Plasma-aided nanofabrication: where is the cutting edge?

EDITORIAL REVIEW

Plasma-aided nanofabrication: where is the cutting edge?

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Abstract

Plasma-aided nanofabrication is a rapidly expanding area of research
spanning disciplines ranging from physics and chemistry of plasmas and gas
discharges to solid state physics, materials science, surface science,
nanoscience and nanotechnology and related engineering subjects. The
current status of the research field is discussed and examples of superior
performance and competitive advantage of plasma processes and techniques
are given. These examples are selected to represent a range of applications
of two major types of plasmas suitable for nanoscale synthesis and
processing, namely thermally non-equilibrium and thermal plasmas. Major
concepts and terminology used in the field are introduced. The paper also
pinpoints the major challenges facing plasma-aided nanofabrication and
identifies some emerging topics for future research.

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

1. Introduction

Plasma-assisted fabrication of intricate nanostructures and
complex nanoassemblies is a topic that is continuously
increasing in importance, both for fundamental research and
for existing and potential industrial applications. Evidence
of this is stronger support from major funding agencies and
industry, a growing number of major research and research
infrastructure programmes, and a rapidly increasing number
of publications. A range of plasma sources and plasma
facilities has been successfully applied to the fabrication of
many different nanoscale structures, features and devices. In
many cases, the performance of plasma-based nanotools has
proved superior to competing nanofabrication methods and
techniques.

It is important to note that this topic is multidisciplinary
and involves knowledge, methods and approaches from a broad
range of disciplines, ranging from stellar astrophysics through
'traditional' nanoscience and nanotechnology, materials
science, the physics and chemistry of plasmas and gas
discharges, to various engineering, health-related and
socio-economic and business subjects. At one extreme,
a variety of nanoscale solid objects are produced in the
plasmas of stellar environments, while at the other, plasma
nanofabrication has had a marked impact on capital investment,
economy, trade and other aspects of our lives. As a
consequence, one can find reports on plasma applications in
nanoscience and nanotechnology virtually anywhere, from
electronic archives to *Science* and *Nature*, not to mention
numerous monographs and edited books (see, e.g. [1–7] and
references therein).

We are pleased to introduce this Cluster Issue on plasma-
aided fabrication of nanostructures and nanoassemblies, whose
aim is to highlight the main features and competitive
advantages of plasma-based nanofabrication approaches,
methods and techniques. The Cluster Issue contains 20
contributions (including this review) representing different
relevant areas [8–26]. These areas are diverse and cover
topics from 'simple' nanoparticles and nanostructured films to
'delicate' quantum dots, nanowires, nanoarrays and elements
of nanodevices. Even though the contributions in this Cluster
Issue highlight only a small fraction of existing and potential

capabilities of plasma nanotools and processes, the reader may nevertheless be overwhelmed by the variety of plasma- and process-specific options and possibilities presented.

This motivated us to write this paper, whose purposes are to explain the structure of the Cluster Issue, the choice of plasmas and processes and the most commonly-used terminology, to highlight some of the most important points and issues raised in individual contributions, and also to give a brief overview of relevant research efforts in a broader context. Ultimately, as the paper title suggests, we are aiming to pinpoint some of the most important milestones achieved in the area of plasma-based synthesis of nanoscale materials and to identify the main directions, opportunities and challenges for the future basic and applied research and R and D efforts in this undoubtedly 'hot' research area. However, we should point out that this paper is in no way an exhaustive review (for reasons including space limitations and our desire not to delay publication of the Cluster Issue). Many issues are discussed only briefly, and the reader is referred to sources of original information; other issues are not considered at all.

The paper is primarily aimed at broad readership with little or no specialist knowledge either in plasma physics or nanoscience. As such, approximately the first third is written using a minimum of technical terms and explaining those that are used in a simple 'commonsense' manner. The remainder of our paper contains discussions and technical details that are likely to require some specialized knowledge. It is worth noting that such a mix is appropriate for many research grant applications, and we would be pleased if this paper were used to generate more competitive research funding in the plasma-based nanotechnology area. Finally, the long list of relevant references will save time and effort for those producing literature surveys for whatever purpose.

This paper is structured as follows. In section. 2 we introduce and justify the structure of the Cluster Issue, outline its main aims and clarify the most important terms used in this and other articles of the issue. The following two sections are devoted to the two main classes of plasma considered here, both of which are at low temperature compared with those present in stellar interiors and fusion devices. Section 3 is devoted to fabrication of nanostructures and nanoassemblies in thermally non-equilibrium plasmas, which are typically at low pressure. In section. 4, relevant efforts using 'thermal' plasmas (plasmas in thermal equilibrium, which are typically at atmospheric pressure) are discussed. Section 5 highlights some of the most important features and competitive advantages of plasma-based nanofabrication techniques and identifies major future challenges and directions of research in the area. The paper ends with a short summary in section. 6.

2. Main issues, aims, concepts and structure

In this section, we specify the main focus of the Cluster Issue, highlight the major aims and explain the most important terms and concepts. We will also justify our choice of specific plasma environments and processes.

2.1. Main issues and aims

This Cluster Issue on plasma-aided nanofabrication is focused on the physics and applications of plasma systems for the fabrication and processing of nanostructured and nanoscale materials, such as functional nanostructured films and coatings, nanoparticles, nanostructures with different dimensionalities (nanotubes, nanorods, nanodots, nanoarrays, etc), self-assembled nanopatterns, nanosized features fabricated by using ultra-fine plasma etching techniques and plasma-based approaches to nanodevice fabrication.

The authors, in collaboration with the Guest Editors, have endeavoured to address some of the following issues in their contributions:

- salient features of plasma-based environments that make them versatile nanofabrication tools;
- competitive advantages of the plasma route(s), with examples of superior performance of plasma-based processes compared with neutral gas-based (e.g. chemical vapour deposition (CVD), molecular beam epitaxy (MBE), cluster beam deposition etc) and other (e.g. wet chemical, electron beam, microlithography, flame) fabrication routes; and
- optimum parameters for, and the physical mechanisms governing, deterministic (highly controlled and pre-dictable) plasma-aided nanoassembly.

Furthermore, we attempted to shed light on the following problems, specifically related to ionized gas (plasma)-based processes and approaches:

- importance of thermal equilibrium (e.g. thermal versus non-equilibrium plasmas);
- effect of the degree of ionization and pressure range of operation;
- role of specific precursor (the building units of nanostructures) and other functional (e.g. surface preparation) species;
- interaction of ions and reactive species with nanostruc-tured surfaces and nanoscale features (e.g. pores and trenches);
- various effects of the low-temperature plasma environ-ments on nucleation/clustering in the ionized gas phase and on solid surfaces;
- control of surface temperature by intense ion fluxes; and
- use of plasma environments to control the self-assembly of nanopatterns on solid surfaces (plasma-directed/guided self-assembly);

as well as other related problems.

2.2. Main concepts and structure

We now define the main concepts and comment on our choice of the structure of this project. First of all, as the title of this paper suggests, two concepts, namely 'plasma' and 'nanofabrication' are put together. Let us define the meanings of both and try to understand what potential benefits one can obtain by combining them.

By plasma, one usually implies a fully- or partially-ionized gas with many unique properties attributable to long-range electromagnetic interactions between charged particles, which do not occur in neutral gases. The plasma is usually composed of electrons and two other categories of species, termed 'ions' and 'neutrals' depending on their charging state.

The intrinsic property of the plasma is to preserve its overall charge neutrality so that the combined number of electric charges on all negatively-charged species is equal to that on all positively-charged species. Species that belong to the 'ion' and 'neutral' categories are the same except for the presence of positive or negative charges in the case of 'ions'. Relevant species can range from individual atoms, molecules, monomers and radicals to chain and aromatic polymers and macromolecules, atomic and molecular clusters, small grains and nanocrystallites and even particle agglomerates and mesoparticles. Amazingly, all these objects can be charge neutral or positively or negatively charged. The electric charge of such particles varies from a single electron charge for most positive and negative ions to hundreds and even thousands of electron charges for solid nanosized clusters and micron-sized grains.

The three ensembles of species in the plasma find themselves in a continuous thermal motion and experience numerous collisions between each other. The rates of such collisions turn out to be critical in determining whether the plasma is in thermal equilibrium or not. Moreover, each of the numerous plasma species j has its own temperature

$$T_j = \frac{2}{3k} \langle \mathcal{E}_j \rangle,$$

where k is the Boltzmann's constant, which serves as a measure of its average kinetic energy $\langle \mathcal{E}_j \rangle$ in thermal motion, where the angular brackets denote averaging over the entire species ensemble. In plasma science, such temperatures are commonly measured in electron volts: $1\,\text{eV} \cong 11\,600\,\text{K}$.

Depending on the species temperatures, plasmas are commonly subdivided into two major categories: high-temperature (or hot for simplicity) and low-temperature (cold) plasmas. Hot plasmas are common in nuclear fusion devices, where temperatures of the abundant species can reach a few thousand eV or even more. At such temperatures, comparable to the temperatures in stellar interiors, matter finds itself in a fully-ionized state. In other words, the plasma contains only electron and ion components. It goes without saying that at such temperatures any solid material not only melts and evaporates but is also stripped of its electron(s) and is therefore itself ionized.

On the other hand, in low-temperature plasmas, for which the species temperatures typically range from fractions to a few tens of eV, in many cases a large fraction of the molecules and atoms remain in a neutral state, corresponding to a very low degree of ionization. Such plasmas are created in gas discharges, when an ac or dc electric current passes through the neutral gas or when gas is subject to an rf or microwave electromagnetic field. Importantly, from the point of view of nanofabrication, large species (clusters, nanosized grains, etc.) have a much better change of formation and remaining in a solid state in low-temperature plasmas than in hot fusion plasmas.

Depending on the relation between the temperatures of electrons, ions, and neutrals, low-temperature plasmas can be in thermal equilibrium ('thermal plasmas') or out of thermal equilibrium ('non-equilibrium plasmas'). In the former case, $T_e \sim T_i \sim T_n$, where subscripts e, i and n denote the electrons, ions and neutrals, respectively. This is possible when collisions

between very light electrons and 'heavy' ions and neutrals are frequent enough to ensure that the average kinetic energy of all particle species is almost the same. Our intuition tells us that this condition would require relatively high pressures. This is why thermal plasmas occur in discharges at high (typically from a few torr to atmospheric) pressures. In thermal plasmas, it is typical to have $T_e \sim T_i \sim T_n \sim 1\,\text{eV}$. This means that the neutral gas environment can be hot enough to melt and even evaporate solid materials. In such plasmas, the degree of ionization is substantial, in many cases approaching full ionization (with some doubly- or even triply-ionized species) in the central higher-temperature regions, but is much lower in the edge or fringe regions.

On the other hand, in low-temperature thermally non-equilibrium plasmas, electron temperatures are usually at least one order of magnitude higher than those of ions and neutrals. For example, in low-pressure dc or rf plasma discharges, ions and neutrals often find themselves at room temperature ($T_i \sim T_n \sim 0.026\,\text{eV}$), whilst the electron temperature is 1–2 eV. In this case, one can expect quite different interactions of plasmas with solids, since the neutral gas is cold and is thus 'solid-state-friendly'. In such plasmas, the degree of ionization is usually relatively low, in the range 10^{-5}–10^{-2}.

It is important to note that there is a further class of low-temperature discharge that occurs in gases at or around atmospheric pressure, but which is out of thermal equilibrium. These 'atmospheric-pressure non-equilibrium discharges' include corona, spark, dielectric barrier and atmospheric-pressure glow discharges. While the collision rate is high, the discharge does not reach thermal equilibrium because it is short-lived, being interrupted before an arc discharge is formed through, for example, the presence of a dielectric barrier.

It is now prudent to define the concepts of nanostructure, nanoassembly and nanofabrication. By nanostructure we mean any solid object with at least one of its dimensions within the nanometre to tens of nanometre range; 1 nm = 10^{-9} m. Commonly known fullerenes, carbon nanotubes and individual nanocrystals of various shapes are the best-known examples. By a nanoassembly we imply any association of atoms in the size range of nanometres to tens of nanometres. The term nanoassembly is therefore a little broader than nanostructure, and elementary nanoassemblies include irregular-shaped fractals, clusters and macromolecules that are larger than 1 nm in size but are hard to term nanostructures. Nanoassembly also incorporates associations (not necessarily regular) of individual nanostructures and elementary nanoassemblies. For simplicity, here we use the term nanoassembly for nanostructured films, nanocrystals, nanoclusters, nanoparticles, nanopatterns and arrays, nanoporous structures—anything that requires an elementary assembly process at a nanometre scale. Nanoassembly can also be a verb, meaning the process of assembly of sub-nanometre-sized building units into anything that exceeds 1 nm in size.

By nanofabrication one usually means the combination of a nanoassembly process and a suitable process environment; for example, synthesis of 2 nm-sized Ge quantum dots on a silicon surface in a germane (GeH_4) plasma. However, common usage suggests that fabrication ultimately means producing some commercially marketable goods. (Otherwise

this is just a sophisticated academic exercise to satisfy scientific curiosity!) Therefore, at the very least, the above combination *nanoassembly + process environment* has to be complemented by one more component: *function* (ultimately related to envisaged applications) to warrant serious consideration as *nanofabrication*. In simple terms, nanofabrication implies production of functionalities, elements, materials and, ultimately, coatings and devices (using just these two examples for simplicity) that contain nanoscale features (e.g. size, nanostructure, nanopores) or have been made by using nanostructures or nanoassemblies as building blocks. Thus, synthesis of a carbon nanoneedle-like (at least potentially operational) microemitter mounted in a nanosized electron emitter cell or ordered arrays of luminescent quantum dots on stepped terraces on Si(1 1 1) surfaces are viable examples of nanofabrication.

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

If we wish to pursue *plasma-aided* nanofabrication, we need to choose the most suitable sort of plasma and optimize it as a *nanoscale* process environment. Fusion plasmas should be immediately taken off the list of eligible candidates because of the extremely high temperatures and limited number of building units (only electrons and the simplest ions are available). This leaves us to choose between two remaining sorts of low-temperature (cold) plasmas, thermal and non-equilibrium plasmas, and decide which sort of plasmas is most suitable for the specified nanofabrication purpose. For the remainder of this paper, we will refer simply to thermal and non-equilibrium plasmas; it will be taken for granted that we are referring to low temperature (or non-fusion) plasmas.

The remarkable difference in neutral and ion temperatures (at comparable electron temperatures) determined our choice of the structure of this Special Cluster Issue. One group of articles addresses various nanofabrication processes in thermal plasmas whilst the other concentrates on the benefits and advantages of using non-equilibrium plasmas. We do not consider atmospheric-pressure non-equilibrium discharges in detail, although one of the contributions [22] does discuss production of carbon black in a gliding-arc discharge, which is a type of atmospheric-pressure non-equilibrium discharges. While they have been used for nanoparticle and coating production, work in this area is not as extensive or as well developed as for the other plasma types. We refer the interested reader to the recent review by Borra [27].

Before we begin a critical overview of the articles contributed to this Cluster Issue, we can try to speculate (using only the knowledge we have so far) on the results to be expected for each type of plasmas. Firstly, in thermal plasmas neutral gas temperatures are much higher than in non-equilibrium plasmas. Therefore, one should expect strong gas temperature-related effects, in addition to those related to high densities. For example, one can expect high-rate nanoparticle nucleation due to the high-density effects on the one hand, and spheroidization (nanoparticles are expected to have smooth spherical shapes) and crystallization due to the

high-temperature effects. The latter two effects are quite similar to post-synthesis annealing of solid particles in high-temperature furnaces. Thermal plasmas are appropriate to synthesize nanostructures that on the one hand require high temperatures for nucleation, accelerated growth, and on the other hand, remain structurally stable at the high neutral and ion temperatures. The most striking example of such nanostructures is the carbon nanotube, discovered by S Iijima in carbon soot generated in a *thermal* arc discharge plasma [28]. Indeed, carbon nanotubes are stable at high temperatures; moreover, their nucleation and growth also benefit from high-temperature plasma environments.

On the other hand, non-equilibrium plasmas are the ideal environment for nanofabrication of anything where process temperature is an issue. Microchip fabrication in microelectronics is perhaps the best example to this effect. Indeed, integrated microelectronic circuitry on a semiconductor platform contains a large number of ultra-thin metal interconnect nanolayers, which will melt at temperatures of $500\,°C$, or even lower due to the continuously shrinking sizes of microelectronic features. It is readily apparent that a direct integration of carbon nanotubes synthesized in a thermal plasma into such a structure would be problematic, if possible at all. Therefore, for such purposes one needs to develop alternative processes and approaches based on low-temperature fabrication environments, such as non-equilibrium plasmas that feature 'cold' room-temperature ions and neutrals. Moreover, non-equilibrium plasmas have an obvious advantage in processing of easy-to-melt materials such as polymers. Another important area discussed in this issue is the synthesis of delicate nanoassemblies that demand low and controlled supply of building material; low-dimensional epitaxial semiconductor nanostructures are good examples in this regard.

The following sections will confirm that the above commonsense-based intuitive conclusions are indeed accurate. We begin our critical overview with the case of non-equilibrium plasmas.

3. Processes based on non-equilibrium plasmas

In this section we highlight some of the most interesting issues raised in the contributions [8–19] related to thermally non-equilibrium plasmas. Typical examples of nanoassemblies that can be synthesized in non-equilibrium plasmas are shown in figure 1. These nanoassemblies feature different dimensionality, structure, elemental composition, function, etc. For example, figure 1(*a*) shows quasi-one-dimensional single-crystalline nanoneedle-like structures; in figure 1(*b*), one can see vertically-aligned quasi-two-dimensional nanofoil-like structures; figures 1(*c*) and (*d*) display arrays of (usually zero-dimensional) quantum dots; figure 1(*e*) shows a cross-sectional view of a solar-cell-grade bilayered crystalline structure made of Si and SiC. Figure 1(*f*) shows an advanced version of one of the most common embodiments of inductively-coupled plasma sources, currently the benchmark plasma processing reactors in the microelectronics industry.

Out of 12 contributions related to non-equilibrium plasmas, the largest group of four articles [8–11] focuses on
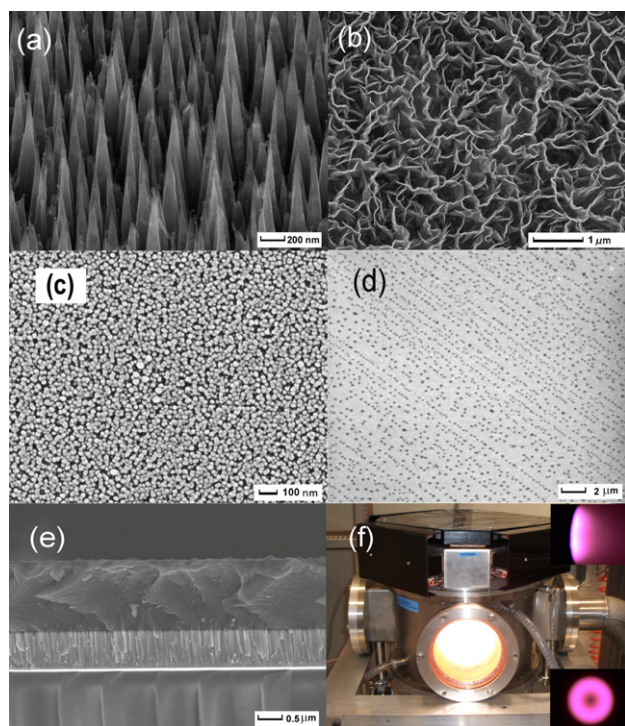
Figure 1. Examples of nanoassemblies (*a*)–(*e*) synthesized in non-equilibrium inductively coupled plasmas (*f*) [50, 63, 64, 75, 92]: (*a*) single-crystalline carbon nanotips (nanoneedle-like structures); (*b*) quasi-two-dimensional vertically aligned nanofoils; (*c*) crystalline SiCN quantum dots; (*d*) ordered arrays of SiC quantum dots; (*e*) cross-sectional SEM image of a bi-layered solar-cell-grade structure; (*f*) source of high-density inductively coupled plasmas with a broad range of capabilities (insets show typical plasma glows). Photo courtesy of S Xu and Plasma Sources and Applications Center, Nanyang Technological University, Singapore (unpublished).

different aspects of plasma-based nanofabrication of silicon-based nanomaterials and elements of nanodevices. This is not a surprise since the most common present-day semiconductor microelectronics platform is silicon-based. The paper by Bell *et al* [13] is relevant to carbon-based nanostructures, which are believed to have the potential to substantially improve the current capabilities of silicon-based micro-/nanoelectronics. Therefore, materials combining silicon and carbon, such as the low-dimensional SiC nanostructures of Cheng *et al* [16], are of exceptional promise for future-generation hybrid silicon-carbon nanodevices. Another three contributions [14, 15, 18] are focused on plasma-assisted synthesis of binary functional materials, such as biocompatible zirconia (ZrO_2) [14], niobium pentoxide (Nb_2O_5) nanowires with excellent catalytic properties [15] and sp^3-bonded boron nitride (5H-BN) for electron field microemitter applications [18]. Different ways of generating ionized vapours of metals and using them for deposition of conformal coatings, filling micro-trenches in ULSI microelectronic technology, and fabrication of self-organized discontinuous (islanded) metal films are discussed in detail in the paper of Anders [12]. In a contribution related to biological applications of plasma-processed nanostructured surfaces, Valsesia *et al* [19] present an interesting hybrid plasma-assisted lithographic technique to fabricate intricate biointerfaces. The remaining contribution

from this group reports on numerical simulation of the growth of nanostructures from ionized and neutral gas environments [17]. It is applicable to a broad range of materials and nanostructures of different structure, shape and dimensionality.

We now discuss these contributions in more detail. The paper by Shieh *et al* [8] details the methods of synthesis of polycrystalline germanium quantum dots on Si and SiO_2, silicon nanograss, Ge nanocones and porous films. Reflecting on the opportunities offered by the plasma-based approach, the authors offer a few interesting examples. First, energetic ions can substantially increase surface reaction rates and reduce the energy barrier for film growth. This is evidenced by a significantly-reduced incubation time of Ge on SiO_2 and the successful deposition of a polycrystalline Ge layer in a 10 min long inductively-coupled-plasma-based process [29]. Another interesting example provides evidence of the advantages of low-pressure, weakly-ionized plasmas in the controlled delivery of building units (this concept is discussed in detail elsewhere [4]). Indeed, one can deliver, in only approximately 0.5 s, exactly as many hydrogen ions as there are atoms on a Si(1 0 0) surface. This high level of control of impinging species can be achieved in inductively-coupled plasmas, which feature high rf power transfer efficiency and high and uniform densities of most of the species involved [30–32]. Depending on the energy of the impinging ions, this feature can be used for controlled and highly-uniform atomic layer etching of Si, which still remains one of the unresolved problems in nanofabrication.

Ion fluxes can also be successfully used to break Si–H bonds and reduce hydrogenation (thus substantially improving the elemental purity) of silicon films, one of the problems that hampers widespread applications of silicon-based nanofilms and nanoassemblies in nanoelectronics. Shieh *et al* [8] report on a number of interesting processes, claiming that plasma (e.g. hydrogen-based) etching can lead to formation of nanograss on Si and an array of Ge quantum dots out of a (presumably fragmented) Ge thin film pre-deposited on SiO_2. These exciting results could be further expanded, e.g. to explore how silicon or germanium-based species etched out of the surface reassemble into nanostructures and how exactly fragmentation of continuous Ge films occurs (for instance, does the Stranski–Krashtanov mechanism common for stress-driven growth of Ge/Si quantum dots occur in this case?). Last but not least, Shieh *et al* [8] explain the relation between the precursor supply, hydrogen termination and catalyst removal/fragmentation on the one hand, and different regimes of nanowire and nanocone growth on the other. These effects are extremely important for the development of deterministic strategies for nanofabrication, and have been studied both experimentally and numerically in relation to a range of nanoassemblies [33–39].

The results reported in contributions [9–11] are excellent examples of the synergy between nanoscience and the physics of complex (dusty) plasmas [40]. All three works describe the use of highly-controlled and predictable reactive silane (SiH_4)-based non-equilibrium plasmas to synthesize ultra-small silicon nanocrystals and create novel materials and elements of devices based on such nanoparticles. Bapat *et al* [9] report on a versatile plasma-assisted process to fabricate perfectly-shaped cubic nanocrystals. This process

has several important plasma-related features. First, synthesis of silicon nanoparticles is carried out in two stages: they are generated remotely (from the deposition substrate) in the active zone of the plasma reactor and then transported using a combination of forces (electrostatic, neutral and ion drag, and thermophoretic [41, 42]) exerted on solid particles in complex plasmas. Second, the unipolar negative charge [43, 44] of the nanoparticles, which they acquire owing to the large difference in electron and ion mobilities, strongly reduces their agglomeration and makes it possible to effectively confine them in a plasma reactor longer than similar neutral particles (owing to the fact that the reactor walls also become negatively charged). Exothermic interactions between the nanoparticles and reactive plasma species facilitate the heating of the nanoparticles, promoting crystallization in the ionized gas phase. The temperatures of the particle surfaces can in fact be several hundred kelvins higher than that of the surrounding gas. It is noteworthy that a significant temperature difference between the catalyst surface and the working gas is a critical factor (not shared by other methods) in the *plasma-assisted* growth of carbon nanotubes and related nanostructures [45–50].

The contribution [9] gives a clear summary of the various process steps involved in the nanofabrication of a device incorporating the crystalline cubic nanoparticles; for more details the reader can be referred to an earlier report [51]. We emphasize that the size of nanoparticles discussed by Bapat *et al* [9] is in the range of a few tens of nanometres; in this case their charge is negative. Future research in this direction could usefully concentrate on providing a convincing explanation of the thermodynamic shape selection of the nanocrystals in question and elucidating the role of surface diffusion processes and hydrogen termination.

The contribution of Roca i Cabarrocas *et al* [10] highlights the uses of smaller (typically in a few nanometre range; however, larger nanoparticles are also considered) silicon nanocrystallites for fabrication of nanodevices in which quantum size effects are essential (e.g. for room-temperature photoluminescence) and growth of polymorphous silicon, a novel type of silicon film. The remarkable manifestation of size-dependent effects is that such ultra-small nanoparticles are in fact *positively charged* as compared with the negatively-charged larger particles discussed above. This change makes it possible to deposit such ultra-small building units on solid surfaces virtually without any major obstacles (such as electrostatic repulsion in the case of larger particles) and also to control their impact energy by imposing a dc potential drop between the plasma and the deposition substrate. Plasma-made polymorphous silicon films are unique because they contain two material phases: a crystalline phase made of plasma-grown ultra-small crystallites and an amorphous (hydrogenated) silicon matrix grown from hydrosilicon radicals. Roca i Cabarrocas *et al* [10] show in several examples how the properties of such films can be effectively controlled by varying process parameters, such as the gas feedstock, working pressure, substrate temperature, etc. In particular, if crystalline structures are formed in the ionized gas phase and then delivered to incorporate into a growing amorphous matrix, polymorphous films are formed. On the other hand, if formation of grains and their crystallization predominantly occurs on the substrate, polycrystalline silicon films are grown.

The paper [10] (as well as other publications, see, e.g. [40, 52]) highlight a recent *paradigm shift* from a common belief that nanostructured silicon films must be synthesized from hydrosilicon radicals (and thus particle formation was regarded as a nuisance) to solid evidence that plasma-generated nanoclusters and nanocrystallites can be controlled and as such serve as viable building blocks of a broad range of nanofilms, not limited to silicon [53–56]. For example, controlling the size of TiO_2 nanoclusters in a plasma-assisted magnetron sputtering process has proved effective in fabricating nanostructured titania films with different ratios of the rutile and anatase phases [57–59], which in turn determines the *in vitro* bioresponse of the films in a simulated body fluid [59]. There is a possibility that ultra-small calcium phosphate nanoclusters play a prominent role in plasma-aided fabrication of nanocrystalline hydroxyapatite [60, 61]. This is consistent with the conclusions of charged cluster theory (CCT) [62], which has been successfully used on a number of occasions to explain unusual, from the atomic- and molecular-assembly viewpoint, nanofilm growth processes that involve positively and negatively charged nanoclusters of different size, structure and composition.

An interesting question arising from the contributions discussed above [8–10] and a number of other reports (see, e.g. [4, 63–65] and references therein) is what exactly causes crystallization of nanoparticles and nanostructures synthesized in plasma environments. In this regard, there appear a few factors that can improve crystallization of plasma-synthesized nanoassemblies. One of the factors is hydrogen atoms that not only terminate dangling bonds on silicon or other surfaces but also are capable of being incorporated into the silicon atomic network and causing its structural relaxation while migrating through it [33] (this issue was also highlighted in the paper of Shieh *et al* [8]). This mechanism is presumably responsible for the remarkable crystallization of nanocrystalline SiC films (grown on silicon substrates with or without a lattice matching AlN interlayer) in reactive plasmas formed from SiH_4, CH_4 and H_2 gas mixtures [66]. In fact, the dynamic deposition and surface diffusion of highly-reactive SiH_x and CH_x ($x = 1, 2, 3$) radicals and their sticking to plasma-activated surface bonds, supplemented by hydrogen atom migration and eventual desorption, leads to structural relaxation of a SiC network to the crystalline state [67, 68].

Another factor in improving crystallization of nanostructures is that due to intense ion bombardment and associated energy transfer, temperatures of plasma-exposed surfaces are higher than those provided by the external substrate heating [45]. In other words, under the same external heating conditions, temperatures on surfaces exposed to a plasma are usually higher. Such higher temperatures are also beneficial for enhancing catalyst activity, which is essential in the growth of carbon nanotubes, nanotips, nanofibres and related structures. In the latter case, additional heating of the surface makes it possible to synthesize nanoassemblies at very low temperatures such as 120 °C [69]. Interestingly, in some cases any additional substrate heating becomes redundant, as is the case of the PECVD of pyramid-like, nanocone-like and nanofibre-like carbon nanostructures (termed the floating temperature growth regime in the original report) [35]. Yet another possibility is that energetic plasma ions cause structural modifications and

eventually relaxation to the crystalline state. There is plenty of experimental evidence to this effect, such as the enhancement of TiO_2 nanocrystal formation by energetic particle bombardment and growth of single-crystalline carbon nanotips at substrate biases ~ -300 V [48, 50, 64]. However, one should exercise extreme caution not to cause any structural damage to nanostructures by overbiasing the substrate. Even though the issue of the causes of crystallization of nanoparticles and nanostructures has frequently been raised in the literature and at conferences, it is still far from resolved.

The paper contributed by Koga *et al* [11] shows the interesting and promising possibility of creating porous low-*k* interlevel dielectric (ILD) materials using SiC-based nanoparticles grown in a reactive plasma. Such materials, with an expected dielectric constant $\varepsilon < 2.0$, are required to fully realize the potential of high-speed signal transmission in ULSI integrated circuitry. To synthesize 20–50 nm sized nanoparticles, reactive plasmas of Ar and $Si(CH_3)_2(OCH_3)_2$ can be used. The transport of such nanoparticles in a plasma discharge is controlled by a number of previously-mentioned forces, including that associated with thermophoresis. Important results of this work include the development of robust strategies for controlled and size-selective deposition of nanoparticle building blocks into specified locations, and also nanopowder management in plasma reactors. Excessive amounts of particulates can significantly affect the operation mode and stability of plasma reactors, especially those with multi-mode operation regimes such as wave-driven and rf discharges [70–72]. It is worth noting that there have been a number of reports of successful use of the thermophoretic force to control nanoparticle motion in the near-substrate areas [73, 74]. Further research in this direction could usefully concentrate on exploring the chemical composition and microstructure of porous low-*k* SiC-based (and other) films, relating them to the specifics of the plasma-based process, in particular those associated with nanopowder-generating regimes.

The variety of plasmas that can be used to fabricate nanostructures and nanoassemblies is very wide, as further suggested by the exciting survey of basic physics and applications of metal plasmas by Anders [12]. It covers the fields of metal plasma production, condensation of energetic ionic species and the processing and synthesis of nanostructures/nanofeatures using such plasmas. The principles of operation of a variety of ionized physical vapour deposition (i-PVD) techniques (modifications of plasma-assisted sputtering, cathodic vacuum arcs and pulsed laser deposition) are examined in the context of their suitability for synthesis and post-processing of nanostructures. One of the main points raised in the contribution is the advantages of using *charged* metal species, whose energy and motion can be precisely controlled in a plasma, in processes where directionality of the condensing species is an issue. A striking example is the use of bias-controlled fluxes of metal ions to fill the gaps in silicon trenches, a process commonly referred to in microelectronic manufacturing as feature metallization. Indeed, a directed and guided flux of metal ions can reach deep inside high-aspect-ratio trenches in silicon; this is not possible to achieve using neutral atoms, which tend to move randomly in space.

This immediately translates into an essential requirement for the develoment of a suitable plasma source: metal atoms have to be effectively ionized while they travel from the point of their release to the deposition substrate. An example of such a versatile plasma reactor is the Integrated Plasma-Aided Nanofabrication Facility (IPANF) [63], which features three dc/rf magnetrons and an external flat spiral rf coil; the latter creates a high-density, highly-uniform inductively-coupled plasma [75], which is used for effective ionization of a variety of building units released from the sputtering targets. The IPANF facility has been successfully used to synthesize a variety of nanostructures of different dimensionality, such as zero-dimensional quantum dots, one-dimensional nanoneedle-like structures and nanowires, two-dimensional nanowall-like structures and multilayered superlattices, heterostructures and nanowells, and three-dimensional nanoassemblies of nearly all imaginable basic shapes [48, 50, 63].

As suggested by Anders [12], different i-PVD systems, vacuum arcs, and pulsed laser deposition (PLD) systems have quite different prospects for nanoscale applications and have their advantages and disadvantages, which are in fact process specific. Among these plasma devices, pulsed magnetron sputtering facilities have an outstanding capability to provide intense fluxes of ionized (with the ionization degree reaching $\sim$70% and even higher, and the possibility of multiple ionization) metal atoms free of macroparticles (which are almost unavoidable in cathodic arc systems). This makes this system suitable for applications demanding controlled dosing of building units, such as synthesis of quantum dot arrays and superlattices with ultra-thin periodic nanolayers. Notably, the macroparticle contamination problem has serious implications not only for cathodic arc systems but also for a range of phenomena in thermally non-equilibrium plasmas (see e.g. [76–78] and references therein).

The contribution of Bell *et al* [13] discusses a number of important *plasma-related* factors that affect the growth and properties of carbon nanotube- and nanofibre-like structures. These factors can be summarized as follows: (i) PECVD makes it possible to synthesize carbon nanostructures on temperature-sensitive materials (this also applies to more generic plasma processing tasks such as film deposition onto or functionalization of polymer surfaces [79]); (ii) the electric field in the plasma sheath appears to be the main factor in achieving nanotube (not only carbon nanotube!) alignment [80], which is not achievable by non-plasma-based methods; (iii) by balancing processes of carbon material delivery to the growth sites and etching it away, one can control the shape of carbon nanostructures; this can be achieved by varying gas feedstock and discharge power. These results are consistent with numerical simulations of deterministic shape control of carbon nanofibre-like structures in a plasma [81].

In this regard, it should be mentioned that the alignment of the nanostructure growth can be controlled by *external* electric fields. For instance, in this way carbon nanotubes can be bent in sharp, pre-determined angles (e.g. 90°) to form L-shaped nanotubes [82]. Moreover, directed ion fluxes from the plasma substantially contribute to the unidirectional growth of Ga-doped ZnO nanorods [83] and AlN columnar nanostructures [84]. As suggested by Bell *et al* [13] the local electric field at the point of growth of carbon nanofibre-like structures can

be enhanced by creating pyramidal shape profiles on silicon substrates; in this case the nanofibres are much longer than those grown on flat substrates. A very interesting suggestion [13] based on a number of earlier reports (see, e.g. [85]) is that C_2H_2 is the most efficient gas feedstock for the growth of related carbon nanostructures. However, the identity of the most important building unit of such nanostructures still remains an open question. The answer to this question is essentially process-specific, depending on microscopic details of structural incorporation of such species into growing nanoassemblies, and its discovery requires a combination of experimental studies and structural investigations using *ab initio* numerical simulations.

The paper of Li *et al* [14] gives an excellent example of how filtered vacuum arc plasmas can be used to synthesize high-quality zirconia (ZrO_2) films with outstanding biocompatibility. Another potential application of zirconia films is as high-*k* gate dielectric materials in nanometre-size microelectronic features. Even though the authors do not provide specific values of the electron, ion and neutral temperatures, we placed this contribution into a category of non-equilibrium plasmas since in cathodic vacuum arcs one usually has $T_e \gg T_i \sim T_n$ with typical values being $T_e \sim 2$–4 eV and $T_i \sim T_n \sim 0.3$–0.5 eV. An interesting conclusion is that the microstructure, surface morphology and phase composition of the ZrO_2 films can be effectively controlled by the process parameters such as the substrate bias, which indicates a possible important role of the plasma ions. Li *et al* [14] also explain the mechanism of bioactivity by negative electric charges acquired by the film surface in a simulated body fluid [86]. A recent contribution [59] challenges this common view and argues that film crystallinity and nanocrystal size are the main factors in inducing the biomimetic response of TiO_2 films, which were also synthesized using non-equilibrium plasmas.

The contribution of Cvelbar and Mozetic [15] tackles a very specific, and one of the most important, problems in the plasma-assisted growth of nanostructures, namely the interaction of reactive plasma-generated species with nanostructured surfaces. Even though several authors have previously considered different aspects of plasma–surface interactions, the uniqueness of the work of Cvelbar and Mozetic [15] is its focus on experimental elucidation of the roles of most important species and their interactions with nanostructured surfaces during the process of plasma-assisted growth of ultra-high-aspect-ratio nanowires. The paper reveals the relation between the creation and consumption of oxygen atoms, and niobium pentoxide (Nb_2O_5) nanowire growth on a niobium foil exposed to oxygen-based plasmas. Notably, the observed decrease of the number density of oxygen atoms is largest when large amounts of Nb_2O_5 nanowires are grown. This conclusion reflects on the very basic nanoscience knowledge that high-aspect-ratio quasi-1D nanostructures (such as nanotubes and nanowires) enable one to dramatically increase the surface area compared with that of a flat substrate, which is the basic principle of operation of nanostructures as chemical catalysts! Interestingly, intense interactions of plasma-generated (e.g. atomic oxygen) species with solid surfaces enable one to synthesize nanoassemblies of Nb_2O_5 and other related oxide materials such as vanadium pentoxide
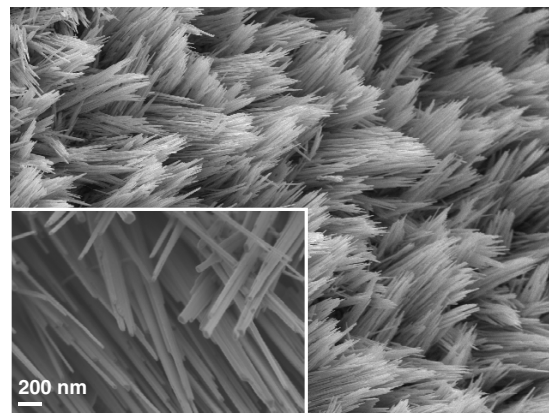

Figure 2. Example of the synthesis of high-aspect-ratio nanowires without any material deposition from the plasma phase. The SEM images show the Nb_2O_5 nanowires grown as a result of interaction of highly-dissociated weakly ionized non-equilibrium oxygen plasma with the surface of a high-purity niobium foil. The average diameter of the single-crystalline Nb_2O_5 nanowires that grow in the (2 1 0) direction is between 50 and 100 nm. Courtesy of U Cvelbar (unpublished).

(V_2O_5) nanowires and smart nanocrystalline coatings [87,88]. Figure 2 shows a unique example of solid phase growth of niobium pentoxide nanowires *without any material deposition from the plasma*. Reactive plasma species etch niobium atoms from the niobium foil; the former combine with oxygen and reassemble on the surface as high-aspect-ratio nanowires. This is an example of another interesting possibility of generation of building units using reactive chemical etching in non-equilibrium plasmas. For different aspects of the related processes and nanostructures, the reader is referred elsewhere [87,89,90].

Cheng *et al* [16] report on the exciting possibility of deterministic assembly of nanocrystalline SiC films using an Ar–H_2 inductively-coupled plasma-assisted rf magnetron sputtering system. The unique feature of this work is in the use of externally-generated high-density inductively-coupled plasmas to ionize Si- and C-based neutral species while they travel from the magnetron target surface to the deposition substrate; remarkably, the temperature on the substrate can be unprecedentedly low ($\sim 400\,°C$). We have already commented on the effectiveness of this procedure when discussing the paper of Anders [12]. The deposition process was carried out in the IPANF facility [63], also mentioned above. A number of articles (see, e.g. [91–94] and references therein) report on plasma-assisted synthesis and the fascinating size-dependent (e.g. room-temperature photoluminescence) properties of quantum dots and nanoparticle films of Ge/Si, SiC, AlN, GaAs, InAlN and other materials. Plasma-assisted synthesis of SiC/Si quantum dot systems has recently been the subject of numerical modelling, which suggests that it is possible to control the elemental composition of the nanodots throughout their entire structure by adjusting the incoming fluxes of the plasma-generated building units and the surface temperature [95]. A more generic approach [96, 97] can explain the evolution of a variety of nanodot systems on surfaces exposed to intense ion fluxes.

As shown in the paper of Levchenko and Ostrikov [17], the effectiveness of the ion contribution to the plasma-assisted
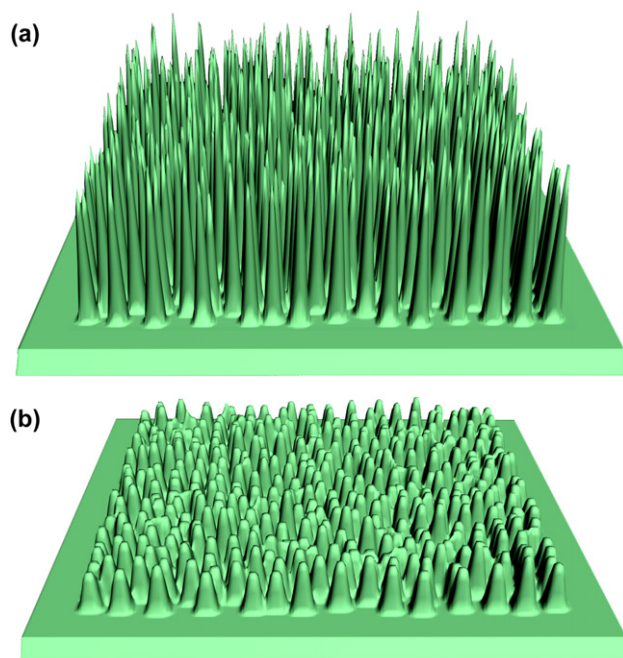
Figure 3. Simulated arrays of vertically-aligned carbon nanotip-like structures synthesized in (*a*) an ionized and (*b*) a neutral gas-based process [38]. Courtesy of I Levchenko (unpublished).

synthesis of nanostructures depends significantly on the dimensionality of such nano-objects. This contribution is devoted to the specific subclass of nanoassemblies that can effectively focus ion fluxes by microscopic electric fields in their immediate vicinity. This strong ion focusing is in fact responsible for effective redistribution of the incoming fluxes of plasma-generated building units and their steering about nanostructured/nanofeatured surfaces. The results of numerical simulations appear instrumental in explaining many important features of plasma-assisted nanostructure growth discussed elsewhere in this Cluster Issue. For example, the results of numerical simulations of the growth kinetics of carbon nanotips in a dense array shown in figure 3 suggest that sharper and taller nanostructures can be synthesized in a plasma-based process (figure 3(*a*)) under the same process parameters as in neutral-gas-based chemical vapour deposition (figure 3(*b*)); the latter process leads to shorter and wider nanocones [38].

Of special interest is the possibility of applying monolayer coatings over the entire surface of high-aspect-ratio carbon nanotubes arranged in dense arrays/forests [98]. This becomes possible because of the outstanding ability of directed fluxes of plasma ions to penetrate into narrow inter-nanotube areas; this is quite difficult, if not impossible, to implement via the neutral gas route [39]. To obtain a full picture of the generation of building units in the plasma and their delivery to nanostructured surfaces [4], the results of multi-scale numerical simulations of ion/neutral dynamics within the plasma sheath area [17] should be complemented by detailed two-dimensional modelling of plasma species and power transfer in a relevant plasma reactor [99].

Komatsu [18] reviews the attractive possibility of using a combination of inductively-coupled rf plasmas and powerful lasers to implement different modifications of 'synergistic' plasma and laser deposition of sp³-bonded boron nitride

and other relevant BN-based nanomaterials. The two basic possibilities discussed are plasma-assisted laser chemical vapour deposition (PALCVD) and plasma-assisted pulsed laser deposition (PAPLD). Successful use of these advanced techniques has made it possible to synthesize boron nitride nanostructures with excellent electron field emission and UV-light emission capabilities. The variety of nanostructures reported includes sp³-bonded 5H-BN nanopowder and cone-like structures, BN nanocomposite powder, BN nanocapsules, BN–B nanoballoons and BN nanofibres. Importantly, Komatsu [18] comments on the roles of the plasma environment in enhancing the performance of hybrid plasma-laser deposition systems. In the PALCVD processes, in particular, reactive plasmas are used to generate the precursor species required for the BN nanoassembly, whereas the surface processes are enhanced photochemically by a pulsed UV laser [100]. The processes are certainly worth pursuing for a broader range of nanofabrication processes and nanomaterial systems.

Interesting examples of using plasmas for plasma-based fabrication of chemical nanopatterned surfaces using reactive plasma etching, with polymer nanospheres as masks, are given in the paper by Valsesia *et al* [19]. The details of the plasma reactor used in this study can be found in earlier work [101]. We emphasize that the use of nanosphere lithography originated from wet chemistry and is not very common for dry plasma etching, which is mostly based on porous masks. Using this technique, it turns out to be possible to create polymeric nanostructures that can induce and sustain bioresponse of bio-interfaces in biomedical applications. It is interesting that the nanostructures undergo substantial transformations depending on the oxygen plasma-based etching time, working pressure, input power and substrate bias. The authors point out the importance of choosing a low pressure for the etching process, since this corresponds to a collisionless plasma regime, allowing anisotropic etching. The functionalized nanopatterned surfaces have shown a remarkable ability to immobilize biomolecules. The results contribute to the development of functional nanopatterned surfaces for advanced biosensor devices. The research could be extended into identification and control of plasma-generated species that create nanoscale surface textures on the one hand, and the species that need to be tethered to the surface to attract biomolecules on the other. For a comprehensive review of the different possibilities of using various plasma-generated functional groups to enhance bioresponse of plasma-processed biointerfaces, the reader is referred elsewhere [79].

4. Processes based on thermal plasmas

We now turn our attention to contributions to this Cluster Issue [20–26] related to *thermal* plasmas.

We first consider the production of nanoparticles in thermal plasmas. Such processes have been studied for some decades; indeed the Tioxide company in the UK has long used dc-arc gas heaters to produce TiO_2 pigment, with particle size of 200 to 400 nm, from $TiCl_4$ precursor on a commercial basis. In 1999, Tioxide became part of the US-based Huntsman group, and with additional sites in Europe and Asia, production has reached 600 000 t per year [102]. It should be noted that combustion-based technology is used as

well as plasma technology in this application [103]. Other industrial processes include that developed by Tetronics Ltd in the UK for production of sub-150 nm aluminium particles in a dc-arc plasma, using aluminium wire as the precursor, helium as the plasma gas and controlled oxidation to passivate the otherwise flammable particles [104].

In their contribution, Li *et al* [20] discuss the production of TiO_2 nanoparticles from an inductively-coupled thermal plasma, using liquid precursors injected into the plasma. As well as its use as a pigment, TiO_2 is widely used as a photocatalyst for the destruction of organic compounds in water and air [105] and has potential applications in dye-sensitized solar cells [106], for solar hydrogen production [107], etc. In these applications, particle size and crystal phase are of fundamental importance. Li *et al* [20] focus on the influence of the quenching method on the properties of the nanoparticles. Transverse and counterflow injection of cold argon and helium are compared, both experimentally and in a computational fluid dynamic model. It is found that counterflow injection of helium is the most successful in reducing particle size, as is required for optimum photocatalytic activity. Mean particle sizes as low as 6 nm are obtained. The results are a nice example of the predictive capability of computational fluid dynamic modelling of thermal plasma processes. In earlier work, researchers from the same group have investigated, for example, synthesis of luminescent Eu^{3+}-doped TiO_2 nanocrystals [108] and TaC nanoparticles from liquid precursors [109], and TiO_2 nanopowders from a micron-size TiC powder precursor [110].

While nanoparticle production is to date the most industrially-important thermal plasma nanofabrication process, in recent years, a range of interesting nanoscale structures have been produced in such plasmas. These include carbon nanotubes and fullerenes, nanostructured films, nanowires, nanoparticle 'towers' and even 'nano-bells' and 'nano-necklaces'. The production of such nanostructures is considered in four of the contributions [21–24].

The paper by Girshick and Hafiz [21] compares two different approaches to synthesizing nanostructured silicon carbide films. In one approach (thermal plasma chemical vapour deposition, or TPCVD) the films grow by chemical vapour deposition on a water-cooled substrate on which the plasma impinges. This method has previously been used for diamond deposition and production of superhard β-SiC films [111]. In the second approach (hypersonic plasma particle deposition, or HPPD), the plasma is quenched by expansion through a nozzle, leading to the homogeneous nucleation from the gas phase of nanoparticles, which form a film when they reach the substrate. This method has also been used to deposit nanoparticle films of Si, SiC, Si–Ti–N, etc. [112,113]. Both methods give high film growth rates (up to 15 μm min^{-1} for TPCVD and 60 μm min^{-1} for HPPD, compared with $\leqslant$ 1 μm h^{-1} for conventional CVD). In both cases, the very steep temperature gradients that can be obtained using thermal plasmas lead to a high degree of supersaturation, and therefore high nucleation rates. While the films produced by both methods have grain sizes of order 10 nm, and are composed chiefly of β-SiC, the TPCVD films are denser and harder. The authors present evidence that the HPPD films are produced by a combination of the impact of previously-nucleated SiC
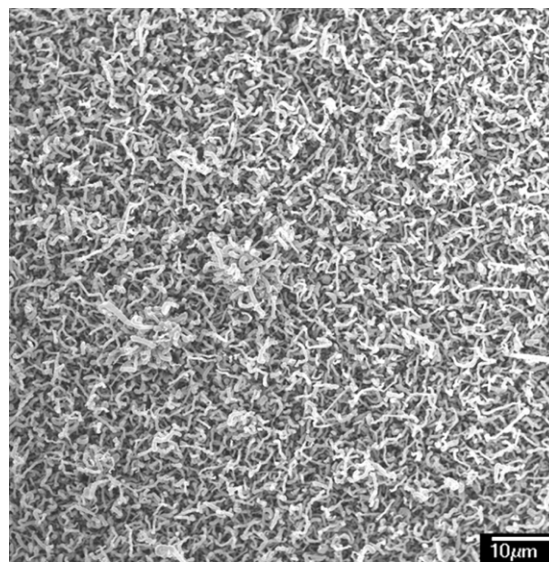

Figure 4. Scanning electron microscope image of silicon nanowires. Reprinted from [114] with kind permission of Springer Science and Business Media.

nanoparticles and the CVD of Si vapour. This dual deposition mechanism gives rise to intriguing possibilities, such as the production of nanoparticle-coated nanowires. In an earlier paper [114], Hafiz *et al* described the formation of single-crystal silicon nanowires. The nanowires are shown in figure 4; figure 11 of Girshick and Hafiz's paper [21] is a higher-resolution image showing the nanoparticle coating. It is postulated that the nanowires grow by CVD onto previously-deposited TiS_2 particles, with the nanoparticle coating being formed by simultaneous nanoparticle impact. There is a range of possible applications in which the high surface area of the nanoparticle and the possibility of electron transport along the nanowires could be utilized, such as dye-sensitized solar cells [106] and solar hydrogen production [115].

The HPPD method has also been used to produce patterned microstructures, using 'aerodynamic lenses' to collimate the nanoparticles into a beam. The process was used to produce towers, lines and two-dimensional patterns with linewidths of the order of tens of micrometres [116]. Figure 5 shows a SiC tower of height 1.3 mm deposited on a stationary substrate; the grain size is about 20 nm.

In their contribution, Gonzalez-Aguilar *et al* [22] provide a review of production of carbon-based nanomaterials and nanostructures in atmospheric-pressure plasmas, both thermal and non-equilibrium. They note that carbon black is one of the oldest nanomaterials used by humans. While a long list of patents for plasma production attests to the efforts to use plasmas for carbon black production, efforts to establish the technology commercially have not passed the pilot plant stage. A wide range of methods for the production of more complicated carbon nanostructures, in particular fullerenes and nanotubes, have also been developed.

Gonzalez-Aguilar *et al* [22] provide an interesting overview of their experience in producing carbon-based nanostructures. They have used a non-thermal atmospheric plasma process to produce carbon black, and a thermal three-phase ac plasma to produce carbon black, fullerenes, single-wall nanotubes, carbon fibres and carbon 'necklaces'. These
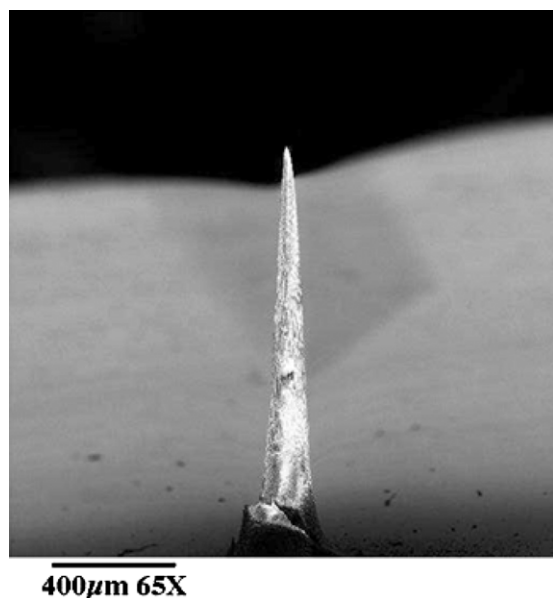
Figure 5. Scanning electron micrograph of an SiC 'tower' composed of 20 nm nanoparticles. Reused with permission from [116], Copyright 2000, American Institute of Physics.
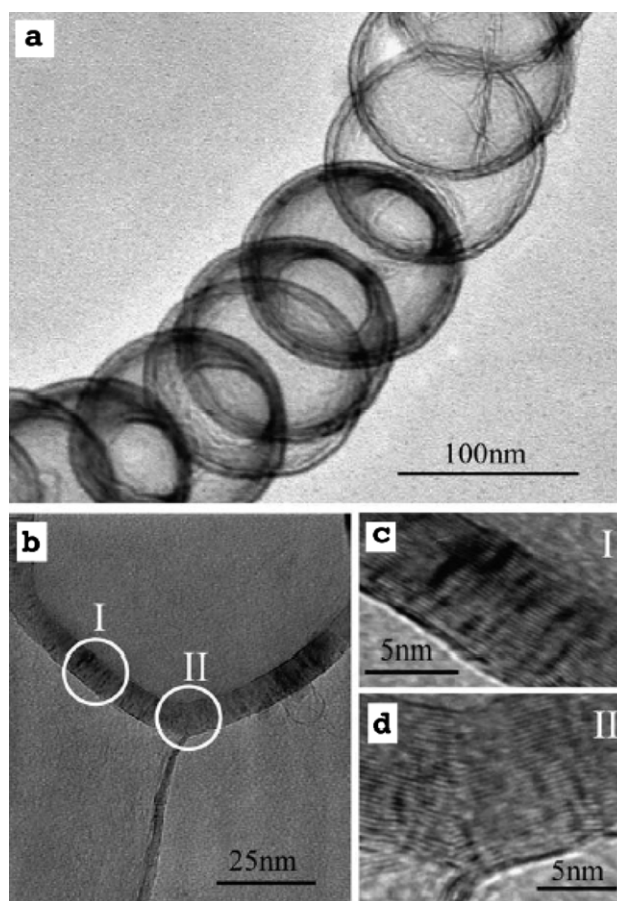

Figure 6. High-resolution transmission electron microscope images of a carbon nanonecklace, which is nearly parallel to the electron beam of the microscope, showing (*a*) the connection between elementary units (nano-bells), (*b*) detail showing the graphene-based shells that make up a nano-bell and (*c*) and (*d*), respectively, details of the regions I and II shown in (*b*). Reprinted from [117] with permission from Elsevier.

'nano-necklaces' can be up to several millimetres long, with outer diameters 50–100 nm, and are composed of joined 'nano-bells', most of which are hollow, although some are filled with the Ni–Co catalyst used in their synthesis. They were described in more detail by Okuno *et al* [117]. Figure 6 shows high-resolution transmission electron microscope images of the connection between the individual nano-bells. Figure 6(*a*) shows the individual nano-bells, while figure 6(*b*) shows they are composed of graphitic sheets. Figures 6(*c*) and (*d*) show that these sheets are separated by about 0.3 nm. Figure 6(*d*) shows the connection between two nano-bells, with the six remaining graphitic sheets from the lower unit surrounding the sheets of the upper unit. Okuno *et al* [117] attribute the growth of the nano-necklaces to the presence of liquid catalytic particles, which requires high temperatures (2000–2700 K), such as only readily attainable using thermal plasma processes.

In their paper, Kim *et al* [23] describe the use of an inductively-coupled plasma to produce high-quality single-walled carbon nanotubes. The precursors are obtained by evaporation of carbon black and metallic catalyst mixtures. The authors note the potential of thermal plasma technologies to produce large quantities of carbon nanotubes in a continuous process. In particular, the high temperatures available lead to a high energy density and an abundance of reactive species, and of course the capacity of thermal plasma technology in an industrial environment is well-proven (as demonstrated by the widespread implementation of applications such as arc welding, plasma spraying and plasma cutting). The particular advantages of the radio-frequency inductively-coupled plasma technology employed by the authors are large plasma volume, longer reaction time (owing to lower gas flow rates), operating parameter flexibility and the absence of electrodes and hence possible contamination. The paper reports continuous production at the rate of $100\,\mathrm{g\,h^{-1}}$ of a carbon soot product, of

which approximately 40% is single-walled carbon nanotubes. This attests to the industrial potential of the process.

A feature of the paper is the use of simple chemical thermodynamic and computational fluid dynamic modelling to infer the optimum conditions for carbon and metal vapour production, carbon and metal cluster formation and single-wall nanotube growth. The authors favour the single-walled nanotube growth mechanism suggested by laser vaporization studies [118], under which homogeneous nucleation of carbon and metals precedes nanotube formation. The importance of an initial rapid quench to allow the formation of metal nanoparticles, followed by a slower quench to favour sustained nanotube growth rather than metal carbide nanoparticle production, is emphasized.

The authors investigate the influence of the grade of the carbon black precursor, the plasma gas and the metallic catalyst composition on single-walled carbon nanotube production. They find that smaller carbon black grain size and reduced sulfur impurity and graphitization are advantageous, as is the use of helium rather than argon as the plasma gas; the latter is attributed to the greater thermal conductivity of helium, leading to more rapid vaporization of the precursors. Finally, the use

of a Ni/Co/Y_2O_3 catalyst is found to improve single-walled carbon nanotube yield.

In his contribution, Keidar [24] clearly and concisely highlights a range of important issues in the plasma-assisted growth of high-quality carbon nanotubes in thermal arc discharge plasmas. It is commonly known that single-walled carbon nanotubes synthesized in arc discharges have a number of indisputable advantages compared with their counterparts grown in thermally non-equilibrium plasmas. These include extra-high growth rates, better structural cohesion and purity, low defect density and the relatively straightforward possibility of large-scale nanotube production; some of these advantages were pointed out by Kim *et al* [23].

What is more surprising is that the presence of metal catalyst on deposition substrates is not always required to synthesize carbon nanotubes in thermal plasmas. In thermal plasmas, the nanotube seed formation can be triggered by metal catalyst released from the specially prepared cathode (or injected otherwise) and often occurs in a region of high carbon and ion density in the inter-electrode gap [119, 120]. This is not so common for nanotube synthesis in non-equilibrium plasmas.

The residence time of the nanotube seed particles in the preferential growth region is critical in determining the nanotube growth process; this particular issue, applicable not only to thermal but also non-equilibrium plasams, is highlighted in [24]. Keidar's paper also contributes to the understanding of the theoretical and practical limits for single-wall nanotube aspect ratio and the most effective plasma-related tuning knobs to control the growth of nanotubes; he also proposes several ways (e.g. use of higher pressures and/or electric fields) to improve the synthesis process.

As suggested by the results of the advanced modelling of the interactions of nanotubes with the plasma environment, the charge on the nanotubes, which ultimately determines their dynamics in the inter-electrode area [119], can change from negative to positive in the areas of depleted electron densities. This can facilitate the nanotube deposition onto negatively-charged surfaces, which is an intrinsic feature of most of the surfaces exposed to the plasma. It is worth noting that a quite similar charge reversal in the plasma sheath area makes it possible for plasma-grown carbon-based nanoparticles to overcome electrostatic repulsion and softly deposit onto nanostructured carbon surfaces [42, 74].

Interestingly, while synthesis of single-walled carbon nanotubes was implemented in the early-1990s in thermal plasmas, it was delayed for at least ten years in non-equilibrium plasmas [121–123]! Difficulties on the way to synthesize *single-walled* carbon nanotubes in thermally non-equilibrium plasmas were highlighted in the review paper of Meyyappan *et al* [5].

One more interesting property of single-walled carbon nanotubes synthesized in arc discharge plasmas is their ability to conduct large currents. Figure 7 shows typical current–voltage characteristics for an arc-produced single-wall carbon nanotube sample until spontaneous ignition occurs [124]. It is believed that the joule heating causes an increase of the sample temperature that, in turn, leads to an increase of the sample resistance. The ignition process is associated with the unique properties of single-walled carbon nanotubes. It
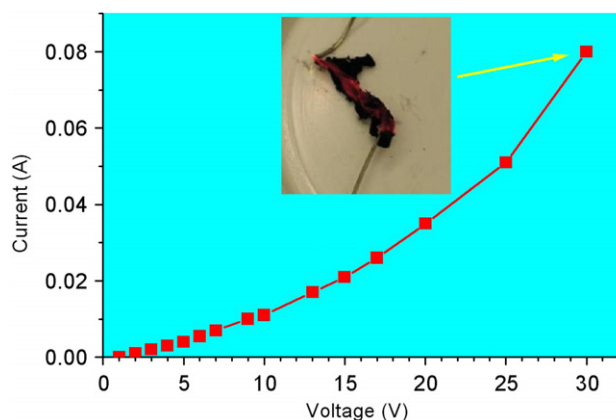

Figure 7. A representative current–voltage characteristic of arc discharge-synthesized single-walled carbon nanotubes when a current is applied across a nanotube sample. Inset shows a sample after ignition [124]. Courtesy of M Keidar (unpublished).

was suggested [124] that controllable ignition and triggering are among possible applications of the current-driven ignition effect in remote triggers and chemical nanoreactors.

Conventional plasma spraying, in which a dc non-transferred arc plasma torch is used to partially melt and deposit particles on a substrate, has recently been comprehensively reviewed by Fauchais [125]. In this Cluster Issue, Fauchais *et al* [25] deal with a much less well-developed plasma spraying method, in which a suspension or solution, rather than solid particles, is injected into the plasma torch. This gives the potential for nanostructured coatings to be deposited. Unlike in conventional plasma spraying, where the injected particles are typically of diameters of micrometres or greater (it is difficult to feed smaller particles without clogging), suspension and solution plasma spraying allow nanostructured coatings to be deposited, with the thickness of individual 'splats' as low as 20 nm. Fauchais *et al* investigate the utility of these techniques through the example of the spraying of the cathode, electrolyte and anode of solid oxide fuel cells. Suspension plasma spraying of yttria-stabilized zirconia (YSZ) was found to permit deposition of dense coatings, as required for the electrolyte. For the anode, porous nickel–YSZ coatings were required; this was obtained by introducing the nickel as a solution of $Ni(NO_3)_2$ in ethanol and the YSZ as a suspension. Spraying of a suspension of $LaMnO_3$ was used to produce porous $LaMnO_3$ cathodes. The properties of the coatings are analysed taking into account the plasma properties and torch phenomena such as the restriking of the anode attachment. This latter phenomenon is a problem in all types of plasma spraying, since it leads to periodic changes in the arc length and position within the plasma torch, and thus to the temperatures to which the injected particles or suspensions are exposed. Overall, the paper demonstrates the versatility of the suspension and solution plasma spraying techniques and their potential for development as industrial processes.

The final contribution, that of Shigeta and Watanabe [26], deals with a sophisticated model of the production of heterogeneous nanoparticles in a thermal plasma. Before discussing this paper, we provide some background on modelling of nanoparticle formation in thermal plasmas. There are three routes by which atoms and molecules in the gas

phase can be converted to condensed particles: homogeneous nucleation, condensation onto an existing particle, and heterogeneous chemical reactions at the surface of a particle. Further, collisions between particles can lead to coagulation, and evaporation leads to a return to the gas phase. Numerical models for homogeneous nucleation and particle growth can be divided into two main classes, 'nucleation-coupled' and 'discrete' models [126]. In the former, a nucleation rate is calculated based on an expression derived from nucleation theory, and this rate is coupled to a model for the evolution of the stable particles. Typically, the first few moments of the particle size distribution are calculated. In contrast, in discrete models, particle formation is simulated by applying the general dynamic equation for aerosols to a discrete representation of the particle size spectrum for monomers, small clusters and particles. The accuracy of discrete models is limited only by the accuracy of the physical modelling of coagulation and evaporation coefficients, by the requirement to group larger particles into 'sections' and by numerical accuracy. Girshick *et al* [127] used a simplified discrete-sectional model (a 'discrete-continuous' model) to investigate iron powder formation from iron vapour in a thermal plasma, and Girshick and Chiu used a discrete-sectional model [128] to investigate nucleation and growth of MgO particles in an Mg–O–Ar plasma. These models were one-dimensional; owing to the computation-intensive nature of the approach, a two-dimensional calculation is prohibitively expensive.

Nucleation-coupled models generally neglect coagulation between clusters and cluster scavenging by stable particles, and also give less information about the particle size distribution, but require greatly less computer space and time. Girshick *et al* [126] showed that by using an appropriate expression for the nucleation rate, very good agreement with the discrete model can be obtained. Nucleation-coupled models have been widely used for over a decade. For example, Désilets, Bilodeau and Proulx [129] modelled the synthesis of Si nanoparticles from $SiCl_4$ precursor using a two-dimensional model, coupling three chemical reactions with nucleation and condensation using a moment approach. Girshick *et al* [130] used a similar approach, also taking into account particle diffusion, coagulation and thermophoresis, to model iron particle formation. A feature of the model is that it also included vaporization of injected iron powder, taking into account the cooling of the plasma through heat transfer to the particles in a self-consistent manner. Murphy [131] modelled the production of Ti nanoparticles from an Ar–H$_2$–$TiCl_4$ plasma in one dimension, using a moment approach coupled to 14 chemical reactions. McFeaters *et al* [132] modelled the production of TiC from TiO_2 and CH_4 in one dimension, using an extensive set of 110 reactions, taking into account homogeneous nucleation and, via simple expressions, soot formation and heterogeneous condensation.

Shigeta and Watanabe [26] have developed a method to model nucleation and heterogeneous condensation, based on the concept of nodal discretization for the particle size space [133]. This allows the size and composition distribution of particles to be predicted. The model thus shares some of the predictive power of discrete models, without the computational expense. However, nucleation is treated in the same manner as nucleation-coupled models, and while

the plasma parameters are obtained in two dimensions, the particle production treatment uses radial averages of plasma temperature and velocity, and is therefore one-dimensional. The model also treats the vaporization of the precursor solid particles in the plasma, although loading of the plasma is not considered. The method has previously been applied by the authors to titanium silicides and borides and molybdenum silicides [134, 135].

In their contribution to this issue [26], Shigeta and Watanabe have introduced an improved formula for heterogeneous condensation and have extended their model to include the effects of particle coagulation and thermophoresis. The first two changes in particular are significant improvements, and the model now has impressive predictive power and flexibility. They have applied their model to the production of heterogeneous nanoparticles from Mo–Si and Ti–Si vapours in an inductively-coupled plasma, generally finding good agreement with measurements of the particle size distribution and composition. Their results identify the importance of heterogeneous condensation and coagulation in the model. A point of interest for designers of nanoparticle production systems is their experimental finding that some precursor powders are not vaporized completely, contrary to the prediction of the model; this is attributed to the time variation of the plasma parameters; it may also be due to variation in particle trajectories and cooling of the plasma due to heat transfer to the particles.

An important problem in thermal plasmas involves the vaporization of liquid and solid precursors, particularly when they are introduced at high rates, as is required for high-rate formation of nanostructures. One major issue is the loading of the plasma that results. Effects that are likely to be important include cooling of the plasma through heating and vaporizing the particles and further through the greatly increased radiative emission in the presence of metallic atoms from the particles [136]. Accurate modelling of the latter would require the calculation of radiative emission coefficients for all elements [137] present, and appropriate treatment of diffusion [138, 139].

A further problem is the nonuniformities, both spatial and temporal, in thermal plasma parameters. We have already mentioned the difficulties caused by the restrike mode in plasma spraying. A more general problem is that of the steep temperature gradients transverse to the plasma flow, which means that species and particles are exposed to different time–temperature histories, and which consequently leads to difficulties in obtaining uniform nanostructure composition.

Another factor of interest in thermal plasmas is the possible charging of particles. This has been considered in some detail in non-thermal atmospheric pressure discharges [27] (it is after all the principle of operation of electrostatic precipitators). However, particle charging in thermal plasmas has not been widely researched. Wang *et al* [140] measured the size and charge distribution of Si and Ti nanoparticles formed in a dc non-transferred arc followed by a hypersonic nozzle and found that while only a few per cent of sub 10 nm particles were charged, almost 50% of the particles larger than 30 nm were charged, with equal numbers of positively- and negatively-charged particles. This was attributed to a balance between attachment of electrons and thermionic emission of electrons.

It is expected that such a bipolar charge distribution will lead to increased coagulation of particles [141], but to the authors' knowledge, this effect has not been included in models.

Charging is an important factor in the production of carbon nanotubes, which occurs in the electrode sheath region of carbon arcs. Keidar *et al* [120] showed that the 'seed particles', from which the nanotubes are formed, are negatively charged owing to the higher mobility of electrons. The transit of the seed particles through the sheath region depends on their aspect ratio; only particles with high aspect ratio are predicted to reach the cathode surface. In his paper in this Cluster Issue, Keidar [24] considered the possibility of positive charging due to thermionic emission. Low electron density was predicted to lead to positive charging and high electron density to negative charging. Keidar further found that application of an electric field could strongly influence nanotube growth. It could be speculated that a proper understanding and exploitation of particle charging effects holds the key to controlled production of complex nanostructures using low-temperature (both thermal and non-equilibrium) plasmas.

The influence of ions on nanoparticle nucleation may also be important. Fisenko *et al* [142] have recently investigated differences between ion-induced nucleation and homogeneous nucleation as well as the collision cross-section for interactions between cluster ions and molecules. Their expression for ion-induced nucleation has been included in a recent discrete-sectional calculation of Tak and Das [143], who found a decrease in mean particle size when ion-induced nucleation was considered.

To end this section we stress that there is certainly a need for progress in the modelling of the production of complex nanostructures. This also applies to non-equilibrium plasma-based processes. Existing models either treat the nanostructure formation processes in an oversimplified manner (e.g. [144]) or use one-dimensional representations of the plasma parameters (e.g. [24, 120]).

5. Issues in plasma-aided nanofabrication

Now, we are in a good position to summarize some of the most important competitive advantages of the plasma-aided nanofabrication over non-plasma-based approaches and techniques. This is done in section 5.1. In section 5.2 we highlight some of the pressing challenges and unresolved issues and map potentially attractive directions for future endeavours in this exciting and commercially-attractive research field.

5.1. Some areas of competitive advantage

We now summarize some of the most clear and important areas of competitive advantage of plasma nanotools and nanoassembly processes. The differences between non-equilibrium and thermal plasmas have been discussed in section 2 and also through the examples given in sections 3 and 4.

A particular advantage of non-equilibrium plasmas is the possibility of directed motion of charged species under the influence of the electric field. This gives the possibility of anisotropic etching of substrates and controlled deposition of nanoassembly building units. In thermal plasmas, the high collision rates mean that directed motion is much less prevalent, except perhaps for larger nanoassemblies such as the nanoparticles and nanotubes considered in [21, 24]. In another aspect, non-equilibrium plasmas can be advantageously used for a range of processes that involve temperature-sensitive materials such as polymers, plastics and ultra-thin nanolayers. Other areas of competitive advantages of non-equilibrium plasmas are also discussed below.

The main competitive advantage of thermal plasmas is the accessibility of high temperatures (high compared with those accessible with combustion-based systems rather than high-temperature fusion plasmas), with regions at temperatures over 20 000 K for transferred arcs and 10 000 K for dc and inductively-coupled rf plasma torches. The high temperatures allow the use of solid, liquid, vapour, gas, suspension and solution precursors, with the possibility of complete dissociation of chemical reactants into atoms. The fact that thermal plasmas are at around atmospheric pressure means that high species densities can be obtained. Moreover, the plasma temperature is largely independent of the chemical reactions (although in the case of high loading, heating and vaporization of precursors can significantly cool the plasma), and there is a very wide choice of both reactive and inert atmospheres. In contrast, combustion-based technologies rely on chemical reactions to heat the gas, and the atmosphere necessarily contains combustible gases and the products of combustion.

The high temperature of thermal plasmas further means that very steep temperature gradients can be obtained, for example by expansion into a low pressure zone, by the introduction of a cold surface, or by mixing of cold gas into the plasma stream. Gas-phase nucleation under high cooling rates becomes pronounced, leading to a high degree of supersaturation and therefore *high nucleation rates*, which allow high-yield synthesis of nanoparticles and nanostructures, not achievable by other methods including non-equilibrium plasma-based ones.

Specific examples of situations in which low-temperature plasmas (both thermal and non-equilibrium unless specified otherwise) can be advantageously and purposefully used include those in which

- specific (e.g. vertical) alignment or electric field-based control of preferential growth directions of nanostructures is required; this applies not only to carbon nanotubes but also to a range of materials and high-aspect-ratio nanostructures;
- directionality of fluxes and penetration of species is necessary; in these cases electric field-driven ions can assist; this advantage is apparent, e.g. in the cases of nanofeature metallization, filling nanopores, and post-processing of dense nanotube arrays; non-equilibrium rather than thermal plasmas are suitable in this case;
- processes are sensitive to high temperatures of the fabrication environments and substrates can easily melt; this is apparent in the case of polymer processing and one of the pressing issues in micro/nanoelectronics; non-equilibrium plasmas are best suited for this purpose and have an indisputable advantage over thermal plasmas and many other methods and techniques;

- crystallization is needed without increasing temperature; plasma-generated crystallization agents (e.g. reactive radicals or subplanted ions) can assist;
- enhanced dissociation of precursor gases is an issue and large yet controlled amounts of specific radicals are required;
- pre-formed building blocks like nanoclusters or nanocrystallites are needed; polymorphous silicon films is one of the examples of this effect;
- otherwise neutral species should be ionized for better control; this is the case in various modifications of ionized physical vapour deposition;
- specific (passivation versus activation) surface preparation is needed; plasmas can offer a great deal of ion- and radical-assisted surface preparation processes;
- it is necessary to enhance catalyst activity but use of other methods is not straightforward; for example, satisfactory fragmentation of catalyst interlayers can be achieved via reactive chemical etching or ion bombardment, but is unavailable or inefficient otherwise;
- both high gas temperatures and high ionized species densities are required; this is a definite advantage of thermal plasmas in, for example, synthesis of single-walled carbon nanotubes in the ionized gas phase;
- condensed precursors are required; thermal plasmas can provide the energy flux necessary for complete vaporization of liquids and solids; intense ion-assisted processes also make non-equilibrium plasmas an efficient source of ionized physical vapour of liquid and solid precursors;
- high-rate production or deposition of nanostructures is required; both thermal and non-equilibrium plasmas can fulfil this requirement. However, thermal plasmas have a clear advantage in the synthesis of large amounts of nanoparticles in the gas phase, whereas non-equilibrium plasmas are better suited for high-rate fabrication of delicate nanoassemblies on solid substrates.

This list represents a few examples of many different possibilities and is by no means exhaustive.

5.2. Directions for future research in the area

Due to the overwhelming variety of possible nanoassemblies, processes, tools and techniques, it would be futile to try to prescribe what should be done in the field in the near future. However, we can highlight some of the most important challenges, unresolved issues and opportunities in plasma-aided nanofabrication that arise from the topics surveyed in this paper.

An overarching goal might be summarized as to fully understand the most effective 'tuning knobs' of plasma-based nanoscale processes with the long-term aim of achieving fully deterministic nanoassembly. Rephrasing the famous statement that Richard Feynman made in his visionary speech 'There is plenty of room at the bottom' [145], one should learn how to create and control the nanoworld, in a plasma environment, plasma species by plasma species, the way we want them. In fact, this is what nature's nanofab does! For more details, the reader is referred to a forthcoming paper [146].

More specifically, one needs to address the yet unresolved problem of self-assembly on plasma-exposed surfaces and in the ionized gas phase and elucidate the roles of charges on plasma-exposed surfaces and plasma-nucleated nanoparticles, electric potentials (or currents) in the vicinity and across the nanoassemblies, ion fluxes and ion-flux-related temperature effects. This will not be possible without precise balancing of delivery and consumption of plasma-generated building units. To this end, one needs to properly identify exactly which species are building units and which ones serve for other relevant purposes, such as surface preparation.

From the point of view of nanotool/process design, those plasma tools and processes that can provide a measured and controlled delivery of building units have the potential to become major competitors to extremely expensive nanofabrication tools such as molecular beam epitaxy. Moreover, there is great potential for plasma nanotools used in combination with other nanoassembly tools such as laser-based methods, chemical vapour deposition, atomic layer deposition (ALD), etc. It is likely that nanofabrication techniques with the prefix 'plasma-assisted/enhanced' will become even more widespread than they are now; the existing examples include PE-CVD, PE-ALD, PE-PLD and i-PVD. It will definitely be worthwhile to further explore the opportunities for hybrid plasma–laser systems to selectively control processes in the ionized gas phase and on solid surfaces.

In the area of plasma etching of nanoassemblies and nanofeatures, a goal is to continue to increase resolution and selectivity and to ultimately be able to etch ultra-deep trenches at and beyond the limit of present-day lithographic tools. It would be wise to pose a deceptively simple question: when the capacity of the highest-resolution lithography is reached (problems are already experienced in the sub-100 nm domain), how can ultra-nanofeatures be etched on essentially self-organized patterns? Are self-organized ultra-nano-trenches/pores filled with metal (a nanoscale analogue of copper metallization of silicon trenches) a myth or reality?

The area of plasma-based synthesis of biomimetic materials and devices and processing of temperature-sensitive polymer bio-interfaces is one of the main areas of competitive advantages of plasma nanotools. It is imperative, however, to be able to identify, generate and control suitable functional plasma species: some species for nanostructure formation and some for surface tethering to attract biomolecules and ultimately improve the bioresponse.

We anticipate that the nanoscale self-organization of nanoassemblies on plasma-exposed surfaces and in the ionized gas phase will be a fertile area for major advances in the field. In this regard, researchers need to learn how to

- control crystallographic growth directions (e.g. pull nanowires out of nanorods) by varying the plasma process parameters;
- predict catalyst nucleation and self-organization, which is essential for the growth of ultra-dense nanotube forests and other nanostructures;
- remove unwanted amorphous deposits, e.g. via plasma etching, and improve nanostructure crystallization, e.g. via atomic/radical crystallization agents or energetic ion bombardment and subplantation;

- properly manipulate energetic ion beams to improve the quality of nanostructures without causing any substantial structural damage;

- manipulate various nanoparticles in the gas phase, in the vicinity of and upon deposition onto solid surfaces; this is required in a broad range of problems spanning from carbon nanotube collection to management of particulate contamination in microelectronics;

- deterministically control self-organization of developing nanostructures into ordered nanopatterns with pre-determined properties;

- remove unwanted contaminants and enable delivery of, e.g. crystalline nanoparticles to specified nanodevice locations by using different plasma forces;

- balance different scenarios of nanoparticle nucleation in the plasma, such as homogeneous nucleation and ion-induced nucleation, the latter being unique to ionized gas environments.

In trying to achieve the above specific nanoassembly-related aims, plasmas should be made stable, reproducible and feature high uniformity of the densities, fluxes and temperatures of the required species. To this end, controlled feed of gaseous, liquid and solid precursors is of outmost importance. Plasmas offer a range of means (from 'simple' thermal vaporization to 'complex' polymerization) to generate the entire spectrum of building units discussed in detail elsewhere [4]. Moreover, the residence time of building units, catalysts and nanoparticles in the plasma reactor should be adjusted to optimize the processes they are meant for. For example, to deterministically control gas-phase synthesis of single-walled carbon nanotubes, metal catalyst nanoparticles should be confined in the plasma long enough to sustain the nanotube growth up to the desired length. In this case, the (usually negative) electric charge the particles acquire in the plasma makes it possible to levitate them in the vicinity of negatively charged surfaces thus increasing the nanotube growth time.

Having read this paper, a researcher might be tempted to make a choice between the thermal and non-equilibrium plasmas in view of their future prospects in the nanoscience research field. The ideal combination is to have a range of versatile plasma tools in the lab; if this is not possible, the best advice would be to try to find the plasma that best suits the needs of the specific nanoassembly problems that are aimed for. Whatever the final choice may be, the list of intriguing problems related to various aspects of plasma-aided nanofabrication is virtually unlimited (as is the number of different possibilities), as exemplified by two major problems in carbon nanotube synthesis that need two different plasmas to resolve. Indeed, the problem of finding ultimate physical limits of nanoparticle production rates in the gas phase will almost certainly require thermal plasmas. On the other hand, in trying to find the absolute minimum of surface temperatures that still can sustain carbon nanotube growth, one needs to deal with thermally non-equilibrium plasmas. Thus, both plasmas have tantalizing future prospects for specific and, more importantly, relevant purposes!

To conclude this section, we pose the following questions:

- Can plasma nanofabrication be developed sufficiently to enable *atomic-scale* processing, e.g. of monoatomic terraces, one of the greatest emerging issues of surface science?

- Is it possible to use plasmas to fabricate structures containing just a few atoms for quantum computing applications via controlled manipulation of small (compared with typical surface densities) numbers of atoms/ions?

- Why do single-walled carbon nanotubes synthesized in thermal arc discharge plasmas have better structural properties than catalyst-enabled/assisted single-walled nanotubes grown from non-equilibrium plasmas?

- What is the influence of nanoparticle charging and charged species in plasmas and on solid surfaces and how can it be utilized for controlled production of a wider range of nanoassemblies?

- In what aspects of nanofabrication are thermal plasmas better than non-equilibrium plasmas and vice versa?

These as well as many other questions and issues are still awaiting definitive resolution. Finally, the field of plasma-aided nanofabrication is full of exciting opportunities in the near future, on scales ranging from undergraduate projects to major national and international research programmes. This field offers an exciting synergy of experimental, theoretical and computational research in a number of different areas of knowledge.

6. Conclusion

This introductory paper, and the articles in this cluster, give some examples of the rapid progress in the field, but cannot give a comprehensive coverage. Moreover, we are by no means experts in every (or even most) aspects of this very broad field. One of the purposes of this paper is to stimulate further research and debate in the field of plasma-aided nanofabrication. We would encourage comments directly to the authors, and submissions to the journal in the form of research articles or substantive comments on issues raised in the Cluster Issue.

We conclude by reiterating that the field of plasma-aided nanofabrication is rapidly expanding. Plasmas, both non-equilibrium and thermal, have many existing and potential advantages over competing technologies, and their exploitation presents great opportunities, both for pure research in understanding mechanisms of nanostructure formation, in applied research in developing novel processes and, it is to be hoped, in new industrial applications.

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References

[1] Poole C P Jr and Owens F J 2003 *Introduction to Nanotechnology* (Hoboken, NJ: Wiley)

[2] Fendler J H 1998 *Nanoparticles and Nanostructured Films: Preparation, Characterization and Applications* (Weinheim: Wiley)

[3] Oehrlein G S 2003 *Plasma Processing of Electronic Materials* (Berlin: Springer)

[4] Ostrikov K 2005 *Rev. Mod. Phys.* **77** 489

[5] Meyyappan M, Delzeit L, Cassell A and Hash D 2003 *Plasma Sources Sci. Technol.* **12** 205

[6] Melechko A V, Merkulov V I, McKnight T E, Guillorn M A, Klein K L, Lowndes D H and Simpson M L 2005 *J. Appl. Phys.* **97** 041301

[7] Ostrikov K and Xu S 2007 *Plasma-Aided Nanofabrication: from Plasma Sources to Nanoassembly* (Weinheim: Wiley).

[8] Shieh J, Lin C H and Yang M C 2007 *J. Phys. D: Appl. Phys.* **40** 2242 (this issue)

[9] Bapat A, Gatti M, Ding Y-P, Campbell S A and Kortshagen U 2007 *J. Phys. D: Appl. Phys.* **40** 2247 (this issue)

[10] Roca i Cabarrocas P, Nguyen-Tran Th, Djeridane Y, Abramov A, Johnson E and Patriarche G 2007 *J. Phys. D: Appl. Phys.* **40** 2258 (this issue)

[11] Koga K, Iwashita S and Shiratani M 2007 *J. Phys. D: Appl. Phys.* **40** 2267 (this issue)

[12] Anders A 2007 *J. Phys. D: Appl. Phys.* **40** 2272 (this issue)

[13] Bell M S, Teo K B K and Milne W I 2007 *J. Phys. D: Appl. Phys.* **40** 2285 (this issue)

[14] Li W, Liu X, Huang A and Chu P K 2007 *J. Phys. D: Appl. Phys.* **40** 2293 (this issue)

[15] Cvelbar U and Mozetic M 2007 *J. Phys. D: Appl. Phys.* **40** 2300 (this issue)

[16] Cheng Q J, Long J D, Chen Z and Xu S 2007 *J. Phys. D: Appl. Phys.* **40** 2304 (this issue)

[17] Levchenko I and Ostrikov K 2007 *J. Phys. D: Appl. Phys.* **40** 2308 (this issue)

[18] Komatsu S 2007 *J. Phys. D: Appl. Phys.* **40** 2320 (this issue)

[19] Valsesia A, Meziani T, Bretagnol F, Colpo P and Rossi F 2007 *J. Phys. D: Appl. Phys.* **40** 2341 (this issue)

[20] Li J-G, Ikeda M, Ye R, Moriyoshi Y and Ishigaki T 2007 *J. Phys. D: Appl. Phys.* **40** 2348 (this issue)

[21] Girshick S L and Hafiz J 2007 *J. Phys. D: Appl. Phys.* **40** 2354 (this issue)

[22] Gonzalez-Aguilar J, Moreno M and Fulcheri L 2007 *J. Phys. D: Appl. Phys.* **40** 2361 (this issue)

[23] Kim K S, Cota-Sanchez G, Kingston C T, Imris M, Simard B and Soucy G 2007 *J. Phys. D: Appl. Phys.* **40** 2375 (this issue)

[24] Keidar M 2007 *J. Phys. D: Appl. Phys.* **40** 2388 (this issue)

[25] Fauchais P, Etchart-Salas R, Delbos C, Tognonvi M, Rat V, Coudert J F and Chartier T 2007 *J. Phys. D: Appl. Phys.* **40** 2394 (this issue)

[26] Shigeta M and Watanabe T 2007 *J. Phys. D: Appl. Phys.* **40** 2407 (this issue)

[27] Borra J-P 2006 *J. Phys. D: Appl. Phys.* **39** R19

[28] Iijima S 1991 *Nature* **354** 56

[29] Yang M J, Shieh J, Hsu S L, Huang I Y, Leu C C, Shen S W, Huang T Y, Lehnen P and Chien C H 2005 *Electrochem. Solid-State Lett.* **8** C74

[30] Xu S, Ostrikov K N, Luo W and Lee S 2000 *J. Vac. Sci. Technol.* A **18** 2185

[31] Ostrikov K N, Xu S and Shafiul Azam A B M 2002 *J. Vac. Sci. Technol.* A **20** 251

[32] Ostrikov K N, Xu S and Yu M Y 2000 *J. Appl. Phys.* **88** 2268

[33] Sriraman S, Agrawal S, Aydil E S and Maroudas D 2002 *Nature* **418** 62

[34] Tsakadze Z L, Ostrikov K, Long J D and Xu S 2004 *Diamond. Relat. Mater.* **13** 1923

[35] Tsakadze Z L, Ostrikov K and Xu S 2005 *Surf. Coat. Technol.* **191** 49

[36] Robertson J 2007 *Mater. Today* **10** 36

[37] Levchenko I, Ostrikov K, Keidar M and Xu S 2005 *J. Appl. Phys.* **98** 064304

[38] Levchenko I, Ostrikov K, Keidar M and Xu S 2006 *Appl. Phys. Lett.* **89** 033109

[39] Levchenko I, Ostrikov K and Tam E 2006 *Appl. Phys. Lett.* **89** 223108

[40] Vladimirov S V and Ostrikov K 2004 *Phys. Rep.* **393** 175

[41] Ostrikov K N, Kumar S and Sugai H 2001 *Phys. Plasmas* **8** 3490

[42] Rutkevych P, Ostrikov K, Xu S and Vladimirov S V 2004 *J. Appl. Phys.* **96** 4421

[43] Ostrikov K N, Yu M Y, Vladimirov S V and Ishihara O 1999 *Phys. Plasmas* **6** 737

[44] Ostrikov K N and Yu M Y 1998 *IEEE Trans. Plasma Sci.* **26** 100

[45] Teo K B K *et al* 2004 *Nano Lett.* **4** 921

[46] Denysenko I B, Xu S, Rutkevych P P, Long J D, Azarenkov N A and Ostrikov K 2004 *J. Appl. Phys.* **95** 2713

[47] Bell M S, Lacerda R G, Teo K B K, Rupesinghe N L, Amaratunga G A J, Milne W I and Chhowalla M 2004 *Appl. Phys. Lett.* **85** 1137

[48] Ostrikov K, Tsakadze Z, Denysenko I, Rutkevych P P, Long J D and Xu S 2005 *Contrib. Plasma Phys.* **45** 514

[49] Hash D B, Bell M S, Teo K B K, Cruden B A, Milne W I and Meyyappan M 2005 *Nanotechnology* **16** 925

[50] Ostrikov K, Long J D, Rutkevych P P and Xu S 2006 *Vacuum* **80** 1126

[51] Ding Y, Dong Y, Bapat A, Nowak J, Carter C B, Kortshagen U R and Campbell S A 2006 *IEEE Trans. Electron Devices* **53** 2525

[52] Vladimirov S V, Ostrikov K and Samarian A A 2005 *Physics and Applications of Complex Plasmas* (London: Imperial College Press)

[53] Chaabane N, Suendo V, Vach H and Roca i Cabarrocas P 2006 *Appl. Phys. Lett.* **88** 203111

[54] Roca i Cabarrocas P, Chaabane N, Kharchenko A V and Tchakarov S 2004 *Plasma Phys. Control. Fusion* **46** B235

[55] Denysenko I B, Ostrikov K, Xu S, Yu M Y and Diong C H 2003 *J. Appl. Phys.* **94** 6097

[56] Oda S 2003 *Mater. Sci. Eng.* B **101** 19

[57] Barnes M C, Gerson A R, Kumar S and Hwang N M 2003 *Thin Solid Films* **436** 181

[58] Barnes M C, Gerson A R, Kumar S and Hwang N M 2004 *Thin Solid Films* **446** 29

[59] Zhou W, Zhong X X, Wu X, Yuan L, Shu Q, Xia Y and Ostrikov K 2007 *J. Biomed. Mater. Res.* A **81A** 453

[60] Xu S, Long J D, Sim L, Diong C H and Ostrikov K 2005 *Plasma Proc. Polym.* **2** 373

[61] Long J D, Xu S, Cai J W, Jiang N, Lu J H, Ostrikov K N and Diong C H 2002 *Mater. Sci. Eng.* C **20** 175

[62] Hwang N M and Kim D Y 2004 *Int. Mater. Rev.* **49** 171

[63] Xu S, Ostrikov K, Long J D and Huang S Y 2006 *Vacuum* **80** 621

[64] Long J D, Xu S, Huang S Y, Rutkevych P P, Xu M and Diong C H 2005 *IEEE Trans. Plasma Sci.* **33** 240

[65] Zhou W, Zhong X X, Wu X C, Yuan L Q, Shu Q W, Li W and Xia Y X 2007 *J. Phys. D: Appl. Phys.* **40** 219

[66] Cheng Q J, Xu S, Long J D and Ostrikov K Low-temperature PECVD of nanodevice-grade nc-SiC, unpublished.

[67] Kerdiles S, Berthelot A, Gourbilleau F and Rizk R 2000 *Appl. Phys. Lett.* **76** 2373

[68] Rajagopalan T, Wang X, Lahlouh B, Ramkumar C, Dutta P and Gangopadhyay S 2003 *J. Appl. Phys.* **94** 5252

[69] Hofmann S, Dukati C, Robertson J and Kleinsorge B 2003 *Appl. Phys. Lett.* **83** 135

[70] Ostrikov K N, Yu M Y and Sugai H 1999 *J. Appl. Phys.* **86** 2425

[71] Azarenkov N A, Denisenko I B and Ostrikov K N 1995 *J. Phys. D: Appl.Phys.* **28** 2465

[72] Ostrikov K N, Yu M Y and Azarenkov N A 1998 *J. Appl. Phys.* **84** 4176

[73] Fontcuberta i Morral A and Roca i Cabarrocas P 2001 *Thin Solid Films* **383** 161

[74] Rutkevych P P, Ostrikov K and Xu S 2005 *Phys. Plasmas* **12** 103507

[75] Xu S, Ostrikov K N, Li Y, Tsakadze E L and Jones I R 2001 *Phys. Plasmas* **8** 2549

[76] Ostrikov K N, Yu M Y and Stenflo L 2000 *Phys. Rev.* E **61** 782

[77] Vladimirov S V, Ostrikov K, Yu M Y and Morfill G E 2003 *Phys. Rev.* E **67** 036406

[78] Ostrikov K N, Yu M Y and Azarenkov N A 1998 *Phys. Rev.* E **58** 2431

[79] Siow K S, Britcher L, Kumar S and Griesser H J 2006 *Plasma Process. Polym.* **3** 392

[80] Bower C, Zhou O, Zhu W, Werder D J and Jin S H 2000 *Appl. Phys. Lett.* **77** 2767

[81] Tam E, Levchenko I and Ostrikov K 2006 *J. Appl. Phys.* **100** 036104

[82] AuBuchon F, Chen L H and Jin S 2005 *J. Phys. Chem.* B **109** 6044

[83] Yan M, Zhang H T, Widjaja E J and Chang R P H 2003 *J. Appl. Phys.* **94** 5240

[84] Mirpuri C, Xu S, Long J D and Ostrikov K 2007 *J. Appl. Phys.* **101** 024312

[85] Chhowalla M, Teo K B K, Ducati C, Rupersihghe N L, Amaratunga G A J, Ferrari A C, Roy D, Robertson J and Milne W I 2001 *J. Appl. Phys.* **90** 5308

[86] Liu X Y, Huang A P, Ding C X and Chu P K 2006 *Biomaterials* **27** 3904

[87] Mozetic M, Cvelbar U, Sunkara M K and Vaddiraju S 2005 *Adv. Mater.* **17** 2138

[88] Lim S P, Long J D, Xu S and Ostrikov K 2007 *J. Phys. D: Appl. Phys.* **40** 1085

[89] Mozetic M, Vesel A, Cvelbar U and Ricard A 2006 *Plasma Chem. Plasma Process.* **26** 103

[90] Cvelbar U, Mozetic M and Ricard A 2005 *IEEE Trans. Plasma Sci.* **33** 834

[91] Shieh J, Ko T S, Chen H L, Dai B T and Chu T C 2004 *Chem. Vap. Deposition* **10** 265

[92] Huang S Y, Xu S, Long J D, Sun Z and Chen T 2006 *Phys. Plasmas* **13** 023506

[93] Xu M, Ng V M, Huang S Y, Long J D and Xu S 2005 *IEEE Trans. Plasma Sci.* **33** 242

[94] Chew K, Rusli, Yoon S F, Ahn J, Ligatchev V, Teo E J, Osipowicz T and Watt F 2002 *J. Appl. Phys.* **92** 2937

[95] Rider A E, Levchenko I and Ostrikov K 2007 *J. Appl. Phys.* **101** 044306

[96] Levchenko I, Korobov M, Romanov M and Keidar M 2004 *J. Phys. D: Appl. Phys.* **37** 1690

[97] Levchenko I and Baranov O 2003 *Vacuum* **72** 205

[98] Tam E, Levchenko I, Ostrikov K, Keidar M and Xu S 2007 *Phys. Plasmas* **14** 033503

[99] Ostrikov K, Yoon H-J, Rider A E and Vladimirov S V 2007 *Plasma Process. Polym.* **4** 27

[100] Komatsu S, Kazami D, Tanaka H, Moriyoshi Y, Shiratani M and Okada K 2006 *J. Chem. Phys.* **125** 084701

[101] Meziani T, Colpo P and Rossi F 2001 *Plasma Sources Sci. Technol.* **10** 276

[102] Kogelschatz U 2004 *Plasma Phys. Control. Fusion* **46** B63

[103] Tioxide Group 1999 *Manufacture and general properties of titanium dioxide pigments*, available at http://www.huntsman.com/pigments/ Media/Manufacture_and_ Generals_Properties.pdf

[104] Deegan D, Chapman C and Pitkethly M 2003 *High Temp. Mater. Process.* **7** 261

[105] Hoffmann M R, Martin S T, Choi W Y and Bahnemann D W 1995 *Chem. Rev.* **95** 69

[106] Gratzel M 2001 *Nature* **414** 338

[107] Murphy A B, Barnes P R F, Randeniya L K, Plumb I C, Grey I E, Horne M D and Glasscock J A 2006 *Int. J. Hydrogen Energy* **31** 1999

[108] Li Y L, Wang X H, Watanabe K and Ishigaki T 2006 *J. Phys. Chem.* B **110** 1121

[109] Ishigaki T, Oh S M, Li J G and Park D W 2005 *Sci. Technol. Adv. Mater.* **6** 111

[110] Li Y L and Ishigaki T 2004 *J. Phys. Chem.* B **108** 15536

[111] Liao F, Girshick S L, Mook W M, Gerberich W W and Zachariah M R 2005 *Appl. Phys. Lett.* **86** 171913

[112] Rao N P, Lee H J, Kelkar M, Hansen D J, Heberlein J V R, McMurry P H and Girshick S L 1997 *Nanostruct. Mater.* **9** 129

[113] Hafiz J, Mukherjee R, Wang X, Marshall M, Twesten R D, Cullinan M, Heberlein J V R, McMurry P H and Girshick S L 2005 *Surf. Coat. Technol.* **200** 1524

[114] Hafiz J, Mukherjee R, Wang X, Cullinan M, Heberlein J V R, McMurry P H and Girshick S L 2006 *J. Nanopart. Res.* **8** 995

[115] Kay A, Cesar I and Gratzel M 2006 *J. Am. Chem. Soc.* **128** 15714

[116] Di Fonzo F *et al* 2000 *Appl. Phys. Lett.* **77** 910

[117] Okuno H, Grivei E, Fabry F, Gruenberger T M, Gonzalez-Aguilar J, Palnichenko A, Fulcheri L, Probst N and Charlier J-C 2004 *Carbon* **42** 2543

[118] Puretzky A A, Geohegan D B, Schittenhelm H, Fan X D and Guillorn M A 2002 *Appl. Surf. Sci.* **197** 552

[119] Keidar M and Waas A M 2004 *Nanotechnology* **15** 1571

[120] Waldorff E I, Waas A M, Friedmann P P and Keidar M 2004 *J. Appl. Phys.* **95** 2749

[121] Kato T, Jeong G H, Hirata T, Hatakeyama R, Tohji K and Motomiya K 2003 *Chem. Phys. Lett.* **381** 422

[122] Li Y *et al* 2004 *Nano Lett.* **4** 317

[123] Kato T, Jeong G H, Hirata T, Hatakeyama R, Tohji K and Motomiya K 2004 *Thin Solid Films* **457** 2

[124] Keidar M, Raitses Y, Knapp A and Waas A M 2006 *Carbon* **44** 1022

[125] Fauchais P 2004 *J. Phys. D: Appl. Phys.* **37** R86

[126] Girshick S L, Chiu C-P and McMurry P H 1990 *Aerosol Sci. Technol.* **13** 465

[127] Girshick S L, Chiu C-P and McMurry P H 1988 *Plasma Chem. Plasma Process.* **8** 145

[128] Girshick S L and Chiu C-P 1990 *J. Aerosol Sci.* **21** 641

[129] Désilets M, Bilodeau J-F and Proulx P 1997 *J. Phys. D: Appl. Phys.* **30** 1951

[130] Girshick S L, Chiu C-P, Muno R, Wu C Y, Yang L, Singh S K and McMurry P H 1993 *J. Aerosol Sci.* **24** 367

[131] Murphy A B 2004 *J. Phys. D: Appl. Phys.* **37** 2841–7

[132] McFeaters J S, Stephens R L, Schwerdtfeger P and Liddell M 1994 *Plasma Chem. Plasma Process.* **14** 333

[133] Prakash A, Bapat A P and Zachariah M R 2003 *Aerosol Sci. Technol.* **37** 892

[134] Shigeta M and Watanabe T 2005 *J. Mater. Res.* **20** 2801

[135] Shigeta M and Watanabe T 2005 *JSME Int. J. Ser. B: Fluid Therm. Eng.* **48** 425

[136] Gonzalez JJ, Bouaziz M, Razafinimanana M and Gleizes A 1997 *Plasma Sources Sci. Technol.* **6** 20

[137] Cram L E 1985 *J. Phys. D: Appl. Phys.* **18** 401

[138] Murphy A B 1996 *J. Phys. D: Appl. Phys.* **29** 1922

[139] Murphy A B 2001 *J. Phys. D: Appl. Phys.* **34** R151

[140] Wang X, Hafiz J, Mukherjee R, Renault T, Heberlein J, Girshick S L and McMurry P H 2005 *Plasma Chem. Plasma Process.* **25** 439

[141] Seinfeld J H and Pandis S N 1998 *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (New York: Wiley)

[142] Fisenko S P, Kane D B and El-Shall M S 2005 *J. Chem. Phys.* **123** 104704

[143] Tak A K and Das A K 2006 Power beams for clean environment and processes *Proc. DAE-BRNS-PSI Symp. on Power Beams for Clean Environment and Processes (Mumbai, 2006)* ed N K Joshi *et al* (Mumbai: Allied Publishers) p 313

[144] Bilodeau J-F, Pousse J and Gleizes A 1998 *Plasma Chem. Plasma Phys.* **18** 285

[145] Feynman R P 1959 There is a plenty of room at the bottom *American Physical Society Annual Meeting (New York, 29 December 1959)*; ed H D Gilbert (New York: Reinhold) reprinted in: *Miniaturization*
See also: http://www.zyvex.com/nanotech/feynman.html.

[146] Ostrikov K 2007 *IEEE Trans. Plasma Sci.* **35** at press.