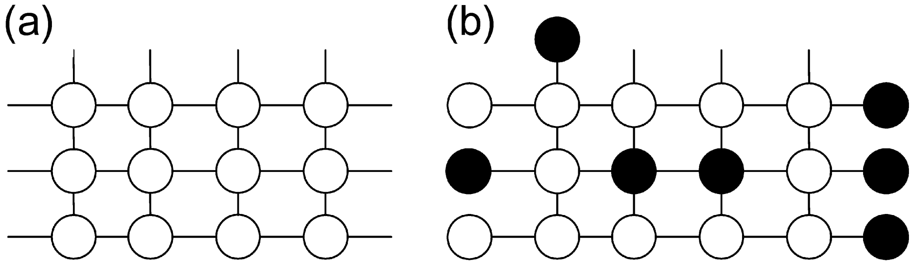

Fig. 1.4 Sketches of (a) pure and (b) hydrogenated nanocrystals.

This requirement is, however, very difficult to implement in many common nanofabrication techniques and is paid a significant attention in this monograph.

Some readers knowledgeable in materials science would immediately raise a reasonable question: a mere surface termination by hydrogen is not enough to consider the material hydrogenated and is usually neglected in the case of macroscopic solids! The most fascinating thing is that if an object is very small, then even a mere surface termination by hydrogen can lead to a substantial percentage of hydrogen atoms (hydrogenation) in the structure. The reason is that the ratio of the numbers of atoms located on the surface and in the interior (which is determined by the surface-to-volume ratio) strongly depends on the size of the nanoscale architecture concerned.

The smaller the size, the larger is the surface-to-volume ratio, and hence, the larger percentage of atoms is located on the surface. In this case, the relative population of dangling bonds available for bonding will be larger and more hydrogen atoms can stick to the surface of the nanoscaled object. What this means is that the chemical reactivity of a sufficiently small nanoparticle is determined by its surface-to-volume ratio and is much larger for sufficiently small nanoclusters. This is why a large variety of nanoparticles made of different materials is used by chemical, polymer, petrochemical, and other industries in numerous technologies utilizing various sorts of chemical catalysis. Thus, we can bookmark two more important issues being the *surface-to-volume ratio* and *reactivity* of the nanoparticles, which makes them invaluable building blocks of nanotechnology.

However, the most amazing thing in the nanoassembly from small clusters is that if one aims to create a new exotic material with very unusual properties, the reactivity of the clusters should not be too high. Our commonsense tells us that the most unusual properties cluster-made materials (materials composed of three-dimensional arrays of discrete, size-selected nanoparticles [33]) would have if they were made of nanoclusters of a small number of atoms but with just a few dangling bonds! In this case the nanoclusters would retain their own structure while combining in a larger assembly; in this case only the clusters would be interlinked. Otherwise, if the number of dangling bonds were as large as the number of the surface atoms, the small nanoclusters would combine together and form a large number of bonds between a large number of atoms from different clusters. Such multiple bonds would result in a much larger strain on the nanocluster structure, which will eventually break to form an object with a little difference from an atom-made assembly.

This simple intuitive assertion leads to a recent groundbreaking discovery that cadmium selenide nanoclusters $(CdSe)_{33}$ and $(CdSe)_{34}$ “self-passivate” their surface bonds to form much smoother surface structures without deleterious dangling bonds, which are drastically different from the common wurtzite structure of bulk CdSe [34]. It is quite typical for nanoclusters that the large surface-to-volume ratio controls the surface reconstruction and makes it stable. This unusual “self-passivation” of the surface (with the high surface ratio) effectively reduces the number of surface dangling bonds. In this case the clusters become less reactive and are less capable to merge together to form larger clusters and maintain their individuality, which is one of the critical requirements for nanofabrication of three-dimensional cluster arrays and cluster-assembled nanomaterials [33].

The above surface self-termination leads to much different structures of small nanoclusters, which in fact turn out to be a lot more strained compared to bulk forms of essentially the same materials. These strained chemical structures of small nanoparticles have numerous implications in nanoscale fabrication [35]. The most remarkable manifestation of this effect is significantly lower melting points of nanoclusters, which makes them ideal building units for epitaxial recrystallization on relatively cold surfaces [36, 37].

We hope that the reader already realized that ultrasmall objects have fundamentally different properties from those of bulk materials of essentially the same chemical composition. These properties can be tuned by adjusting the sizes, shapes, chemical structure, elemental composition, and surface-to-volume ratio.

Moreover, if arrays of a large number of nanostructures are concerned, there appear a few other essential issues such as *size and shape uniformity* of individual nanostructures across the pattern/array, controlled ordering of the nanostructures in the array, and interstructure spacings. These important parameters of individual nano-objects and their arrays need to be precisely controlled during the nanofabrication process. We are thus fully aware of the most important issues we will be looking at when trying to synthesize nanoscale assemblies in plasma-aided nanofabrication.

This is the stop point for now and it would be prudent to ask if there are any questions as what we normally do at the end of every lecture. And as it often happens, we sometimes forget to define some most essential things we were talking about in the lecture. Just like in this case: we will not be surprised if a reader would look again at the title of this book and finds out that we have not yet properly defined what the nanofabrication is in the first place! Well, our commonsense can help again: nanofabrication apparently means fabricating something very small, with the sizes in the nanometer range. So far, we have not discussed all the possibilities in this regard. Indeed, there might be a very large number of approaches, techniques, and processes to fabricate different sorts of nanoscale objects. Taken into account that the number of such nanoassemblies rapidly increases, so is the number of suitable fabrication and characterization tools and processes, the number of possibilities can be virtually infinite.

From the very fundamental perspective, the nanofabrication can be defined as the process of assembly of subnanometer-sized building units (e.g., atoms, ions, radicals) into larger objects (e.g., nanostructures, nanopatterns, nanostructured films) with feature sizes in the nanometer range [36]. This approach is commonly known as a bottom-up approach and heavily relies on self-organization (also commonly termed self-assembly) of building units (BUs) in a suitable nanofabrication environment or manipulation and stacking of such BUs externally (e.g., by a tip of a scanning tunneling microscope).

The other fundamental possibility is understood as a top-down approach, which relies on carving larger objects to reduce their size (this, e.g., can be achieved by using chemical etching, which removes some BUs) and also includes creation of nanosized void features such as tiny trenches in silicon wafers with sub-100 nm linewidths. Put in a simple language, the nanofabrication is a set of means to manipulate (e.g., move, stack, remove, control self-organization) the building units in a suitable environment and create nanoscale assemblies.

Wait a minute! We have just said “in a suitable environment” and started this introductory chapter with defining a plasma. Thus, we have no choice but to pose a now clearly obvious question: is the (low-temperature) plasma environment suitable for nanoscale applications or not and how to choose the right plasma for specific nanoscale applications?

1.3
Plasma-Assisted Synthesis of Nanomaterials

The answer to the first part of the question posed in the last sentence of Section 1.2 is a definite “yes”! There is a plethora of convincing evidence to this effect and it will be a futile attempt to try to produce an exhaustive review of all nanofilms, nanoparticles, nanostructures, porous nanofeatures, etc. ever fabricated by using plasma-based tools. It is amazing that the groundbreaking Iijima’s discovery of carbon nanotubes was made in a carbonaceous soot synthesized by arc discharge plasmas [13]! Let us now consider a few representative examples of most common nanostructures and nanofilms synthesized by using low-temperature plasmas.

The first common example of plasma applications in nanotechnology is the synthesis of materials with nanoscaled features, commonly referred to as nanostructured materials. Such features can include some elements of surface morphology (e.g., humps, bumps and valleys of the nanometer size), internal inclusions, granular structure and some others. One such example is given in Fig.1.5 showing a high resolution transmission electron micrograph of ultrasmall ($\sim$4–5 nm in size) ultrananocrystalline inclusions in an amorphous silicon matrix. This nanostructured, mixed-phase material has been synthesized in the Plasma Sources and Applications Center, NIE, Nanyang Technological University, Singapore by using low-temperature plasmas sustained in reactive mixtures of silane, hydrogen, and argon gases. Under certain plasma-based process conditions, it turns out possible to achieve quite high crystalline fractions and elemental purity, which is often quite challenging, if possible at all, to implement via other, nonplasma-based routes. Quite similar nanostructured materials, showing a very strong dependence of their nanocrystalline contents and degree of hydrogenation on the plasma parameters, have been synthesized by a number of research groups including but not limited to the University of Orleans and Ecole Polytechnique (France), Kuyshu University (Japan) and the University of Minnesota (USA) [38–50].

Work in this direction emerged at the cross-roads of physics of semiconductors and dusty plasmas, the two research fields that hardly can be put close to each other by our commonsense. Briefly, since the mid-1980s amorphous silicon (*a*-Si) has been among the most promising materials for photovoltaic applications. Among the main issues in the fabrication of amorphous silicon-based solar cells there have always been (and in fact, still remain!) a low deposition rate, relatively poor photostability, and a few others. Amorphous silicon films for microelectronic applications are commonly synthesized from reactive silane (SiH_4)-based plasmas (some other gases such as argon and hydrogen are used for passivation and activation of the growth surface). Amazingly, but in the late 1980s to early 1990s it was observed that silane-based plasmas are prone of small solid particles, which are now commonly termed dust grains or simply dusts; the plasma that contains such particles is known as the "dusty" (or "complex") plasma [11, 51–54].

The observations showed that under some conditions large clouds of ultrasmall particulates are formed in silane-based plasmas; such conditions were commonly termed as "dust/powder generation regime(s)." Some of the dusts are too small to be detected by optical means and/or seen by a naked eye. The size of such particles is very broadly distributed but in most cases remains within the nanometer range. The first thing that comes into mind is