

Preface

Applications of low-temperature plasmas for materials synthesis and processing at nanoscales and fabrication of nanodevices is a very new and quickly emerging area at the frontier of physics and chemistry of plasmas and gas discharges, nanoscience and nanotechnology, solid-state physics, and materials science. Such plasma systems contain a wide range of neutral and charged, reactive and nonreactive species with the chemical structure and other properties that make them indispensable for nanoscale fabrication of exotic architectures of different dimensionality and functional thin films and places uniquely among other existing nanofabrication tools. By nanoscales, we imply spatial scales in the range between ~ 1 nm and a few hundred nm ($1 \text{ nm} = 10^{-9} \text{ m}$).

In our decision to write this book we were motivated by the fact that even though basic properties and applications of low-temperature plasma systems had been widely discussed in the literature, there have been no systematic attempt to show the entire pathway from the development of suitable advanced plasma sources and plasma-based nanofabrication facilities with the required parameters and operation capabilities to the successful nanoscale synthesis.

We started our research in the area of the plasma-based synthesis of nanomaterials, in a sense, from behind, only in mid-2001 after the establishment of the Advanced Materials and Nanostructures Laboratory (AMNL) within the Plasma Sources and Applications Center (PSAC) of Nanyang Technological University in Singapore. At that time we had a few RF plasma sources and also RF diode and DC magnetron sputtering facilities and, inspired by a number of breakthrough works on plasma-based synthesis of carbon nanotubes, nanoparticles, and various nanostructured films, decided to follow this exciting and very hot direction of research. At that time the nanomaterials research was among the top research priorities and we managed to secure a couple of million dollars in competitive research and infrastructure grants, established a new Plasma Sources and Applications Center, secured space for the AMNL, purchased our own field emission scanning electron microscope, hired people, purchased catalyzed templates and other necessary stuff and

jumped straight into running experiments on nanostructure synthesis by using whatever plasma sources were available at that time in the lab.

However, to our great disappointment, we did not manage to reproduce many of the successful experiments on plasma-assisted synthesis of carbon nanotube-like structures, although all the recipes had been strictly followed. On almost the same substrates, at exactly the same substrate temperatures and working gases the nanostructures either did not grow at all or grew quite differently; in many cases the quality of the nanopatterns was very far from what had previously been reported in the literature.

At that time, there existed a widely accepted opinion that in the growth of carbon nanotubes, the role of the plasma environment is merely in providing vertical alignment of the nanotubes in the electric field, which originates due to charge separation in the plasma sheath between the plasma bulk and the nanostructured surfaces. The role of the ionized gas component was in most cases simply sidestepped or disregarded. Our disappointment was getting even worse when we tried to use different plasma rigs and found out that the results were actually very different in different vacuum chambers, although the process conditions, including surface temperature, were very similar. That led us to an intuitive guess that the observed differences had something to do with the plasma rather than surface conditions.

A bit later, when we realized that the plasma ion bombardment can substantially modify the surface during pretreatment, and also increase the surface temperature during the actual deposition stage, we tried to maintain the substrate DC bias, the main control tool of the ionic fluxes crashing into the surface, the same during the experiments in different plasma chambers. But the results were not the same again. This led us to an intuitive conclusion that the plasma does play a prominent role in the nanostructure synthesis and it is not merely the commonly accepted vertical alignment.

Early in 2003, when trying again and again to synthesize carbon nanotubes from a mixture of methane, hydrogen, and argon, we inadvertently forgot to turn an external substrate heater on. This heating element was supposed to heat our samples to temperatures at least as high as 550–600 °C, commonly used in most of the successful experiments at that time. To our biggest surprise, carbon nanostructures emerged and covered the entire substrate, and most amazingly, in a fairly uniform fashion! This eventually led us to the discovery of what we later called the “floating temperature regime”. In this growth mode, the Ni/Fe/Co-catalyzed silicon substrates do not need to be externally heated at all and the growth temperatures are about the same as that of the neutral gas in the plasma reactor (or higher if ion bombardment is significant). This very unexpected and fascinating result was reported at the Gaseous Electronics Conference in San Francisco in October 2003.

Unfortunately, due to significant delays with the reliable substrate temperature and temperature gradient measurements and also bad luck with the editors and referees of a few journals which publish the results quickly (again, Murphy's law!), we did not manage to publish this result until January 2005 (the corrected proof had been published online since March 2004). At about the same time, the literature was virtually flooded by numerous reports on "lower, even lower, lowest" substrate temperatures that enable the plasma-assisted synthesis of various carbon-based nanostructures (just to mention commonly known single- and multiwalled nanotubes, nanofibers, nanocones, nano-pyramids, etc.).

This plasma-related "nanotube growth without heating" paradox was eventually resolved and conclusively related to the additional heating of solid surfaces by the plasma ions; this heating on its own can add more than 100 degrees to the surface temperature.

This is just one example evidencing that "the plasma does matter"! Very fortunately, we realized that reasonably quickly and decided to develop a new and versatile plasma facility, which would enable a direct control of the nanoassembly processes by the independently created and manipulated, in a controlled fashion, low-temperature inductively coupled plasma.

Before that, we had moved a long and thorny way along the trail of plasma source development and knew which main issues needed to be resolved before a successful plasma source could be created. Some of relevant attempts are described in Chapter 2 of this book. Not surprisingly, our new plasma facility, which soon evolved into the very successful Integrated Plasma-Aided Nanofabrication Facility (IPANF), turned out extremely useful in synthesizing not only "trivial" carbon nanotube-like structures but also a large variety of semiconductor quantum confinement structures of different dimensionality discussed in Chapter 5 of this monograph.

We emphasize that despite an enormous number of existing research monographs, textbooks, and edited volumes related to nanoscience and nanotechnology on one hand and the physics and applications of low-temperature plasmas on the other hand, we are not aware of any research monographs showing a consistent and complete "success story," which begins from the development of original plasma sources and processes and ends up with the evidence of successful synthesis and/or processing of nano-materials.

This monograph is based on collaborative research of the authors and their teams, which they started in 1999 in Singapore and continue, via a number of international linkage projects even after Kostya (Ken) Ostrikov moved to the University of Sydney, Australia and established his own Plasma Nanoscience research team. Over the years, this collaboration also involved a large number of researchers from different countries, which eventually led to the establishment of the International Research Network for Deterministic Plasma-Aided Nanofabrication.

The scope of this monograph lies within the “Plasma Nanoscience” sub-field at the cutting edge interdisciplinary research at the cross-roads where the physics and chemistry of plasmas and gas discharges meets nanoscience and materials physics and engineering. This work certainly does not aim at the entire coverage of the existing reports on the variety of nanostructures, nanomaterials, and nanodevices on one hand and on the plasma tools and techniques for materials synthesis and processing at nanoscales and plasma-aided nanofabrication on the other one (even though it provides a very long but certainly not exhaustive list of relevant publications). Neither does our monograph aim to introduce the physics of low-temperature plasmas for materials processing. We refer the interested reader to some of the many existing books that cover the relevant areas of knowledge [1–11]. This work has a clear practical perspective and aims to demonstrate to the wide multidisciplinary academic and research community how important is to properly select and develop suitable plasma facilities and processes. This work also poses a number of open questions, which are expected to stimulate the interest of researchers from different areas toward more extensive use of plasma nanofabrication tools.

To make this undoubtedly very “research-heavy” monograph easily understood, at least in very basic terms, to a person with a basic high-school knowledge of physics and chemistry, we decided to write an introductory Chapter 1, which, first of all, explains what is the plasma, what is the nanotechnology and how these two things link together. After a brief overview of the main issues of the nanotechnology and plasma applications in nanofabrication, we give some basic ideas how to choose the right plasma-based process for the envisaged nanoscale application. The structure of this monograph will be introduced immediately after the most important things are clarified.

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