Chapter 1

Introduction

1.1   Introduction

It has been said that nanometer is "a magical point on the length scale; for this it is the point where the smallest man-made devices meet the atoms and molecules of the natural world."[1] Indeed, nanotechnology mania is sweeping through all fields of science and engineering.

Generally speaking, the scale of atoms and molecules is less than one nanometer. Chemists have provided a bottom-up method to synthesize various nanostructures in these years. In this dissertation, we will attempt to show a bottom-up method for fabricating carbon and silicon nanostructures based on a new phase segregation concept.

Carbon and silicon are two essential elements in industry. For example, it is extensively used in petroleum industry, while silicon is widely utilized in semi-conductor industry. Thus, the nano-sized carbon and silicon structure have attracted lots attentions lately. This thesis will present different types of carbon materials, such as carbon nanotubes, porous carbon, and graphitic carbon, and various types of silicon materials, such as silicon nanoparticles, porous silicon, and silicon nanowires.

1.2   Nanostructure of Carbon Materials

1.2.1   The Structure of Carbon

Solid carbon exists as graphite, diamond, and other phase such as the fullerenes, which have structures related to that of graphite. Graphite and diamond are two of the most interesting minerals. Graphite consists of planar sheets of sp^2 hybridized carbon atoms in a hexagonal network. Diamond, each carbon atom is sp^3 hybridized and linked tetrahedral to

its four neighbors. They are identical chemically - both are composed of carbon (C), but physically, they are very different. The important physical difference is their hardness. The hardness of minerals is compared using the Mohs Hardness Scale,[2] a relative scale numbered 1 (softest) to 10 (hardest). Graphite is very soft and has a hardness of 1 to 2 on this scale. Diamonds are the hardest known natural substance and have a hardness of 10. The reason for the differences in hardness and other physical properties can be explained with the molecular models below.

The crystal lattice of graphite (Figure 1.1)[3,4] composed of graphene layers, which the carbon sheets are bounded by weak van der Waals forces between each other. The weak bonding forces hold the sheets together. Because these forces are weak, the sheets can easily slide past each other. The sliding of these sheets gives graphite its softness for writing and lubricating properties. Graphite is a good electrical conductor with an electrical conductivity in the range of 10^4 S/m at room temperature.[5] However, graphite is normally formed at temperature over 2773 K. At lower decomposition temperatures, the degree of ordering in the graphite lattice can be considerably less. For example, on substrates such as quartz or alumina, turbostratic carbon is formed at 1173 K.[6] Graphitization of turbostratic carbon causes its transformation to be well-ordered graphite. Oriented graphite can be formed at relatively low temperature; however, the presence of metal catalyst such as Fe, Co, Ni is needed.
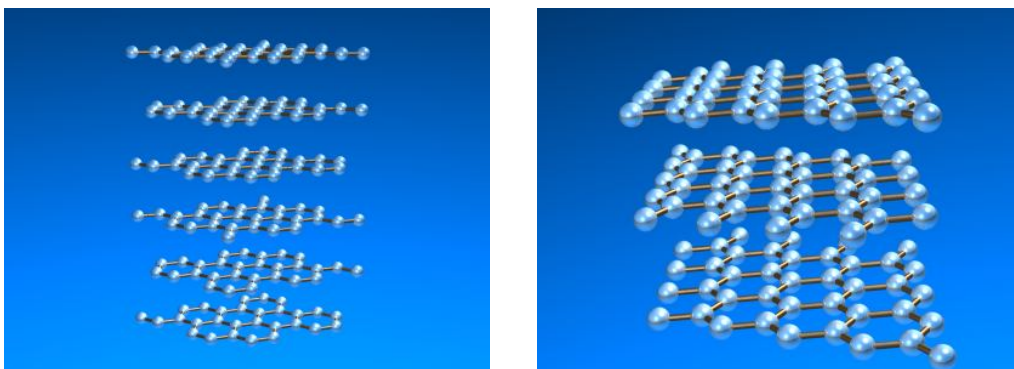

Figure 1.1 The crystal structure of graphite.[3]

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The unique properties of graphite materials have lots of applications such as selective adsorption, energy storage, catalyst support, and fuel cell catches people's attention for further reserch.[7-10] The graphitic carbon can also be expected to perform as a high-rate and high capacity anode materials in lithium ion battery applications.[11]

Each carbon atom in diamonds is strongly bonded to four adjacent carbon atoms located at the apices of a tetrahedron. The four valence electrons of each carbon atom participate in the formation of very strong covalent bonds (Figure 1.2).[3,4] These bonds have the same strength in all directions. This gives diamonds to have great hardness. Since there are no free electrons to wander through the structure, diamonds are excellent insulators. In principle and in practice graphite may be converted into diamond by the application of heat and pressure. One method used to synthesize industrial diamonds recreates the geological conditions that produce natural diamonds by compressing graphite at pressure over 80 kbar and temperatures above 1773 K. During the past study, significant progress has been made on experimental techniques for synthesizing diamonds by the decomposition of hydrocarbon gases. Particularly notable is the finding by Setaka and colleagues[12] that, using three different chmical-vapor-deposition (CVD) methods, diamonds can be grown from a methane-hydrogen mixed gas on various substrates such as silicon.
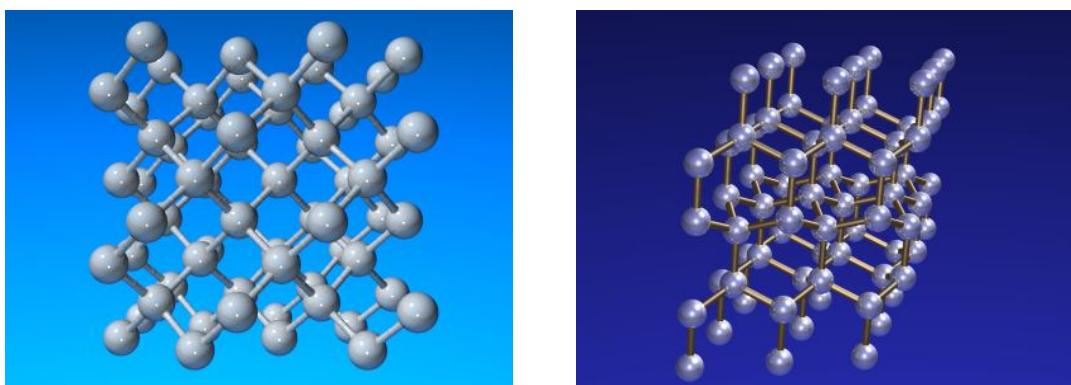

Figure 1.2 The crystal structure of diamond.[3]

1.2.2   Carbon Nanotubes

The discovery of carbon nanotubes (CNTs) by Iijima in 1991[13] created much excitement and research into the properties of nanometer-scale cylindrical carbon networks. They are typically composed of 2 to 50 concentric cylindrical shells with outer diameters, a few tens of nm and lengths on the order of μm. Each shell has the structure of a rolled up graphene sheet with the sp^2 carbon forming a hexagonal lattice (Figure 1.3).[3] CNTs produced by pyrolysis of propylene show a significant increase in the degree of ordering of the (002) planes after heated to 2800 ^{o}C under Ar flow,[14] so well-ordered graphite wall structure can be obtained.[15]

Theoretical studies of nanotubes have predicted that they will have unusual mechanical, electrical, and magnetic properties of fundamental scientific interest and possibly of technological importance. Potential applications for CNTs with the highest thermal conductivity, the highest strength of any materials, and outstanding filed emission properties have been suggested.[16-18] They show tremendous promise in a wide varieties of applications, inclusive of chemical sensors, biosensors, electronic, interconnects, field emitter, and scanning probes.[19-22] Nevertheless, no one can deny that the real opportunities for carbon nanotube chemistry still exist in the future.
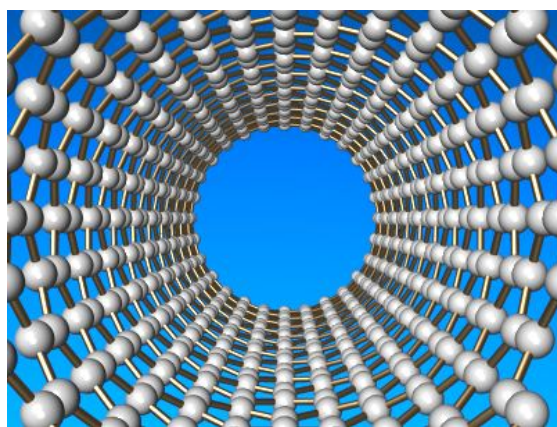

Figure 1.3 The structure of carbon nanotube.[3]

There is probably no other material with so much potential; however, there still are so many challenges for the preparation of the carbon nanotubes,[23-25] and a task or challenge to be dealt with studying their purification from catalyst residues, solving random orientation, and controlling chirality into semiconducting and metallic nanotubes. All of these challenges lie in front of us; nevertheless, pure carbon nanotubes still cost more than gold.
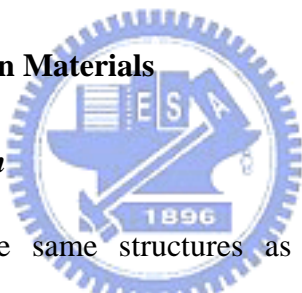
1.2.3 Porous Carbon

The demand for porous materials in industrial applications and in our daily life is increasing. Porous carbon materials, especially those containing micropores or mesopores, are equipped with various applications such as used as adsorbent[26] and catalyst supports.[27] High-porosity of carbons, which is given a name — activated carbon, are generally prepared from activation by using either physical or chemical methods.[28-30] In chemical activation, the carbonization and activation are accomplished in a single step by carrying out thermal decomposition of the raw material impregnated with certain chemical agents. The advantages of chemical activation are low-energy cost due to temperatures (773 to 1073 K) lower than those needed for physical activation, and high product yields. Physical activation involves in gasification of the char, obtained from carbonization of the raw material, oxidation with steam, carbon dioxide, air or any mixture of these gases in the temperature range from 1073 to 1373 K. However, the pore size and structure cannot be easily controlled through the activation process, thus the well-controlled pore size distribution has imposed serious problems concering the applications. Various types of inorganic templates have been used to design and control the pore structure of porous carbon materials. Using mesoporous silica materials as the template for carbon preparation has been proved to be a promising technique in producing carbons with uniform mesopores and widely used approach.[31-34]

According to the International Union of Pure and Applied Chemistry (IUPAC), the pores of a porous materials are classified in three groups: micropores (width d < 2 nm),

mesopores (2 nm < d <50 nm) and macropores (d > 50 nm).[35] Most commercial activated carbons have a specific surface area of the order of 800 - 1500 m^2/g. The maximum of the distribution curve on their volume versus their radii is mostly in the microporous range of 0.4 - 2.0 nm. However, the mesopores can serve as the main transport arteries for the adsorbate. Therefore, mesopores of porous carbon materials play a very important role in adsorption, especially in new applications, such as catalyst supports, battery electrodes, capacitors, and gas storage and bio-medical engineering applications. For such applications, the carbon materials should possess not only high surface area, but also high ratio of mesopores or macropores to micropores, because many macromolecules and ions larger than the pore diameter of micropores are not able to enter and transport the micropores.

1.3　　Nanostructure of Silicon Materials

1.3.1　The Structure of Silicon

Element silicon has the same structures as diamond. The atoms are bonded tetrahedrally with covalent bonds (Figure 1.4).[3,4] However, in silicon, the energy gap is smaller than diamond. A few electrons can cross the gap at 298 K, making silicon a semiconductor. In addition, at higher temperatures, the more energy is available to excite electrons into the conduction bands, the conductivity of silicon increase. The small conductivity of silicon can be enhanced at normal temperatures if the silicon crystal is doped with certain other elements. For example, an n-type semiconductor, that conductivity is increased by doping arsenic atom having more valence electrons than the atoms in the host crystal. When semiconductors are doped with boron element having fewer valence electrons than the atoms of the host crystal, called p-type semiconductors.
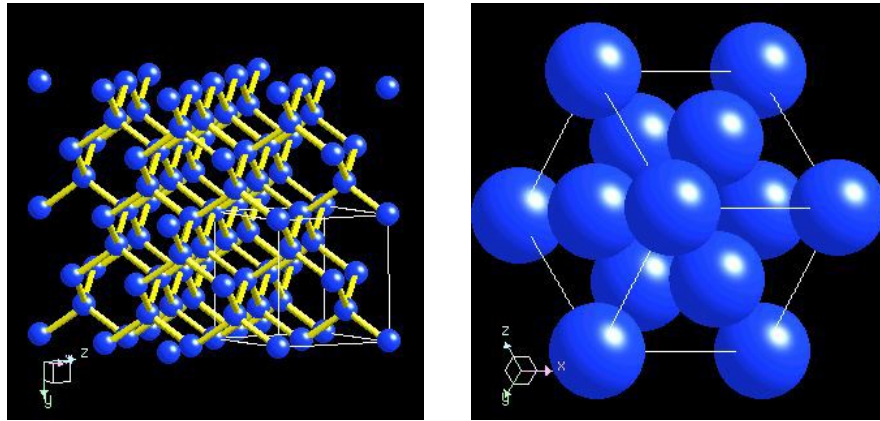
Figure 1.4 The crystal structure of silicon.[3]

### 1.3.2 Porous Silicon and Silicon Nanoparticles

Silicon nanoparticles display optical and electronic properties depending on lowering melting point decreases in size.[36] Such properties are thought to have important applications in the development of optoelectronic devices. Silicon nanoparticles can be made by a range of different methods including the gas or solution phase decomposition of silanes, hydride reagents and the electrochemical etching of silicon wafers.[37-39]

Porous silicon has been demonstrated to yield visible light emissions at room temperature.[40] Such a behavior is primarily attributed to electron confinement in the nanocrystals that constituted the porous structure. There are many methods used to fabricate porous silicon. Porous silicon have primarily been produced by etching bulk silicon using hydrogen fluoride (HF) solutions.[41] The development of a gas-based method for the fabrication is another technique.[42] Such a considerable surface area provides a large number of potential binding sites which draw great attention in porous silicon for chemical, bio-sensing application, biocompatible material.[43-46]

1.3.3 Silicon Nanowires

Research on conventional 1-D semiconducting materials has been noticed. Among them, silicon nanowires have special properties. Thus, silicon is the most widely used and studied semiconducting materials. When silicon nanoscale formed, such as nanocrystal,

porous silicon, quantum well, and nanowirs, have appealed to scientists due to their peculiar physical properties, such as light emission, field emission, and quantum confinement effect. Previous studies have demonstrated that the synthesis of semiconductor nanowires can be achieved by using catalyst-assisted vapor-liquid-solid (VLS) growth, solution phase approach, pulsed laser ablation, and molecular beam epitaxy etc.[47-50] SiNWs also have been produced by an oxide-assisted methods, and however, this approach generally yields a broad diameter distribution, bulk defects, and a thick surface oxide layer.[51] Silicon nanowires (SiNWs) with well- controlled diameter have been synthesized by using well-defined Au nanocluster catalysts and silane (SiH_4) was used as the vapor phase reactant.[52] The potential use of low-dimensional silicon structure for optoelectronic device, includes silicon-based light-emitting diodes.[53] Moreover, luminescent silicon may be acted as a useful fluorescence agent in biological systems.[54]
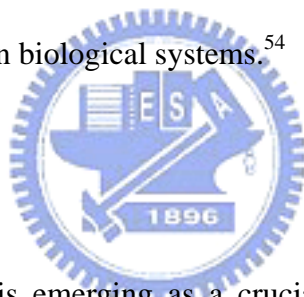
1.4   Growth methods

Nanomaterial synthesis is emerging as a crucial technology in nanotechnology to develop building block for nanometer-scale devices. There are many strategies used to synthesize a various types of nanostructures. Template-mediated growth has become one of the popular methods to fabricate nanostructures over large area and it would get well-aligned and dimension-controlled materials that can be obtained through this advance. Furthermore, a developed experimental method is desired in order to reduce and simplify experimental steps. For example, the reactants or/and products not only served as reactors in the synthesis process, but also acted as self-templates to assist growth. We will introduce the hard template-assisted methods and self-templated approaches as follows. These methods would be provided simple and efficient process to obtain nanostructure materials. According to the synthesis process, our reaction happens in the vapor and solid interface. Two models

are used to explain the growth mechanism - vapor-liquid-solid (VLS) and vapor-solid (VS) growth.

1.4.1 Hard Template Assist Growth

Anodized aluminum oxide (AAO) template, one of the hard templates is usually used as an assistant. Porous AAO membrane is formed via the anodization of aluminum metal in acidic agent solution, which has been demonstrated in detail recently. Several researchers have reported that pore size and pore distribution of AAO have been completely controlled by adjusting the anodization conditions of the oxidation voltage, temperature and the electrolyte.[55-58] For each AAO membrane, their pore density can be achieved 10^{11} cm^{-2} of pores and pore diameter can be controlled from 5 to 400 nm. Thus, narrow pore distributions can be formed by changing the applied voltage and the electrolyte. Every fine pore distribution of AAO membrance should be regular hexagonal pore structures that has some excellent characteristics such as high pore density, thermal stability, chemical stability and easily removed by acidic or basic treatment. As a result, AAO templates are widely used in synthesizing 1-D nanostructure materials including nanowires, nanotubes, nanocomposites and so on. These 1-D nanostructure molds could be molded by loading precursor into AAO pores with some approaches just like vapor-phase evaporation, liquid-phase injection, solution-phase chemical or electrochemical deposition.

Growth of CNTs has been provided an efficient approach to the production of aligned arrays of CNTs by using AAO template.[59] These CNTs had uniform diameter, highly ordered and perfectly vertical to the plane of AAO template.

1.4.2 Self Template Phase Segregation Assist Growth

In nature, the mineralogy having various types of species and morphologies have been noticed by scientists. The composition of these mineral are inorganic, inorganic salt and/or metal alloy. The phase segregation of the different compositions in the mineral are induced and believed to assist formation which is affected by several environment factors,

such as pressure and/or temperature.[60] The other case is in polymer science, the theoretical phase segregation for diblock ot triblock copolymers, composed of two chemically different components, could be self-assembled into various ordered nanostructures spheres, cylinders and lamellae.[61] Micelles have convenient and flexible structures functioning as nanoreactors or self-templates that is another example.

Core-shell heterostructure nanowires and tubular nanowires have recently been synthesized.[62-64] By combining different types of nanostructures in an axial or radial direction, the variety of functions may be realized. Nanostructures, including nanowires or nanotubes, often display high chemical reactivity due to their low dimensionality and a high surface area. The reactivity leads to the nanostructure oxidation and contamination, resulting in dramatic changes in morphology and properties of nanostructures. Thus, it is extremely important to have a protective sheath made of thermally and chemically stable materials on grown nanowires to enhance their performance. Many types of nanowires have a protection layer to form a core-shell structure via different methods. Previously, metallic nanowires, coated silicon dioxide have been produced by VS reactions and by laser ablation technique.[65] Literature reported that hexagonal boron nitride has served as an insulating and/or protective shield for nanostructure encapsulating within.[66,67] Another case is graphite carbon layer coating which can act as a chemically inert protecting layer. Several routes have been developed to prepare carbon nanotube in relation to composite heteronanostructures.[68,69] Recently, nanowires can be produced via carbon materials which not serve as nanoreactors for simple thermal reaction process, and the formation of protective carbon can be served as the sheath coating on the nanowires in order to prevent their surface oxidation and/or hydrogenation.[70]

1.4.3 Vapor-Liquid-Solid Growth

The VLS process[71-73] has been an important approach in growth of quasi-one-dimensional (1-D) nanostructures. In the VLS process, a metal catalyst is

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rationally chosen from the phase diagram by identifying a metal that is in liquid state at the growth temperature and serves as the site for adsorbing the incoming molecules. Thus, it is phase-segregated at the growth front and leads to the growth. The metal liquid droplet serves as a active site for absorption of gas-phase reactant. 1-D nanostructure growth begins after the liquid becomes supersaturated in reactant materials and continues as long as the catalyst alloy remains in a liquid state and the reactant is available. During the growth, the catalyst droplet directs the 1-D's growth and determines the diameter of the 1-D. The growth terminates when the temperature is below the eutectic temperature of the catalyst alloy or the reactant is not available.

1.4.4   *Vapor-Solid Growth*

In vapor-solid (VS) growth of nanowires, structural defects play an important role in both the nucleation and the growth. The differing from VLS growth of nanowires that catalyst or initiator are required in the growth of the nanowires. The morphological feature of VS grown nanowires is that there exists a conical tip at the end of the nanowires. The classical VS method for whiskers growth also merits attention for the growth of nanometer 1-D materials.[74] In this process, the vapor is first generated by evaporation, chemical reduction or gaseous reaction. The vapor is subsequently transported and condensed onto a substrate. The VS method has been used to prepare oxide, metal whiskers with micrometer diameters. The requirements for 1-D crystal growth, such as the presence of a dislocation at the vapor-solid interface, are still a matter of controversy in 1-D VS growth.

Previously, our group reported that addition of poly(dimethylsiloxane) (PDMS) to a solvent-free vapor-solid reaction growth (VSRG) process assisted Cu nanowire formation significantly.[75] A simple high yield synthesis of Ag nanowires which is carried out by using $AgNO_3$ and $(Me_3Si)_4Si$ were prepared in a sealed tube under low pressure at 400 K.[76]

1.5   Goal of this thesis

In this thesis, a phase segregation concept in the inorganic field is proposed to dramatically affect the morphology of carbon and silicon nanostructures via vapor-solid reaction grown. The new approach has been provided to built-up the nanostructures more easily.

We employ C_6F_6 to react with Na, and then a unique type of porous carbon material was formed. The self-generated NaF acts as the nanotemplate to shape the carbon material into the observed porous structure. 1-D CaF_2/a-C (amorphous carbon) and MgF_2/a-C core/shell nanowires can be generated easily in one step. The MF_2 (M=Ca, Mg) and a-C can act as reactors and extend cooperatively as interdependent self-templates to assist growth. A simple experimental setup to fabricate high quality graphitic carbon materials with various porous, fibrous, and lamellar structures at relatively low reaction temperature and catalyst free has been developed. High quality single crystal and defect free silicon nanostructurs, such as clustered-nanoparticles, porous, wire-like, coral-like, and lamellar morphologies, can be obtained via simple experiment design. These experimental results will be discussed in the following chapters in detail.

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