Engineering of Transition Metal-Assisted Graphene and Carbon Nanotubes Formation in Transmission Electron Microscopy

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Abstract

Carbon-based advanced nanomaterials are important for the devices of next generation, such as in field effect transistors, sensors, nanoelectronics, nanocomposites and flexible displays. In recent years, one-dimensional carbon nanotubes (CNTs) and two-dimensional graphene have become new members of the carbon family. They are ideal model materials for low-dimensional sciences, and are regarded as the key materials for future nanoscience and nanotechnology. For the device applications, their controllable synthesis and position control should be indispensable. In this thesis, these issues are challenged by dynamically observing their formation process in atomic dimension inside transmission electron microscopy (TEM).

For the *in-situ* TEM dynamical observation, the sample preparation is a key factor. Firstly, platinum (Pt)-, palladium (Pd)- and cobalt (Co)-included amorphous carbon nanofibers (CNFs) as well as pristine (pure) CNFs were fabricated on the edges of graphite foil by argon (Ar^+) ion irradiation with and without a supply of those metals at room temperature. Also, the controllable synthesis of copper-carbon nanoneedles (Cu-CNNs) with higher Cu concentration than C directly on an edge of Cu foil by Ar^+ ion irradiation with a supply of C during ion irradiation was achieved. They were featured by the amorphous carbon structure with the inclusion of metal nanoparticles. For a comparison, Cu-coated pristine CNFs were also prepared. For those samples, dynamic TEM observation was performed by *in-situ* current-voltage (I-V) measurement and/or direct heating in TEM.

In-situ I-V measurement of both Cu-CNNs and Cu coated CNFs in TEM revealed for the first time that current increased gradually at the beginning and suddenly steeply increased with applied voltage due to the transformation from amorphous carbon to graphene catalyzed by Cu. After the formation of graphene, current density as high as 10^6 A/cm^2, which is comparable to that of Cu film in normal interconnect application was achieved. Graphene formation was due to the Joule heating induced by the electron current flow. Compared with Cu-coated CNFs, the formation temperature of graphene as low as 1073 K was realized for Cu-CNNs, thanks to the reduction in melting point induced by the size effect of Cu nanoparticles dispersed in the Cu-CNNs.

In-situ I-V measurement of Pd-included CNFs in TEM resulted in the formation of graphene which involves the thermomigration starting from the middle part of the structure. This thermomigration also was due to Joule heating induced by the electron current flow. It also proved that Pd possessed a good ohmic contact with carbon materials. This implies that it can be replaceable to gold as an electrode for carbon interconnection application.

Different from the Pd and Cu cases, the *in-situ* I-V measurement of Co-included CNF showed that Co nanoparticle in CNF migrated through electromigration phenomenon and resulted in the formation of Co-capped CNTs due to the current induced Joule heating. This implies that movement of Co particle is controllable, thus being advantageous to apply it to fabricate a probe for magnetic force microscopy (MFM), because CNTs probe with a magnetic particle on the tip is known to be ideal for the better performance of MFM.

In-situ I-V measurement of Pt-included CNF in TEM led to the formation of a multilayer CNTs through electromigration behavior of Pt nanoparticles. The driving force for the transformation was current induced Joule heating. The movement of Pt nanoparticles were controllable and by using this controllable movement, the connection of two CNTs was achieved. So, the application of this controllable migration of Pt will open a door for nanosoldering of carbon nanostructure.

Thus, this thesis demonstrated the potential of engineering the controllable formation of graphene and CNTs as well as position control by solid phase reaction for various future device applications.

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Chapter 1

Introduction

1.0 Background of the Study

In Richard Feynman's famous speech entitled "There is plenty of room at the bottom", he emphasized about the manipulation and rearrangement of things in atomic scale to achieve the mechanical and atomic sized devices and components [1]. He concluded that the development of technologies to construct such small systems would be interdisciplinary, combining fields such as physics, chemistry and biology, and would offer a new world of possibilities that could radically change the technology around us. Since then, the technological world are being developed rapidly in almost all technological areas towards nanotechnology. However, this development is inadequate as the giga-scale miniaturization of those technologies faces difficult challenges in terms of materials, architectures, fabrication and integration of nanoscale active and passive elements. Also, there are many questions on the expected performance in terms of reliability, speed, compatibility and power consumption [2]. To continue with the current speed of development of nanofabrication, highly strong, controllable, flexible and conductive materials with wide range of optical and electronic properties are essential.

Among the nanomaterials, carbon nanomaterials are anticipated as key materials

that underpin major advances in all areas of science and technology due to their unique electronic, optical, thermal, mechanical and chemical properties [3, 4]. The discovery of hollow carbon sphere named C_{60} buckyballs or fullerene in 1985, and the Nobel Prize awarded to Curl, Kroto and Smalley, obviously marked the beginning of this nanocarbon era [5, 6]. The research in nanocarbon continuously developed by the discovery of 1 dimensional carbon nanotubes (CNTs) by Sumio Iijima in 1991 [7, 8]. One decade later, the discovery of 2 dimensional graphite structure called graphene by Geim and Novoselov which led them to be awarded the Nobel Prize in Physics further highlights the high expectations for nanocarbons, in particular for applications in electronics and material sciences [9-11]. Among those allotropes of carbon, CNTs and graphene are of importance to modern science and technology since they provide exciting challenges and opportunities for chemists, physicists, biologists and materials scientists.

Although CNTs and graphene have been employed in many nanotechnology applications including interconnections, nanosensors, medicals and so on, the detail information about these nanomaterials still need to be answered before it can be fully utilized in various applications [12-15]. These fundamental information will be significant to control the CNTs and graphene growth, as well as knowledge and explanation about their properties in desired applications. Current studies on nanostructured materials, including nanowires, nanocrystalline and nanotubes (NTs) have discovered many of 'unusual deformation' phenomena compared with their bulk parts, such as high strength, nano-piezoelectric effects and unusual plastic deformation behaviors [16]. Nanostructured materials can stand a larger dynamic range of elastic and plastic strains compared to conventional materials. Furthermore, Richard Feynman in his speech in 1959 also talked about the importance of manipulation and control of materials

on a small length scale, such as the fabrication of molecular machines [1].

To achieve the manipulation and control of materials in nanoscale, nano-manipulation in scanning electron microscopy (SEM) has been proved to be a powerful technique for in–situ manipulating, structuring, characterizing, and assembling as-grown nanomaterials and as-fabricated nanostructures [17-19]. However, the best resolution of a high grade commercially available SEM is typically around 1–2 nm in an ideal environment which is not satisfactory for high resolution investigation. To solve this problem, transmission electron microscopy (TEM) has come in the picture. The higher resolution of the TEM allows for a more detailed and especially local analysis of the structural properties of the nanostructures [20-23]. Therefore the selection of a nanostructure with the desired properties is possible. Furthermore, the ultra-high vacuum (UHV) in the TEM and the low generation of secondary electrons leads to a much reduced deposition of contamination on the samples [20]. Thus, the in-situ nanomanipulation or nanoengineering in TEM opens the path to understand the mechanism of nanocarbon formation and its properties. In the following sections, recent progress in CNTs and graphene research will be introduced including the controllable synthesis, proposed growth mechanism, CNTs/graphene-based electronic devices and in situ TEM investigations. After that, the motivation and organization of this thesis will be presented.

1.1 Controllable Synthesis of Graphene and Carbon Nanotubes

Graphene and CNTs has been explored as promising candidates for future nanoelectronic applications as a result of their superior properties, atomic thickness and plethora of applications. To achieve this aims, graphene and CNTs must be synthesized in a controllable manner. Thus, the controllable synthesis of graphene and CNTs is of

great interest and received more attention recently.

1.1.1 Graphene with Controlled Size and Shape

A variety of benzene ring arrangements in the two-dimensional space creates graphene sheets with different shapes, sizes, edges and layer structures. Besides that, the different covalent or noncovalent bondings with other atoms lead to different doping or modification of graphene sheet, which create graphene materials with various properties [24]. For example, depending on the width and edge configurations, graphene nanoribbon can act as metallic or semiconducting materials [25, 26]. Graphene nanoribbon with a width narrower than 10 nm will possess semiconducting properties, because of the confinement of the electron wave function. Also, the bandgap of the nanoribbon can be tuned by varying their width. The narrow nanoribbon will create a material with larger bandgap [26].

For graphene with larger width, the properties of graphene nanoribbon are mainly determined by the edge configurations. Zigzag nanoribbons possess half-metallic properties with a good conductivity, while armchair nanoribbons could have either metallic or semiconducting, depending on their widths [27]. On the other hand, doping or chemical modification of graphene can modify their properties. N-type graphene can be synthesized by doping nitrogen atoms at the edges of graphene hexagonal ring [28, 29]. Figure 1.1 below summarizes present techniques for synthesizing graphene with controlled sizes, shapes. edges, layers, doping and assembly. These various types of graphene are potential candidates for fabricating nanodevices or nanocircuits where each type of graphene can function as a different component based on their properties [30].

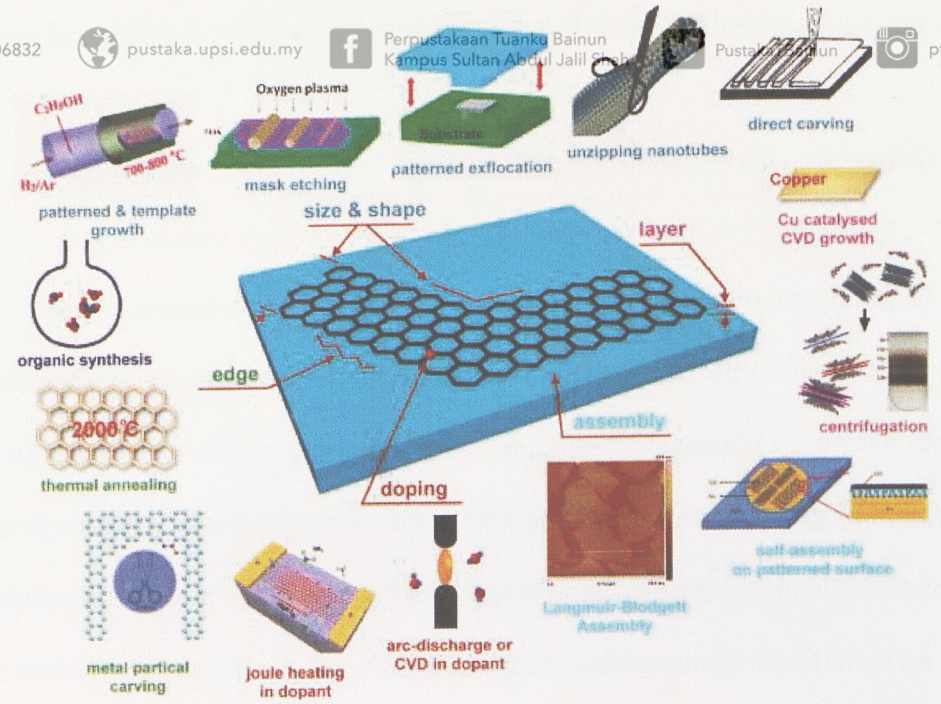

Figure 1.1. The present techniques for synthesizing graphene with controlled sizes, shapes, edges, layers, doping and assembly [24].

To achieve the practical applications, well-defined graphene is essential. However, conventional techniques usually produce graphene with various sizes, shapes and layer numbers due to random exfoliations and growth process. This problem remains challenges and limits the fundamental research and practical applications of graphene. To date, more attention has been given on the controllable synthesis of graphene. Chemical vapor deposition (CVD) is a well-known technique to controllably produce various types of nanomaterials. Many groups have reported on the epitaxial growth of single and few layers graphene on catalyst metals such as Cu, Ni, Pt and Co which was deposited on the wafer [31-33]. Several groups have revealed the patterned growth of graphene using catalyst pattern in CVD [34, 35]. The graphene growth takes place only on the surface of catalyst pattern and thus resulting in graphene pattern (Figure 1.2 (a)). However, in the application point of view, the drawback of this technique is the presence of catalyst metals

which need to be removed. Reina *et al.* reported the etching process of a metal catalyst and the transfer process of graphene to another substrate using polymethylmethacrylate (PMMA) (Figure 1.2(a)). Some of the researchers reported on using of polydimethylsiloxane (PDMS) stamps or a floating process to transfer the graphene patterns for applications (Figure 1.2(b)) [32, 35].

Besides that, patterned graphene is also synthesizable using an electron beam, ion beam, laser or scanning probe microscopy (SPM) tips. Also, Joule heating is used to reshape rough edges of graphene into armchair or zigzag edges. The atomically smooth straight edges can also be attained by carving graphene sheets with thermally activated metal nanoparticles. On the other hand, focus laser beam thinning was developed to control the number of layers of graphene [24, 36].

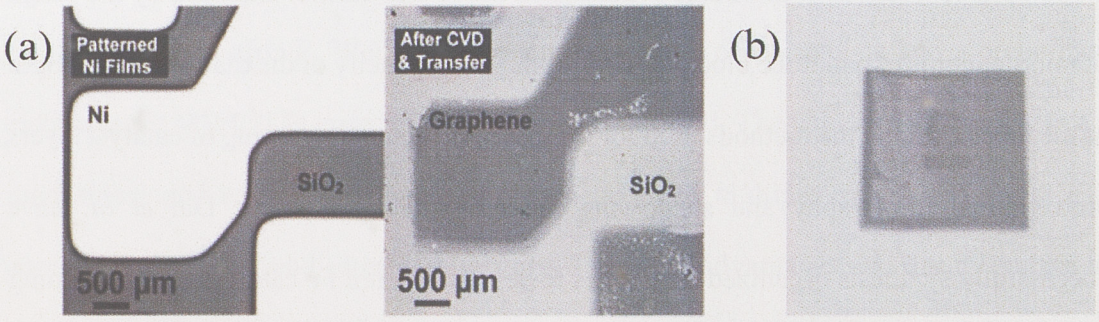

Figure 1.2. Controlled epitaxial growth of graphene and its applications. a) Photo images of the prepatterned Ni films on a SiO_2/Si substrate and the grown graphene pattern after transferring to another SiO_2/Si substrate. b) Photo image of the grown graphene pattern after transferring by PDMS stamp. [32, 35]