Chapter 30

Carbon Nanostructures by PECVD: Few Case Studies

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30.1 Introduction to the World of Carbon Nanostructures

Carbon is one of the most abundant element of nature and its nanostructures have different exciting application from drug delivery to X-ray generation. Both sp^2 and sp^3 hybridized nanostructures of carbon are very useful for several important applications. Graphene and carbon nanotubes (CNTs) are the most popular form of carbon nanostructures and both of them are sp^2 hybridized. Graphene is the single layer of graphite and this wonderful material and rolls up to form a cylindrical structure forming CNTs. This type of CNTS are called single walled-CNTs (SWCNTs); similarly, multiple graphene cylinders can roll together to form multi-walled CNTs (MWCNTs). Multiple layers of graphene sheets standing one over another can form either multi-layered graphene or graphene nanowalls (GNWs). GNWs are simply multi-layered graphene sheets stacked over one another in rotationally random manner. All these sp^2 hybridized nanostructures can be used for making miniature X-ray devices, gas sensors, for drug delivery etc. Nano-crystalline diamond (NCD) is probably the best example of sp^3 hybridized carbon nanostructure which essentially retains all excellent properties of diamond but easier to synthesize in lab. The development of these nanostructures are being done by different methods, but plasma based synthesis is probably the most popular one. Large scale synthesis of these nanostructures can be achieved by arc plasma CVD, modified fluoride bed reactor. Among all the plasma synthesis techniques microwave plasma CVD (MPECVD) is one of the most popular method worldwide for synthesis of pristine carbon nanostructures for basic physics study and applications. Development of carbon nanostructures especially CNTs and GNWs in many cases require coating of a $\sim$20 nm layer of 3-D transition metals (eg. Fe, Ni, & Co). However, in present days researchers have developed techniques to synthesize carbon nanostructures even without a catalyst layer on metallic substrates like Inconel, SS and Kovar for practical applications.

30.2 Typical Synthesis Procedures of Carbon Nanostructures

As discussed in the earlier section, MPECVD is preferred choice for deposition of carbon nanostructures due to its higher operating pressure, faster deposition rate and comparatively higher operating temperature (800-1000 °C). A typical MPECVD system has a 2.45 GHz magnetron (2-5 kW) for microwave generation, transmission line, a three-port circulator, water cooled dummy load, cross coupler, three stub tuners, a sliding short and a mode converter. Figure 30.1 shows schematic with all components marked and an actual MPECVD chamber for the deposition of these nanostructures. For synthesis of carbon nanostructures,

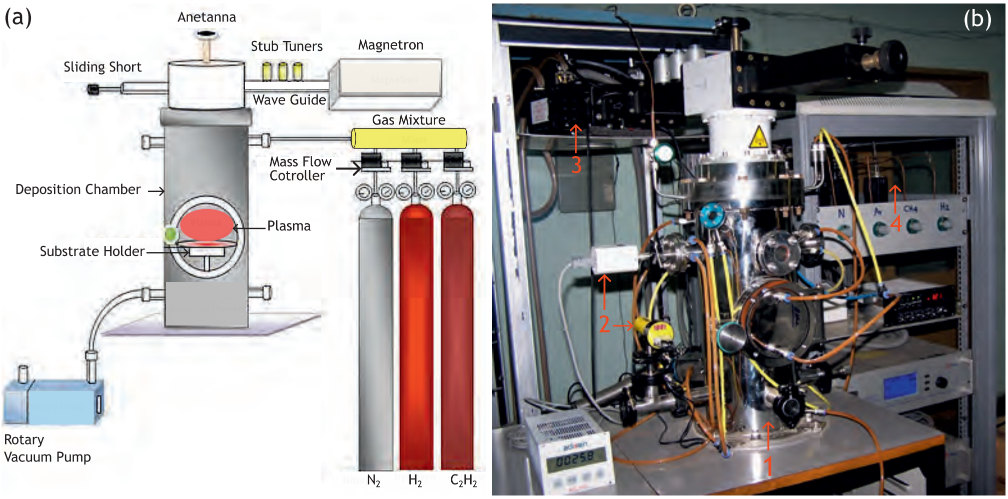

Figure 30.1: MPECVD system: (a) Schematic and (b) actual image. Here, 1, 2, 3 and 4 correspond to deposition chamber, vacuum gauges, magnetron and mass flow controller, respectively.

operating pressure is kept in the range of 18-40 Torr and a suitable gas mixture of H_2, N_2 and C_2H_2 is sent for the deposition at powers between 500 W to 1.2 kW for generation of these nanostructures. High quality CNTs, GNWs and NCDs can be deposited using MPECVD system. The basic physics of deposition methods and nano-science leads to discovery of many exciting phenomena like co-deposition of two very differently hybridized nanostructures or observation of splitting inside D Raman bands of GNWs. GNWs and CNTs also show excellent field emission properties which can be used for development of field emission based miniature X-ray sources. A few brief case studies below will help to peek into the world of carbon nanostructures.

30.3 Case Studies

30.3.1 Co-depostion of different carbon nanostructures

Researches have shown that there is an exciting way in MPECVD where two different sp^2 hybridized (CNTs and GNWs) and one sp^2 and another sp^3 for GNWs and NCDs respectively can be deposited in a single experiment at separate locations in the reaction chamber. The basis remains finding a window where two different nanostructures can be deposited simultaneously. One needs to prepare substrates in such manner that each one favors a different deposition. Eg. if one wants to deposit NCD and GNWs together one must prepare the substrate for NCD with seeds of diamond particles and keep the pressure high ~35 Torr. The ions and radicals inside plasma sheath then follows their respective favorable chemistries for deposition. Choice and surface treatment of the substrate is important for a particular type of co-deposition while precursor flow rate is the major controlling factor. An unscratched Si surface used as attenuator on top of the actual Inconel substrate with comparative high flow rate of precursor gas (~20 SCCM) leads to the growth of GNWs on the attenuator and CNTs are then synthesized on Inconel. Instead, a scratched Si surface as attenuator with relatively lower precursor flow rate (~5 SCCM) results in the deposition of NCD on Si and CNTs are again deposited on Inconel. Both these substrates must be kept inside plasma sheath for co-deposition to happen.

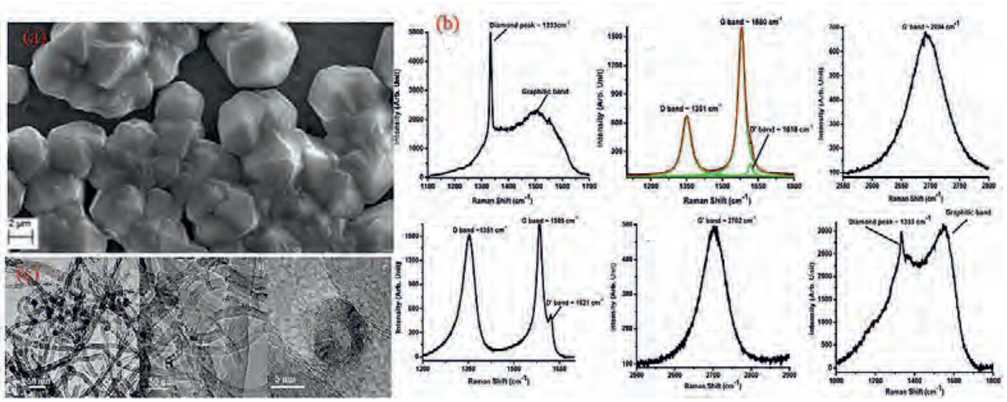

Figure 30.2: (a) Well faceted diamond crystals deposited by MPECVD, (b) Raman spectroscopic results showing deposition of diamond, GNWs CNTs and NCDs, and (c) HRTEM images showing deposition of high quality multi-walled CNTs.

30.3.2 Substrate heat treatment and microwave attenuation for CNTs

For direct growth of CNTs on metallic substrates like Inconel, substrate heat-treatment prior to deposition and microwave attenuation during deposition helps in tremendous improvement of deposition rate and field-emission current density of deposited nanostrcutures. All these informations are gathered when nanostructures are studied by suitable characterization methods like electron microscopy (FESEM, HRTEM) and X-ray diffraction (XRD). Studies revealed that heat-treatment causes opening up of Inconel grain boundaries where 3-D transition metal segregates. This in turn, helps in improving deposition rate while microwave attenuation reduces microwwave reflection from metal surfaces efficiently enhancing residence time of the dissociated precursor. Understanding becomes simpler when one thinks that microwave and metal are incompatible together. Although plasma will absorb most of the applied microwave power for its generation sustenance but reflection from metal will cause problem in deposition. This problem is resolved when one places a microwave attenuator on top of the metallic substrate. A simple Si piece can act as attenuator and deposition still can take place between the gap of the substrate and attenuator.

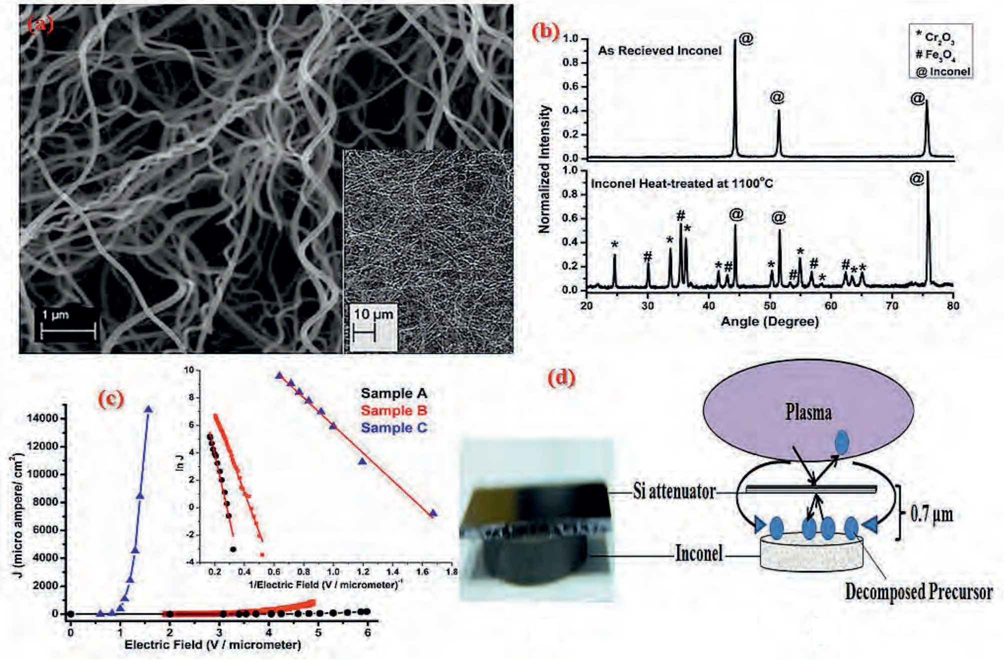

Figure 30.3: (a) pristine CNTs deposited by MPECVD, (b) XRD spectra showing effect of heat-treatment, (c) drastic improvement in sample C with heat treatment and microwave attenuation, and (d) schematic representation of microwave attenuation.

30.3.3 Synthesis of GNWs and hybrid nanostructures on thin metallic wires

Like section 30.3.2, in this case using an attenuator is difficult because of the geometry of the substrate; a metallic wire typically of 1-3 mm diameter. For this purpose, a double-layer plasma as shown in the following image, needs to be generated to confine plasma on metallic wire to generate pristine GNWs and hybrid nanostructures. This type of substrates are important for practical applications like miniature X-ray devices for use in dentistry and brachytherapy. Figure 30.5 shows deposition of GNWs on different metallic substrates.

Figure 30.4: Deposition of GNWs on different metallic substrates.

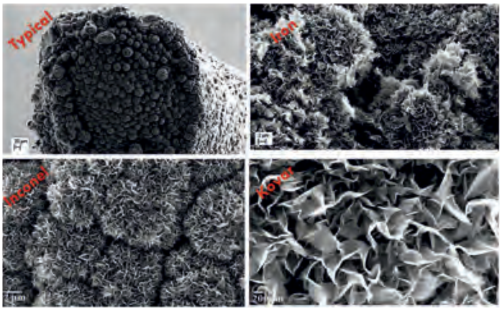

Figure 30.5: Deposition of GNWs on different metallic substrates.

MPECVD can also be used to synthesize hybrid nanostructure of GNWs and CNTs could be deposited on metallic wires which shows excellent field emission. Clear bamboo-like defects which increases local density of states (LDOS) of pi-electrons are observed in these nanostructures. These nanostructures are not only excellent field emitters but their repeatable and stable electron emission might hold the key in developing a miniature X-ray source.

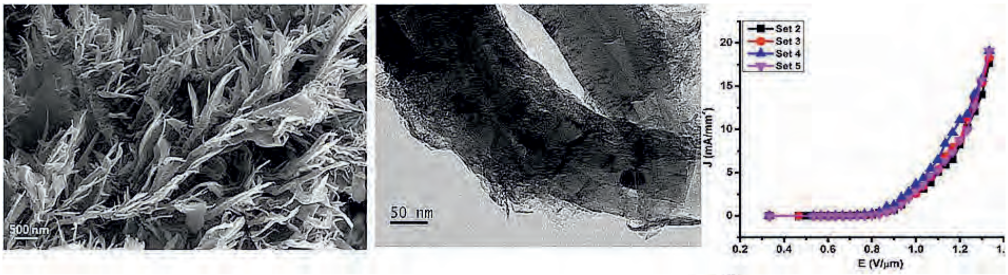

Figure 30.6: Hybrid nanostructures with very high and repeatable field emission performance.

Frequently Asked Questions

Q1. How the heat treatment helps in improving density of carbon nanotubes on Inconel?

Q2. What is the signature Raman peak for diamond?

Q3. Explain from Fig.30.6 why D band splitting has been observed in GNWs?

Q4. How carbon nanostructures can be used for X-ray generation?

Q5. What is the typical experimental condition for generation of carbon nanostructures by microwave plasma CVD?