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Abstract

This review paper presents historical perspectives, recent advances and future directions in the multidisciplinary research field of plasma nanoscience. The current status and future challenges are presented using a three-dimensional framework. The first and the largest dimension covers the most important classes of nanoscale objects (nanostructures, nanofeatures and nanoassemblies/nanoarchitectures) and materials systems, namely carbon nanotubes, nanofibres, graphene, graphene nanoribbons, graphene nanoflakes, nanodiamond and related carbon-based nanostructures; metal, silicon and other inorganic nanoparticles and nanostructures; soft organic nanomaterials; nano-biomaterials; biological objects and nanoscale plasma etching. In the second dimension, we discuss the most common types of plasmas and plasma reactors used in nanoscale plasma synthesis and processing. These include low-temperature non-equilibrium plasmas at low and high pressures, thermal plasmas, high-pressure microplasmas, plasmas in liquids and plasma–liquid interactions, high-energy-density plasmas, and ionized physical vapour deposition as well as some other plasma-enhanced nanofabrication techniques. In the third dimension, we outline some of the 'Grand Science Challenges' and 'Grand Socio-economic Challenges' to which significant contributions from plasma nanoscience-related research can be expected in the near future. The urgent need for a stronger focus on practical, outcome-oriented research to tackle the grand challenges is emphasized and concisely formulated as *from controlled complexity to practical simplicity in solving grand challenges*.

(Some figures in this article are in colour only in the electronic version)

1. Plasma nanoscience: a brief introduction

Have you ever considered what makes a difference when nanoscale solid objects are produced using precursors in different states of matter? Such nanoscale objects, and nanomaterials made from them, are known to have very different electronic, structural, mechanical, optical, etc properties compared with bulk materials with the same chemical composition [1, 2]. But does it really matter *how they are produced*? What effect does the use of gaseous rather than liquid precursors have in the assembly or processing of such nanomaterials? What changes can one expect in

the atomic- and mesoscopic-level arrangements due to the difference in the assembly pathways? How can the properties of these materials be enhanced by optimizing the nanoscale assembly processes?

Let us now pose a further question: what will be the effect on the structure and properties of a nanoscale object if a given fraction of the gas molecules or atoms (for example, in open air, in a gas container or in gas bubbles dissolved in a liquid) used in its production or processing are ionized? In very basic terms, this is the most fundamental question of plasma nanoscience.

For example, carbon nanotubes (CNTs), the most common basic building blocks of present-day nanotechnology,

can be synthesized using a large variety of approaches, specific techniques, precursors and process environments. However, when an ionized gas (plasma) is used, not only can the growth temperatures be dramatically reduced but also the CNTs usually become vertically aligned and in many cases have superior properties compared with those produced using many other nanoscale synthesis techniques. Properly aligned nanotube arrays show much better performance in many applications, ranging from their more traditional uses as electron field emitters and as vertical interconnects in nanoelectronics to more recent applications in drug/gene/protein delivery systems, cellular control and renewable energy conversion devices. Thus, the plasma environment promotes vertical alignment of the nanotubes and as a result, properties required for specific applications can be achieved. But *how exactly*? *Which mechanism* plays the key role? Why is it so difficult to achieve this using neutral-gas-based processes? How can one improve the nanotube properties, synthesis process efficiency and the CNT performance in applications by tailoring the plasma environment?

This is just a typical example of the type of problem addressed by the plasma nanoscience field. The production, processing and performance testing of any object or set of objects with at least one nanoscale dimension, composed of atoms of any chemical element and produced using any type of ionized gas (plasma) is of interest in plasma nanoscience. Of particular importance is how the plasma affects synthesis and processing at nanoscales. However, the converse, namely how spatial localization to sub-micrometre dimensions affects plasma-related phenomena, is also critically important.

So, what is the scope of plasma nanoscience? In principle, it covers any combination of (a) nano-objects; (b) materials and (c) ionized-gas-assisted processes used in their production [3]. The number of possibilities is unlimited and it is very easy to get lost in this three-dimensional space. One can also add a variety of natural or technological environments to stress that the processes used can be naturally occurring (e.g. nanoparticle nucleation and growth in space) or artificial (e.g. nanomanufacturing). This is why it is particularly important to study only those combinations of the above points (a), (b) and (c) that not only make sense (e.g. it is unlikely that one would choose to use a hydrocarbon gas to produce silicon nanowires) but also *that really matter*.

Here we have arrived at perhaps the most important point—what does 'really matter' actually mean? 'Matter' for whom or for what? In this paper we will aim to clarify in particular why one should engage in plasma nanoscience research and why this research really matters.

The very brief answers to these non-trivial questions are:

- One should engage in this research simply because it is a rapidly developing and fertile field at the cutting edge of many seemingly unrelated disciplines that generates large amounts of exciting new knowledge, in particular concerning how matter can be uniquely and exotically arranged at nano- and subnanoscales using a collection of charged particles (a plasma).

- This research helps us to address several of the 'Grand Socio-economic Challenges' faced by humankind.

It is therefore crucial to select the nanoscale objects and materials relevant to technological advances that may substantially contribute to the solution of the above grand challenges. For example, metal oxide nanowires are a new platform for the novel energy conversion devices needed to solve the renewable energy grand challenge. Arrays of gold nanoparticles are basic elements of cheap point-of-care biomedical sensors that will assist in addressing the preventative healthcare grand challenge. Ionized-gas-assisted processes, in turn, should be developed not only to allow production of nanomaterials with the required functionality and performance but also with the aim of addressing the critical requirements associated with the Earth's sustainability. These requirements are intimately related to the grand challenges and include energy- and matter-efficiency, environmental and human health compatibility, reasonable simplicity, scalability, affordability, cost-effectiveness, adaptability (e.g. to prevailing conditions in developing countries) and commercial viability, to mention just a few.

It is important to stress that 'Grand Science Challenges' and 'Grand Socio-economic Challenges' are in many cases very closely related. For example, to decrease the cost (a socio-economic target) of photovoltaic renewable energy produced by quantum-dot-enhanced silicon-based solar cells, one has to discover a revolutionary new way of drastically enhancing the yield of electron–ion-pair (exciton) generation, which is a major scientific challenge. As another example, the global socio-economic demand to continuously improve microprocessor performance in computers and communication devices while maintaining the cost at existing or even lower levels, drives the science-related miniaturization grand challenge.

This briefly explains the notion of which research endeavours really matter at present and how these efforts should be organized, concentrated, and if possible, coordinated, in virtually any scientific field, including plasma nanoscience. More details on the scientific, technological and socio-economic challenges that plasma nanoscience research helps us to tackle are presented in this review and the truly multidisciplinary collection of papers in this Special Cluster Issue on 'Perspectives and Challenges in Plasma Nanoscience'.

2. Brief historic perspective

Low-temperature plasmas have been applied to materials synthesis, structuring and processing for decades. However, learning how to use such plasmas to allow these processes to occur at nanoscale dimensions has only become critical since the rapid growth of nanoscience and nanotechnology in last two decades. Remarkably, Iijima's discovery of CNTs, which was made using arc-discharge plasmas [4], gave nanoscience and nanotechnology a major boost. Indeed, CNTs have rapidly become one of the most important building blocks in this exciting and rapidly developing science and technology field. Before this pioneering discovery, only a handful of published works reported on using plasmas to process or produce

nanoscale objects. By the mid-1990s to early 2000s, several striking advantages of plasma applications at the nanoscale, such as the vertical alignment of CNTs, had been demonstrated [5–7]. This, in turn, led to the very rapid increase in the number of publications in this area.

This expansion proceeded into different dimensions. Successful applications of ionized gases in nanoscale synthesis and processing were reported for

- a larger and larger number of nanoscale objects, structures, architectures, arrays and patterns, with a continuously increasing structural complexity and improving functionality;
- both basic nanotechnology approaches, namely top-down and bottom-up nanofabrication;
- a rapidly expanding variety of materials systems, which started from simple carbon- and silicon-based systems and expanded into a very large number of organic and inorganic materials, including complex multi-element systems, polymers and even biological cells and tissues;
- a multitude of ionized gas systems which currently range in size from the weakly ionized plasmas of stellar envelopes with astrophysical dimensions down to the micrometre dimensions of microplasmas. These systems use precursors in all three basic states of matter (solid, liquid, gas) and produce ionized gases with vastly different properties such as densities, temperatures, lifetimes, reactivity and thermal non-equilibriums;
- a very broad range of applications ranging from more traditional microelectronics (which to a very large extent is based on plasma-assisted processes) to health care, medicine, nutrition, agriculture, energy conversion and storage, environmental monitoring and remediation, national security, space missions, to mention just a few.

Selected research milestones included ionized-gas-assisted nanoparticle generation, confinement and post-processing; growth control and alignment of one-dimensional nanostructures; synthesis of single-walled carbon nanotubes (SWCNTs) in a plasma; a major paradigm shift from traditional avoidance of nanoparticle contamination towards device-quality nanoparticle production; mass production of carbon nanostructures; high-precision etching and advances in nano- and atomic-level etching; catalyst-free nanowire synthesis; chirality control in SWCNTs; precision doping and surface passivation (e.g. hydrogenation or oxidation) of ultra-small low-dimensional materials such as nanocrystals; graphene hydrogenation and oxidation which in turn lead to unique structures and properties; etc. These achievements have been covered in this Special Cluster Issue and a number of recent monographs, review papers and other relevant publications [8–32].

The number of relevant publications is currently a few thousand per year compared with only a few tens per year in the early- to mid-1990s. The most rapid acceleration in the number of publications was experienced in the mid-2000s. This is not coincidental as by that time the outstanding capabilities of ionized-gas-based nanofabrication tools and processes had become widely accepted. More importantly, there was clear

evidence of a major paradigm shift: from earlier trial-and-error and phenomenological approaches to quasi-deterministic approaches based on an in-depth understanding of plasma-related effects and insights into elementary processes involved at multiple spatial and temporal scales. Indeed, further progress of the field required a deep understanding of the underlying physico-chemical mechanisms that led to the many and various newly discovered plasma-related phenomena that in turn resulted in new and fascinating nanoscale structures and assemblies. A growing multidisciplinary research community needed to know *when a plasma should be used*, *how the plasma works* and *which plasma process to use*, well before attempting to synthesize or process any specific nanomaterial. This demand in particular led to a dramatic increase in the number of studies primarily aimed at explaining the mechanisms by which unique plasma-related properties are translated into highly unusual materials properties. These studies in turn helped plasma-based nanotechnology to find its place among the most versatile nano-tools of the nano-age and heralded the advent of plasma nanoscience as a distinct research field.

3. Setting the directions: approach and aims of this Special Issue

The interest of a broad multidisciplinary community in plasma nanoscience has been demonstrated not only by a rapidly and steadily increasing number of publications (including major reviews, monographs and edited books) that cover a vast variety of scientific and engineering disciplines, but also by a large number of relevant conferences, symposia, workshops and special sessions, collaborative international projects, scientific exchanges and special issues of leading journals. This Special Issue continues the theme of the Special Cluster Issue on Plasma-Aided Fabrication of Nanostructures and Nanoassemblies published in Journal of Physics D: Applied Physics in April 2007 [33]. The earlier issue focused on providing some typical examples of applications of two major classes of low-temperature plasmas, namely thermal and non-equilibrium plasmas, in nanofabrication.

This issue is structured very differently and aims at a more exhaustive coverage of the main areas involved in plasma nanoscience research. In a sense, the selected content has a four-dimensional structure that not only reflects the three major categories (nanoscale objects, materials systems, and ionized-gas-based processes used) highlighted in section 1 but also a range of applications that are highly relevant to a few major 'Grand Socio-economic Challenges'.

A similar structure is adopted in this review paper. For simplicity, the scope has only three dimensions—specific nanomaterials (combining the categories of nanoscale objects and specific materials), ionized-gas/plasma-based processes and discharge types, as well as the intended applications. The papers included in this Special Issue are mentioned in each of these categories. We also provide a brief and non-exhaustive overview of some of the relevant areas not covered in the Special Issue. For example, this paper also highlights some of the most recent advances and future perspectives in the field recently presented at the Second International

Symposium on Plasma Nanoscience (iPlasmaNano-II) which was held in December 2010 in Australia [34]. In most cases, we aim at summarizing (and wherever possible, referencing) the points that (in our view) most clearly and succinctly reflect current status and the challenges and opportunities in any particular area in the three-dimensional (nanomaterials systems (section 4), ionized-gas-based processes (section 5) and applications (section 6)) space. When discussing the applications, we will also comment on the most relevant 'Grand Socio-economic Challenges'. We will also discuss some of the emerging scientific challenges at the intersection with other highly topical fields that at present are rapidly gaining momentum.

Therefore, our effort is primarily directed towards pointing out the most significant (largely in our own view, although many experts in specific areas were consulted) achievements and highlighting the main future directions and expected advances in any particular area, rather than detailed discussions of specific technical details or the physico-chemical mechanisms involved. For these details, the reader should refer to the relevant original publications; the list of references in this review is by no means exhaustive.

4. The first dimension: micro- and nanoscale objects and materials systems

In this section, we discuss several examples of the most common nanoscale objects of different dimensionality, their arrays and nanomaterials based on them. Wherever possible, emphasis is made on relevant plasma-specific effects.

4.1. Carbon nanotubes

CNTs are arguably the most common example of a nanostructure in whose growth the application of low-temperature plasmas brings many important benefits. Formation of the CNTs in most cases requires catalyst nanoparticles to support the nanotube nucleation and growth. These nanoparticles play several critical roles. In particular, the catalyst nanoparticles lower the energy barriers for incorporation of carbon atoms into the developing graphitic walls, provide specific areas (e.g. edges or terraces) for these walls to nucleate/develop, determine the radial dimensions of the nanotubes, help us to separate the CNTs from other structures in the arrays/patterns, support and facilitate diffusion of carbon atoms before they reach the walls, support nucleation of caps of SWCNTs and to a very large extent determine their chirality [35–38].

The energy required to produce carbon atoms (by dissociation of carbon-based precursors in the gas phase or on the surface), to allow them to diffuse through the catalyst and then to incorporate into the nanostructures largely determines the process temperatures. In plasma-based processes, these temperatures are remarkably lower (by up to several hundred degrees) than in the equivalent neutral gas-based processes [39]. In addition, growth rates can be much higher and the nanotube quality can be markedly better if appropriate plasmas are used.

At present, a large variety of plasma-based CNT growth approaches and techniques is available; they range from more traditional thermal plasmas of arc discharges and low-pressure, non-equilibrium plasmas to the more recent non-equilibrium plasmas operated at atmospheric pressures. Plasmas are also commonly used for selective doping (for example, to control the conductivity type for applications in electronics and photovoltaics) and functionalization (e.g. to allow selective attachment of specific objects including biomolecules, DNA and proteins). In many cases, plasmas lead to superior results in terms of selectivity and stability. In simple terms, plasma-produced species may stick better to the CNT surface (which has no dangling bonds) compared with those produced using many other treatment techniques.

Generally, production and post-processing of CNTs using plasmas is one of the most established and widely used nanoscale processes (representative examples are shown in figure 1; they cannot be described here due to space constraints). The mechanisms of the plasma-related phenomena in CNT growth and processing are relatively well understood. However, detailed quantitative studies that convincingly relate the elementary processes in the plasma bulk to the nanoscale processes (e.g. those confined to the size of catalyst nanoparticles) are essentially missing. Advanced multi-scale numerical modelling and simulation are expected to bridge this gap [42–51]. This challenge is generic and applies to virtually all nanoscale objects and systems produced using ionized gas environments.

There are many important challenges in this direction. For example, avoiding nanotube damage by energetic ions that are produced in the plasma and accelerated in the plasma sheath still remains a major problem despite years of research. This is why some atmospheric-pressure plasma systems, in which ion energies are fairly low due to the high rate of collisions, may have clear advantages [52]. It still remains unclear how to use plasma-specific mechanisms (e.g. selectivity and surface energy control) to allow the as yet elusive chirality control of SWCNTs, to separate metallic and semiconducting SWCNTs and to process a specific region of a nanotube with nanoscale and sub-nanoscale precision. In the multi-walled CNT growth, it still remains very difficult to effectively control the number of walls.

Among other major issues for the years ahead, one should pinpoint the overwhelming need to avoid *any* catalyst in the nanotube growth and in particular, enable direct integration of CNTs in the currently silicon-dominated nanodevice platforms. Recently, many novel (e.g. semiconductor nanoparticles, metal oxide nanoparticles and non-traditional metals such as gold) catalysts have been demonstrated to support CNT growth. However, any catalyst introduces very substantial losses through electron and heat transport; this is particularly critical for nanoelectronic and energy conversion applications. At present, other than artificial carbon pre-seeding (e.g. by implantation, manipulation or other means of carbon-rich surface formation), there are no reliable means to completely eliminate catalysts in CNT growth.

CNT-related research is widely represented in this Special Issue and many important experimental and modelling aspects are covered [53–61].
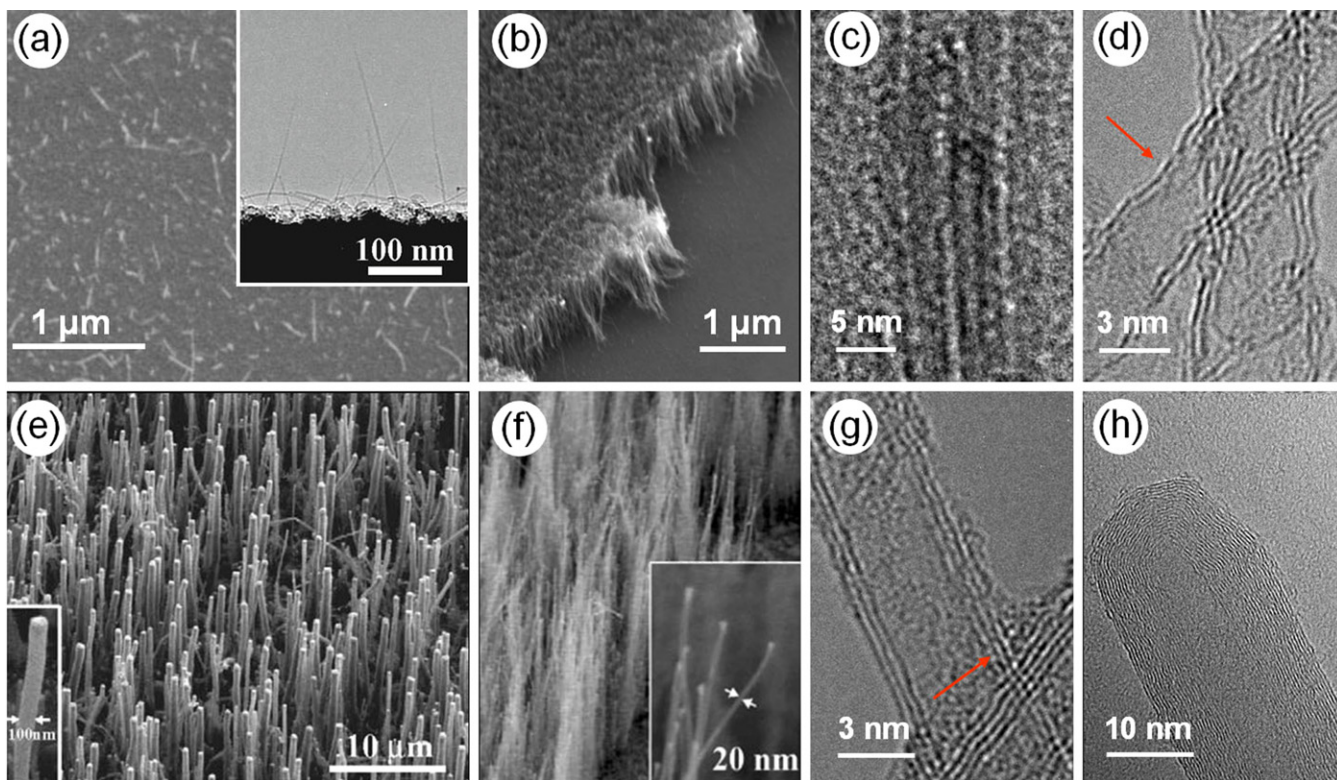
Figure 1. Plasma synthesized CNTs with tailored alignment or structure. SEM images of diffusion plasma CVD synthesized SWCNTs for the case of (*a*) individually freestanding and (*b*) vertically bristling growth or (*e*), (*f*) multi-walled carbon nanotubes during vertically aligned growth [40]. The number of carbon nanotube walls can be tailored in low-temperature microplasmas with a size of Ni catalyst and results in (*c*) single-walled, (*d*) double-walled, (*g*) triple-walled and (*h*) multi-walled structure shown by TEM micrographs [41]. Courtesy of Hatakeyama (*a*), (*b*), (*e*), (*f*) and Sankaran (*c*), (*d*), (*g*), (*h*). Parts of original images reproduced with permission from Wiley-VCH and ACS.

4.2. Graphene, graphene nanoribbons/nanoflakes/nanosheets and related structures

Graphene, a single sheet of graphitic carbon, is the nanostructure that has generated the most excitement in recent years. The Nobel Prize in Physics 2010 was awarded to Geim and Novoselov for their discovery of this truly two-dimensional material, previously deemed impossible [62, 63]. The exceptional conductivity, hardness and optical transparency of graphene are extremely attractive for a large number of applications.

There are a number of related structures such as graphene nanoflakes and nanosheets (a relatively small number of flat graphene layers, typically less than ten), graphene nanoribbons (same as above but for bent graphene layers), and carbon nanowalls (a large number of graphene layers of total thickness ∼10 nm or more). These structures also have many unique properties, mostly related to very high reactivity of the sharp edges of multiple graphene sheets and a pronounced electron confinement when the number of graphene sheets is small. Examples of thin graphene nanosheets and carbon nanowalls of different morphologies produced using hydrocarbon-based rf plasmas are presented in figure 2.

Among plasma-related methods to produce graphene and graphene nanoflakes, one should mention plasma-enhanced chemical vapour deposition (PECVD) on metal catalysts (e.g. Pt, Pd and Cu) with appropriate lattice matching. This

possibility was demonstrated using both non-equilibrium and thermal plasmas under a range of process conditions. Plasma-assisted thermal CVD (e.g. using dc or rf plasma discharges placed along the direction of the precursor gas flow) has allowed a substantial reduction in the process temperatures required for graphene growth, by as much as 200 K [64]. Another possibility is to promote rapid evaporation of Si atoms from thin carbon-rich SiC layers. This is not widely used in plasma-based graphene production, mostly because very high surface temperatures (∼1200 °C and even higher) are required, which are very uncommon in plasma-based processes. However, plasmas can be used for very effective heating of very thin surface layers, which may eliminate the need to heat the whole substrate. In addition, the diffusion, desorption and evaporation barriers can also be reduced on plasma-exposed surfaces. Under such conditions, Si atoms tend to leave the surface even faster than upon conventional thermal surface activation [65]. This possibility awaits experimental realization.

Plasma-based post-processing of graphene (and also graphene-derived materials such as graphene oxide) has proved very effective in modifying graphene's surface energy, which in turn resulted in dramatic changes in the structural and electronic properties. Indeed, plasma-assisted surface hydrogenation led to the formation of hydrogen-terminated bent graphene sheets that is now termed graphene [66, 67]. The underlying mechanism is related to the reduction in the
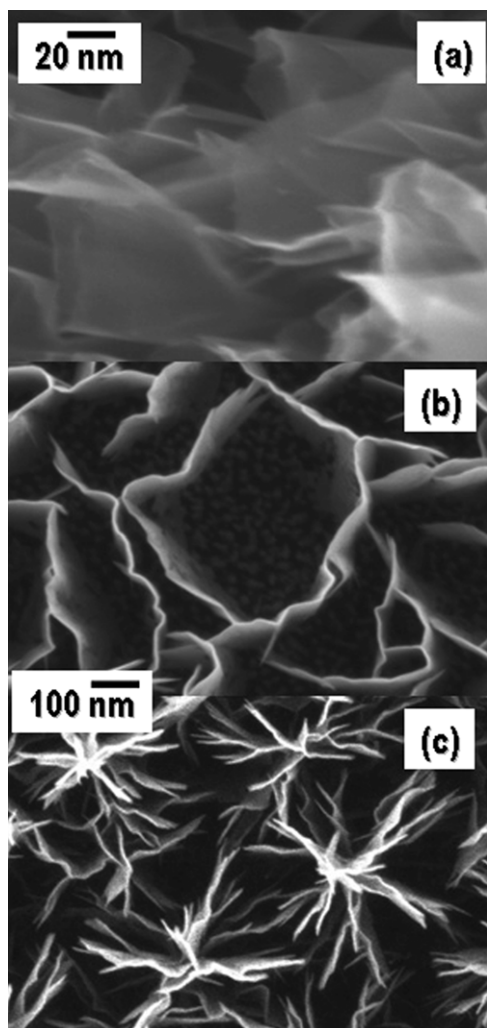
Figure 2. Scanning electron micrographs of (*a*) graphene nanosheets and (*b*), (*c*) carbon nanowalls of two typical morphologies. Courtesy of Kumar, Seo and Ostrikov.

surface energy per unit area upon surface hydrogenation. This in turn makes it possible to increase the surface area by bending the graphene sheet without increasing the total surface area. Hydrogen plasmas can also be used for highly selective low-temperature etching of graphene edges without introducing defects in the basal plane [68]. Plasmas have also been used for the effective atomic-layer-precision thickening of films that contain only a few graphene layers.

The non-equilibrium nature of the plasma (electron energy is typically 1–2 orders of magnitude higher than that of the heavy species) contributes strongly to the very high dissociation rates of molecular gases (such as hydrogen in this example) and the creation of a large number of reactive atomic and radical species. This is also critical in enabling effective oxygenation of graphene surfaces in a plasma [69], which in turn results in the change in the type of electrical conductivity, from semi-metallic in conventional graphene to semiconducting in plasma-oxygenated graphene. In other words, effective plasma oxygenation has proved very useful in solving the important problem of opening the bandgap in the normally bandgap-less graphene. This opens

exciting opportunities of using graphene not only as highly conducting channels but also as semiconducting logic elements in nanoelectronics.

Plasmas have also been instrumental in the production of graphene nanoribbons. One possibility that has been demonstrated relies on plasma-assisted unzipping of multi-walled carbon nanotubes partially buried in a polymer matrix [70, 71]. These structures are usually surface-supported and have excellent prospects for applications in chemical and environmental sensors owing to the reactivity of their edges, and in nanofluidics [72] because of the presence of conducting channels with nanoscale dimensions.

Carbon nanowalls contain a relatively large number of vertically aligned graphene sheets and are usually attached to a surface by their edges [73]. It is remarkable that they can be grown directly on silicon surfaces without any catalyst, in striking contrast to nanotubes. Interestingly, this has only been possible when the surface is exposed to a plasma. Despite a large number of proposed models, there is currently still no clear understanding of these striking experimental observations. This is clearly an interesting opportunity to unveil the underlying physical mechanisms of the plasma-enabled growth of the carbon nanowalls.

Material quality and nanostructure type selectivity are perhaps one of the main issues in the plasma-assisted synthesis of graphene, graphene flakes and graphene nanosheets. For example, a common problem in graphene growth over large catalyst surface areas is the frequently observed formation of two- and even three-dimensional islands instead of the expected single graphene layers over large surface areas. Development of an understanding of carbon monolayer formation through plasma-controlled bottom-up self-organization and the basic mechanisms of this control is an obvious research opportunity.

Plasmas offer the possibility of large-scale graphene production; using thermal plasmas of arc discharges appears promising [74–76]. However, post-synthesis separation of different carbon structures that are simultaneously produced is a significant hurdle yet to be overcome.

Relevant papers from this Special Issue [53–61, 77, 78] provide further insights.

4.3. Other carbon-based nanomaterials

The variety of carbon-based nanomaterials that have been produced and/or post-processed using plasma-based techniques is overwhelming and it is impossible even to mention all of them. We will present only a few representative examples. Structure-wise, these materials have either a pure sp^2 (graphitic nanocarbons) or sp^3 (diamond-like nanocarbons) structure, or a mixture of these phases. Moreover, the relative contents of crystalline and amorphous phases can vary widely.

In addition to CNTs, some examples of graphitic nanocarbons include carbon nanofibres [10, 79–81], carbon nanopipettes [82], single-crystalline nanotips [83], carbon nanocones [84, 85], carbon nanowires [87], single- and multi-walled fullerenes [88], carbon nanocages [89, 90] and carbon nanospheres [91]. Plasma-assisted growth of both free-standing and surface-supported carbon nanostructures has

been demonstrated. In many cases, these structures require some catalytic material (e.g. Ni) and relatively high process temperatures to initiate their growth. The arrangement and activity of the catalyst nanoparticles are quite similar to those in CNT growth. Issues that are still not fully resolved include control of incubation times in the catalyst nanoparticles, maintaining their catalytic activity throughout the growth, preventing the nanoparticles from being buried by amorphous carbon, and prevention of catalyst metal diffusion into the substrate [92]. Low-temperature plasmas have been demonstrated to provide effective remedies to most of the above issues in some specific cases; a broader range of possibilities (e.g. enabling simultaneous activation of catalyst NPs of different sizes) has been predicted using numerical simulations [93] but has yet to be confirmed experimentally.

Two of the greatest challenges are predicting which specific nanostructure is going to emerge out of a given catalyst nanoparticle array, and choosing appropriate plasma process conditions to enable a reasonable degree of selectivity between different types of structures. This challenge is generic and applies to most of the nanomaterials that require catalytic growth. This is particularly difficult to address given the current strong thrust to enable all-in nanofabrication processes, in which all the steps (from catalyst preparation to synthesis and post-processing) are conducted in the same reactor. It is therefore very important to be able to perform a reasonable analysis of the catalyst nanoparticle arrangement (which in many cases proceeds via controlled or guided self-organization [94]) *in situ*, without major interruptions of the process flow. This problem can be avoided by attempting to eliminate catalyst nanoparticles; recent reports on the plasma-assisted, catalyst-free synthesis of hierarchical microcone-nanowire structures and arbitrary patterns of multi-walled carbon nanotubes using dense microwave plasmas [95, 96] suggest the potential application of plasma-based tools. However, this would require the development of revolutionary new approaches, which might be based on a combination of top-down nanofabrication (with a continuously increasing precision and resolution) and bottom-up self-organized nanostructure growth.

For many applications, carbon nanostructures have to be capped or decorated with metal nanoparticles. In particular, this is required for carbon nanostructures with non-reactive surfaces (e.g. hydrogen-terminated nanofibres or tubular structures without active sites or bonds) to increase their reactivity in sensing applications, to modify the electronic structure and control electron transport by creating nanoscale metal-dielectric–semiconductor junctions, as well as to fabricate electric contacts on the nanostructure surfaces. Recent publications show several examples of such intriguing possibilities [97, 98].

An interesting recent trend has been the production of carbon nanostructures under non-equilibrium conditions. Relevant examples include synthesis of nanodiamond and exotic carbon nanostructures such as nanoshells and nanocages. Synthesis of diamond-like nanomaterials (diamond is a thermodynamically less-stable carbon allotrope than graphitic carbon) usually requires very high pressures

and temperatures. These non-equilibrium process conditions prevent re-arrangement of diamond-like carbon to graphite during the relatively fast synthesis. In a plasma environment, synthesis of nanodiamond crystals and ultra-nanocrystalline diamond films can be implemented under relatively low (well under atmospheric) pressures and moderate process temperatures [99, 100]. However, to mitigate the higher energy cost of the synthesis of the more non-equilibrium nanodiamond structures, plasmas of relatively high energy density and species concentrations (e.g. microwave plasmas) are commonly used. Plasma-assisted synthesis of nanodiamond is a relatively well established and advanced process developed over the last couple of decades [99, 100]. Diamond nanocones and nanorods are other examples of plasma-produced sp^3 carbon nanostructures [101, 102].

One of the main challenges is the ability to control facet expression (and hence reactivity) in diamond nanocrystals. The possibilities of such control have been predicted theoretically by *ab initio* density functional theory (DFT) computations [103]. However, we are not aware of any clear experimental confirmation in the plasma-related literature. Another important present-day challenge is the introduction of precisely dosed levels of dopants into small carbon nanocrystals. This problem is generic and applies to most nanocrystalline systems. For instance, introduction of nitrogen-vacancy colour centres is being pursued to allow room-temperature single photon generation, single-spin readout and, ultimately, effective quantum control in nanodiamond [104]. Nanodiamond facet expression and control of the level of doping in a plasma are exciting opportunities for future research. Such control is critically required in several biomedical and IT applications of nanodiamond including magnetic resonance imaging (MRI) and quantum computing.

Extreme non-equilibrium conditions have been demonstrated to produce exotic carbon nanostructures such as carbon nanoshells and nanocages [105]. These conditions were produced, for example, in transient spark discharges between different electrodes (e.g. graphite and metal) at atmospheric pressures. The very high transient temperatures achieved in these discharges and the high rates of cooling made it possible to capture the as-nucleated carbon nanostructures in metastable states. The controlled production of metastable nanostructures and nanoarchitectures is a vast and presently largely unexplored field. Thermal and chemical non-equilibrium conditions in a variety of plasmas have the potential to allow this as yet elusive control [106].

Some of the above and other interesting relevant aspects are discussed in this Special Issue [53, 77, 107, 108].

4.4. Metal nanoparticles

As mentioned in previous sections, arrays or patterns of metal nanoparticles provide the essential catalytic support for the growth of CNTs and other nanostructures. This also applies to a very large number of other materials systems (e.g. silicon, germanium and other semiconductors; oxides, nitrides, oxynitrides, etc). Metal nanoparticle arrays are also

used in plasmonic and sensor devices. In plasmonic devices, the choice of material is mostly dictated by the available electron densities in the metal and the possibility of locating the plasmonic resonance in the optical range, as well as of achieving reasonably low losses in plasmonic structures [109]. These devices confine light to deep-subwavelength dimensions where a variety of nanoplasmonic phenomena can unfold and lead to unprecedented concentration of optical energy to volumes with a characteristic length scale typically between 2 and 20 nm [110]. In sensor devices, the metal nanoparticles are chosen for their ability to react with the sensing media and undergo a change to their optical or electrical properties. Metal nanoparticle arrays are also used as nano-resistors in nanoelectronic applications. Nanoparticle sizes and interparticle spacing can be adjusted to enable specific electric charge transport and resistivity mechanisms [111, 112]. The metal nanoparticle arrays are produced using a large variety of ionized gas-based techniques, including PECVD of metal-organic precursors and effective manipulation of metallic vapours (ionized physical vapour deposition, iPVD) [113]. The range of relevant deposition systems will be discussed in section 5.

The formation of a nanoparticle array in many cases involves pre-deposition of thin nanolayers followed by fragmentation upon heating. This fragmentation can be implemented directly in the plasma or in a separate post-annealing step. However, the resulting arrays are usually very non-uniform, both in terms of nanoparticle size and location. Attempts to use nano-templates (e.g. anodized porous alumina or monolayer sphere lithography) are, on the other hand, limited by their intrinsic spatial resolution [114]. For example, tiny metal nanoparticles that support the growth of SWCNTs cannot be produced in this way; a controlled self-organization-based approach needs to be used instead. Exposure to low-temperature plasmas has proved useful to improve the nucleation density and size and position uniformity of the self-organized metal nanoarrays; these possibilities have been predicted numerically and demonstrated experimentally (figure 3) [92, 115]. Interestingly, control of self-organized nanoparticle arrays in a plasma can be implemented at reasonably low temperatures. This is not only advantageous to meet the main requirements for nanofabrication but also to minimize diffusion of metal atoms into the substrates, which is a significant issue in high-temperature catalytic growth of a large number of nanostructures.

Metal nanoparticles can also be produced (e.g. using iPVD systems) and processed (e.g. using PECVD of functional overcoats of a very large number of materials) in the ionized gas phase and then deposited onto the substrate. The ability of low-temperature plasmas to (usually) negatively charge both the nanoparticles and the substrate surfaces leads to the possibility to levitate the nanoparticles in fairly steady positions and post-process them during the confinement time [8, 116].

It is also important to stress that plasma-based techniques have been used to produce arrays or patterns of metal nanoparticles on the surfaces of a variety of nanoscale and microscopic objects of different dimensionalities. These objects include but are not limited to carbon nanosheets and
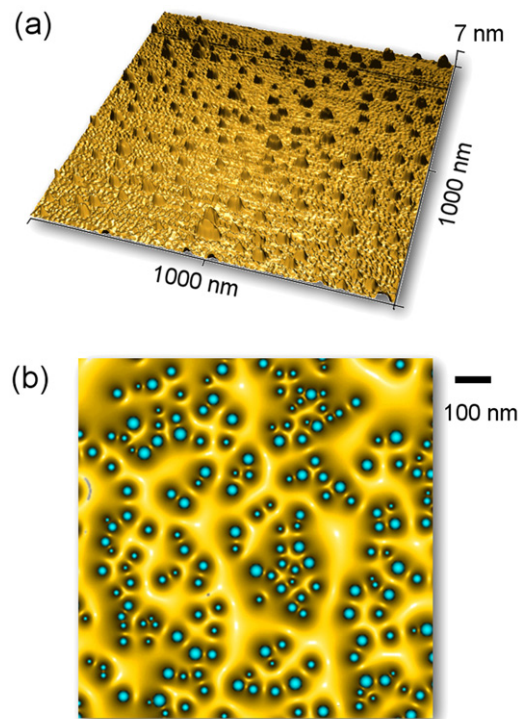

Figure 3. (*a*) Atomic force micrograph and (*b*) simulated pattern of self-organized arrays of nickel nanoparticles on a SiO$_2$ substrate exposed to low-temperature plasmas [115]. Courtesy of Levchenko.

dielectric (e.g. SiO$_2$) and semiconducting (e.g. metal oxide) nanowires [117, 118].

The apparent challenges include mastering the ability to characterize and control the formation of nanoarrays and nanoparticles, identifying and optimizing the most useful plasma-specific effects. For example, it still remains unclear how to control the locations at which nanoparticles nucleate, and then their correlated development into self-organized nanoarrays. It is also very challenging to control the expression of specific (e.g., high-index) crystalline facets of metal nanoparticles on plasma-exposed surfaces. A reasonable level of control is currently available in surface science experiments [119] that are usually conducted in ultra-high vacuum, whereas plasma experiments are conducted at pressures orders of magnitude higher [18]. Generally speaking, this challenge is related to the ongoing efforts to bridge the gap between plasma physics and surface science [18].

Some of these and other important issues are discussed in this issue [58, 107, 120–125].

4.5. Silicon nanoparticles and nanostructures

Silicon nanoparticles and nanostructures represent a very important class of plasma-produced nanomaterials. Due to natural abundance of silicon compounds, the present dominance of silicon-based micromanufacturing platforms, as well as silicon's very useful electronic and optical properties, these nanomaterials hold outstanding promise for applications not only in microelectronics but also in photovoltaic solar cells and biomedical devices of the next generation, to mention just a couple of examples. Silicon-based nanomaterials can be
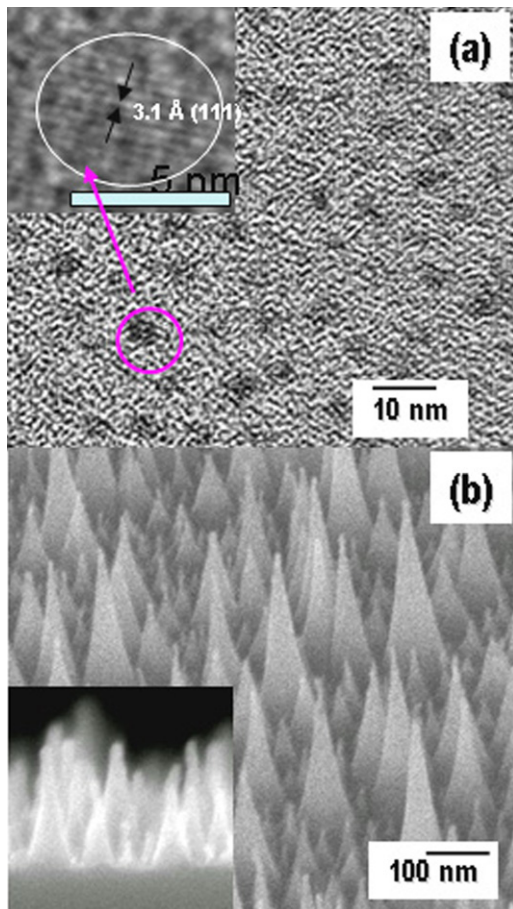
Figure 4. (*a*) Transmission electron microscope image of silicon quantum dots embedded in an *a*-Si matrix produced in reactive silane-based plasmas [128] and (*b*) scanning electron microscope image of single-crystalline silicon nanotips fabricated using Ar + H$_2$ plasmas [143]. Insets show (*a*) a single quantum dot and (*b*) a cross-sectional view of the silicon nanotips.

produced and processed both in the ionized gas phase and on the surface. There are several options for their fabrication. The most common option heavily relies on PECVD using the highly toxic and flammable silane (SiH$_4$) precursor, although some other and less toxic precursors such as tetra-ethyl-ortho-silicate (TEOS) are also widely used. In this way, one can produce a variety of silicon nanoparticles in the gas phase, on the surface, or embedded in an amorphous silicon matrix [126–128]. Some examples of such possibilities are shown in figure 4. Gas-phase synthesis and detection of silicon-based nanoparticles followed by their deposition on the surface is relatively well understood and has been one of the major thrusts in dusty plasma research in the last two decades [129–131]. These nanoparticles were initially considered merely as deleterious contaminants in nanoscale plasma processing (e.g. etching in microelectronic fabrication) and significant efforts were applied to develop reliable strategies to avoid them [132]. However, as the feature sizes in nanoelectronics reduced, the potential dangers posed by silicon nanoparticles increased very significantly, as one nanoparticle wrongly deposited in a feature of similar dimensions could damage the whole integrated circuit. Research on the elimination of

such nanoparticles or prevention of their growth has therefore recently become even more significant.

On the other hand, the ability to grow the nanoparticles in a controlled fashion and then deposit them onto specified areas with micrometre (and even higher) precision has led to a major paradigm shift. Indeed, the silicon and other nanoparticles that were previously considered to be deleterious have become among the most valuable building blocks in nanotechnology [132]. A significant success was achieved in the synthesis, processing and nanodevice integration of plasma-produced hydrogenated silicon and some other semiconducting nanocrystals [20, 135]. More importantly, plasma-based processes enabled very effective shape and size control of such nanocrystals. In particular, the formation of silicon nanocrystals of nearly perfect cubic shapes has been demonstrated in hydrogen-containing gas mixtures. This can be attributed to the very effective dissociation of hydrogen molecules in non-equilibrium plasmas (see other subsections for further examples) which in turn results in complete termination of the surfaces of silicon nanocrystals [136]. We emphasize that the thermodynamically preferred shape of hydrogen-terminated silicon nanoparticles is cubic rather than more smoothly curved (e.g. close to spherical) for bare silicon [137].

Therefore, the plasma creates a chemically and thermally non-equilibrium environment in which the effective surface passivation results in the formation of otherwise very reactive, high-surface-energy facets. If this surface termination can be reversed (similar to the case of reversible hydrogenation of graphene) before the cubic structure can revert to the thermodynamically preferred round shape, one can obtain very reactive silicon nanocrystals with a large number of active surface bonds. This possibility, although thought to be achievable relatively straightforwardly via oxygen-plasma-assisted hydrogen reduction or argon-plasma-assisted surface activation, still awaits reliable practical implementation.

The formation of silicon (or other) nanostructures on the surface can also be implemented in several ways. One way would be to deposit the plasma-grown (or plasma-injected) nanoparticles onto the specified microscopic locations. This possibility was predicted using numerical modelling and simulation of nanoparticle trajectories [133]. Most recently, it was demonstrated experimentally that ion-induced focusing and microscopic electric fields near charged microstructured Si surfaces lead to exotic three-dimensional assemblies (e.g. multi-leaf flower-like structures) of charged Cu nanoparticles produced by spark discharges [134]. There is an opportunity to extend this interesting possibility to three-dimensional structures made of charged silicon nanoparticles.

Another possibility is to use catalytic PECVD to develop quasi-one-dimensional silicon nanostructures (e.g. nanorods or nanowires) on the surface. Plasma-based processes result in the nucleation and growth of such nanostructures (of the same thickness) at temperatures (by as much as a couple of hundred degrees) and gas pressures remarkably lower than in thermal CVD [138–140]. Furthermore, the nucleation of silicon nanowires is adversely affected by the Gibbs–Thomson effect, which causes a large increase in the nucleation threshold (and

hence the minimum surface temperature and supersaturation level of the precursor atoms) for thinner nanowires. Recent results reveal that plasma-specific effects of localized heating, enhanced diffusion and faster supersaturation in the metal (e.g., gold) catalyst lead to the minimization or even almost complete suppression of the Gibbs-Thomson effect [141]. This explains frequent experimental observations of the possibility to grow much thinner silicon nanowires in a PECVD process conducted at the same temperature and gas pressure as thermal CVD [138–140]. This offers excellent prospects to harness the truly two-dimensional electron confinement effects in thin quantum wires that are critically needed for many advanced applications such as energy conversion and gas sensing. In addition, faster nanowire nucleation also prevents the catalyst nanoparticles from being buried by amorphous carbon deposits before they are lifted off the substrate by silicon layers nucleating underneath.

It is also possible to use reactive plasmas to profile the silicon surface with nanometre precision. A combination of reactive plasma etching and redeposition of the as-etched material can lead to the formation of self-organized patterns of quasi-one-dimensional silicon nanostructures such as silicon nanopyramids, nanocones, nanowires, nanograss and hierarchical two-tiered structures [142–146]. These surfaces feature excellent antireflection and water-repellent properties and offer exciting applications in optoelectronics, photovoltaics and biomedical devices.

In particular, interaction of Ar + H_2 plasmas with the surface of p-type Si wafer not only results in the formation of anti-reflective textures on the surface but also leads to the conversion of the conductivity type from the p-type to the n-type in the near-surface layer. This in turn leads to the simultaneous formation of a p–n junction, which otherwise normally requires several fabrication steps such as thin layer deposition and selective doping. The photovoltaic response that can be obtained from such simple solar cells produced via a single-step plasma exposure and subsequent electrode deposition is very strong. Indeed, the photovoltaic conversion efficiency of 11.9%, short-circuit photocurrent up to 32 mA cm^{-2}, open circuit voltage of 530 mV and fill factor reaching 70% have been reported very recently [147]. The understanding of the underlying mechanism of the p–n junction formation, and in particular, the role of quantum confinement effects that arise from the tips of sharp silicon nanostructures, represent an excellent opportunity for future research.

Silicon etching can be performed with and without the use of masks. Self-assembled nanosphere monolayers or other pre-deposited features can be used as nanoscale etching masks. The mechanisms of maskless etching (which has been demonstrated to yield silicon nanograss and other silicon nanostructures) [142–144] are not properly understood; this represents a very significant research opportunity. More importantly, plasma-assisted surface nanotexturing can be performed using simple combinations of non-toxic gases such as argon and hydrogen, in addition to more reactive etching gases such as Cl_2, CF_4 and SF_6. These nanoscale textures, in turn, determine the electronic densities of states (electronic and optical properties) as well as the phononic properties of

the nanostructured silicon [152]. This not only significantly enhances the application potential but also the possibilities for characterization (e.g. by additional nanotexture-specific Raman fingerprints) of this class of nanomaterials.

Among many other challenges, we would stress the need to properly understand the underlying mechanisms for nucleation, growth, facet arrangement, reversible surface termination and activation, and atomic-precision doping of silicon nanocrystals. Once this understanding is obtained, effective controls for these processes, and the development of the most suitable plasma-based processes, reactors and safety equipment, will be possible. Precision doping may be implemented by highly controlled and transient incorporation of appropriate dopants (e.g. boron or nitrogen or elements of the same groups) during the nucleation stage or, alternatively, carving small silicon nanocrystalline structures from pre-doped silicon wafers. The ability of plasmas to add or remove dopants may also be used to form nanoscale p–n (and more complex junctions) in the same plasma reactor using a very small number of process steps [154].

Related papers from this Special Issue [55, 125, 148–154] provide more insights into this area. Further discussion of nanoscale plasma etching can also be found in the following subsections.

4.6. Other inorganic nanoparticles and nanostructures

Nanoscale plasma processing has been successfully applied to several classes of materials in addition to more traditional carbon- and silicon-based nanomaterials discussed above. The ability of plasma-based systems to handle precursors in gas, liquid and solid states, as well as to implement various combinations of chemical and physical methods of processing precursors and substrates, have made it possible to remarkably expand the range of binary, ternary, quarternary, etc materials systems into the nanomaterials domain.

For example, the ability of non-equilibrium plasmas to produce atomic oxygen and nitrogen species (which otherwise is a non-trivial task because of very high dissociation energy barriers) in a variety of radical, excited and ionic states, has led to the possibility of very effective synthesis of oxide and nitride nanostructures using both low- and atmospheric-pressure plasma discharges [23, 155–157]. Nano-oxides of some semiconducting elements (e.g. silicon and germanium) and of a large number of light and heavy metals have been successfully produced. The variety of reported morphologies is also huge, spanning all three dimensionalities from tiny quantum dots to complex three-dimensional nanoarchitectures. Some examples of such structures are displayed in figure 5.

The range of demonstrated and envisaged applications is also very broad. For example, metal oxide nanostructures and nanoparticles find numerous uses in photovoltaic, electrochemical, thermoelectric and photochemical energy conversion, as well as environmental and bio-sensing. Such nanoparticles are also used for targeted cancer therapies and to deliver heat and reactive oxygen species to selected areas affected by tumours.

A very interesting and truly plasma-enabled effect is the production of metal oxide nanostructures directly on metal
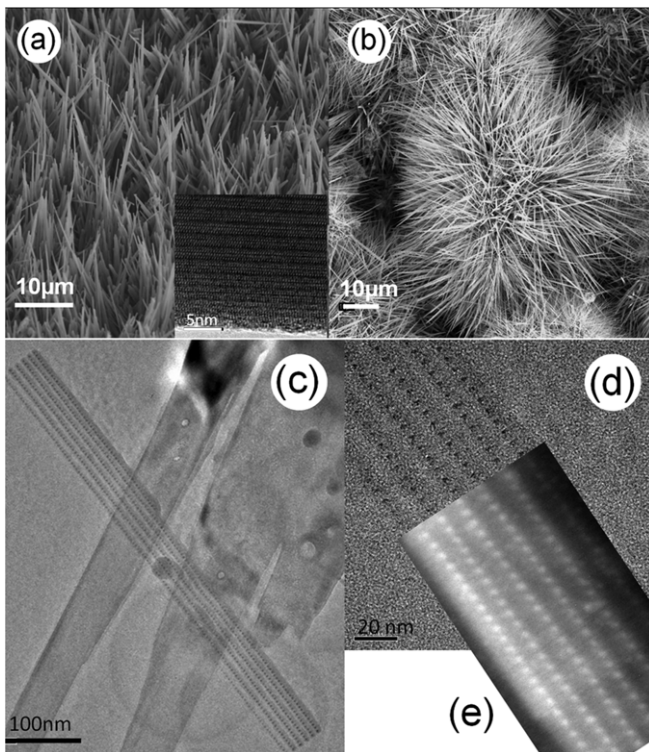
Figure 5. Representative examples of metal oxide nanostructures produced using plasmoxi-nanotech: scanning electron microscope images of (*a*) niobium oxide (Nb_2O_5) nanowires and (*b*) gallium oxide (β-Ga_2O_3) nanowires, and molybdenum oxide nanotubes in (*c*) bright-field image, (*d*) high-resolution electron microscope image and (*e*) Z-contrast high-resolution scanning transmission electron microscope image. Courtesy of Cvelbar, Chen and Sunkara.

surfaces without using any metal-organic precursor gases or external sources of metal atoms [24, 158–163]. This possibility relies on the direct contact of metal surfaces with reactive oxygen plasmas. This process is extremely fast; only a few tens of seconds to a couple of minutes is usually required to develop nanostructures of various sizes and morphologies (e.g. nanodots, nanoneedles, nanopyramids, nanobelts, tapered and straight nanowires) and made of a range of oxide materials including but not limited to SiO_2, CdO, Fe_2O_3, Nb_2O_5, V_2O_5, WO_2, WO_3 and CuO_2. For comparison, many thermal and chemical processes for the growth of similar nanowires require at least several hours [167].

Physically, the non-equilibrium plasma dissociates oxygen molecules very effectively and unusually high dissociation degrees (in some cases reaching 50% or even higher [168]) can be achieved. The oxygen atoms in turn find themselves in various excited states, which in turn creates the possibility to release their energy into atomic-scale interactions on the metal surface. For example, recombination of oxygen atoms on small nanoscale surface features (e.g. hillocks) is believed to lead to the creation of localized ultra-small hot spots [24, 163, 164], where the plasma-exposed material is activated (in some cases even melted as the melting temperature dramatically decreases with size and also depends on the nano-alloy composition) to accommodate oxygen atoms. After the as-formed nano-alloy is supersaturated with

oxygen, nucleation takes place. It is important to stress that this process does not require any external substrate heating.

Thus, reactive plasmas represent an ideal all-in environment for this simple and effective process, which is scaleable for mass production of high-quality (perfectly single-crystalline in this case) nanostructures, and has excellent potential for commercialization. It is also of interest to note that this simple plasma-enabled process makes it possible to tailor nanowire structure at the atomic level. Indeed, a unique periodic oxygen vacancy ordering has been reported [165]. A conclusive understanding of this fascinating phenomenon, alongside reliable measurements of surface charge distributions, local temperatures in the hot spots, nanowire incubation times, as well as an explanation of the nucleation selectivity, have not yet been reached.

Currently, there is a very strong thrust towards using atmospheric-pressure plasma systems (both thermal and non-equilibrium plasma systems—from large-scale arc-discharge plasma reactors to tiny microplasmas) to produce a large variety of metal oxide nanostructures and nanoarchitectures [23]. These approaches benefit from the natural presence of oxygen in the air; however, care has to be taken to avoid large amounts of nitrogen being incorporated into the developing nanostructures. This is an example for which tailoring of electron energy distribution functions (EEDFs) in the plasma to enable selective dissociation of oxygen molecules leaving nitrogen molecules intact (the dissociation threshold of N_2 is higher than of O_2 by several eV) is a very promising approach. This approach can also be used to produce carbon nitride-based nanomaterials with tailored carbon and nitrogen contents. Since the dissociation energies of CH_4 and N_2 are very different (4.55 eV and 9.74 eV, respectively), the EEDFs can be tailored (e.g., by adding Ar to a $CH_4 + N_2$ gas mixture) to maximize the dissociation rates in any desired range of energies [166].

Another important area is the plasma-assisted doping of semiconducting and oxide nanomaterials to control the type of conductivity. For example, it is currently very difficult to obtain p-type conductivity in ZnO nanofilms and nanocrystals as well as to alter the type of conductivity in very thin near-surface areas of semiconductor crystals. Several recent results suggest that plasma-assisted doping has strong potential to provide a relatively simple solution of these important problems [169, 170]. However, the mechanisms that convincingly relate the reactivity of the plasma species to specific reactions on the surface and inside the material during the growth or within a thin sub-surface layer still need to be understood.

Despite the many widespread uses of reactive oxygen plasmas for nanoscale synthesis and processing of a large variety of inorganic nanomaterials (as well as soft organic matter of the following section), this area is expected to significantly mature and expand in the future, eventually leading to the *plasmoxy-nanotech* of the future. For more comprehensive discussions of the relevant topics, the reader is referred to other papers in this Special Issue [58, 149, 171–173].
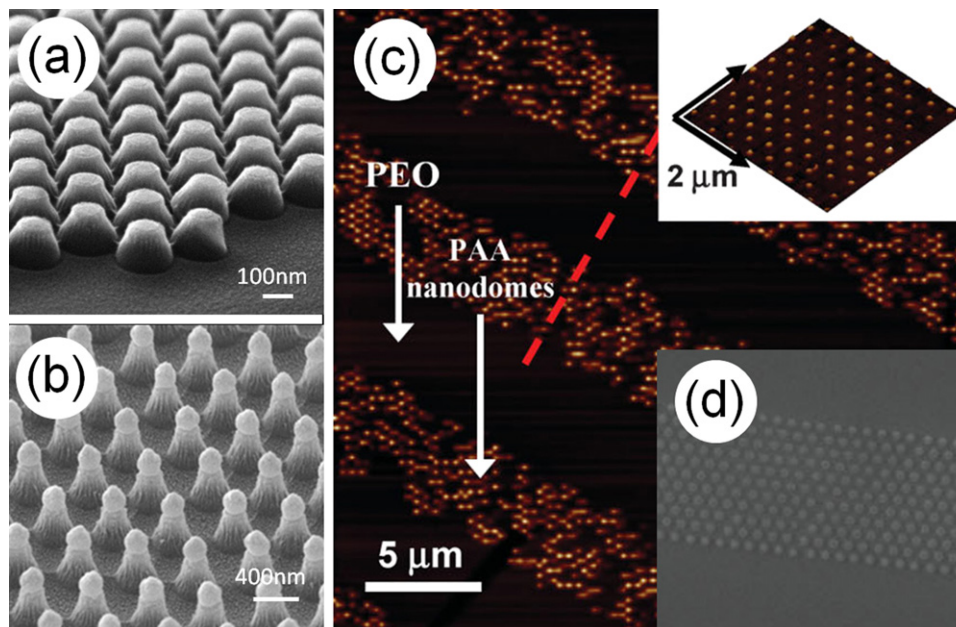
Figure 6. Representative examples of soft organic nanostructures via plasma processing. Scanning electron microscopy (SEM) images of (*a*) nanosize polystyrene (PS) beads on poly(acrylic acid) (PAA) obtained by colloidal lithography [177, 184] and (*b*) beads etched with oxygen plasma [179]. (*c*) Atomic force microscopy (AFM) image of the patterned lines containing PAA nanostructures after removal of the residual PS; the upper-right inset shows the magnified AFM image of the nanostructured area showing the hexagonal packing [178]. (*d*) SEM image of the PS nanoparticles after oxygen plasma etching [178]. Parts of original images reproduced with permission from IOP Publishing and Wiley.

4.7. Soft organic nanomaterials

In addition to hard carbon-based nanomaterials, low-temperature plasmas have been successfully used for the synthesis, micro- and nanostructuring and functionalization of soft and temperature-sensitive (e.g. polymeric) materials. Some representative examples are shown in figure 6. In these applications, discharges are usually operated at low power levels to reduce any damage that may arise due to heating of the surface by the plasma. Similarly to the case of hard matter, there are two means of developing nanoscale structures and features on polymer surfaces. The first route is to use PECVD of complex organic precursors (plasma polymerization [174, 175]); however, the overwhelming complexity of the plasma chemistry significantly restricts control of the growth. The second approach, based on surface nano-texturing or profiling using low-temperature reactive plasmas, is therefore more commonly used. More importantly, such plasmas are significantly less complex than most of those derived from organic and metal-organic precursors in PECVD. Indeed, plasmas of relatively simple combinations of inert (e.g. Ar and He) and mildly reactive (e.g., O_2 and N_2) gases are commonly used. The underlying mechanisms of the plasma–polymer interactions in this case are mostly expected to be chemical (e.g. etching) rather than thermal (to avoid melting and evaporation) or based on physical impact (to avoid surface damage due to sputtering). It is thus reasonable to use, for example, oxygen plasmas with relatively low degrees of dissociation and ion energies (sheath potentials) near the surface. A good example of a suitable plasma reactor is the high-density, low-pressure inductively coupled oxygen plasma.

Similarly to many hard materials such as silicon, plasma etching approaches for soft materials are based on mask-assisted or maskless lithography. For instance, dense self-organized monolayers of polystyrene (PS) nanospheres in the few hundred nanometre size range have been successfully used to etch underlying polymerized acrylic acid (PAA) films and create ordered arrays of nanosphere-capped tapered conical nanostructures of various morphologies [176, 179].

Surface texturing can be complemented with additional control of surface energy, which in turn determines surface wettability, one of the critical factors in the attachment of biomolecules and cells. In this case, fluorine-containing reactive gases such as CF_4 may serve both purposes. Indeed, CF_x and F radicals not only etch the polymer surface but also increase fluorine content, which in turn enhances water-repellent (hydrophobic) properties of the structured polymer surfaces. Concurrent nanostructuring and fluorination of polystyrene surfaces using fluorocarbon (e.g. CF_4) etching gases has recently been demonstrated [180, 181]. Using this technique, one can create a variety of morphological features including nanodot and nanodome patterns as well as nanowall-like ribbons and other structures. It is important to stress that no additional masking is required to produce these features.

It is believed that surface textures on plasma- and ion-beam-exposed surfaces develop through a mechanism that is essentially based on self-organization. For example, the formation, patterning and density of nanodots and ripples on the surface can be effectively controlled by tailoring the exposure to the plasma and ions [182, 183]. This opens exciting opportunities for controlling nanoscale surface roughness in a number of applications.

This nanoscale patterning and texturing, in combination with plasma-enabled selected-area surface functionalization (e.g. by OH–, COOH–, NH_x–, etc groups that interact with biomolecules) [185, 186] has great promise for the production of bio-interfaces that are capable of controlling interactions with biological objects. These interactions in many cases proceed via bio-recognition and attachment of specific proteins to plasma-functionalized nano- and microstructured surfaces, followed by intracellular signalling that in turn controls cell viability, proliferation and differentiation [187].

Another important and rapidly emerging area of applications of plasma-produced and processed soft organic nanomaterials is thin-film organic electronic, optoelectronic and photovoltaic devices. Such organic (or plastic) materials are expected to enable flexible and less fragile devices that are based on synthetic polymers or polymers produced from recycled agricultural products [188]. Organic semiconductors are presently used in the development of next-generation display panels based on organic light-emitting diodes (OLEDs), 'plastic' electronic devices based on organic field effect transistors (OFETs) and low-cost organic solar cells [189–191]. Organic polymers with different types of conductivity were demonstrated [192]. However, there is a significant challenge to enable effective control of the conductivity type using plasma polymerization, especially in nanostructured and composition- and structure-graded polymers.

There are many significant challenges, such as the ability to predict the self-organized patterns that emerge as a result of plasma–surface interactions (both in mask-assisted and maskless cases) and select the most suitable plasma process parameters. The mechanisms underlying the formation of the features and structure also need to be properly understood. Future research on plasma-formed or processed bio-interfaces offers many exciting opportunities for interdisciplinary collaborations, in particular investigating the specific mechanisms by which plasma-processed or functionalized nanoscale surface structures and features interact with proteins and cells. It is still not very clear exactly which patterns and structures should be created and how exactly they should be post-processed or functionalized to enable highly selective bio-recognition, attachment and ultimately control of specific types of cells. This class of application has many features in common with inorganic bio-nanomaterials, which will be briefly discussed in the following subsection.

More details of the ongoing research efforts and perspectives in this area can be found elsewhere in this Special Issue [121, 184].

4.8. Nano-biomaterials

Low-temperature plasma-assisted processes have been used to fabricate and process a range of nano-biomaterials. These materials are used as bioimplants and scaffolds in reconstructive surgery or dentistry, in drug, gene and protein delivery systems, as implanted biosensors and other medical devices, and in other applications. Some polymeric nano-biomaterials have already been discussed in the previous

subsection; here we will briefly mention a few examples related to different nanomaterials. Relevant examples include various nanoparticles for applications including biomedical imaging (e.g. luminescent semiconducting nanocrystals for tracing intravascular drug delivery capsules or the already mentioned nanodiamond for MRI imaging), drug, gene and protein delivery, and targeting and aggressive treatment of tumour cells [193, 194]. Hard diamond-like carbon (DLC) coatings with specific microstructures have been used (e.g. in combination with biocompatible polymers and suitable metal alloys) to improve biocompatibility and durability of cardiac and vascular stents. Nickel–titanium (NiTi) shape memory alloys and more recently DLC-coated poly-acryl-ether-ether-ketone (PEEK) have been used to construct automatic scoliosis correction devices [195–198]. Nanostructured hydroxyapatite bio-ceramics and silica bioglass fabricated using plasma-assisted techniques have been used to coat biomedical implants for use as artificial hip and knee joints and teeth [199–203]. Furthermore, arrays of nanodiamond crystals show excellent biocompatibility and are currently used as the main functional element in the bionic eye research that is set to revolutionize ophtalmologic technologies [205]. Optometry and vision science and applications also substantially benefit from plasma-coated/processed contact lenses that offer excellent anti-microbial properties, safety, flexibility and durability when worn on the eye [206].

Interestingly, properties of nanocrystalline phases of many biomaterials determine their *in vitro* bio-response in biocompatibility assessment. For example, nanoparticles of rutile and anatase, two phases of titanium dioxide (produced under different plasma process conditions), showed quite different size-dependent *in vitro* responses in simulated body fluid [204].

Plasma-processed arrays of multi-walled CNTs can also be used as effective drug and protein delivery systems (figure 7) [207]. In these applications, plasma-related effects are used to control the wetting properties (e.g., switch-over between dominant hydrophillic and hydrophobic responses) of the nanostructured surfaces [208, 209]. In turn, this will allow the controlled storage and release of the drugs or proteins in future clinical applications. In particular, delivery of bone morphogenetic proteins (BMPs) is promising as a truly alternative way of bone reconstruction without the need for invasive reconstructive surgery using bioscaffolds or implants. Other biological and medical applications of CNTs are discussed in more detail elsewhere [210].

The above representative examples cover only a small range of possibilities in which plasma-specific effects play a significant role in the development of microstructure and degree of crystallinity, and in controlling the surface energy and other properties of biomaterials. Many of these attributes appear to be important biocompatibility factors. Despite a very large number of reports on successful uses of low-temperature plasmas for the fabrication of viable biomaterials, there is little knowledge about the link between the plasma process parameters used to produce specific biocompatibility factors (in particular those related to nanoscale surface topography or structure) of the biomaterials and the specific bioresponses
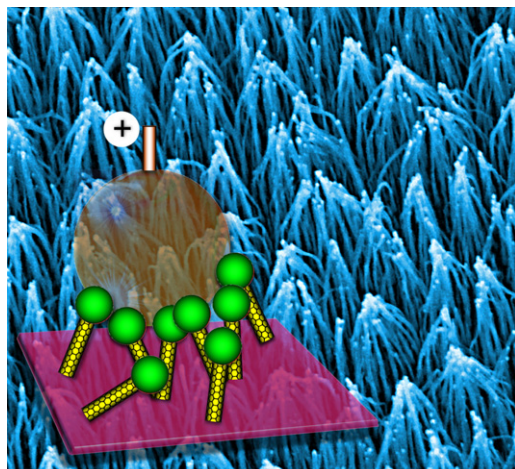
Figure 7. Plasma-processed forests of multi-walled carbon nanotubes have controlled water-repellent properties which can be optimized to enable precisely dosed and timed drug delivery [207, 209]. Courtesy of Han and Levchenko.

Figure 8. Atmospheric-pressure plasma jets have excellent potential to improve wound and cancer treatment. An example of melanoma skin cancer treatment by such a plasma jet is shown. Courtesy of Levchenko.

of relevant cell types. This represents a major opportunity for interdisciplinary research. Another challenge is to expand the scope of plasma nanoscience research into plasma-aided nanofabrication of the multi-shell functionalized nanoparticles of interest to nanomedicine. An example of this possibility is presented by Kong *et al* [211] in this Special Issue. Another paper from this issue examines plasma- and nanoparticle-related nanosafety issues [212].

4.9. Biological objects

Plasma interactions with biological objects has become one of the most topical areas of research. The most common examples include using thermally non-equilibrium cold atmospheric-pressure plasmas (produced, for example, in dielectric barrier discharges or plasma jets) for bacterial inactivation and biofilm removal (e.g. plasma sterilization of food and for dental hygiene and medical treatments [213–216]) and plasma medicine (e.g. wound healing, blood coagulation and skin cancer therapies) [217–220]. An example of the application of a cold atmospheric-pressure plasma jet for treatment of skin cancer is shown in figure 8. The plasmas produce a variety of reactive oxygen- and nitrogen-based species in different neutral, ionized and excited states (O, O*, OH, O_2^-, H_2O_2, NO*, NO_2^-, OONOH, etc; some of the species can be long-living and therefore have a realistic opportunity to induce biologic effects during their lifetime [221]), in addition to other ionic species, electric fields and UV radiation. These factors in combination have effects that vary depending on the particular cell type (figure 9). The reported effects include but are not limited to apoptosis (programmed death), cell membrane rupture, and control of rates of cell division, migration and proliferation.

Impressive advances have been made in this field in recent years. However, there are many challenges ahead, not only in converting the promise of plasma health care and medicine into commercial and clinical applications, but also in understanding the specific mechanisms of interactions of plasma species with
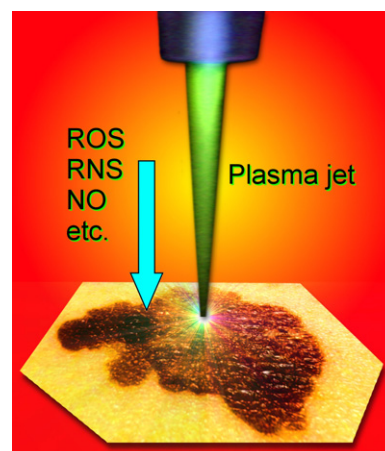
cells. In particular, it is not clear how particular reactive species generated in the plasma induce and affect cellular responses, both at the cellular and intracellular levels. Put simply, a cell is covered by a membrane, which contains a very large number of organelles both inside and on the surface. The major issue is to determine the optimum doses of the selected plasma species in specific (e.g. ionized, excited, radical) states that should be delivered to the targeted cells to induce the desired responses (apoptosis, migration, division, etc). Importantly, only the targeted cells should receive the required treatment while other cells should be left intact. Given the microscopic size of the cells, this poses the question of selectivity of plasma–cell–surface interactions at the *microscopic level*. Moreover, it would be reasonable to question if the entire surface of the cell should receive the prescribed dose of the plasma species or if only specific organelles in localized areas should be affected.

Given the nanometre dimensions of organelles (for example, cilia are nanowire-like structures which are believed to be responsible for activation of intracellular signalling pathways) on the cellular surface, nanoscale selectivity may thus become an important issue. Is it indeed possible to produce and deliver only a small number of reactive species to a small nanoscale area (e.g. the tips of the cilia) and in this way tell the cell what to do? If this simple action could trigger an intracellular command, for example, 'start programmed death', then it may not even be necessary for a large number of reactive species to find their way to DNA (which is contained in the cell nucleus) through nuclear pores having passed through or bypassed the membrane, endoplasmic reticulum, ribosomes, and the many other structures and interfaces in the intracellular space. Likewise, how can transport of the reactive species be controlled with nanometre precision in the intracellular space, for example to deliver oxygen species to oxidize a specific DNA strand or nucleotide or to target a specific protein or virus (which have nanometre dimensions)? We can confidently state without exaggeration that this is not only a billion-dollar question but is also a major challenge at the interface of biological and physical sciences.

Plasma nanoscience research can help us to solve some of the above problems. On the one hand, delivery of plasma-created species with nanoscale precision is one of the key plasma-specific effects [222, 223] and should be explored in the context of interactions of the ionic species with microscopic objects on cellular and tissue surfaces. On the other hand, plasma-produced and appropriately functionalized and/or impregnated nanoparticles can be used for targeted delivery of reactive species, heat, and radiation to localized areas both on the surfaces and in the interior of the cells. This approach, although without the use of plasma-assisted techniques, is presently widely used in nanomedicine, in particular in the area of targeted cancer therapies [225–228]. The combination of atmospheric-pressure plasma discharges and nanoparticles may also resolve the intrinsic limitations of plasma medicine to surface treatments. Initial reports on dramatic improvement of cancer treatment efficacy using the combination of plasmas and nanoparticles [224] are very encouraging. However, the toxicity of any nanoparticles used should be assessed rigorously before clinical application [212, 229].

There is a realistic possibility that the plasma species and nanoparticles act synergistically to enhance their 'own' effects. For example, plasma functionalization and surface coating/modification may reduce the toxicity of nanoparticles, for example through the formation of active biological media (e.g., protein coronas) that associate with plasma-modified nanoparticle surfaces [230, 231]. The mechanisms of transport and cellular control (e.g., apoptosis) associated with reactive radical species and nanoparticles are also quite different [232, 233]. One can thus expect that these effects can act synergistically and complement each other. The nanoparticles can be used for the effective delivery of the reactive radicals into the intracellular space. The combined use of the nanoparticles and reactive radicals may reduce the doses of each of them (e.g. to induce a specific effect on cells) compared with what would be required if they were used separately. This issue is particularly important since 'only the dose makes a thing not a poison' (e.g. a desired biomedical effect can be achieved), according to the Paracelsus' rule [234]. However, the effectiveness and the rates of release of the radicals as well as the nanoparticle uptake (e.g. by inracellular vesicles [235]) will depend on the prevailing intracellular biokinetic mechanisms under specific conditions. Since many equations of physico-chemical kinetics (e.g. involved in the description of nanostructure development and plasma–surface interactions) are structurally quite similar to the equations of biokinetics (e.g. of radical species), this offers an exciting opportunity to develop truly interdisciplinary approaches for the comprehensive analysis of interactions of plasmas and nanoparticles with living cells, tissues and organisms.

The area of microscopic interactions of reactive plasma species and plasma-produced, processed and transported nanoparticles with biological objects is essentially unexplored and offers exciting opportunities for future research and multidisciplinary collaborations. The reader is referred to the contributions of Kong *et al* [211] and Han *et al* [212] to this Special Issue for further details.

4.10. Nanoscale plasma etching

Plasma etching is perhaps the first well-established plasma-enabled technology for which the issues of downscaling to the nanometre domain had to be addressed. As the feature sizes of integrated circuits continuously decrease, new challenges arise to enable further downscaling without compromising structural and material quality and ultimately performance in microelectronic applications. Indeed, as these sizes decrease, so does the required precision in maintaining the geometrical (e.g. shape and aspect ratio), structural and compositional quality of the features involved. More importantly, the mechanisms that determine the interactions between the plasma species and the surface features, structures and layers become fundamentally different when the dimensions become very small. In this case, atomic-level processes determine the mechanisms and energetics of chemical reactions on the surface, which may become very different from those involved in etching of bulk or microscopic materials. The ability to control the selectivity, rates, anisotropy and other attributes of the plasma etching processes in fabricating objects of truly nanoscale dimensions is one of the greatest challenges for the present-day nanotechnology.

Plasma etching is a complex process that simultaneously involves a very large number of plasma species (electrons, ions, radical and non-radical neutral species) as well as chemical reactions both in the gas phase and on the surface. All these species have their own characteristic times and pathways of interactions with solid surfaces. In reactive chemical etching, relatively long-living (ionic or neutral) radicals combine with specific atoms of the surface and form volatile compounds that in turn remove the atoms from the etched material. As a result, some features on the surface are formed. Interestingly, several species often work synergistically to dramatically increase the etching rate. These effects are quite similar to the ion-assisted production of carbon and silicon species required for the growth of CNTs and nanofibres and silicon nanowires [80, 141]. As mentioned above, the etching process may or may not involve etching masks. Plasma etching is one of the most established plasma-based processes [236]; the progress and future challenges in the nanoscale plasma etching of a large variety of materials are well documented [237–240].

Specifically addressing the issue of *nanoscale* etching, we pinpoint the major challenges in achieving atomic layer etching (ALE) as well as reaching the ultimate limits in highly anisotropic etching of very-high-aspect-ratio features of nanoscale thickness. These abilities require effective control of the (relative) fluxes of ionic and neutral radical species, and in particular, their delivery to the specific nanoscale areas that need to be etched.

For example, in developing a high-aspect ratio trench, one should deliver the reactive etching species to the very bottom of the trench without letting them interact with the side-walls, thus avoiding undesirable sidewall etching. Currently, aspect ratios of deep silicon trenches as high as about 100 have been reported [241]. An example of a high-aspect-ratio silicon feature is shown in figure 10. Similarly to the processing of dense arrays of vertically aligned CNTs [246, 247], the ions have a much better capacity for deep penetration. However, limited
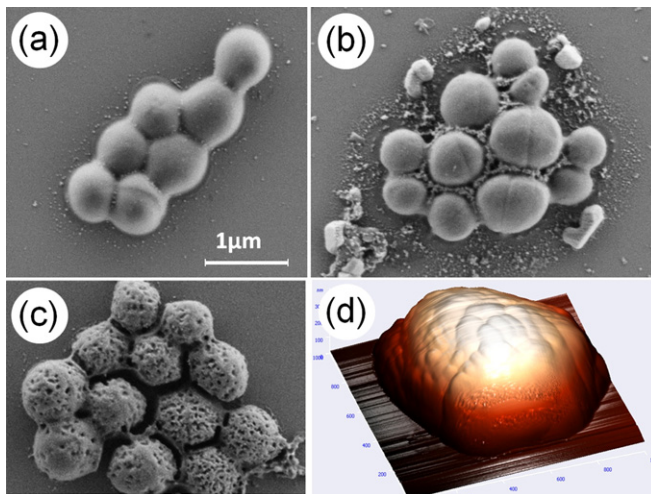
Figure 9. An example of low-temperature plasma degradation of *staphylococcus aureus* bacterial cells with neutral atoms: (*a*) untreated cells, (*b*) removal of capsule and (*c*) degradation of cell wall [214]. (d) Atomic force microscopy image of selective removal of bacterial capsule. Courtesy of Junkar and Cvelbar. Parts of original images reproduced with permission from AIP.
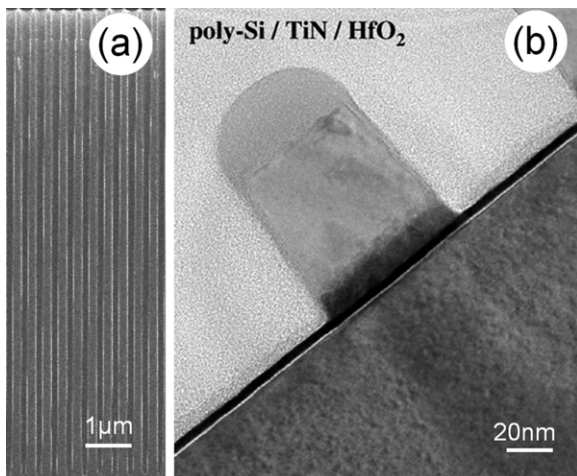

Figure 10. An example of a high-aspect-ratio thin trench in a silicon wafer etched in reactive plasmas (*a*) [241] and transmission electron microscopy image of a poly-Si/TiN/HfO₂ etched gate stack (*b*) [242]. Parts of original images reproduced with permission from AAAS and Elsevier.

charge dissipation leads to undesirable charge buildup inside the features; this in turn prevents more ions from penetrating and further advancing the nanofeature etching process. To control the charge buildup, pulsed processes have recently been introduced, with the pulse timing (duration of 'on' and 'off' sequences) adjusted to deliver the required ion dose during the pulse and allow the charge to dissipate or neutralize between pulses [243]. Despite these impressive advances, precise control of selective species penetration and reactions in nanometre-scale regions still represents a major challenge for the coming years.

In ALE (which in a sense is quite similar to the atomic layer deposition), a monolayer of adsorbed atoms is first deposited on the surface. This process needs to be self-limiting so that only a single layer is deposited. After evacuation of

the reactor, the second reactive species, which can effectively remove some of the adsorbed atoms (so that only one layer of the material is etched) is introduced. This process should also be self-limiting; the second species are only expected to interact with the adsorbed species rather than with the substrate being etched. Recent results of numerical modelling support this possibility [244]; however, selection of the self-limiting steps, development of viable ALE processes and understanding the specific roles of the plasma-related effects still require substantial effort.

In mask-assisted etching, the resolution of lithographic techniques is rapidly nearing its physical limits (believed to be several tens of nanometres). These limits may be reduced to the 20–30 nm range (and possibly lower) with the advent of extreme UV (EUV)-based lithography which relies on state-of-the-art excimer lasers, plasma excimer lamps or the dense plasma focus (DPF) of *Z*-pinch devices, which can produce EUV bursts with wavelengths as short as 13.5 nm. Etching approaches based on self-organized masks (such as a monolayer of polymer spheres or a polymer surface with roughness in the nanometre range produced by plasma exposure) represent a relatively new trend in nanoscale plasma etching and are rapidly gaining momentum. On the other hand, mask-free approaches, although widely used (e.g. for the formation of silicon nanograss discussed above), still lack controllability, and require a proper understanding of the self-organization mechanisms involved.

These arguments suggest that nanoscale plasma etching is also an area where groundbreaking results may be expected in the near future. Several papers [150, 151, 154, 245] in this Special Issue are directly related to this exciting topic.

5. The second dimension: plasmas of interest

In this section, we will very briefly overview some of the most common types of *low-temperature* plasmas and also some of their salient properties that are particularly useful in plasma-aided nanofabrication. Because of space constraints, only a few typical examples of applications of such discharges are selected. We will also highlight the associated challenges and expected advances in the years ahead.

5.1. Low-temperature, non-equilibrium, low-pressure plasmas

Low-temperature, non-equilibrium, low-pressure plasma discharges are the most common in nanoscale fabrication (e.g. nanoelectronics and solar cell manufacture). Such plasmas are operated in a very broad pressure range using a very large variety of gas compositions and excitation sources (mechanisms of power delivery to the plasma). The plasmas are non-equilibrium, i.e. $T_e \gg T_i, T_n$, where T_e, T_i and T_n are the electron, ion and neutral temperatures, respectively. Some of the most common embodiments include dc plasmas, capacitively coupled plasmas (CCPs), inductively-coupled plasmas (ICPs), microwave plasmas (MWPs), and wave-driven (e.g. helicon or surface-wave) plasmas [251–253]. Some plasma-aided nanofabrication facilities are built as
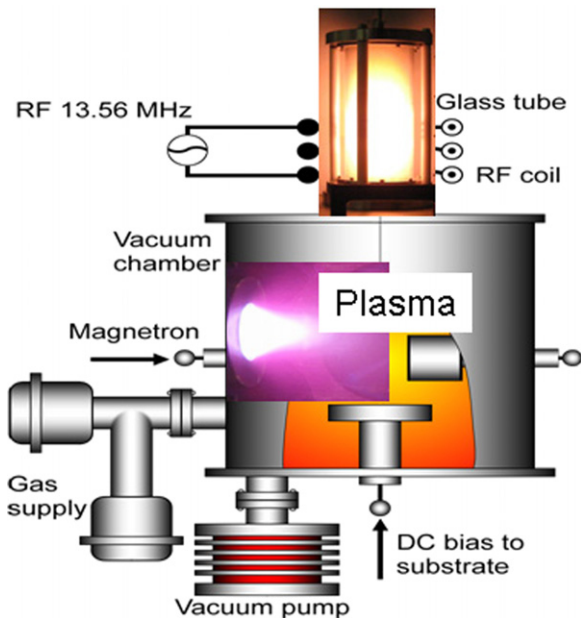
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Figure 11. A hybrid plasma-aided nanofabrication plasma facility at the Plasma Nanoscience Centre Australia can be operated in various modes. A simultaneous use of PECVD and magnetron sputtering modes is depicted.

hybrid systems [254]. For example, the reactor shown in figure 11 can be operated in thermal CVD, PECVD, dc, rf or pulsed magnetron sputtering and a few combined modes (e.g. PECVD and magnetron sputtering shown in the figure), with the added possibilities of remote and direct plasma operation, substrate manipulation, internal and external substrate heating, and independent ion extraction.

Nanofabrication processes using these plasmas are conducted *in vacuo* and are usually intended for high-precision, high-quality, yet relatively low-yield processes, such as reactive ion or radical etching of semiconductor wafers for nanoelectronics. The lower densities and higher sheath potentials of dc plasmas and CCPs make them more suitable for applications where ion-related damage is not an issue and low amounts of matter are required. On the other hand, high-density ICP and MW plasmas with low sheath potentials can be useful for high-rate deposition of low-energy species, which is an important requirement in the fabrication of thin-film silicon-based solar cells [154]. Some of the plasmas, such as ICPs [248, 250] or surface-wave-driven microwave plasmas [249] can be switched between different (e.g. low- and high-density) operating modes. The strong thermal non-equilibrium of such plasmas leads to increased radical production in the gas phase, in part due to electron-impact reactions [248], which eventually leads to the dramatically reduced temperatures needed for the nucleation and growth of most of surface-supported nanoscale objects. Non-equilibrium, low-pressure plasmas are also commonly used for the production and post-processing of relatively small quantities of free-standing nanoparticles, using the ability to charge and levitate such particles near the sheath edge.

Scaling up the plasma reactors to solar cell and large display panels is one of the most significant challenges for

this type of plasmas. Present-day technology uses plasma reactors that can process silicon wafers with surface areas of up to $\sim$10–11 m^2. Maintaining uniformity and precision of the nanoscale plasma processing over such large areas is one of the major problems that needs to be overcome in the near future. Ongoing efforts on the design and optimization of such large-area plasma reactors are focused on either developing a single high-power (e.g. microwave) source and distribution of the input power over different areas of the reactor (e.g. using waveguides) or utilizing arrays of plasma sources (e.g. internal ICPs) with a relatively low power input to each of them [255].

5.2. Thermal plasmas

At higher pressures (above about 0.1 atm) all the species involved tend to thermalize because of the much higher rates of collisions. The temperatures of the electrons, ions, and neutrals are very close to each other ($T_e \sim T_i \sim T_n$); thus, all the species find themselves in thermal equilibrium [256]. Typical densities of these species in thermal plasmas are much higher than in low-pressure non-equilibrium plasmas, with electron densities usually reaching 10^{23} m^{-3}. Hence, one can expect very high fluxes of matter and energy in nanoscale synthesis.

Thermal plasmas are usually produced by arc discharges between two conducting (e.g. graphitic or metal) electrodes or in radio-frequency ICPs. Arc discharges can be divided into transferred arcs, in which one of the electrodes is the workpiece (the material being processed), and non-transferred arcs, in which both electrodes are inside a plasma torch, and a jet of plasma is produced from the torch aperture. All types have found very wide industrial application, in processes such as arc welding [257], plasma spraying [258], plasma cutting [259], waste treatment [260] and metallurgy [261].

Transferred arc discharges are the most energy efficient, but temperature distributions are very non-uniform (see figure 12 for a typical two-dimensional profile and photograph of this type of plasma discharges). Near the cathode, the temperature can be as high as 20 000 K, while at the discharge periphery it can be just a few hundred kelvin [263]. Temperatures are lower in non-transferred arcs and rf ICPs, reaching about 15 000 K and 12 000 K respectively, but the distributions are more uniform, particular in rf ICPs.

The high energy densities of thermal plasmas allow complete evaporation of virtually any material (including those with very high melting temperatures such as carbon or tungsten). Rapid quenching of the plasma to promote nucleation can be achieved by relying on the large temperature gradients and flow velocities in the case of transferred arcs, or by the introduction of cold gas or liquid. A wide range of nanoparticles and nanostructures have been produced, in some cases on a commercial basis, including metallic, ceramic and core-shell nanoparticles [17, 172], nanostructured surfaces [172] and carbon nanostructures including CNTs, graphene and fullerenes [59, 74]. The high densities of precursors mean that very high rates of nanoparticle formation and deposition can be achieved.

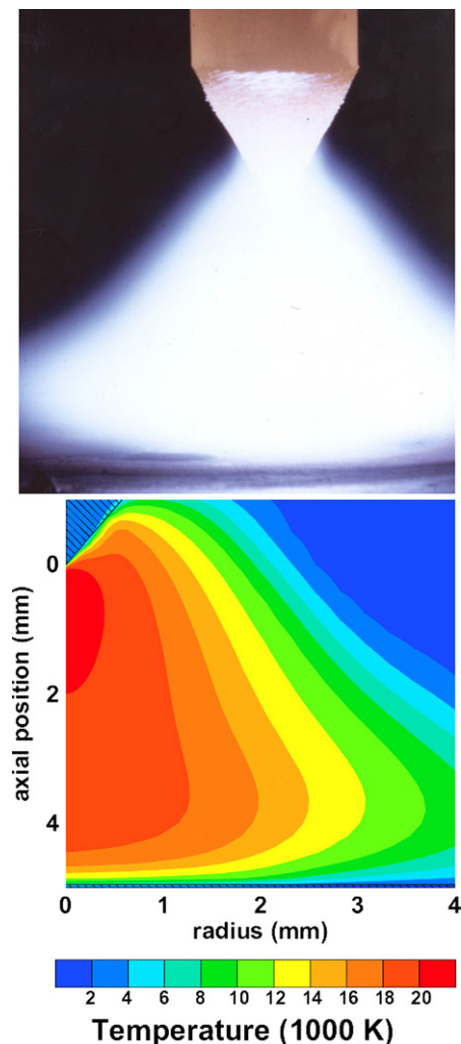Important problems arise from the high-temperature gradients, which mean that production of nanostructures of

Figure 12. A photograph and calculated two-dimensional temperature field in a typical atmospheric-pressure transferred arc discharge in argon, obtained as described in [262].

uniform composition and size is difficult, particularly in transferred arcs. Further work is also required on the control of nanostructure size and quality, and the separation of different structures produced simultaneously.

An extended discussion of all the issues is contained in a paper in this Special Issue [172].

5.3. Low-temperature, non-equilibrium, high-pressure plasmas

As mentioned above, effective collisions between the electrons, neutrals and ions thermalize the plasma. If the plasma is short-lived or is maintained by sufficiently short pulses, the energy exchange between different species may not be effective and some of the species may have much higher energies than others. The first situation is the case, for example, in the plasma streamers generated under transient conditions of frequent surface charging and discharging in dielectric barrier discharges [264]. This is also possible in the relatively stable plasma bullets produced in atmospheric-pressure plasma jets [265]. The second situation is realized in nanosecond

repetitive plasma sparks [266], in which the species cannot effectively thermalize due to the transient application of the external power.

In addition to widespread applications in plasma hygiene and medicine, the first two types of discharges can also be used for surface processing (e.g. increasing the wettability, roughening, oxidation and nitriding), rather than nanoscale synthesis, which usually requires additional precursor materials and raises additional safety concerns (e.g. when using methane or acetylene to produce CNTs). Spark discharges have only recently attracted significant attention for nanofabrication. Nonetheless, by varying the electrode material, one can produce metal oxide nanoparticles [267] as well as highly non-equilibrium structures such as carbon nanocages [105].

5.4. High-pressure microplasmas

There is another possibility to achieve thermal non-equilibrium at atmospheric pressures, by reducing the plasma size to micrometre or even sub-micrometre dimensions [22]. This size reduction leads to a major restructuring of the plasma, including a significant increase in the electric field in the inter-electrode space. This in turn leads to a large increase in the electron energy, which results in non-Maxwellian electron energy distributions. Smaller discharge dimensions in turn lead to much higher rates of neutral collisions with the electrodes and walls which therefore reduces the temperature of the neutrals. This highly unusual thermal non-equilibrium leads to very high chemical reactivity and much enhanced rates of radical production, which is of benefit for nanoparticle production (e.g. via radical polymerization) in the gas phase.

A variety of discharge configurations has been used to produce nanoscale objects. For example, hollow-cathode metal tubes have been used for the synthesis of silicon, nickel, iron, and nickel–iron alloy nanoparticles using reactive precursor gases (silane, nickelocene and ferrocene) [268, 269]. In another example, using gas jets with a metal wire electrode, various metal oxide nanostructures and nanoarchitectures have been produced (figure 13) [58, 270]. It has also been shown that the microplasmas can control the formation of self-organized nanopatterns on solid surfaces [271, 272]. However, the underlying mechanisms still need to be understood. Another apparent challenge is to determine the smallest possible size of the plasmas that can be sustained, and then use such plasmas for energy-efficient nanoscale synthesis and processing. Indeed, such small plasmas would be required to achieve truly matter- and energy-efficient nanofabrication of tiny objects [55].

5.5. Plasmas in liquids and plasma–liquid interactions

Plasmas produced by electric discharges in liquids have many interesting properties that make such plasmas suitable for nanoscale synthesis. Liquid evaporation creates rapidly moving high-density vapours in which the plasma can be created. Such plasmas have high density and are usually strongly nonequilibrium [273]. These two features lead to very high rates of chemical reaction that in turn create a unique reactive plasma environment. The discharges in liquids can
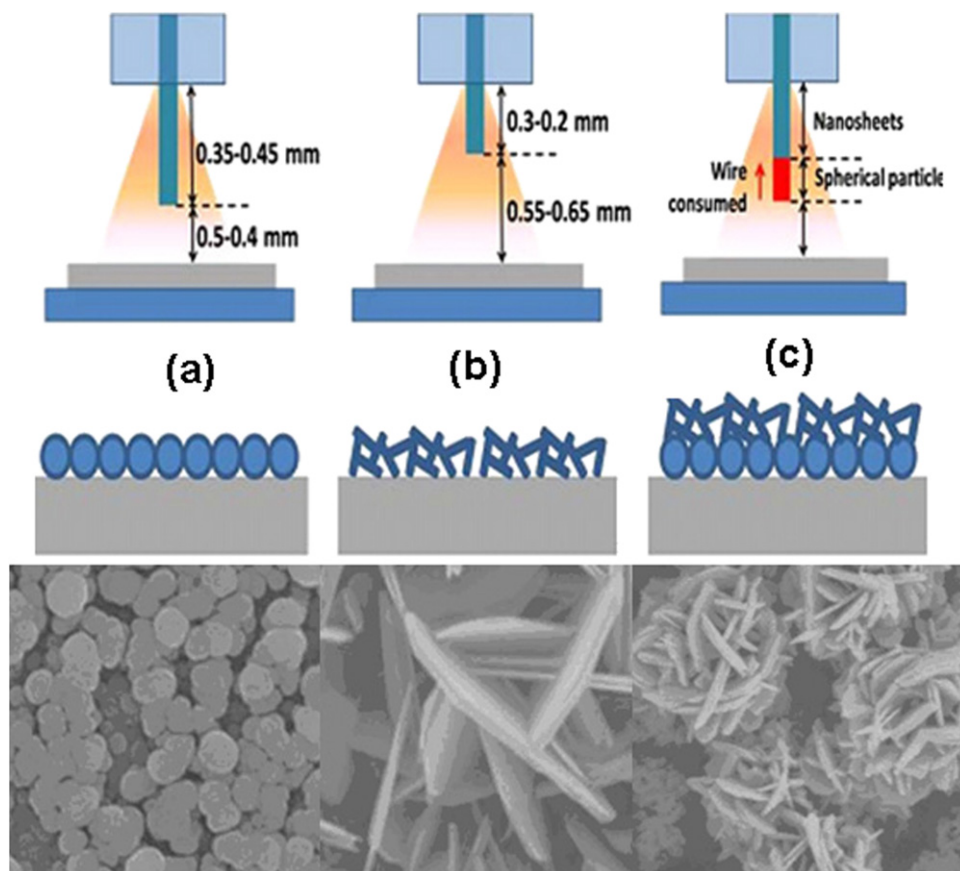
Figure 13. An example of atmospheric-pressure microplasma nanofabrication of molybdenum oxide nanostructures and nanoarchitectures. The resulting morphology (nanospheres, nanosheets, and nanospheres decorated by nanosheets) can be effectively tailored by varying the distance between the substrate and the Mo wire electrode [157]. Parts of original images reproduced with permission from IOP Publishing.

be produced under both high-voltage (e.g. using pulsed dc excitation of a few kilovolts) and low-voltage (e.g. using arc discharges) conditions.

There are two main routes to producing nanoparticles using discharges in liquids. The first relies on specific electrode materials and is very convenient for synthesizing metal or metal oxide nanoparticles, quite similar to arc-discharge-based processes in gas environments. A related option is to use solutions of metal-organic precursors; this type of process is a 'liquid-phase equivalent' of conventional PECVD. The most recent advances include the production of iron nanoparticles using pulsed arc discharges in liquid nitrogen at cryogenic temperatures [274] and the synthesis of carbon-based nanomaterials in supercritical fluids [275]. Other demonstrated applications of solution plasmas include film deposition, surface modification (e.g. oxidation and nitriding) and production of carbon-based nanomaterials. This class of materials processing is commonly termed *solution plasma processing* [276].

The second route for involving liquids in plasma-aided nanoscale synthesis is to create an external plasma that is brought into contact with the liquid [277, 278]. This approach creates many exciting possibilities not only to treat liquids (e.g. water purification) and immersed tools (e.g. sterilization of medical instruments) but also to produce nanoparticles of different compositions and shape. One of the interesting features of this approach is the possibility to use metal

salt solutions instead of metal-organic precursors; this is an example of a safe and an environment-friendly technique. This approach is commonly termed *plasma electrochemistry*; we believe it can also be referred to as *immersion plasma processing*.

Generating plasmas in liquids makes it possible to increase the plasma density, thereby reducing the minimum size of the plasma, which is expected to be at least a few multiples of the Debye length. Nanoscale corona-like glows were produced by remotely generated pulsed discharges in water using CNTs as electrodes [279]. These glows are localized near the nanotube tips and further research to identify and harness their plasma-specific properties is required.

Nanoscale solution and immersion plasma processing are new and rapidly expanding fields. There are many opportunities to make progress in these areas, for example by contributing to a better understanding of plasma production, plasma–liquid interaction, nanoparticle nucleation and growth mechanisms, and to developing reliable diagnostic approaches and tools.

For more information, the reader is referred to relevant papers [58, 280] in this Special Issue.

5.6. High-energy-density plasmas

High-energy-density plasma devices, such as the DPF and *Z*-pinch, have traditionally been used for nuclear fusion

purposes. These discharges are very short (typically in the 10–100 ns range) and produce very high-density plasmas ($n_e \sim 10^{26}$–10^{28} m^{-3}). Exposure of materials to such high-energy-density plasmas leads to deposition of very significant amounts of energy, typically several joule, in an extremely short time. For example, Z-pinch devices can produce fluxes of energetic (up to tens of kV) ions with very high area densities $\sim 10^{19}$ m^{-2} per pulse. This creates extremely non-equilibrium conditions upon the very rapid deposition of the above energy onto the surface [120].

Under such conditions, it is possible to effectively evaporate solid targets (e.g. metals) and produce a fully ionized vapour of the evaporated target material that may condense elsewhere (e.g. on the deposition substrate or a nanoparticle collector) in nanoparticle form [281]. The ions can be produced in very-highly-ionized states (with charge numbers to +10 and even higher) and have energies in the kilovolt range. In DPF devices, more than $\sim 10^{18}$ ions per shot can be produced [282]. Another possibility is to expose solid surfaces to such high-energy-density plasmas and in this way modify material surfaces. Self-organized nanoscale patterns are frequently observed upon such exposure.

As mentioned above, the plasmas and the associated materials processing are both run under extremely non-equilibrium conditions, under which it is extremely difficult to relate the heat and matter exchange upon energetic ion condensation to the properties of the nanomaterials formed. To allow the formation of truly metastable nanomaterials, it is imperative to achieve very high energy dissipation (cooling) rates, in addition to the already available ultra-high rates of energy deposition [106]. Given the extreme non-equilibrium and short time scales of these processes, the issues of process predictability and controllability, as well as energy and cost-efficiency, require significant attention in the future. For more details, please refer to the paper of Surla and Ruzic in this Special Issue [120].

5.7. i-PVD and other plasma-enhanced nanofabrication techniques

Processes in which an ionized vapour of a normally solid material is produced via physical processes such as sputtering or heating are commonly referred to as iPVD [113]. The ionized vapour in turn can condense either in the gas phase or on the deposition substrate to form nanoparticles or films. Relevant techniques to produce such ionized vapours include anodic arcs, filtered cathodic arcs, various modifications of magnetron sputtering including high-power impulse magnetron sputtering (HIPIMS) and pulsed laser ablation (PLA; also known as pulsed laser deposition). Very different ion densities are produced in the different processes; they are typically $\sim 10^{16}$–10^{18} m^{-3} for dc and rf pulsed magnetron sputtering, $\sim 10^{18}$ m^{-3} for filtered cathodic vacuum arcs and $\sim 10^{21}$ m^{-3} for PLA. The precursors for nanostructure production produced in these approaches can be in various states, including atomic, radical, ionic, solid nanocluster and liquid droplet.

The specific technique is chosen depending on the actual requirements of a particular nanofabrication process; both top-down and bottom-up nanofabrication approaches have been used. For example, HIPIMS deposition [283] can be suitable for processes when a relatively large amount of material needs to be deposited over a relatively short period of time, for example, to produce a thin metal nanofilm to be used as a catalyst for CNT growth. PLA operated in a nanosecond regime usually produces highly stoichiometric liquid droplets no matter how complex the structure of the ablation target. Upon redeposition, this results in the formation of complex structures of the same elemental composition. Using small doses of the ablated material, very small nanoscale objects such as semiconducting quantum dots can be produced [284]. On the other hand, femtosecond laser pulses produce finely tuned fluxes of atomic matter, which offers excellent prospects for the formation of subnanometre layers.

Important challenges include developing the ability to control the release and transport of building units, and to adjust the ion energy to create the optimum conditions for nanostructure nucleation and growth upon energetic condensation. Reliable *real-time* tools and approaches for plasma diagnostics and growth process monitoring are also required. Increasing of the range of applications of existing iPVD systems is another priority; some iPVD systems have been used to produce thermoelectric materials and also to process (e.g. coat, heat and melt) nanoparticles as discussed in the contributions of Wiggers [286] and Kersten [123].

Owing to space constraints, we are not able to review, or even mention, all the existing hybrid techniques, in which low-temperature plasmas are used to enhance other deposition techniques. Here we will only note a few representative examples, such as plasma-enhanced magnetron sputtering deposition, which has been used to produce a variety of catalytic nanolayers and nanoparticles *in situ* [14], plasma-enhanced PLA, which has been used to fabricate ZnO nanomaterials [287], plasma-enhanced molecular beam epitaxy of nitride nanomaterials [288] and plasma-enhanced atomic layer deposition of monoatomic layers [289]. The use of the plasma produces many benefits, in particular increased dissociation of reactive gases, reduced process temperatures, better precursor utilization and higher throughput.

6. The third dimension: cutting-edge applications and grand challenges

Having discussed the two first dimensions (nanoscale objects and materials in section 4 and types of plasmas in section 5), here we will briefly mention some of the most important areas in which nanotechnology-driven innovation has the potential to help solve the 'Grand Socio-economic Challenges' faced by humankind. To be more specific, we will focus on the areas related to nanoelectronics, energy, health and the environment in which we anticipate that nanoscale materials, and devices produced using plasma nanoscience approaches, may make substantial contributions. We will restrict ourselves to mentioning some of the best-known applications.

6.1. Nanoelectronics

In the field of nanoelectronics [290], major advances and changes are expected in the coming years. One can also expect that plasma-based nanotechnologies will continue to make the prime contribution. The anticipated advances will be associated with the continued improvement of precision and resolution of top-down nanofabrication, possibly to tens of nanometres and below. Continuously increasing precision and throughput of nanoscale plasma etching on the one hand, and the advent of new nano-lithography tools based on plasma sources of extreme ultraviolet radiation on the other, have outstanding potential to drive the expected improvements in top-down nanofabrication.

In parallel, the importance of bottom-up nanofabrication, which is based on controlled or guided self-organization of nanostructure patterns and arrays, will continue to increase. This will happen in part because of the possibility of producing self-organized patterns and arrays of very small nanoscale objects that are not achievable via top-down approaches. Plasma-specific effects can in turn offer several effective control capabilities for these self-organized processes.

It is expected that several new materials will need to be integrated into the currently dominant silicon-based micromanufacturing platform. These materials include graphene, CNTs and semiconducting nanowires, to mention just a few. Plasma-based approaches have shown excellent results in the production and processing of such nanomaterials. The low-loss and energy-efficient integration of these nanomaterials into nanodevices is a significant related challenge. For this reason, reliability of operation and simplicity of production, in addition to reasonable cost, are becoming very important issues in nanofabrication.

6.2. Energy

Major advances are expected in the application of nanomaterials and plasma technologies for the solution of the 'Grand Energy Challenge' [291, 292]. The main areas in which it is anticipated that plasma nanoscience research will contribute are the fabrication of nanomaterials and devices for energy conversion, energy storage, light emission and sequestration (e.g carbon dioxide capture). Since energy conversion is fundamentally determined by elementary processes at nano- and subnanometre scales, the understanding of the underlying mechanisms of energy exchange between photons, electrons, holes and phonons and their transport over nanometre lengths in energy conversion nanodevices is becoming an issue of paramount importance [55, 291].

Fabrication of photovoltaic solar cells for renewable energy generation is probably the most important area of application of plasma-made and processed nanomaterials in the foreseeable future. Of particular interest are low-cost, highly-efficient thin-film silicon-based cells, various tandem cell configurations with high conversion efficiency, as well as quantum-dot-enhanced solar cells of the third generation [55, 154]. An example of a third-generation, thin-film silicon-based photovoltaic solar cell enhanced by gold nanoparticles deposited on top of the cell (for plasmonic enhancement of light

capture via forward light scattering) and with a fairly uniform three-dimensional array of silicon quantum dots within a functional silicon layer (for bandgap tailoring and multiple exciton generation) is shown in figure 14.

Opportunities for cutting-edge research include elaboration of novel physical mechanisms to increase the efficiency of light trapping (e.g. using surface plasmon resonances in plasma-produced gold nanoparticle arrays [293, 294] or precisely tailored surface micro- or nano-texturing using plasma exposure), photocarrier generation (e.g. bandgap tailoring in functional layers to maximize the hot carrier contribution or enabling multiple exciton generation by producing regular arrays of plasma-produced nanocrystals [299, 300]), as well as improving exciton transport and capture in the electric circuit (e.g. by improving the quality of the nanomaterials involved). Commercial opportunities include development of large-scale plasma reactors for the production of truly large-area solar cell panels, as well as integrated cluster equipment for all-in-one synthesis and production of the functional layers of the solar cells. One can also expect that the use of plasma-based nanotechnology will substantially reduce the production costs of photovoltaic devices. Additional opportunities also exist in the incorporation of plasma-made carbon-based nanomaterials (e.g. CNTs and nanowalls) [56, 78] with appropriate plasma-assisted doping in photovoltaic solar cells. These nanomaterials offer drastically different mechanisms of carrier generation and transport compared with the existing silicon-based platform.

An important issue that affects the development of any particular platform for energy conversion devices is commercial viability. This is one of the reasons why photovoltaic cells based on flexible and cheap organic nanomaterials and also on hybrids of soft (polymer) materials and other nanomaterials (e.g. fullerenes, CNTs, nanowires, etc) are increasingly gaining momentum [295]. However, the photoconversion efficiencies of this type of devices require a substantial improvement [296]. Low-cost atmospheric-pressure plasma processing holds and outstanding promise not only in the structuring of organic photovoltaic materials but also in tailoring their carrier generation and electric conductivity properties, as well as the practical implementation of large-scale roll-to-roll industrial manufacturing processes.

There are many opportunities to contribute to the rapid development of other energy-related areas. Indeed, production of low-cost, high-quantum-yield quantum dot- and quantum well-based semiconductor nanomaterials (e.g. InN and GaN) as well as light-emitting organic nanomaterials is crucial for the development of the new-generation of low-cost, high-efficiency solid-state lighting. Solid-state sources such as light-emitting diodes (LEDs) are the ultimate high-brightness and energy-efficient light sources of the future [285, 297].

Production of the next-generation of thermoelectric devices will help recover the enormous waste heat produced by industries, urban transport, and households. Major fundamental advances are needed to truly incorporate nanomaterials into highly efficient thermoelectric energy generation, in particular, to simultaneously increase electric
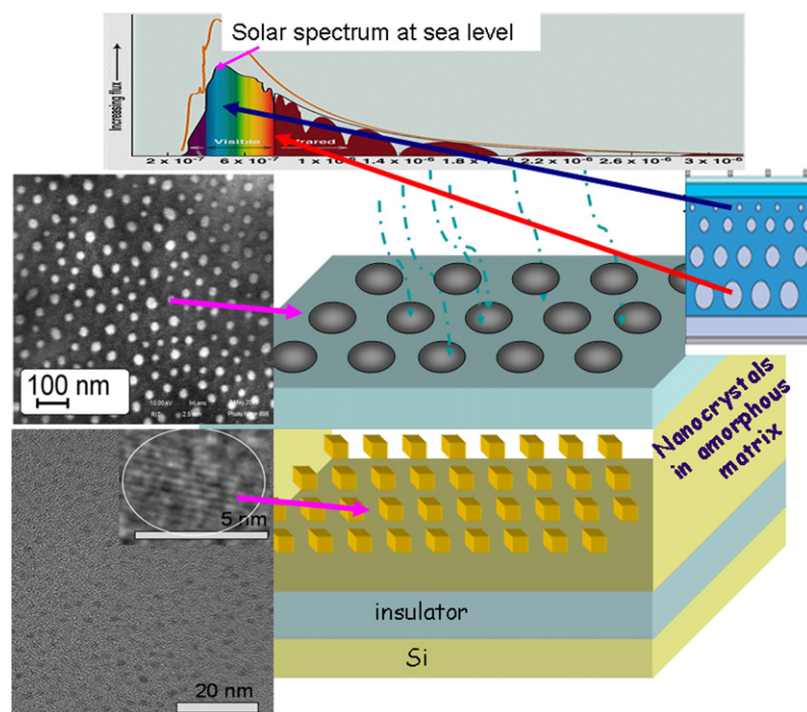
Figure 14. Thin-film, silicon-based photovoltaic solar cells of the third generation substantially benefit from the involvement of plasma nanotechnology. Arrays of gold nanoparticles on top of a transparent conducting oxide layer serve to enable effective light trapping by using forward scattering on electromagnetic fields of surface plasmons excited in the gold nanoparticles. Silicon nanocrystals in the main functional layer (amorphous silicon in this example) can be arranged in layers of different sizes to enable effective trapping of photons from the entire solar spectrum. Layers with smaller and larger nanoparticles can effectively interact with higher- and lower-energy photons respectively. Fascinating quantum phenomena such as multiple exciton generation and generation of several excitons by a single photon passing through different nanocrystals are possible.

conductivity (to minimize Joule losses) and decrease thermal conductivity (to reduce parasitic thermal leakage) far beyond what is achievable by using conventional bulk thermoelectric materials. For more details of contributions of plasma-based technologies to the solution of this problem please refer to the relevant paper from this Special Issue [286].

Other energy conversion routes such as electrochemical (fuel cells), photocatalysis and photosynthesis (solar fuels), piezoelectric (conversion of mechanical energy into electric), and solar thermophotovoltaic (using solar heat to generate photons and then direct them into a photovoltaic cell) are also expected to receive a major boost through the utilization of unique properties of nanomaterials. For example, the efficiency of photocatalytic hydrogen production has been increased by the use of nanotube arrays in place of unstructured films [298]. Equally important are various means of energy storage and heat management such as electrochemical batteries, capacitors and supercapacitors, chemical storage of hydrogen, heat sinks based on nanomaterials with high thermal conductivity and several others. A variety of nanotechnology approaches will continue to be exploited to develop nanomaterials with suitable properties. Some of the possibilities of using plasma nanotechnology to contribute in this direction are also reviewed [53, 149] in this Special Issue.

Energy technologies currently have enormous environ-mental impact, which in part is evidenced by continuously increasing levels of carbon dioxide emissions. Solutions to this problem, one of which may be using nanoporous or other

sorbent materials for CO_2 capture [301], are matters of the utmost importance. Various nanoporous materials produced using plasma nanotechnology should be examined for their suitability to solve this problem.

6.3. Health and the environment

There are numerous important challenges related to health and the environment. We take a very broad view of the term environment, including the workplace, the natural environment on Earth, and extending to outer space.

Health-related challenges include plentiful and balanced nutrition and water supply, as well as effective and accessible preventative health care and medicine. Environment-related challenges include workplace safety (with a particular emphasis on nanosafety because of the primary focus of this paper in nanotechnology), the maintenance of a clean natural environment, and a cataclysm-free near space.

Substantial contributions that a plasma-based nano-technology can deliver to the first area (health-related challenges) have been discussed above in relation to nano-biomaterials, plasma medicine and health care and plasma hygiene. Some relevant applications to briefly mention here include effective cancer therapies; biophotonic imaging; wound healing; blood coagulation; sterilization of medical instruments, the oral cavity and food packaging; delivery systems for drugs, DNA and genes; biocompatible implants for hip and knee joints and eye cornea; biocompatible scaffolds

for reconstructive surgery and biosensors for health and point-of-care disease monitoring.

The second, environment-related area, can also substantially benefit from the involvement of plasma nanoscience research. Indeed, plasma-made nanowire-based oxygen monitors [161] can be used as prime safety detectors in the workplace, in particular, in laboratories that use reactive gases or in the areas where insufficient oxygen supply may cause asphyxiation. Detailed discussion of nanosafety aspects by Han *et al* [212] in this Special Issue lead to the conclusion that plasma-based nanotechnology has several unique features that make it one of the safest and most environmentally friendly nanotechnologies.

On the scale of the Earth, a multitude of plasma-specific phenomena related to the charging and dynamics of space dust make significant contributions towards predicting space weather. For more details please refer to the paper of Popel *et al* [302] in this Special Issue.

On the scale of the Universe, phenomena related to plasmas (which constitutes more than 99% of visible matter in the Universe) also play a major role in the nucleation and growth of carbon and other nanoparticles which in turn form interstellar dust. These processes take place in the relatively cold environments of massive (e.g. red giant) stars. The condensation of (e.g. carbon) material ejected from the hot stars takes place where the gas temperature and the ionization degree of the plasma are low [303]. The role of the plasma in the nucleation of interstellar dust particles has been discussed in the literature (e.g. by invoking the ion-assisted nucleation mechanisms) [3, 16], yet solid modelling and experimental results to clearly substantiate this are essentially missing. This represents another outstanding opportunity to reveal the role of plasma-nanoscience-related phenomena in the processes of stellar evolution and the balance of energy and matter in the Universe.

7. Conclusions

We hope that this review paper, as well as the other papers in this Special Issue, have convinced you that plasma nanoscience is a very interesting and fertile field in which one can expect many exciting discoveries and viable practical applications in the years ahead. The examples and challenges mentioned in our paper represent only a small subset of the numerous existing research achievements and the possibilities for future research.

One important issue to stress is the inherently multidisciplinary character of the field, which is set to expand into many areas that previously were considered totally unrelated. Plasma nanoscience research bridges the physics of plasmas and gas discharges, nanoscience and nanotechnology, quantum physics and chemistry, nano- and optoelectronics, materials science, physical chemistry, crystallography, surface science, optics and photonics, plasmonics, environmental and life sciences, cellular biology, microbiology, biochemistry, electrical and electronic engineering, mechanical and aerospace engineering, and other fields.

Therefore, synergies between the plasma and nanoscale objects (e.g. nanoparticles) have driven the applications of the physics of plasmas and gas discharges well beyond its traditional scope. On the other hand, many research and technology fields benefit from the their synergies with plasma- and nano-related research. This is one of the reasons why research results in plasma nanoscience and nanotechnology are published in a very large range of journals; the number of such publications is rapidly increasing. The number of successful applications of various plasma environments, systems, tools and processes to produce nanoscale objects of any dimensionality and virtually any structure and elemental composition; architectures, arrays and patterns of these objects with unique and highly controllable properties; and nanodevices in which these objects are integrated is also becoming larger and larger. The applications of plasma-made nanomaterials have also spread well beyond traditional microelectronic manufacturing and hard coatings into areas ranging from renewable energy generation through regenerative medicine to environmental monitoring and remediation.

The scientific discoveries and advances that will continue to drive further developments in the field are expected to occur at the boundaries between several disciplines. In particular, groundbreaking discoveries might be expected in the ability to control energy and matter at nanoscales, which has recently been accepted as essential for a sustainable future of humankind [304, 305]. Plasma-specific control of elementary processes of energy and matter exchange on surfaces with nanoscale dimensions, self-organization of large patterns of nanoscale objects, and nucleation and development of exotic nanostructures under highly non-equilibrium conditions, hold outstanding promise for contributing to the solution of this 'Grand Science Challenge' [106, 306]. For more detailed discussions, the reader is referred to the paper by Ostrikov in this Special Issue [55].

Many exciting opportunities exist in the application of plasma-based nanoscale synthesis and processing to produce arrays of quantum structures (e.g. quantum dots—the artificial atoms). These hold great promise as a means towards realization of the currently elusive coherent quantum control [307]. This possibility is often referred to as the second quantum revolution, and is needed to realize the long-held dream of a purpose-designed and precisely controlled quantum world. In the quantum realm, one can manipulate the quantum mechanical degrees of freedom such as electron spin and photon polarization, as well as achieving quantum entanglement and superposition. The present-day challenge is to make these effects a reality in loss-prone environments at room temperatures. This capability needs to be extended into mesoscopic systems of artificial atoms that can retain their quantum coherence for a reasonably long period, in spite of thermal fluctuations, noise, dephasing due to interactions with the substrate, etc. These made-to-order mesoscopic systems are set to enable long-range emergent quantum phenomena including entangled many-body states, long-range quantum order and strongly correlated quantum interactions not only between individual objects but also between systems (e.g. patterns or arrays) of such objects.

Interfacing biological, plasma and nano-worlds at micro- and nanoscales also represents a grand opportunity in the coming decades. This will ultimately lead to high-precision control at cellular and intracellular levels using nanoscale and atomic-level stimuli from reactive plasmas and plasma-produced or processed nanoparticles. This control is in turn needed to resolve many health challenges such as cancer, neurodegenerative diseases and viral infections. One can anticipate the advent of plasma nanomedicine and plasma-nano-health care in the near future.

Environmental and health-friendliness is another prominent feature of plasma nanotechnology [212]. In this area, there is a myriad of scientific opportunities to develop reliable nanosafety standards and assessment protocols for plasma-produced and processed nanoparticles and nanostructures. This assessment is also vital for the understanding of interactions of plasma-synthesized or functionalized nano-objects with living cells, tissues and organisms.

These and many other ongoing and anticipated advances in the plasma nanoscience field are set to substantially contribute to the solution of several 'Grand Socio-economic Challenges' related to a sustainable development of humankind. These challenges include energy, environment, preventative health care and medicine, food and water. As nanotechnology in general is moving into the practical, outcome-driven domain [308], the focus of plasma nanoscience also needs to be directed towards applications closely related to these 'Grand Socio-economic Challenges'. Otherwise, there is a danger of losing the current strong levels of topicality and of interest from other research, engineering, and business fields.

To conclude this paper, we decided to formulate a simple catchphrase that would reflect the current trends and future opportunities in the plasma nanoscience field. After recalling the earlier years of research, when the primary focus was on the ability to control emergent self-organization phenomena in complex (e.g. hierarchical) nanoscale systems, the significant advances that have been made in this direction, and putting these advances into the practical, outcome-oriented context, one can finally arrive to the conclusion that plasma nanoscience should move in the direction *from controlled complexity to practical simplicity in solving grand challenges* [309].

Acknowledgments

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