International Journal for Innovative Engineering and Management Research
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IJIEMR Transactions, online available on 10th Mar 2019. Link :http://www.ijiemr.org/downloads.php?vol=Volume-07&issue=ISSUE-03

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Volume 07, Issue 03, Pages: 235–240.

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SYNTHESIS AND CHARACTERIZATION OF CARBON NANOWALLS BY ICP-CVD USING ALUMINIUM ACETYLACETONATE PRECURSOR

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ABSTRACT
A new method of synthesis of carbon nanowalls using acetylacetonate as metal organic precursor is presented. The films were deposited in ICP-CVD generated argon plasma by varying gas flow rate, plasma power, substrate temperature and reactor pressure. The precursor-feeding rate into the plasma chamber was controlled by the argon gas flow. No catalyst or other carbon gas source was added to deposit such structures.The wall size of CNWs was strongly influenced by the aluminium content present inside the film, plasma parameters like substrate temperature, plasma power and gas flow rate. The smallest wall size observed was 5nm. All films were analysed using SEM, XRD, Raman and TEM techniques in order to characterize the morphology of the samples. XPS, EDX, SIMS, and NRA were used for chemical analysis.The structuring of CNW layers was performed successfully with a pulsed power laser. The resulting cathodes exhibited fairly aligned and efficient field emission (FE) at onset fields for 1 nA of 10-20 V/μm. Local FE measurements of selected CNW patches revealed promising maximum current values up to about 100 μA.

INTRODUCTION
Recent years have seen a rapid growth of interest in carbon nanostructures because of their various applications in electro-chemical devices, field emitters and sensors. The discovery of carbon nanotubes by lijima has attracted the interest of researchers in graphite like materials. Simultaneously, two dimension carbon structures have also been discovered in various forms like carbon nanohorns , carbon nanoflakes , carbon nanoflowers , carbon nanosheets and carbon nanowalls. The major applications of two-dimensional carbon nanostructures can be electron field emitters and capacitor electr odes. In 2002, Wu et al. observed for the first time carbon wall-like structures which were perpendicular to the substrate. They were called carbon nanowalls (CNWs). It was studied by TEM that CNWs consist of few graphene sheets standing on the substrate.

According to the dimensionality carbon materials can be divided into the following categories:

Three-dimensional (3D) (Diamond, Graphite)

Two dimensional (2D) (Graphene)

One dimensional (1D) (Carbon nanotubes)

Zero dimensional (0D) (Fullerenes)

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BRIEF DESCRIPTION OF CNWS

Two dimensional CNWs are nanostructured graphite sheets with edges, which are composed of planar graphene sheets standing vertically on the substrate. The sheets are few nanometers thick and form a network of wall type structures. The most important features of CNWs are high aspect ratio, large surface area and sharp edges. Hence, CNWs can be very useful in nanoelectronics. The most common tool for fabrication of CNW is chemical vapor deposition. It is well known that CNWs and similar structures have been grown using various CVD methods such as RF capacitively coupled plasma assisted by H radical injection, radio frequency inductively coupled plasma, electron beam excited plasma, microwave plasma, DC plasma hot filament CVD, helical wave plasma, and by sputtering of a glassy carbon target.

CHARACTERIZATION OF CNWS

CNWs have been characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, X-ray diffraction, X-ray photo electron spectroscopy, secondary ion mass spectroscopy and spectroscopic ellipsometry. Considering a variety of possible applications of CNWs, the important factors for studies are the growth controls of CNWs including spacing, thickness, morphology, crystalline and electrical properties. CNWs have a high density of atomic scale graphitic edges that are potential sites for electron field emission. This might lead to applications in flat-panel displays and light sources. Researchers have studied the field emission properties from CNWs and related structures. The key properties of CNWs are vertically standing walls with a high surface to volume ratio which makes them ideal gas storage materials. Several nanoparticles such as Ni, Co, Ni, Fe and Pt were also deposited on the surface of CNWs. CNWs were also used as a template for synthesizing mesoporous materials with high surface areas.

OBJECTIVES

The focus of this study is the fabrication and characterization of 2D carbon nanowalls. In the early work, CNWs were mainly formed by using H2 and reactive organic gases (carbon sources). In order to go one step further, we introduce a deposition method by metal organic precursor. In this process, there is no need of introducing any organic gas or additional H radicals. Following the systematic study of the effect of aluminium on the morphology of the CNWs and its electron emission properties, we shall carry out the deposition at various substrate temperature, argon gas flow and plasma power.

More importantly, we could also draw some conclusions to achieve high quality CNW devices. High quality CNWs devices are very important in further investigation for uniform field emission properties of CNWs. Special attention has been given to answer the following questions/tasks:

- Is it possible to deposit CNWs without using organic gas and without injecting H+ radicals additionally?
- To investigate the possibilities of the film depositions at various plasma conditions and study the effect on morphology as well as field emission properties.

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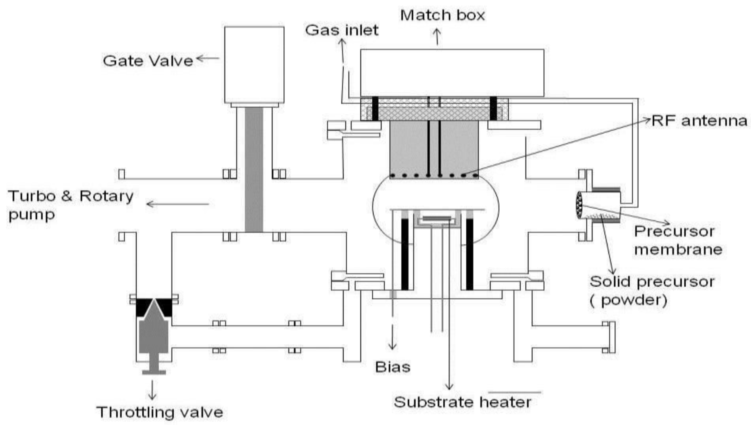
 Is Al improving the properties of the films? How does it affect the morphology of CNWs?
 Deposition in O2/Ar plasma results alumina films or is it possible to deposit CNWs in this condition too?
 How do the edges and defects affect the properties of CNWs?

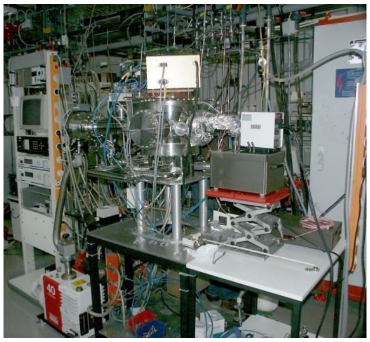
EXPERIMENTAL TECHNIQUES

Chemical vapor deposition

Chemical vapor deposition is a chemical process which is used to produce thin solid films. In this process, the gaseous molecules (which are called precursors) are introduced in a chemical reaction and then solid material growths at the surface form a film (powder etc). CVD is used in very wide areas like the production of powder, fibers and coatings. Very wide research on CVD has proved that it can produce mostly any kind of material like metals, non-metals, compounds of carbon and silicon like oxides, nitrides, and borides.
When the chemical process is proceeded with a plasma, it is called plasma enhanced CVD. Plasma is generated in an electromagnetic field which is set between two electrodes (top electrode and ground substrate). An electron collision takes place with gas molecules and forms ions and reactive neutrals. The total charge neutralizes with all reactive elements and sustains plasma inside the reactor. Plasma enhanced CVD is very useful for low substrate temperatures. In brief, CVD can be designed according to need but the basics of CVD are the dispensing gases, the temperature control and the produced bi-products. Sustaining the plasma is additional in plasma CVD.



A schematic diagram of ICP-CVD used for CNWs deposition



A picture of ICP CVD

CHARACTERIZATIONS METHODS

ELECTRON MICROSCOPY

An electron microscope is a type of microscope that produces an electronically-magnified image of a specimen for detailed observations. The electron microscope uses a particle beam of electrons to illuminate the specimen and create a magnified image of it. The microscope has a greater resolving power (magnification) than a light-powered optical microscope, because it uses electrons that have wavelengths about 100,000 times

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shorter than visible light (photons), and can achieve magnifications of up to 1,000,000x, whereas light microscopes are limited to 1000x magnification. Electron microscopes are used to observe a wide range of biological and inorganic specimens including microorganisms, cells, large molecules, biopsy samples, metals, and crystals. Industrially, the electron microscope is primarily used for quality control and failure analysis in semiconductor device fabrication.

X-RAY DIFFRACTION METHODS

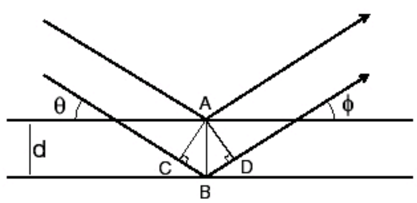
With the help of X-rays, it is now possible to determine the special arrangement of the structural units of a substance in the crystalline state and hence X-rays can be employed in investigating the interior of a crystal. The most important feature of the crystals of a substance is that the interfacial angles remain constant although the shapes and sizes of individual crystals differ considerably. Making use of this fact, Havy (1784) suggested that crystals are built up of small units having the same interfacial angles as the crystal. The distance between the atoms in crystals have been found to be roughly equal to 10-8 cm. So optical and elctronic microscopy cannot be used in this field. It was suggested by Von Laue (1912) that it might be possible to direct X-ray on crystals because:

 The crystals act as a three dimensional natural grating for X-Rays.

 X- rays act as part of the electromagnetic radiation.

 X-ray are actually the radiation of very small wavelength probably of the order of 10-4cm

Since its discovery in 1912 by Von Laue [115] X-ray diffraction has provided a wealth of important information to science and industry. For example, much of the spacing of atoms in crystalline material has been directly deduced from diffraction studies. These studies proved to be of immense importance in understanding the physical properties of metals, polymeric materials and other solids.



Diffraction of X- rays by crystals

XPS ANALYSIS

Al 2p peaks as a function of the precursor flow rate are shown in Figure 38. The continuous lines show the experimental data while the fits are drawn as dashed lines. The asymmetry of the peaks indicates the existence of two aluminium species in the samples: Al4C3 and Al2O3. The spin-orbit split (=0.4 eV [137]) of the Al 2p line could not be resolved within the resolution of our equipment. The Al 2p line was fitted using two peaks spaced 1.6 eV apart (see the inset of Figure 38), the 74.6 eV peak being due to aluminium carbide and the peak at 76.2 eV being attributed to spurious aluminium oxide. The signal is clearly dominated by aluminium carbide (80-90% of the integrated peak area). No significant variation of the binding energy was found in

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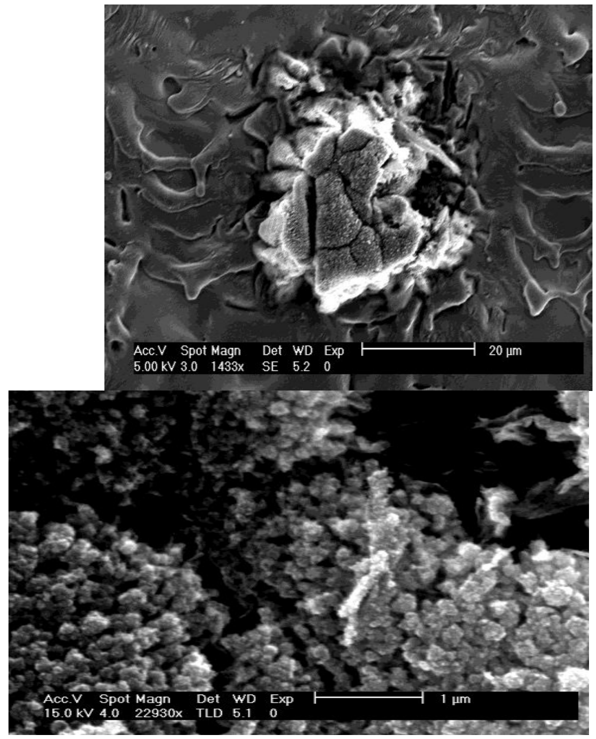
comparing the different films indicating similar aluminium environments for all precursor concentrations. The total area of the Al 2p peak correlates well with the concentration of aluminium due to the variation of the argon flow found by SIMS Figure 39 shows a comparison of the emission from the C 1s state between two CNW samples prepared at increasing argon flows.

FESM OF CARBON NANOWALLS

The FE properties of the laser-structured CNW cathodes were measured with a field emission scanning microscope (FESM) at a vacuum of 10-9 mbar using a tungsten anode of truncated cone shape with adjusted diameter (□a=30 μm) at a gap Δz . In order to investigate the FE mechanism and achievable current limit of the CNWs, local current-voltage measurements were performed on selected patches (e.g. the numbered ones in Figure 49 d). The local field was always calibrated by means of V(z) plots . From a detailed top view SEM image of the CNW-block, it looks cracked ,(Figure 48 left) as well as looks like inhomogeneous CNW spherical aggregates (Figure 48 right). Therefore, the current jumps and different FE properties are possible during the measurements. In order to investigate the homogeneity and the alignment of an emission from the cathode, seven (two) voltage scans at fixed field emission current (at 1nA) were performed in different areas of the cathode with Øanode = 30 μm (3 μm).

Medium Figure (a, b) and high resolution voltage maps show that most emitting areas of the cathode emit at a field of 10-20 V/μm. Voltage maps of the cathode showed fairly visible alignment of emission and nearly a 100 % of emitting CNW-blocks but with moderate homogeneity.



Top view SEM image of untested CNW-block: CNW- block looks shattered into many pieces (on the left) and CNW spherical aggregates (on the right)

FUTURE SCOPE

In future, the structuring of CNWs for device fabrication is possible. The work intends to signify that CNWs can be produced by different metal organic precursors like titanium metal organic precursor etc. To explore the properties of CNWs synthesized by different sources, it will be worth investigating in the field of graphene-based nanostructures. The initial results of field emission of CNWs sample are encouraging, but further optimization is required to exploit their full potential for device applications. In the direction of

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aluminium oxide, it is possible to deposit single phase α aluminium oxide films at low substrate temperatures. However, further research is required to tailor the plasma parameters that match the energy required for the formation of α Al2O3.

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