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Controlled Synthesis and Characterization of Metal Oxide Nanowires by Chemical Vapor Deposition on Silicon and Carbon Substrates

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by

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Abstract

Nanotechnology and nanomaterials have attracted considerable interest and are predicted to revolutionize many materials and technologies that we use in everyday life. In the past few years, significant research has focused on one dimensional metal oxide nanostructures due to their unique properties and potential applications in various fields from nanoelectronics to energy. However, controlled synthesis of these nanostructures is still a challenge.

The objective of this thesis is to synthesize metal oxide nanowires by chemical vapour deposition directly on various substrates. The nanostructures include (i) silicon oxide nanostructures on silicon substrate, (ii) manganese oxide nanostructures on silicon substrate, and (iii) manganese oxide nanostructures on carbon paper substrate.

Firstly, silicon oxide nanowires were synthesized on silicon substrate by a VO_2 assisted chemical vapor deposition. Networked features of silicon oxide nanowires were found. Systematic study on the nanowire growth has indicated that morphology and composition of the final products are considerably sensitive to the catalyst components, reaction atmosphere and temperature. These results will help in better understanding the growth process of silicon oxide nanowires.

Secondly, manganese oxide nanostructures were synthesized on silicon substrate by chemical vapor deposition method. It was found that MnO nanowires are high density and single crystalline with average diameter of 150 nm. These nanowires were characterized using FESEM, EDX, TEM and XRD. The synthesis process and effects of growth parameters such as temperature, heating rate and source/substrate distance on the morphology, composition and structure of the products were systematically studied.

Finally, manganese oxide nanostructures were synthesized on carbon paper substrate by chemical vapor deposition method. It was revealed that manganese oxide nanowires and nanobelts can be selectively grown on carbon paper substrate by using a catalyst (gold) assisted or catalyst free thermal evaporation of manganese powder under an argon gas atmosphere. Various effects of growth parameters such as temperature, catalyst and buffered substrate on the growth product were also systematically investigated by using SEM, TEM and XPS.

Keywords: Silicon oxide, manganese monoxide, nanowire, nanobelt, chemical vapor deposition, growth mechanism

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Abbreviations

CVD – Chemical vapor deposition

SEM – Scanning electron microscope

TEM – Transmission electron microscope

HRTEM – High-resolution transmission electron microscope

XRD – X-ray diffraction

SLS – Solid liquid solid

VLS – Vapor liquid solid

VS – Vapor solid

Chapter One: Introduction to One-Dimensional Nanomaterials

1. Nanotechnology

1.1. Introduction

In 1965, Intel co-founder Gordon E. Moore stated that

> *"The complexity for minimum component cost has increased at a rate of roughly a factor of two per year ... Over longer term, the rate of increase is a bit more uncertain although there is no reason to believe that will not remain nearly constant for at least 10 years*"[1]

Later he altered his projection to a doubling every two years, and this statement has been empirically proven since 1970s as shown in figure 1. This means that every 24 months the density of transistors on integrated circuits doubles.

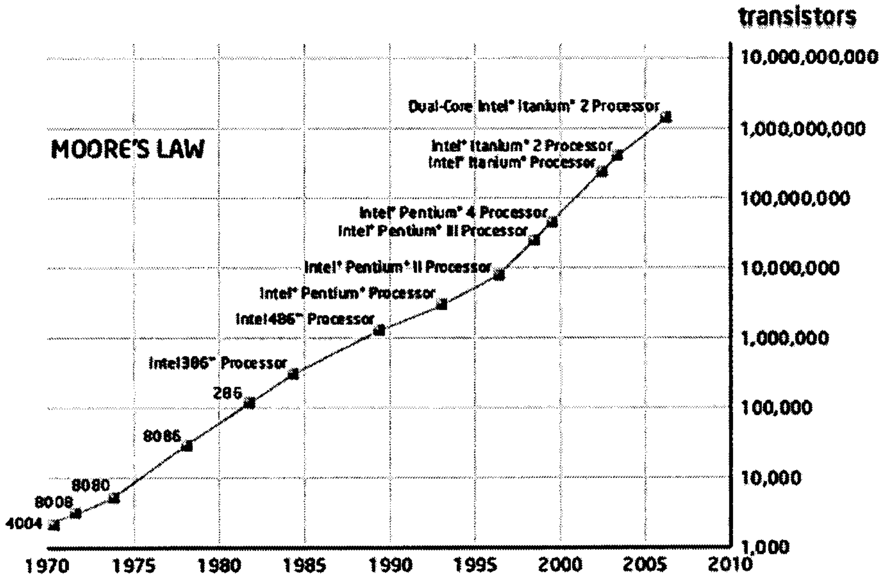

Figure1. "Moore's law" plot of transistor size versus year. The trend line illustrates that the transistor size has decreased by a factor of 2 every 18 months (diagram copied from Intel website)

It is obvious that using conventional microchip technologies, electronic industry would reach its limit of transistor density on a single wafer. In order to be able to follow Moore's prediction, new technologies such as nanotechnology are needed to develop to give electronic industries access to move from micrometer scale to smaller scales such as nanoscale.

Nanotechnology, a term coined in the 1970s refers to the development of and use of techniques to study physical phenomena and construct structures as well as incorporation of these structures into applications. This technology deals with small sized materials. The typical dimension spans from subnanometer to several hundred nanometers [2]. Although size is a convenient way of defining the area, it alone is not enough to distinguish the nanoscale material from microscopic material. For example there is no line of demarcation that separates structures at 120 nm from that of 100 nm. In practice nanotechnology has more to do with the investigation of novel properties that manifest themselves at that size scale, and of the ability to manipulate and artificially construct structures at that scale [3].

Nanotechnology might be new, but the use of nanosized material and research on nanometer scale is not new at all. It is known that in the fourth century A.D. Roman glass makers were fabricating glasses containing nanosized metals. The great varieties of beautiful colors of the windows of medieval cathedrals are due to the presence of metal nanoparticles in the glass. Photography is an advanced and mature technology, developed in eighteen and nineteenth centuries which depend on the production of silver nanoparticles [4]. In addition the study of biological systems and engineering of many materials such as colloidal dispersion and catalysts have been in the nanometers regimes for centuries. Use of colloidal gold has a long history, though a comprehensive study on the preparation and properties of colloidal gold was first published in the middle of 19th century. Colloidal gold was and is still used for treatment of arthritis. A number of diseases were diagnosed by the interaction of colloidal gold with spinal fluids obtained from the patient [4].

What is really new about nanotechnology is the combination of the ability to see and manipulate matter on the nanoscale and understanding of atomic scale interactions in recent decades.

Predication about the promise of nanotechnology can be traced back to Feynman's classic 1959 talk where he stated: "the principles of physics, as far as I can see, do not speak against the possibility of maneuvering thins atom by atom."[5]. Feynman proceeded to describe building with atomic precision and outlined a pathway involving a series of increasingly smaller machines and in recent decades due to intensive research on this technology such predications are coming to reality. Nanotechnology enables industries to manufacture smaller, lighter, stronger and cleaner products which lead to huge commercial applications in various fields such as semiconductors, electronics, medical, automotive and energy. For example in electronics, in long term, huge amount of work is being done to commercialize semiconducting nanotubes for electronics. Similarly, work is being carried out to scale up spintornic molecules containing two atoms in an organic system such that spin can be transferred from one to the other and sensed. For mid-term opportunities nanostructured material using atomic cluster deposition show promise of for interconnects and sensors whose small size and ability to integrate onto silicon logic circuits using lithography or other imaging techniques coupled with low temperature assembly promise rapid response and low cost. But from immediate opportunities of nanotechnology in electronic industry, enhanced shielding materials, solders, conductive adhesives, are now possible as nanosized material become available and economic[6]. Other opportunities exist in composite conductors. Recently a group reported the synthesis of the fabrication of conductive polymer composite (density of $0.05 gcm^{-3}$) using nanostructured material. These polymers find wide applications in electromagnetic interference shielding, electrostatic discharge protection and actuators [7].

Nanomaterials and nanostructures also increase the efficiency of many types of energy conversion devices (photovoltaic, thermoelectric, battery and fuel cell). This area will get increased attention as the energy supply and demand equation becomes more complex. Fuel cells, specially proton exchange fuel cells (PEMFCs) are now attracting enormous interest for various applications such as low/zero emission vehicles, power source for small portable electronics [8,9,10]. There are several challenges in the commercialization of PEMFCs [10,11]. One of these challenges are the high cost of noble metals used as catalysts such as Pt. Currently, in commercially offered prototype fuel cells, very small portion (20-30%) of Pt is used efficiently. In order to obtain higher utilization of Pt, numerous studies have been carried out. Recently it has been reported that nanomaterials such as nanotubes [12] and nanowires [13] are suitable material for Pt support in PEMFC and enhance the performance of fuel cells due to their various advantages such as huge surface area. This will improve the Pt utilization by securing the electronic route from Pt to supporting electron in PEMFCs.

These examples indicate that nanotechnology is a multidisciplinary field requiring knowledge of chemistry, physics, material science, engineering and most often biology to fully exploit its advantages. Also, there are many challenges to be addressed before nanotechnology can be effectively used in different fields.

1.2. Challenges in Nanotechnology

Although many of the fundamentals have long been established in different fields such as in physics, chemistry, material science, researchers in the field of nanotechnology face many new challenges that are unique to nanostructures and the applications of these materials.

One of the challenges in nanotechnology is integration of nanostructures into or with macroscopic systems. Some observers suggest that a future tagline for nanotechnology might be "Nano Inside" since the value of nanotechnology will be realized by its successful integration into more complex structures and devices that span length scales from nano all the way to macroscopic world of humankind. This reflects the fact that many of the first uses of nanotechnology will be for microtechnology both in terms of fabricating devices and in understanding their behavior.

Integrating the unique and valuable functional properties of nanotechnology with complex and multi length scale structures poses significant scientific and manufacturing challenges. Understanding and predicting fundamental behavior of systems that span many length scales requires new knowledge concerning [14]:

1) the control of optical and electronic energy transfer coupled across multiple length scales
2) the coupling of mechanical forces across nano, micro and larger scales, including the control of fluidic transport
3) the integration of biological and synthetic materials and control of the interface between the different components

Another challenge is building and demonstration of novel tools to study at nanometer level what is being manifested at macro level. Although material properties such as electrical conductivity and dielectric constant tensile strength are independent of dimensions and weight of the material but in practice, system properties are measured experimentally. The small size and complexity of nanoscale structures make the development of new measurement technologies more challenging than ever. Measurements of physical properties of nanomaterials require extremely sensitive instrumentation while the noise level must be kept very low.

There are other challenges that arise only in the nanometers scale and are not found in the macro level. For example, doping in semiconductors has been very well established process. However, random doping fluctuations become extremely important at nanometer scale, since these fluctuations would be no longer tolerable in the nanometer scale. Making the situation further complicated is the location of the dopant atoms. Surface atom would certainly behave differently from the centered atom. The challenge will be not only to achieve reproducible and uniform distribution of dopant atoms in nanometer scale, but also to precisely control the location of dopant atoms. To meet such a challenge the ability to monitor and manipulate the material processing in the atomic level is crucial.

In addition to the above challenges, successful nanoscale manufacturing is also one of the key issues of development of nanotechnology. This requires the ability to control materials synthesis at nanometer scale with sufficiently high reliability and yield to be cost effective. Various processes have been developed for the synthesis of different nanostructures. For example most experts would agree that self assembly promises to be an important tool for nanoscale manufacturing; however it still is in an early stage of development [14].

For fabrication and processing of nanomaterials and nanostructures, the following challenges must be addressed [2]:

1) Overcome the huge surface energy, a result of enormous surface area or large surface to volume ratio.
2) Ensure all nanomaterials with desired size, uniform distribution, morphology, crystallinity, chemical composition and microstructure that altogether result in desired physical properties.
3) Prevent nanomaterials from coarsening through either Ostwald ripening or agglomeration as time evolutes.

These fabrication challenges are generalized for all the type of nanomaterial. But nanomaterials based on different fields of study have been categorized into several types. Each type of nanostructures has its unique difficulties in the fabrication process. This has attracted many researchers to develop various methods to synthesize different nanostructures.

2. Nanomaterials

Nanomaterials are one of the building blocks of nanotechnology. Depending on the application and purpose of nanomaterials, they have found various definitions. But they can be generally defined as materials with physical structures which at least one their dimension is between 1-100nm [4]. Nanomaterials due to their application are the fastest growing area in material science and engineering [15]. These materials have distinctly different physical and chemical properties from those of a single atom (molecule) and bulk matter with the same chemical composition. This is because many properties of solids depend on the size range over which they are measured. Microscopic details become averaged when investigating bulk materials. At macro- or large scale range ordinarily studied in traditional fields of physics such as mechanics, electricity and optics the sizes of the objects under study range from millimeters to kilometers. The properties of these materials are averaged properties, such as the density and elastic moduli in mechanics, the resistivity and magnetization in electricity and magnetism. When measurements are made in the micrometer or nanometer ranges, this is not the case [4]. This is why some of the important issues in nanoscience relate to size effects, shape phenomena, quantum confinement and optical excitations of individual and coupled finite systems [16].

Based on the above definition of nanomaterials, they can be classified into three major groups [5,17,18].

1) Zero-dimensional (0D) nanomaterials
2) One-dimensional (1D) nanomaterials
3) Two-dimensional (2D) nanomaterials

Table1. Typical dimensions of nanomaterials along with examples of material used in these types of groups for various applications [19]

Type of nanomaterial	Nanostructures	Size	Materials
0D	Quantum dots Nanocrystals Nanoparticles	Diam. 1-10nm Diam. 1-100nm	Metals, semiconductors, Magnetic material Ceramic oxides
1D	Nanowires Nanorods Nanobelts Nanocables Nanotubes	Diam. 1-100nm	Metals , semiconductors oxides, sulfides, nitrides Carbon, layered metal chalcogenides
2D	Thin films	Thickness 1-1000nm	A variety of material

2.1. Zero-Dimensional Nanomaterials

Zero-Dimensional nanomaterials are material with all three of their dimensions below 100 nm. Clusters, nanoparticles and quantum dots can be classified as 0D nanomaterials. There have been many reports of synthesis nanoparticles of various materials such as insulators, semiconductors, metals and magnetic materials for different applications. Some of these applications include:

(i) Security: authentication and anti-forgery [19]

(ii) Life science: diagnostics, biological sensors drug delivery and replacement for luminescent and fluorescent dyes in biological probes. For example, for biological process and subcellular metabolic process tracking, quantum dots are joined with biological receptors that can recognize and attach to specific component of living system. Quantum dots offer advantages over conventional fluorescent probes because they can be turned to emit over a wide range of colors yet require only a single excitation source to drive emission.

(iii) Electronics: data storage LEDs. For example, there have been reports of potential use of cadmium sulfide nanoparticles as the next generation phosphors for general illumination applications [14]. Also, there have been many reports of silicon quantum dots generating light where bulk silicon as an indirect band gap semiconductor does not have this capability [18-21].

Many techniques, including both top-down and bottom-up approaches have been developed and applied for the synthesis of nanoparticles. Top-down approaches include milling or attrition, repeated quenching and lithography. Nanoparticles produced in these methods usually have relatively broad size distribution and they may contain significant amount of impurities. Bottom-up approaches are far more popular in the synthesis of nanoparticles and many methods have been developed. For example, nanoparticles such as Pd, Au [22], TiO_2 [23], Si [24, 25], and MnO_x [26, 27] were synthesized by homogeneous nucleation from liquid or vapor, or by heterogeneous nucleation on substrate.

For fabrication of nanoparticles, a small size is not the only requirement. For any practical application the processing conditions need to be controlled in such a way that resulting nanoparticles have the following characteristics [4]:

1) Identical size of all particles
2) Identical shape or morphology
3) Identical chemical composition and crystal structure
4) Individually dispersed or monodispersed

2.2. Two Dimensional Nanomaterial

Two-Dimensional nanomaterials, are structures with one of their dimensions below 100 nm. Thin films and thin layers are among 2D nanomaterials. Perhaps these are the simplest and most well developed form of nanomaterials that are built one atomic layer at a time. Many modern optical, electronic and magnetic devices are manufactured using this technology [14]. Examples of application of thin films can be found in resonator technology [14, 28, 29]. Thin film resonator technology has been under development for over 40 years as means to reach higher frequencies, obtainable with conventional quartz crystal technology. Using advances in micro-electronic processing, thin films of piezoelectric materials are used to fabricate resonators and filters over range of 500MHz to 20GHz [30,31]. Another major application of 2D nanomaterial can be in automobile industry and surface coating technology for various purposes such as protection [32,33]. In addition in recent years, there have been many reports of using thin films in energy technologies such as solar cells [34] and lithium ion batteries [35].

Due to diverse applications of 2D nanomaterial, as mentioned above, deposition of thin films has been a subject of intensive study for almost a century and many methods have been developed and improved. Although there are many methods of these materials, generally thin film deposition involves predominantly heterogeneous processes including heterogeneous chemical reactions, evaporation, adsorption and desorption of growth surfaces, heterogeneous nucleation and surface growth [4].

2.3. One-Dimensional Nanomaterials

One-Dimensional nanomaterials might be the latest type of nanomaterials synthesized and studied for various applications compared to other types of nanomaterials. These structures have been called by a variety of names including: whiskers, fibers or fibrils, nanowires and nanorods. In most cases, nanotubes and nanocables are also considered as 1D nanostructures. But generally 1D nanomaterials are divided into two major groups of nanotubes and nanowires.

2.3.1. Nanotubes

Nanotubes are 1D nanomaterials with hollow structures. There are many reports about nanotube synthesis of various organic and inorganic materials. But one type of the well known nanotubes synthesized are carbon nanotubes. Following the discovery of carbon nanotubes in 1991 [36], synthesis of these nanostructures have attracted tremendous attention due to their superior mechanical properties, unique electronic behavior and their potential applications in various fields. These nanotubes are unique allotropes of carbon due to configuration of the carbon atoms that form the nanotube structure. Carbon nanotubes possess many desirable properties, including high mechanical strength and flexibility, excellent electrical and thermal conductivity. These collective set of properties makes carbon nanotubes very desirable material for many applications including high strength composite materials, nanoscale transistors and fuel cell electrodes.

There have been reports of nanotubes structures based on other materials such as titania nanotubes [37], Fe and its oxides [38,39], Ni [39], Co [39], Si and SiO_2 [40] and manganese oxide [41,42]. Compared to carbon nanotube studies, inorganic nanotubes started much later due to the difficulties in synthesizing these structures. Like carbon nanotubes, these inorganic nanotubes exhibit unique properties which make them ideal candidates for various applications such as catalyst, energy technologies and electronics.

2.3.2. Nanowires

Nanowires, nanorods and nanobelts constitute an important class of 1D nanostructures which provide models to study the relations between electrical transport, optical and other properties with dimensionality and size confinement. In comparison with quantum dots and carbon nanotubes, the advancement of these 1D nanostructures has been slow until very recently, as hindered by the difficulties associated with the synthesis of nanowires with well controlled dimension, morphology, phase purity and chemical composition [43]. These materials are expected to play important roles as interconnects, functional components in the fabrication of nanoscale electronic and optoelectronic devices and electrochemical applications. Many studies have demonstrated the unique properties of nanowires and nanorods, such as superior mechanical toughness [44], high luminescence efficiency [45] and higher catalytic activity.

Until now nanowires with different compositions have been explored, while large part of these work have been focused on semiconductor systems. Researchers have reported the synthesis of nanowires such as Si and its oxides [46-48], Ge [49, 50], GaN [51], GaAs [52], ZnO [53], WO_x [54], V_2O_5 [55], Mn_3O_4 [56], Al_2O_3 [57] and so on. These nanowires with various properties have applications in energy technologies such as fuel cells, solar cells, and batteries, In order to study of new physical properties and applications of these materials, the current challenges still are controlled synthesis with controlled size, morphology, microstructure and chemical composition. To do so, the increased understanding of growth mechanisms is critical.

3. Growth mechanisms of Nanowires

The synthesis of nanowires with controlled composition, size purity and crystallinity requires a proper understanding of the nucleation and growth process at the nanometer regime. Many techniques have been developed for the synthesis and formation of one dimensional nanostructured materials. Recently, 1D nanostructures have been fabricated using nanolithographic techniques such as electron beam or focused ion beam writing, proximal probe patterning and X-ray lithography. These methods are generally not very cost effective and rapid for the purpose of making large quantities of the 1D nanostructures. Several other ways of growing nanowires such as laser ablation, and template assisted growth have also been explored. Laser ablation and template assisted approaches provide large quantities of nanowires but do not control over the composition, size or orientation direction of nanowires. However, chemical methods tend to be superior and provide an alternative strategy for nanowire generation. Chemical methods include solution and vapor based methods and precursor methods as well as solvothermal, hydrothermal and carbothermal methods.

In these methods, several strategies have been developed for 1D nanostructures with different levels of control over the growth parameters. These include [19]:

1) the use of the anisotropic crystallographic structure of the solid to facilitate 1D nanowire growth
2) the introduction of a solid-liquid interface to reduce the symmetry of a seed
3) the use of templates with 1D morphologies to direct the formation of nanowires
4) the use of supersaturation control to modify the growth habit of a seed
5) the use of capping agents o kinetically control the growth rates of various facets of a seed
6) self assembly of 0D nanostructures

Based on these strategies, chemical methods developed for the growth of nanowires can be categorized in different ways. In some cases, these methods can be divided into four groups such as [4]:

i) Spontaneous growth: this is driven by the reduction of Gibbs free energy or chemical potential. The reduction of Gibbs free energy is commonly realized by phase transformation or chemical reaction or the release of stress. This group includes methods such as vapor deposition growth or stress induced re-crystallization.

ii) Template base synthesis: in this group nanowires are deposited on templates with nanosized channels. The most commonly used and commercially available templates are anodized alumina membranes. The difference of methods in this group is usually in the process of deposition of material. Electroplating, electrophoretic deposition colloid dispersion melt and solution filling are some of the methods belonging to this group.

iii) Electrospinning: this method was originally developed for generating ultra thin polymer fibers. In this method electrical forces are used to produce polymer fibers with nanometer scale diameters.

iv) Lithography: includes various techniques such as ion beam lithography, electron beam lithography and X-ray lithography. In these methods generally nanoscale features are defined in a thin film of photoresist and material are deposited in these channels.

Researchers have also categorized the chemical methods into:

1) solution based approaches to nanowires
2) nanowire growth in the gas phase

3.1. Solution-based approaches to nanowires

This synthetic strategy for nanowires makes use of anisotropic growth dictated by the crystallographic structure of a solid material or confined and directed by templates or kinetically controlled by supersaturation, or by the use of appropriate capping agents.

3.1.1.Non-Template methods

Many solid materials such as polysulphur nitride (SN_x) grow into 1D nanostructures and this habit is determined by the highly anisotropic bonding in the crystallographic structure [19]. Other materials such as selenium, tellurium and molybdenum chalcogenides are also easily obtained as nanowires due to the anisotropic bonding which makes the crystallization occur along the c-axis favoring the stronger covalent bonds over the relatively weak van der Waals forces between the chains [19].

Gates et al. [58], synthesized a spherical colloidal suspension/dispersion of amorphous (a-) selenium dissolved in the solution precipitates out as nanocrystallites of triagonal Se (t-Se). During aging of this dispersion in the dark, the a-Se dissolves slowly in the solution and subsequently crystallizes out slowly on a t-Se seed. The intrinsic anisotropic nature of t-Se building blocks that is extended, helical chains of Se atoms in the triagonal phase assembles ultimately into nanowires of t-Se.

These non-template directed methods are readily extended to a range of other solid materials whose crystallographic structures are characterized by chain like building blocks.

3.1.2. Template methods

Template-based synthesis of nanostructured materials is a very general method and can be used in fabrication of nanorods, nanowires and nanotubules of polymers, metals, semiconductors and oxides. In this technique, the template simply serves as a scaffold against which other kinds of materials with similar morphologies are synthesized. In other words, the *in situ* generated materials are shaped into a nanostructure with its morphology complementary to that of the template.

Various templates with nanosized channels have been explored for the template growth of nanorods and nanotubules. The most commonly used and commercially available templates are anodized alumina membranes. Other membranes have also been used as templates such as nanochannel array glass, radiation track-etched mica, and mesoporous materials, porous silicon by electrochemical etching of silicon wager, zeolites and carbon nanotubes. Alumina membranes with uniform and parallel porous structures are made by anodic oxidation of aluminum sheet in solution of sulfuric, oxalic or phosphoric acids. In addition to the desired pore or channel size, morphology, size distribution and density of pores, template materials must meet certain requirements. First template material must be compatible with the processing conditions. For example an electrical insulator is required for a template to be used in electrochemical deposition. Secondly depositing materials or solution must wet the internal pore walls. Thirdly for the synthesis of nanorods or nanowires the deposition should start from the bottom or one of the template channels and proceed from one side to another.

The nanowires themselves can be used as templates to generate the nanowires of other materials. The template may be coated onto the nanowire forming coaxial nanocables [59] or it may react with the nanowires forming a new material [60]. In the physical approach the surface of the nanowires could be directly coated with conformal sheaths made of a different material to form coaxial nanocables. Subsequent dissolution of the original nanowires could lead to nanotubes of the coated material. The sol-gel coating method is a generic route to synthesize coaxial nanocables that may contain electrically conductive metal cores and insulating sheaths.

Template directed synthesis of nanorods covered by carbon and other materials has been reported in the literature. Sloan et al., [61] found out that single walled carbon nanotubes can be filled up to 50% by silver by employing the KCl-UCl_4 and AgCl-AgBr eutectic systems to produce nanowires.

3.1.3. Solution-liquid-solid process

This method was developed by Buhro's research group [62] and was first applied for the synthesis of InP, InAs and GaAs nanowires with solution-phase reactions at relatively lower temperatures (below 230°C). In a typical procedure a metal (e.g. In, Sn, Bi) with low melting point was used as a catalyst and the desired material was generated through the decomposition of organometallic precursors.

Holmes et al. [63] used colloidal catalysts to control the diameters of silicon nanowires grown by solution-liquid-solid growth. Bulk quantities of defect free silicon nanowires with nearly uniform diameter ranging from 4 to 5 nm were grown to a length of several micrometers. In their study it was found that supercritical conditions are required to form the alloy droplets and to promote silicon crystallization. The diameter and length of nanowires grown by solution liquid solid methods can be controlled by controlling the size of liquid catalyst and the growth time.

There have been other solution based methods such as solvothermal processes developed for the synthesis of 1D nanostructures. These methods have been extensively examined. For example, in solvothermal process, a solvent is mixed with certain metal precursors and possible crystal growth regulating or templating agents such as amines. The solution mixture is placed in an autoclave kept at relatively high temperature and pressure to carry out the crystal growth and assembly process. The methodology seems to be quite versatile and has been demonstrated to be able to produce many different crystalline semiconductors nanorods and nanowires.

3.2. Vapor phase growth of nanowires

Vapor phase growth is commonly used to produce nanowires, starting with simple evaporation technique in an appropriate atmosphere to produce elemental or oxide nanowires. Generally differences between methods in this group are [19]:

1) Mechanisms used for the synthesis of nanostructures mostly depend on the composition of nanowires and conditions of the process
2) Vapor generation sources

To understand the process of nanowire growth for better control of their microstructure and composition in vapor phase growth methods, several mechanisms have been proposed. Vapor-liquid-solid (VLS), Vapor solid (VS), Solid-liquid-Solid (SLS) and oxide assisted growth are some of the major mechanisms studied for this purpose.

3.2.1. Vapor-liquid-solid growth

The growth of nanowire via a gas phase reaction involving this process has been extensively studied. Wagner in 1960's, during his studies on the synthesis of large single crystalline whiskers, proposed this mechanism. According to this mechanism, the anisotropic crystal growth is promoted by the presence of a liquid alloy solid interface [19]. His mechanism was widely accepted and applied to understanding the growth of various nanowires, such as Si and Ge. As an example, Xia et al. [64] explained the growth of Ge nanowires using Au clusters as solvent at high temperatures based on the Ge-Au binary phase diagram shown in figure 2.

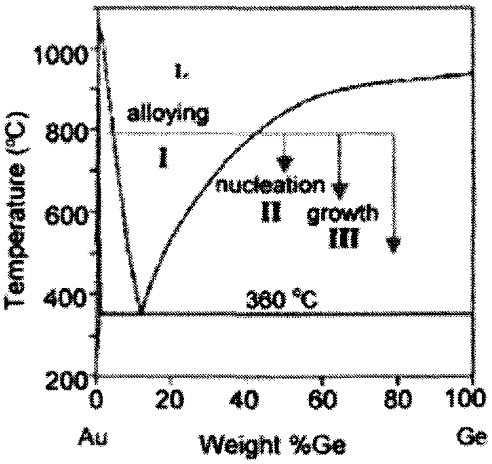

Figure2. Ge-Au Binary phase diagram [64].

The schematic diagram of Ge nanowires grown using VLS mechanism is illustrated in figure 3. According to this diagram and Ge-Au binary phase diagram the Ge and Au will form a liquid alloy when the temperature is higher than the eutectic point. The liquid surface has a large accommodation coefficient and is therefore a preferred deposition site for incoming Ge vapor. After the liquid alloy becomes supersaturated with Ge, Ge nanowire growth occurs by precipitation at the solid-liquid surface. A real time observation of Ge nanowire growth conducted in an *in situ* high temperature transition electron microscope showed a sequence of TEM images which directly mirrors the proposed VLS mechanism. This VLS method has been exploited in the past several decades to produce 1-100μm diameter 1D structures (whiskers). By controlling the nucleation and growth it is possible to produce nanowires.

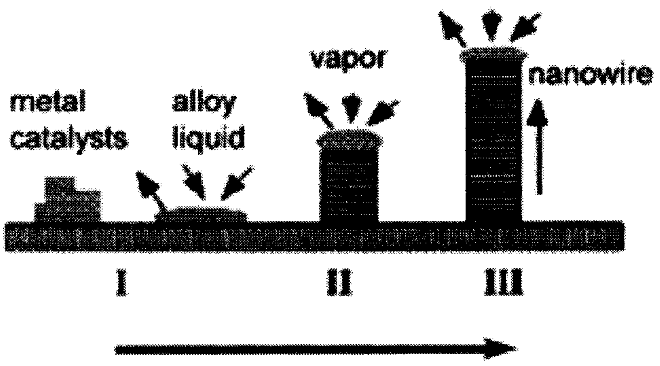

Figure3. Schematic diagram of Ge nanowire grown using VLS mechanism [64].

The synthesis of nanowires using this mechanism requires several conditions. The requirements for this mechanism include:

1) Catalyst and source material: by knowing the equilibrium phase diagram one can predict the catalyst material and growth conditions for the VLS approach.
2) Method to vaporize the source material and melt the catalyst

Nanowires grown by this method usually have certain features which help identify their growth mechanism. For example, most of nanowires synthesized using the VLS process have a catalyst droplet at their tip. But this is not always the case and depends on the interaction of liquid catalyst droplet with the substrate. There have been reports of nanowire synthesized using VLS method with catalyst particles at the base of nanowires [65-67]. This is similar to growth process of carbon nanotubes.

3.2.2. Vapor-solid growth

Besides VLS mechanism, the classical vapor solid method for whiskers growth has also been reported for the growth of 1D nanomaterials. 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. Hence it is possible to synthesize 1D nanostructures if one can control its nucleation and subsequent growth process. Sears was the first to explain the growth of mercury whiskers by axial screw dislocation induced anisotropic growth in 1955. The mercury whiskers or nanowire were grown by a simple VS method at -50°C under high vacuum. Subsequently a lot of research was devoted to studying the growth of nanostructures using this methods and researchers revealed that the growth of nanorods or nanowires is not necessarily controlled by the presence of defects [2].

Usually nanowires and nanorods grown by VS method are single crystals with fewer imperfections. The formation of 1D nanostructures through this method are due to anisotropic growth. Several mechanisms are known to result in anisotropic growth. For example:

1) Different facets in a crystal have different growth rates
2) Presence of imperfections in specific crystal directions such as screw dislocation
3) Preferential accumulation or poisoning by impurities on specific facets

Also in case of synthesis of nanowires and nanorods, it is known that the impurities have differential adsorption on various crystal facets in a given crystal and the adsorption of impurity would retard the growth process. Impurity poisoning has often been cited as one of the reasons which resulted in anisotropic growth during synthesis of nanowire and nanorods [2].

Using this method, nanowires for oxides of Zn [68], Sn [69], In [70], Mg [71] and Ga [72] has been attempted.

3.2.3. Oxide assisted growth

In contrast to the well established VLS and VS mechanism, there have been reports of nanowire growth using different processes. One of these processes is oxide assisted nanowire growth. Lee et al., reported the synthesis GaAs nanowires by oxide assisted laser ablation of mixture of GaAs and Ga_2O_3 [44]. The GaAs nanowires have lengths up to tens of micrometers and diameter in the range 10-120 nm. The oxide assisted nanowire growth mechanism was further applied for production of various nanostructures such as Si and SiO_x [73], Copper sulphide [45], boron [74] and MgO [75] nanowires. The nanowire growth via this process is not very clear and researchers have proposed various steps for the growth process depending on the materials.

3.2.4. Solid-liquid-solid growth

In general, a high temperature is required in the growth of nanowires by methods mentioned above. Recently it has been reported that at these temperatures, another growth process can be activated called solid-liquid-solid (SLS). This process is similar to VLS mechanism but doesn't fall in the category of vapor based approach for nanowire synthesis.

There are few reports of synthesis of 1D nanostructures following SLS and mostly focus on silicon based material. Yan et al. [46], reported the synthesis of Si nanowires following this mechanism using Ni as catalyst. They proposed that since the concentration of Si in the vapor phase was negligible at temperatures they carried out the experiments and because the substrate was covered only by a thin layer of Ni therefore the only possible silicon source was from the silicon substrate. Figure 4, shows a schematic diagram of silicon nanowires grown using Ni as catalyst via SLS growth mechanism.

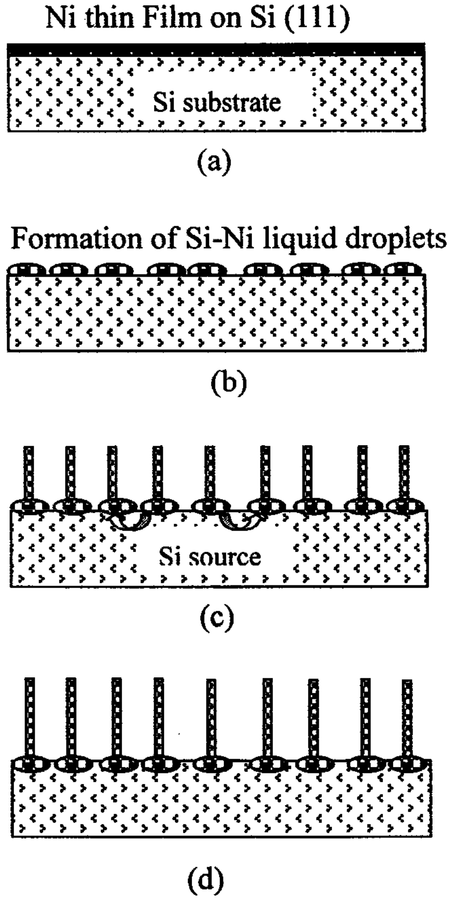

Figure4. Schematic diagram of Si nanowire synthesized using Ni catalyst via SLS growth mechanism [46].

They proved that the Ni layer reacts with Si substrate at high temperatures and from eutectic liquid alloy droplets and after supersaturation of the droplets by silicon diffused through the substrate nanowires are synthesized [46].

There have been reports of other vapor based synthesis mechanism, such as carbothermal reactions which mostly based on the type of material.

4. Synthesis methods

Base on these growth mechanisms, several vapor deposition methods have been developed for the synthesis of 1D nanostructures. The two most important techniques are:

1) Physical vapor deposition (PVD)
2) Chemical vapor deposition (CVD)

4.1. Physical vapor deposition

PVD is a process of transferring growth species from a source or target and deposit them on a substrate to often form thin films, but by adjusting the conditions (such as templates and catalysts) it can be applied for the synthesis of nanostructures of certain material. The process proceeds atomistically and mostly involves no chemical reactions. Various methods have been developed for the removal of growth species from the source or target.

In general, PVD methods can be divided into two major groups: evaporation and sputtering. In evaporation, the growth species are removed from the source by thermal means. In sputtering, atoms or molecules are dislodged from solid target through impact of gaseous ions (plasma).

Nanowires synthesized using PVD are usually composed of low melting material such as SnO_2 [76] and CdS [77]. However, using sputtering and plasma enhanced vapor deposition systems researchers have reported the synthesis of some relatively high temperature nanowires.

4.2. Chemical vapor deposition

CVD is the process of chemically reacting a volatile compound of a material to be deposited with other gases to produce a nonvolatile solid that deposits atomistically on a suitable placed substrate [78]. CVD processes for deposition of thin films have been very extensively studied and very well documented, largely due to the close association with solid state microelectronics, however synthesizing nanowires using these methods is at it early stages. Figure 5 shows schematic diagram of nanowires synthesized using a simple CVD method. In this process source material is involved in gas phase reactions and depending on process conditions, nanostructures are deposited on the substrate. This simple process has been used to synthesize many nanowires such as SiO_2 [48], SiC [79], (Ga, Mn)N [80], Mn_3O_4 [56], ZnS [81].

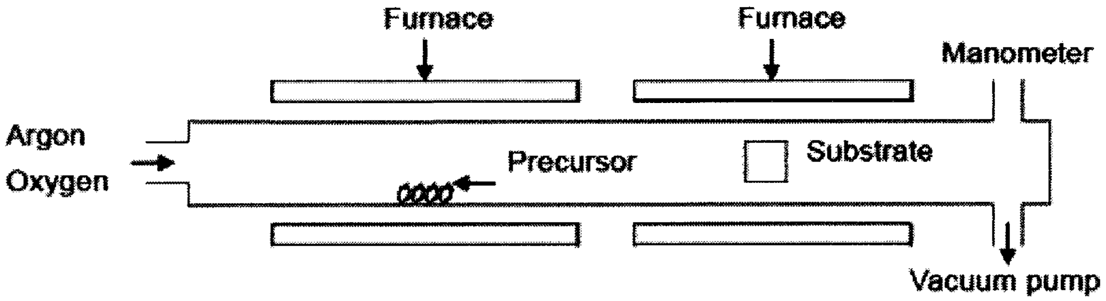

Figure5. Schematic diagram of nanowires synthesized using a chemical vapor deposition method.

Because of the versatile nature of CVD, the chemistry is very rich and carious types of chemical reactions are involved. Gas phase reactions and surface reactions are intricately mixed. In addition a variety of CVD methods and CVD reactors have been developed depending on the types of precursors used, the deposition conditions applied and forms of energy introduced to the system to activate the chemical reactions desired for the deposition process. For example when metalorganic compounds are used as precursors, the process is generally referred to as MOCVD (metalorganic CVD). Kang et al, synthesized SiC nanowires on Si (100) substrate using Ni as a catalyst and Dichloromethylvinylsilane as a single molecular precursor by MOCVD method [82]. There have also been reports of synthesizing ZnO [53], GaN [51], InP [83], etc When plasma is used to promote the chemical reactions, this is called a plasma enhanced CVD or PECVD. There have been few reports of synthesis of nanowires using this method. Jung et al [47], synthesized cone shaped silicon nanowires using this method. The nanowires were synthesized according to VLS growth mechanism. They used Au as the catalyst and silicon was supplied by introducing SiH_4 in to the chamber. Other CVD methods are laser enhanced or assisted CVD [84] and aerosol assisted CVD or AACVD [85].

5. Thesis Outline and Research Goals

As mentioned in the introduction section, synthesis of 1D nanostructures is one of the key factors for developing nanomaterials and applying them in various potential applications. Chemical vapor deposition method was employed for the synthesis of several nanowires (silicon dioxide and manganese monoxide) for a variety of applications. The effects of process parameters on the final product deposited on the substrates were studied. Nanostructures were characterized using various techniques and possible growth mechanisms were proposed for the synthesis of nanowires deposited.

Chapter 2 is divided into two parts. In the first section, a detailed description of CVD method used for the synthesis of silicon dioxide nanowires on silicon substrate and various experiments carried out to study the effect of parameters such as hydrogen, catalysts and temperature is given. Also, characterization methods applied on the nanostructures are explained. In the second section, similar to the previous section, experimental procedures for the synthesis of manganese monoxide nanowires on different substrates such as silicon and carbon paper are explained and the techniques used for characterization of manganese nanostructures are described.

Chapter 3, networked silicon oxide nanowires were synthesized by a VO_2 assisted chemical vapor deposition at 1000°C without supplying any gaseous or liquid Si source. TEM and SEM observations indicate that the silicon oxide nanowires have smooth surfaces with uniform diameters of 30-100 nm, and their lengths reach to several hundred micrometers. XPS results show that the atomic ratio of silicon to oxygen is about 1:2. Systematic study on the nanowire growth has indicated that morphology and composition of the final products are considerably sensitive to the catalyst components, reaction atmosphere and temperature. In VO_2 assisted growth of SiO_2 nanowires, when H_2 is not introduced to the atmosphere vanadium oxide rod like structures are deposited on the silicon substrate. But for SiO_2 nanowires synthesized using Au, without using H_2 gas it has been seen that the surface of the substrate is covered non-uniformly by very short nanowires. The mechanism of the growth of these nanowires is proposed to be solid-liquid-solid (SLS) process. It is also found by increasing the temperature up to 1200°C, the growth mechanism of SiO_2 nanowires changes from solid-liquid-solid (SLS) to vapor-solid (VS) processes since wire like structures can be formed without any catalyst or H_2 gas introduced to the system. These results will help better understand the growth procedure of silicon dioxide nanostructures and synthesize composite nanostructures such as metal silicides for various applications.

Chapter 4, single crystalline MnO nanowires were successfully synthesized on silicon substrate via simple vapor deposition method. The MnO nanowires were characterized as single crystal fcc structure with an average diameter 150 nm and length up to 100μm. The synthesis process and effects of growth parameters such as temperature, heating rate and source/substrate distance on the morphology of nanostructures were systematically studied. By controlling the growth parameters, silicon oxide nanowires and composites of silicon oxide sheet and manganese oxide microwires were also synthesized. One-dimensional MnO nanowires have great potential applications in catalyst and battery technologies.

Chapter 5, preliminary results of synthesis of manganese oxide nanostructures on carbon paper have been described. These nanostructures were synthesized based on the results of manganese oxide nanowires on silicon substrate. Results indicate that the morphology of nanostructures and their mechanism change drastically when gold is not used as a catalyst. These nanostructures are expected to be used in electrochemical applications such as fuel cells and batteries.

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Chapter Two: Experimental Procedures

1. Silicon oxide nanostructures

1.1. Synthesis

The synthesis of silicon oxide nanowires was carried out in a horizontal tube furnace (LINDBERG /BLUE, Mini-Mite Tube Furnace, Model: TF55035A). Silicon (100) wafers were used as the substrate.

In this method, silicon wafer acted as source of silicon as well as a substrate for the growth of nanowires. Various experiments were carried out to optimize the growth parameters including temperature, gas composition and catalyst material as well as study their effects on the morphology of structures synthesized on the substrate. A summary of experiments conducted in this section is shown in Table 1.

Table1. Summary of experimental conditions studied for the synthesis of silicon oxide nanostructures

Temperature (°C)	Gas	Additives
950-1000	Ar/H_2	VO_2 powder
950-1000	Ar/H_2	Au layer (3-5nm)
950-1000	Ar/H_2	VO_2/Au
950-1000	Ar	VO_2 powder
950-1000	Ar	Au layer (3-5nm)
950-1000	Ar/H_2	---
1200	Ar/H_2	VO_2 powder
1200	Ar/H_2	Au layer (3-5nm)
1200	Ar/H_2	---

To synthesize the nanowires using VO_2 powder, a 5mm x 10mm substrate together with the 150mg of VO_2 powder were placed 10mm apart in an alumina boat which was transferred into the furnace. A schematic diagram of method used for the synthesis of silicon oxide nanostructures is illustrated in figure 1. A flow of high purity argon (200sccm) was used to before heating the system to remove part of the oxygen in present in the chamber. The furnace was heated to 1000°C in 15minitues and kept at this temperature for 5 h. Meanwhile, a constant flow of high purity argon (200 sccm) and hydrogen (20 sccm) was maintained. At the end of experiment, white wool like products were found on the silicon substrate.

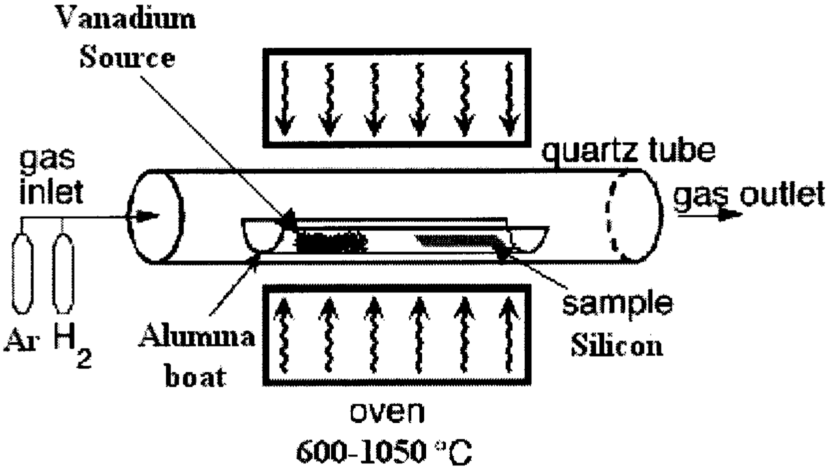

Figure1. Schematic diagram of CVD method used for the synthesis of silicon oxide nanostructures.

To synthesize silicon oxide nanowires using gold catalyst, a 2-5 nm thick gold layer was sputtered on the 5mm x 10mm silicon substrate using Emitech K550X sputter coater. After sputtering, similar growth process was used in the absence of VO_2 powder to synthesize the nanostructures.

1.2. Characterization

The nanowires synthesized were characterized using various methods to better understand the effects of different growth parameters and propose a growth mechanism.

The general morphology of nanowires was observed using a Hitachi S-4500 field-emission scanning electron microscopy (FESEM) operated at 5.0 kV. Due to nonconductive nature SiO_2 nanostructures, under FESEM at high voltages or high magnifications, nanostructures were charged (charging effect of insulators) causing difficulties in imaging the nanowires. In order to obtain better images, some of the samples were sputtered with a thin layer of gold before SEM observation to overcome the charging problem.

JEOL 2010F transmission electron microscopy (TEM) operated at 200 kV was used to study single SiO_2 nanowires. Selective area electron diffraction (SAED) pattern was taken using this TEM to determine the crystal structure of these nanowires. For composition data, the nanostructures were analyzed by Kratos Axis Ultra Al(alpha) X-ray photoelectron spectroscopy (XPS) operated at 14 kV.

2. Manganese monoxide Nanostructures

2.1. Synthesis

2.1.1. Silicon substrate

Manganese oxide nanowires on silicon substrate were synthesized by vapor deposition method. Schematic diagram of the CVD setup used in the growth process of these nanostructures is shown in figure 2.

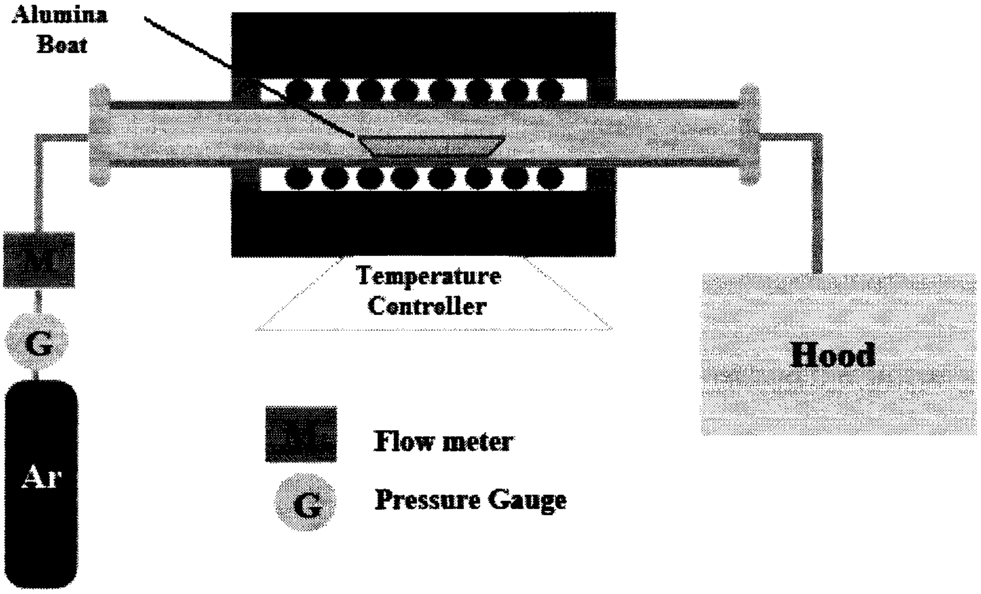

Figure2. Schematic diagram of CVD method used for the synthesis of manganese oxide nanostructures using manganese powder.

In this method of manganese powder (99%, Aldrich) was used as the source material. Before the growth procedure, a 5mm x 10mm silicon wafer was coated with a 3-5 nm thin gold layer as catalyst using Emitech K550X sputter coater. Gold was chosen based on the binary phase diagram of manganese and gold (figure 3). It can be seen that these material have eutectic point in their phase diagram which makes gold a possible catalyst for the synthesis manganese based nanostructures using VLS mechanism.

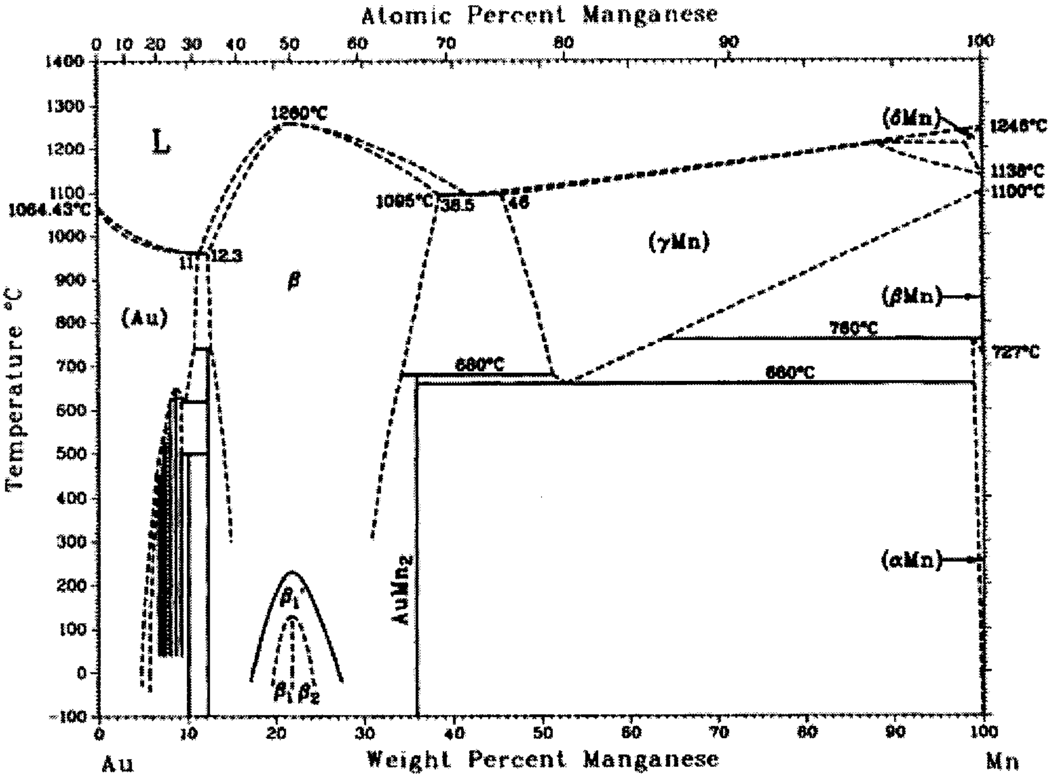

Figure3. Simplified binary phase diagram of Au-Mn, showing eutectic point around 960°C.

200mg of Manganese powder was placed in alumina boat and the silicon substrate (Si) was placed over the powder covering the source. The distance between the powder and the substrate was carefully controlled by the height of the alumina boat at about 2-5mm. A schematic diagram of source/substrate is shown in figure 4.

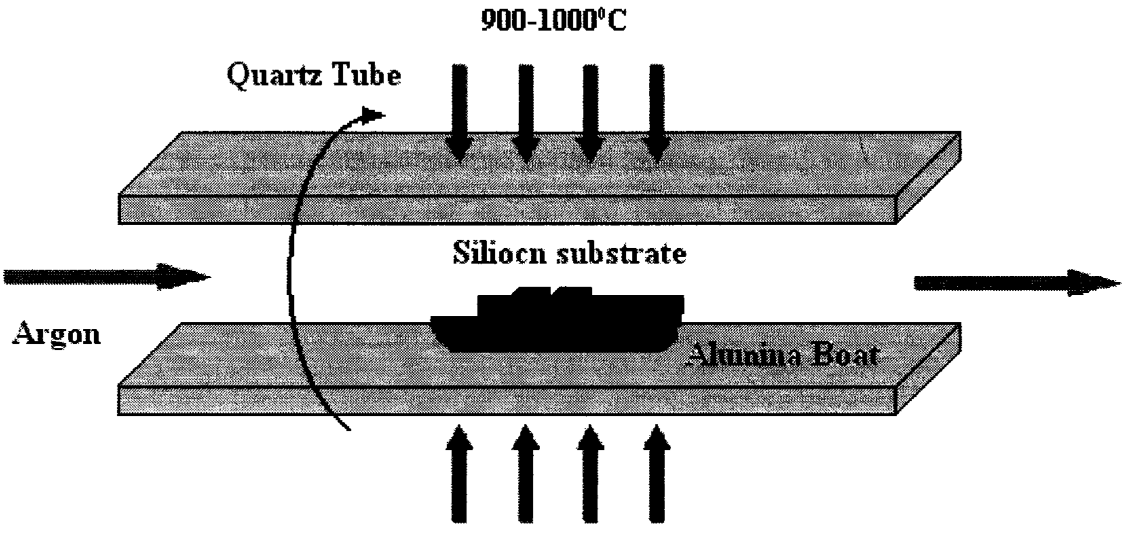

Figure4. Schematic diagram showing substrate-source setup in the quartz tube of CVD process for the synthesis of manganese oxide nanostructures on silicon substrate.

The boat was placed at the center of quartz tube and transferred into a horizontal high temperature resistance furnace. The oxygen in the system was partially removed by introducing high purity argon (200sccm) into the chamber before heating the system for 20minitures. The system was heated to 900-1000°C (based on the binary phase diagram) at controlled heating rates (5°Cmin^{-1} - 50°Cmin^{-1}) for 2 h. During the process, a constant flow of high purity argon (200 sccm) was maintained as carrier medium. Various parameters such as temperature of the system, heating rate and source/substrate distance were varied to control the morphology of the products. After the furnace was cooled down to room temperature, light green products were found on the substrate. The growth conditions studied for the synthesis of manganese oxide nanostructures on silicon substrate have been summarized in table 2.

Table2. Summary of experimental conditions applied to study the effect various growth parameters on the morphology of structures deposited on the silicon substrate

Temperature (°C)	Heating rate (°C/min)	Source/substrate distance (mm)
<900	5	2
900	5	2
930	5	2
950	5	2
1000	5	2
930	10	2
930	50	2
930	5	4
930	5	6

2.1.2. Carbon paper substrate

Manganese oxide nanostructures on carbon paper were synthesized using a simple CVD method. Similar to the procedure used in the previous section, a 5mm x 10mm carbon paper was placed on top of 200mg of pure manganese powder in an alumina boat at a 2-5mm distance. The boat was put in a quartz tube and transferred in to horizontal furnace. The system was heated up to 900-1000°C while a constant flow of argon (200 sccm) was maintained in the quartz tube.

In this section, in addition to studying the effects of temperature, source/substrate distance and heating rate, the effects of gold layer on the morphology of nanostructures deposited was also studied. The gold layers with different thicknesses were sputtered on carbon paper using Emitech K550X sputter coater.

2.2. Characterization

The morphology and composition of resultant products on the substrate were characterized by Hitachi S-4500 field-emission scanning electron microscopy (SEM) operated at 5.0 kV and energy dispersive X-ray spectroscopy (EDX).

Philips CM10 transmission electron microscopy (TEM) and a Jeol 2010 FEG HRTEM operated at 200 kV were used to study the structure of single nanowires and selected area electron diffraction (SAED) operated at 80 kV was applied to determine the crystal structure of the nanowires.

For surface sensitive analysis of silicon nanowires synthesized on the silicon substrate Kratos Axis Ultra Al(alpha) X-ray photoelectron spectroscopy (XPS) operated at 14 kV was used.

Chapter Three: Vanadium Oxide Assisted Synthesis of Networked Silicon Oxide Nanowires and Their Growth Dependence*

1. Introduction

In recent years, a great deal of attention has been placed on low dimensional materials, such as thin films, nanowires, nanotubes and nanoparticles. Among these nanomaterials, research on one dimensional (1D) materials such as nanowires and nanotubes have increased dramatically due to their anisotropic shape and variable stoichiometry which can offer interesting physical and chemical properties and makes them suitable for various applications. Recently, 1D silicon oxide (SiO_x) nanostructures have attracted considerable interest because of their properties and applications in various technologies such as optics, electronics and chemical sensors [1-5].

Until now, diverse synthesis methods such as vapor transport [1], bio-mimetic strategies [2], laser ablation [3], physical and thermal chemical evaporation [4,5], thermal oxidation [6] and solution methods [7] have been used to prepare silicon based nanostructures with different morphologies including nanowires [1], nanotubes [7] and nanoflowers [8]. Vapor transport methods are often used to grow silicon based nanowires because of their simple systems and fast growth rates compared to solution base methods. Some mechanisms have been proposed for the growth of silicon oxide nanowires using

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*** This paper will be submitted to Journal of Crystal Growth.**

vapor transport methods such as vapor-liquid-solid (VLS) mechanism and vapor-solid mechanism. In these methods, a source material, e.g. Si powder and catalyst like Au (VLS process), is used to grow Si based nanowires [9]. Some studies of growing silicon oxide nanowires directly from silicon substrate without any external silicon source have recently been reported [10-12]. Park et al. [10] synthesized amorphous SiO_x nanowires using Au and Pd-Au alloy as catalysts. Kim et al. [11] found that SiO_x nanowires can be grown from Cu coated silicon substrates. Lee et al. [12] reported the growth of silica nanowires from silicon substrates covered with thin films of TiN/Ni. Some reports using other catalysts such as Fe, Ga, Ga-In and Co have also been presented [11]. Generally, metal particles have been commonly employed as the catalyst to obtain silicon oxide nanowires and solid-liquid-solid (SLS) growth mechanism has been proposed for these processes. However, there are few reports on the catalytic effects of metal oxide on growing silicon oxide nanowires.

In this study, it has been found that uniform silicon oxide nanowires with distinct network features can be synthesized in bulk with the aid of VO_2 powder. Further, we found that the network characteristic of silicon oxide nanowires can be significantly enhanced by combining VO_2 and gold as the co-catalyst. Furthermore, we can obtain SiO_2 nanowires and VO_x nanowires with the control of hydrogen in the system.

In addition, detailed influence of different parameters, such as type of catalyst, atmosphere of the experiment (gases introduced into the system) and temperature has been systematically investigated. The growth process and mechanisms has also been discussed.

2. Results and Discussion

2.1. Effect of Catalyst

In order to study the effect of catalysts on the morphology of silicon oxide nanostructures synthesized on the Si substrate, different options of catalysts were used including Au, VO_2 and Au-VO_2. Figure 1 shows SEM images of silicon oxide nanostructures synthesized using these catalysts at 1000°C, in Ar/H_2 atmosphere for 5 hours. SEM observations illustrate that each catalyst affects the morphology of the deposited nanostructures in different ways.

Figure 1a and 1b show SEM images of networked silicon oxide nanowires synthesized using co-catalysts of VO_2 and Au in the mentioned conditions. As seen in the low magnification SEM image of these nanowires (fig.1a), using the VO_2 powder and a gold thin layer on silicon substrate together, high density of networked silicon oxide nanowires covering the substrate uniformly can be synthesized. The diameter of these nanowires is between 30-70 nm and their length reaches up to tens of micrometers. Higher magnification image of these networked structures (fig.1b) reveals that silicon oxide nanowires have branched structures, suggesting simultaneous nucleation and growth of the nanowires. In some cases, these branched nanowires bundle together forming rope like structures. Metallic catalysts such as Ga [15] and Sn [16] have also been reported to grow similar silicon oxide nanostructures.

SEM images of silicon oxide nanowires synthesized using gold as catalyst are shown in figures 1c and 1d. It can be seen (fig.1c), high density of nanowires is synthesized on the substrate. High magnification SEM image (fig.1d) of these nanowires reveals that the nanostructures are composed of thick nanowires and thin nanowire-bundles, possibly due to excess of gold on the surface of the silicon substrate. In addition, these images reveal that the morphology of silicon oxide nanowires is similar to the results from co-catalyst of VO_2 and gold, having curved and smooth surface. But compared to the well dispersed network of nanowires grown by the co-catalysts, these nanowires have shorter lengths and wider diameter distribution from 20nm to 200nm as seen in figure 1c. The synthesis of silicon oxide nanowires using gold directly from silicon substrate was previously reported by several other groups. For example, Xing et al. [9] used a silicon substrate coated with a 5nm-thick gold layer in hydrogen and 200 torr at 1000°C. Park et al.[10] reported the synthesis of silicon oxide nanowires using gold catalyst directly from the substrate without the use of hydrogen in higher temperatures. They also used an alloy of Pd-Au as catalyst to synthesize silicon oxide nanowires. According to their reports, silicon oxide nanowires could be grown at lower temperature around 1000°C using the alloy catalyst in respect to nanowires grown only with the use of gold at 1150°C.

Figures 1e and 1f show SEM images of silicon oxide nanowires synthesized by heating the silicon substrates with only VO_2 powder at 1000°C in Ar/H_2 atmosphere. Randomly oriented nanowires are seen and bundles are formed in some areas but completely covering the substrate (fig.1e). Figure 1f shows a high magnification image of these bundles. It can be seen that, similar to nanowires synthesized using the co-catalyst, the silicon oxide nanowires synthesized using only VO_2 powder are highly tangled together forming networked structures in low densities. Compared to nanowires grown by gold, these nanowires have lower density but longer length up to tens of micrometers.

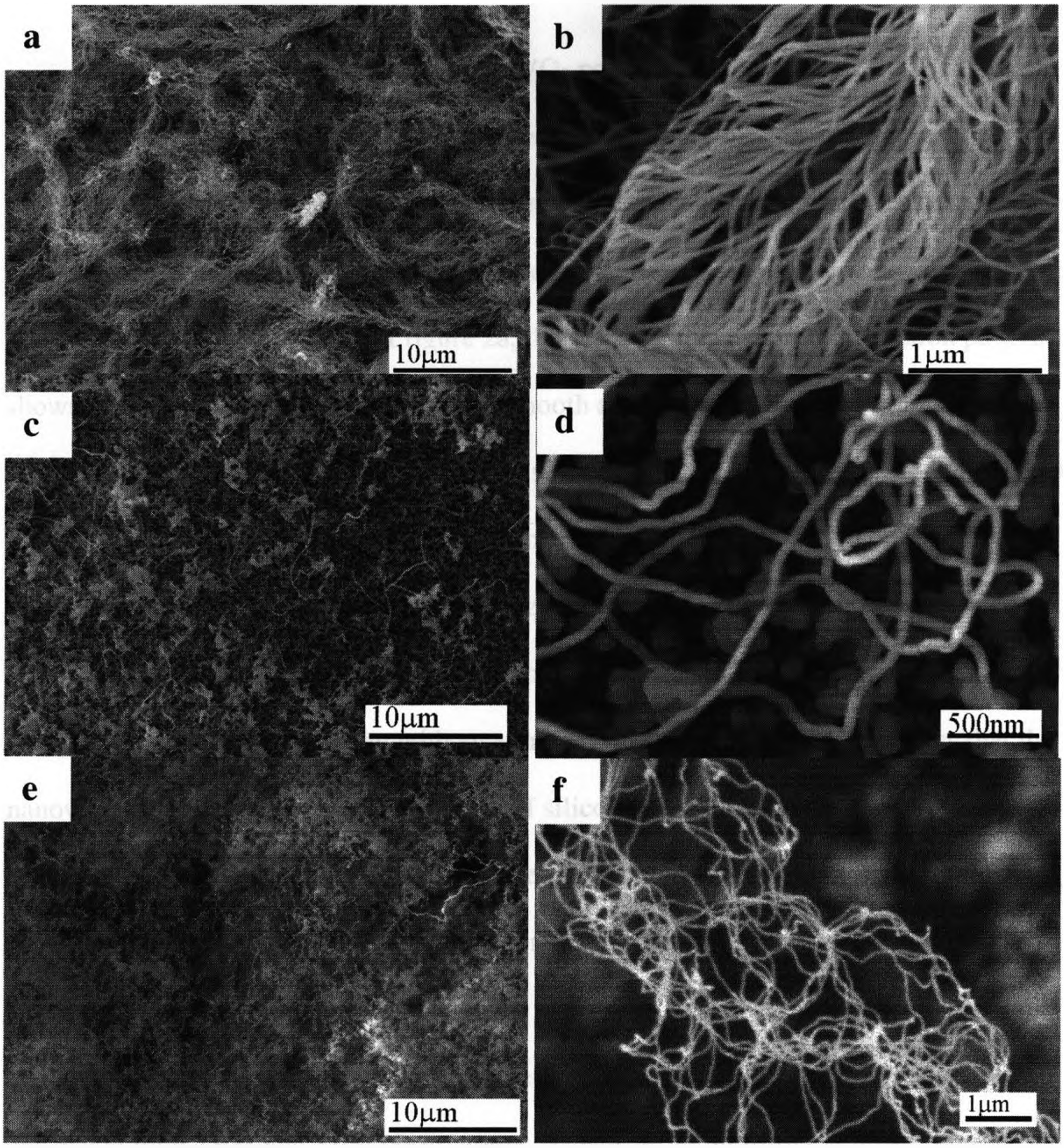

Figure1. Typical SEM images of silicon oxide nanostructures synthesized using various catalysts by simple thermal annealing of silicon substrate. a) Low magnification of silicon oxide nanowires synthesized using the co-catalyst of VO_2 and Au. b) Increased magnification of silicon oxide network of nanowires synthesized using the co-catalysts. c) Low magnification of silicon oxide nanowires synthesized using gold catalyst. d) Increased magnification image of gold assisted grown silicon oxide nanowires with uniform diameter of these nanowires along their length with a with bundles of nanowires on the background. e) Low magnification image of silicon oxide nanowires synthesized using VO_2 as a catalyst. f) Increased magnification image of these silicon oxide network of nanowires.

For a detailed study of the effect of VO_2 powder on the synthesis of silicon oxide nanowires, TEM observations and XPS measurements were carried out. Figure 2a shows a typical TEM image of the silicon oxide nanowires. The observation reveals that no catalyst particles were found at the tips of the nanowires and the nanowires were clean. In addition, as shown in the inset of figure 2a, the selected area electron diffraction pattern shows that the nanowires are amorphous, smooth and curved morphology of nanowires can be observed. This is similar to reports using other catalysts in these temperatures [10-12]. In TEM observations, it was seen that the nanowires have diameters in the range of 30-100nm similar to the nanowires synthesized using both VO_2 powder and gold catalyst.

The XPS spectrum (fig.2b) of these nanowires illustrates that they are mainly composed of silicon and oxygen with an atomic ratio close to 1:2. This indicates that the nanowires synthesized by thermal heating of silicon substrates with VO_2 powder are mainly SiO_2 nanowires. The carbon peak seen in the XPS spectrum could be from impurities such as carbon oxides absorbed on the silicon oxide nanowires or in the XPS chamber.

No catalyst peaks (vanadium) can be observed in the XPS spectrum which is consistent with TEM and SEM observations. This is different from the result reported by Yang et al. [1], who synthesized amorphous silica nanowires by heating the silicon with a mixture of hydrous zinc chloride and vanadium dioxide powder. In their case, vanadium particles were detected on the tip of silicon oxide nanowires.

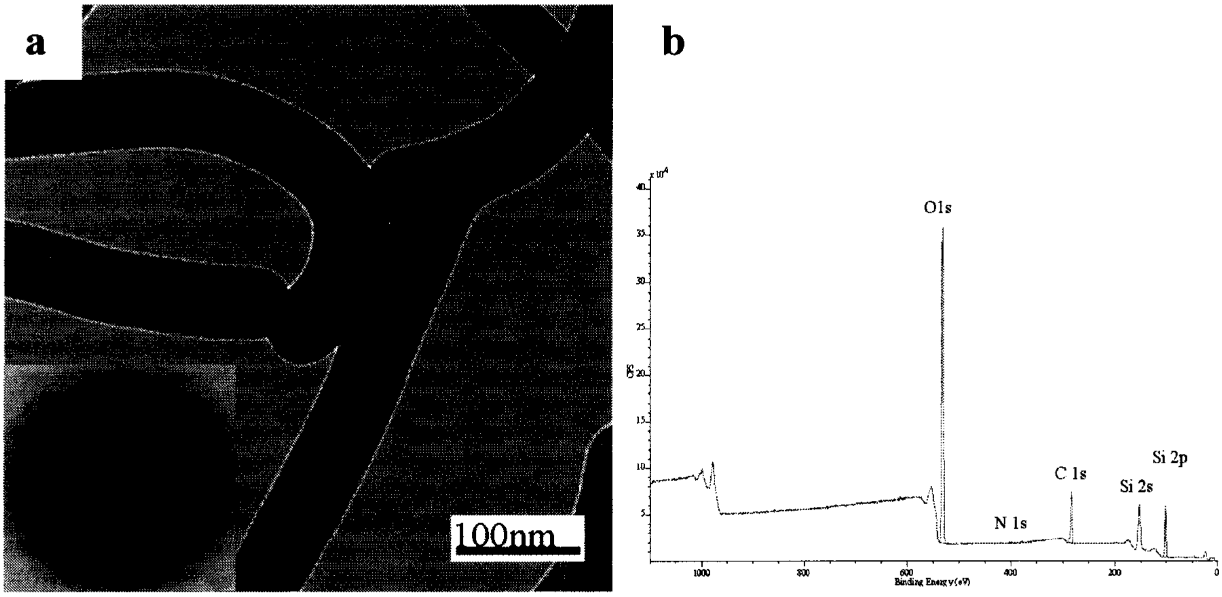

Figure2. a) TEM image of silicon oxide nanowires showing smooth morphology and a diameter of 50-70 nm. The SAED pattern shown in the inset reveals a characteristic diffusive ring pattern indicating that silicon oxide nanowires are completely amorphous. b) XPS spectrum of silicon oxide nanowires with silicon to oxygen peak ratio of approximately 0.5, there were no peaks for VO_2, suggesting that the nanowires are pure silicon oxide nanowires.

2.2 Effect of Hydrogen

A number of studies have reported the growth of silicon oxide nanowires from silicon substrate with various catalysts under H_2 atmosphere. Lee et al. [12] used TiN/Ni coated silicon substrate in H_2 atmosphere and synthesized amorphous silica nanowires. Xing et al. [9] reported the growth of silicon nanowires from silicon coated with gold in H_2 atmosphere, a similar condition to our experiment. Recently, Shoa et al. [14] reported the synthesis of low oxygen content silicon nanowires from a single quartz crystal in H_2 atmosphere in relatively high temperatures.

In this study, it was found that the presence of H_2 is essential for the growth of high density of the nanowires in temperatures around 1000°C. Figure 3a shows SEM image of silicon substrate heated with VO_2 powder in only Ar atmosphere at 1000°C.

Unlike previous results using H_2 (figs.1e, 1f), the substrate is covered by rod like structures with variable diameters. EDX results on these structures reveal that these structures are mainly comprised of vanadium and oxygen and the silicon peak is mainly from the substrate itself. According to these observations, H_2 inhibits the deposition of vanadium oxide on the silicon and results in the growth of silicon oxide nanowires. In addition, some controlled experiments were conducted with only Ar/H_2 gas and silicon substrate in the chamber. No products were deposited on the substrate. It can be concluded that both H_2 gasand VO_2 powder are crucial for the growth of high-density networked silicon oxide nanowires.

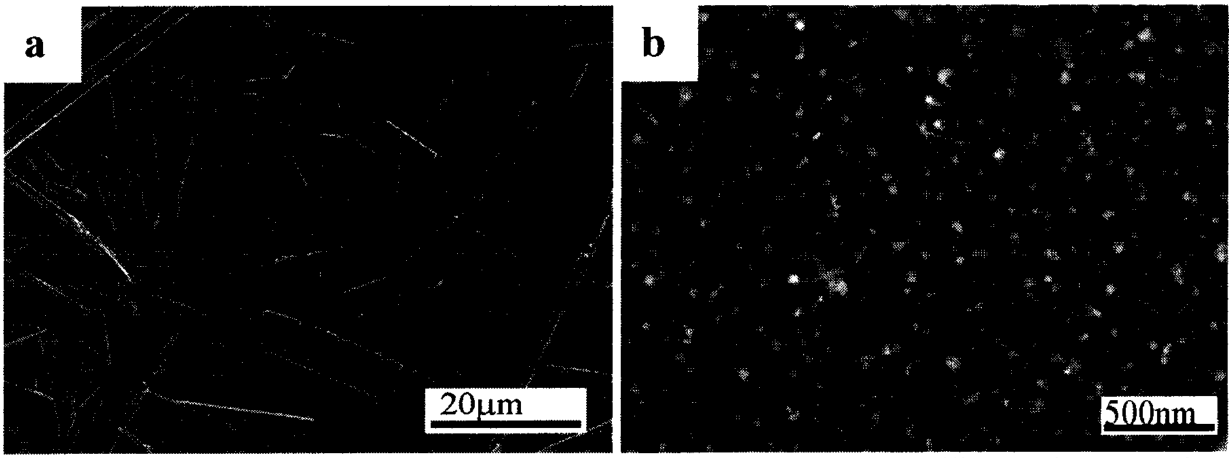

Figure3. SEM images showing the effect of hydrogen in the synthesis of silicon oxide nanowires. a) SEM image of vanadium oxide structures synthesized on silicon substrate by thermal annealing of silicon substrates in vicinity of VO_2 powder without the presence of H_2 in atmosphere. b) SEM image of low density of silicon oxide nanowires synthesized on silicon substrate coated with gold without the use of H_2 gas.

SEM image of silicon substrate coated with gold in Ar atmosphere at 1000°C (fig.3b) shows that very small nanowires are synthesized on the substrate and there are a few bundles of silicon oxide nanowires non-uniformly distributed on the substrate.

Therefore, the results indicate that H_2 gas in the atmosphere increases the density of silicon oxide nanowires synthesized from the substrate.

It should be noted that in the two cases, a wide range of H_2 flow rate has been applied (60 sccm-180 sccm) and the results indicate that the growth of the silicon oxide nanowires is not sensitive to the amount of hydrogen.

2.3 Effect of Temperature

Temperature also plays an important role on the synthesis and growth mechanism of silicon oxide nanowires. Some studies of synthesizing silicon oxide nanowires directly from the substrate in a range of temperatures from 950°C to 1400°C have been reported previously [2, 6, 14]. In the present study, a series of experiments were conducted to study the effect of temperature on the synthesis of silicon oxide nanowire. It was found that silicon oxide nanowires can be synthesized above 950°C using VO_2 powder or Gold as catalysts in Ar/H_2 atmosphere. The main difference between the nanowires grown in different temperatures is their density and diameter. As the temperature is increased, the density and average diameter of nanowires increases dramatically (from 100 nm to 500 nm). But in temperatures higher than 1200°C, it was seen that silicon oxide wire-like structures with large diameters can be synthesized even without either catalysts or H_2 gas. It was also seen that the products on the substrate are a mixture of microfibers and nanowires and have wide range of diameters from 100 nm to over 1 μm.

From these results, it can be concluded that the presence of catalyst and H_2 is necessary in generating silicon oxide nanowires at lower temperatures (~950°C). At higher temperatures (~1200°C), neither catalyst nor H_2 is necessary in growing silicon oxide micro and nanowires.

Table 1 summarizes the results from various conditions studied for growing silicon oxide nanowires.

Table1. Effect of different parameters on the synthesis of SiO_2 nanostructures

Temperature (°C)	Gas	Additives	Final Morphology
950-1000	Ar/H_2	VO_2 powder	SiO_2 networked nanowires networks
950-1000	Ar/H_2	Au layer (3-5nm)	SiO_2 nanowires
950-1000	Ar/H_2	VO_2/Au	High density SiO_2 networked nanowires
950-1000	Ar	VO_2 powder	VO_x microrods
950-1000	Ar	Au layer (3-5nm)	Non-uniform short SiO_2 nanowires
950-1000	Ar/H_2	---	None
1200	Ar/H_2	VO_2 powder	SiO_2 microfibers
1200	Ar/H_2	Au layer (3-5nm)	SiO_2 microfibers
1200	Ar/H_2	---	SiO_2 microfibers

2.4 Growth mechanism

Some mechanisms have been proposed for the growth of silicon oxide nanowires such as vapor-liquid-solid mechanism (VLS) [21, 22]. In this process, Si atoms in the vapor phase are dissolved into the mediating alloy liquid droplets formed at high temperature and then Si nanowires precipitate from the supersaturated alloy droplets [5]. This mechanism requires gaseous Si source material and one of its characteristic is the solidified particles at the tip of nanowires. But in the present study, no external silicon source was used. Based on TEM and SEM observations of silicon nanowires grown in relatively low temperatures (~1000°C), no particles were formed on the tip of nanowires. Therefore, other mechanisms may be responsible for the growth of these silicon oxide nanowires

In the case of silicon oxide nanowires synthesized using gold, according to several studies, solid-liquid-solid (SLS) mechanism can be the governing mechanism. In this process, the gold catalyst layer forms liquid droplets with silicon from the substrate due to low eutectic point of Au-Si alloy (ca.370°C). Then, silicon atoms diffuse through the substrate-liquid interface into the liquid droplets. When the silicon concentration in the droplets reach the saturation level,, the excess silicon atoms precipitate as nanowires on the interface of droplet and atmosphere [13]. Since similar conditions to previous reports have been used in our experiments, this mechanism might be responsible for the growth of silicon oxide nanowires using gold catalyst.

Yang et al. [1] reported the synthesis of silicon oxide nanowires with vanadium acting as the catalyst. They observed the vanadium particle on the tip of nanowires and proposed VLS mechanism for the growth of nanowires. But it still remains unclear why VO_2 can promote the growth of silicon oxide nanowires in this study since catalysts particles were not detected at the nanowire tip. However, there are similarities in the surface morphology of silicon substrate after the synthesis process and growth conditions used between silicon nanowires grown using gold and VO_2. Consequently, SLS mechanism can be ascribed to the VO_2 assisted growth of silicon nanowires.

In this case, the powder was very close to the substrate and it could touch the substrate in some places and acted as the catalyst forming liquid droplets and enabled the growth of silicon oxide nanowires following SLS mechanism. Through SEM observations, some silicon oxide nanowires were seen on vanadium powders on the silicon substrate.

It should be noted that H_2 plays an important role in this mechanism. A number of studies have reported the synthesis of silicon oxide nanowires in H_2 atmosphere using catalyst in relatively low temperatures or at higher temperatures without the use of catalysts [4, 13, 14]. In this study according to the experimental results on the effect of H_2 gas, it was seen that the presence of H_2 gas in the annealing atmosphere increases the density silicon oxide nanowires synthesized using gold as catalyst (fig. 1c,d, and fig. 3b) and can positively decrease the synthesis temperature of the silicon oxide nanowires. Also, H_2 gas prevents the deposition of vanadium oxide structures on silicon substrate and enhances the growth of silicon oxide nanowires. Previous reports have proposed that the role of H_2 is to enhance the supersaturation of liquid droplet and build up the driving force for the precipitation of silicon as silicon nanowires [9, 13]. This might be true to some extent. However, since we have also used argon instead of H_2 and there are distinct differences in the results in both cases, effect of hydrogen is supposed beyond the statement claimed in these studies. Considering the studies done by Kuribayashi et al. [19] on the shape transformation of silicon trenches, the activation energy for diffusion under a low hydrogen pressure is much higher than that under ultra high vacuum conditions. This suggests that surface diffusion of silicon atoms is enhanced in the presence of small amount of hydrogen in the atmosphere which can explain the synthesis of high density silicon oxide nanowires in the current experiments.

For silicon oxide nanowires synthesized at higher temperatures (~1200°C) as reported by Zhang et al. [20], various conditions including different catalysts were used and none of any metal/Si droplets were detected on the tips of nanowires, proposing a vapor-solid (VS) mechanism for the silicon oxide nanowires synthesized at 1200°C temperature.

Considering the melting point of silicon oxide, silicon and the thickness of the native silicon oxide on the substrate, it has been mentioned in various studies that, at temperatures around 1200°C and above, silicon and native silicon oxide can react according to the following reaction [20]:

$$Si_{(S)} + SiO_{2(S)} = 2SiO_{(G)}$$

The product of this reaction in the gas phase can react as shown below and SiO_2 is formed in the solid phase.

$$2SiO_{(G)} = SiO_{2(G)} + Si_{(G)}$$

$$Si_{(G)} + O_{2(G)} = SiO_{2(S)}$$

In this mechanism, catalyst is not necessary and the sources of oxygen can be residual oxygen in Ar and the CVD chamber.

As seen by changing the temperature, the mechanism involved in synthesizing silicon oxide nanostructures changes and the deciding factor for the yield and morphology of these nanostructures varies as well. Thus, it is believed that the present work provides better understating of the synthesis mechanism and further studies are currently being done on different materials.

3. Conclusion

In summary, we have successfully synthesized the silicon oxide nanowire network with diameters of 30-100nm by heating the silicon substrate with VO_2 powder at the temperature around 1000°C. In addition, it was found that the mixture of VO_2 and gold as co-catalysts enhances the achievement of silicon oxide nanowires with network characteristic. The microscopic characterization indicates that SLS mechanism governs the synthesis of these nanowires at lower temperatures (<1000°C), while VS mechanism dominates at higher temperature (~1200°C). Further, the presence of H_2 gas is important in elevating nanowire density at temperatures below 1000°C but at higher temperatures (~1200°C), mixture of microfibers and nanowires are synthesized without the use of any metal catalyst or H_2.

Acknowledgments

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Chapter Four: Synthesis and Characterization of Single Crystalline MnO Nanowires by Vapor Phase Deposition Method[*]

1. Introduction

Featuring their variable oxidation states, manganese oxides have attracted substantial attention due to their superior magnetic, electrical and chemical properties, which promise great potential in superconductivity, catalysts, sensors, battery, corrosion and high temperature applications [1-7].

In recent years, considerable research has been focused on nanostructured manganese oxides [3-13]. It has been well documented that nanostructured manganese oxides possess unique electronic, optical and magnetic properties, showing quite different behaviors compared to their counterparts in bulk phase due to their anisotropic feature in morphologies, size and shape. Moreover, properties of the manganese oxide nanostructures can be readily modified by tailoring their size and structure [8]. Studies on MnO nanoparticles and nanorods have shown that these nanostructures exhibit ferromagnetic behavior while bulk MnO is anti-ferromagnetic [5, 9,14]. Seo et al, [15] reported the size dependent magnetic behavior of colloidal Mn_3O_4 and MnO nanoparticles, which can be used for sensor applications. Chen et al [11] also showed that manganese oxide nanorods have high specific capacitance and a good reversibility, which makes them an excellent candidate as an electrode material for electrochemical capacitors. Apart from magnetic properties, it has been reported that MnO nanocrystals

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[*] **This paper will be submitted to Journal of Material Research.**

have higher oxygen reduction activity compared to bulk MnO in alkaline aqueous solutions [8]. Further, Yang et al [10] showed that one-dimensional manganese monoxide nanostructures exhibit catalytic function on the oxidation and decomposition of the methylene blue dye with H_2O_2. More recently, Lahann [16] reported that MnO nanowires could separate water and oil. Therefore, it can be seen that MnO nanostructures can be used in various applications as electrodes in electrochemical applications. However, the synthesis of mono-phase manganese oxides with well-controlled dimensionality and single crystal structure is still a major challenge [17].

So far, several methods have been developed to synthesize nanostructured manganese oxides with different morphologies such as nanowires and nanorods. Yang et al [10] synthesized manganese oxide nanorods using heat treatment of nanostructured precursors of γ-MnOOH. Park et al [5] reported the growth of MnO nanospheres and nanorods by thermal decomposition of Mn-Surfactant complexes. Wang et al [17] synthesized manganese dioxide nanowires and nanorods by hydrothermal method based on the redox reactions of MnO_4^- and Mn^{2+}. In addition, other methods such as reflux [18], sol-gel [19] and different types of hydrothermal processes [4, 6, 20,21] also have been used for the production of manganese oxide nanostructures. Further, the influence of different growth parameters in these methods has been extensively studied [20-22]. However, vapor phase deposition methods have been rarely employed to synthesize mono-phase manganese oxide nanowires [12, 23,24] due to uncontrollable phase transformation of multivalent manganese oxides (MnO_2, Mn_2O_3 and Mn_3O_4).

In the present work, we report a facile way of synthesizing high density, single crystalline and highly pure MnO nanowires using a vapor deposition method. Detailed influence of experiment parameters on the final product has been systematically investigated to control the morphology and phase structure of the manganese monoxide nanowires. Keeping the starting materials unchanged, manganese oxide nanowires, silicon oxide nanowires, and the nanocomposites of silicon oxide nanowalls on manganese oxide microwires were selectively obtained.

2. Results and Discussion:

Manganese oxide nanowires were synthesized on a silicon substrate after optimization of various growth parameters. The general morphology of the products was initially observed by SEM technique. Figure 1a shows a typical SEM image of the product. It reveals that the product consists of dense nanowires that uniformly cover the silicon substrate. The length of the resultant nanowires is up to 100μm. EDX spectrum, as shown in Figure 1b, indicates that the nanowires are mainly composed of manganese and oxygen. The weak silicon peak in the spectrum comes from the silicon substrate.

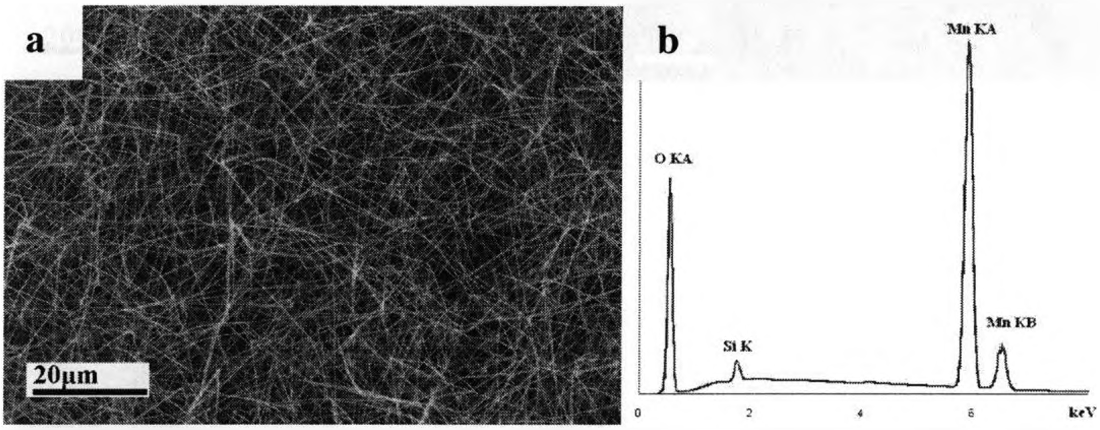

Figure1. a) SEM images of manganese oxide nanowires synthesized on silicon substrate with 3-4nm, showing uniform coverage of silicon substrate. b) EDX spectrum of manganese oxide nanowires on silicon substrate with 3-4 nm gold.

TEM observations indicate that diameter of the nanowires ranges from 70-250 nm with a mean value of 150 nm. Figure 2a shows a typical TEM image of a single nanowire with the diameter of around 170 nm. The selected area electron diffraction (SAED) pattern (Figure 2b) taken from this nanowire reveals single crystalline nature of the nanowire and the reflections can be indexed as (220) crystal plane of face centered cubic (fcc) MnO phase. HRTEM analysis (Figure 2c) of manganese monoxide nanowires shows that the nanowire have relatively smooth surface. The clear lattice fringes in Figure 2c confirm high quality crystallinity of the nanowire. The inter-planar spacing is measured as 0.25 nm corresponding to the {111} plane of MnO crystal structure.

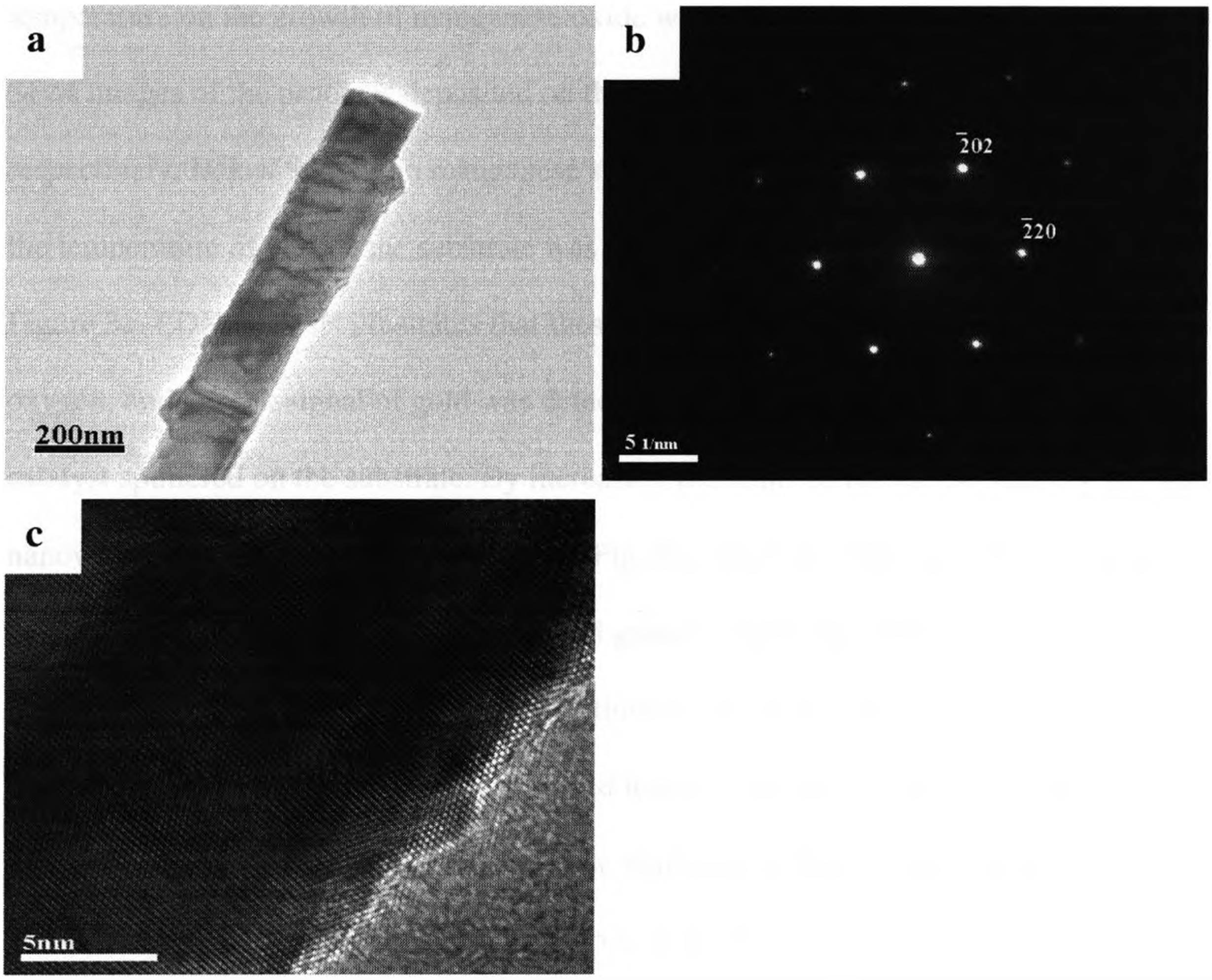

Figure2. a) TEM image of a MnO nanowire with a diameter of about 150 nm. b) SAED pattern of the nanowires which corresponds to fcc-MnO phase. c) HRTEM image of manganese oxide nanowires.

During our experimental process, it has been found that morphology of the structures is very sensitive to the involved growth parameters, such as synthesis temperature, distance of source (manganese powder)/substrate and heating rate of the reaction system. In order to understand the growth mechanism of the MnO nanowires, effects of the growth parameters on the nanowires composition and structure were systematically studied.

2.1 Effect of temperature

Based on a group of experimentally optimized parameters, influence of temperature on the growth of manganese oxide was initially investigated. Figure 3 shows SEM images of the products deposited on the substrate at 900°C, 930°C and 960°C, respectively. Below 900°C, no manganese structures were obtained on the substrate. At the temperature of 900°C, the substrate was covered with microparticles as shown in Figure 3a. EDX analysis illustrates that these particles mainly consist of manganese and oxygen, and a weak signal of gold was detected as well. Here, this is due to the gold as catalyst sputtered on the substrate. By increasing the temperature to 930°C, very straight nanowires were observed on the substrate (Fig.3b), which is identical to the manganese oxide nanowires grown under the optimized growth conditions. While some nanowires have very sharp tips, other nanowires have thicker tips up to 150 nm in diameter. At a higher temperature of 960°C, the density and length of nanowires increases (Fig.3c). However, the nanowires synthesized at these temperatures have rougher surfaces and non-uniform diameters along their length up to 350 nm.

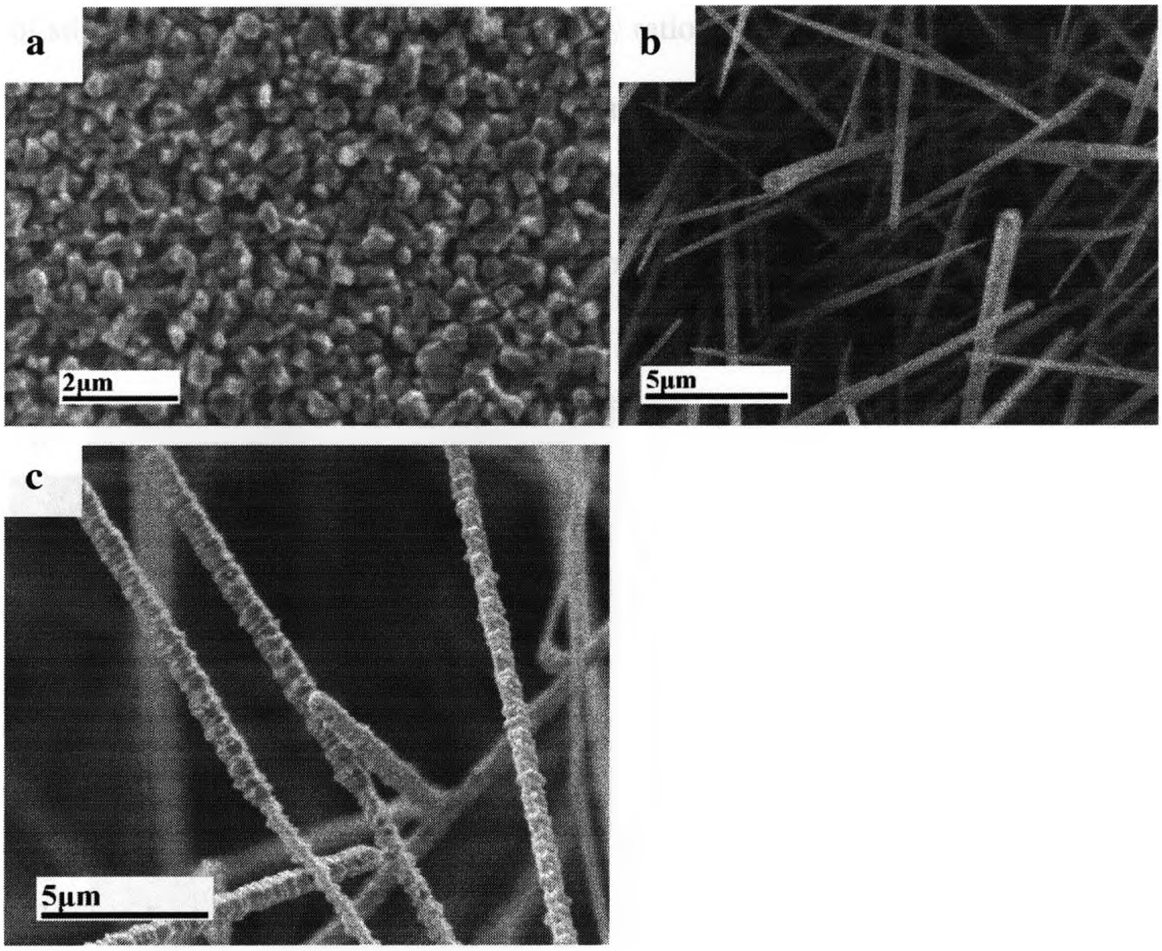

Figure3. SEM images showing the effects of synthesis temperature on the nanostructures. a) Particles deposited on the substrate in temperatures at 900°C. b) Nanowires synthesized in 930°C. c) Nano & micro-wires synthesized in temperatures 960°C.

2.2 Effect of source/substrate distance

Besides the synthesis temperature, the distance of source/substrate is shown as a significant factor affecting not only morphology but also composition and phase structure of the product. When the distance of source/substrate is less than 2 mm, manganese oxide nanowires were obtained. Increasing the source/substrate distance to more than 6 mm, the substrate was covered with high density of thin and tangled nanowires with the morphology completely different from the manganese oxide nanowires mentioned above, as shown in Figure 4a. XPS results shown in Figure 4b indicate that the nanowires consist of silicon and oxygen with the stoichiometry ratio of 1 to 2 (SiO_2). According to TEM observations (Figure 4c), SiO_2 nanowires have a narrow diameter range of about 70 nm and the diffraction pattern shown in inset of figure 4c illustrates amorphous nature of these nanowires. When the distance was kept at 4 mm, the products were composed of a mixture of manganese oxide nanowires and silicon oxide nanowires.

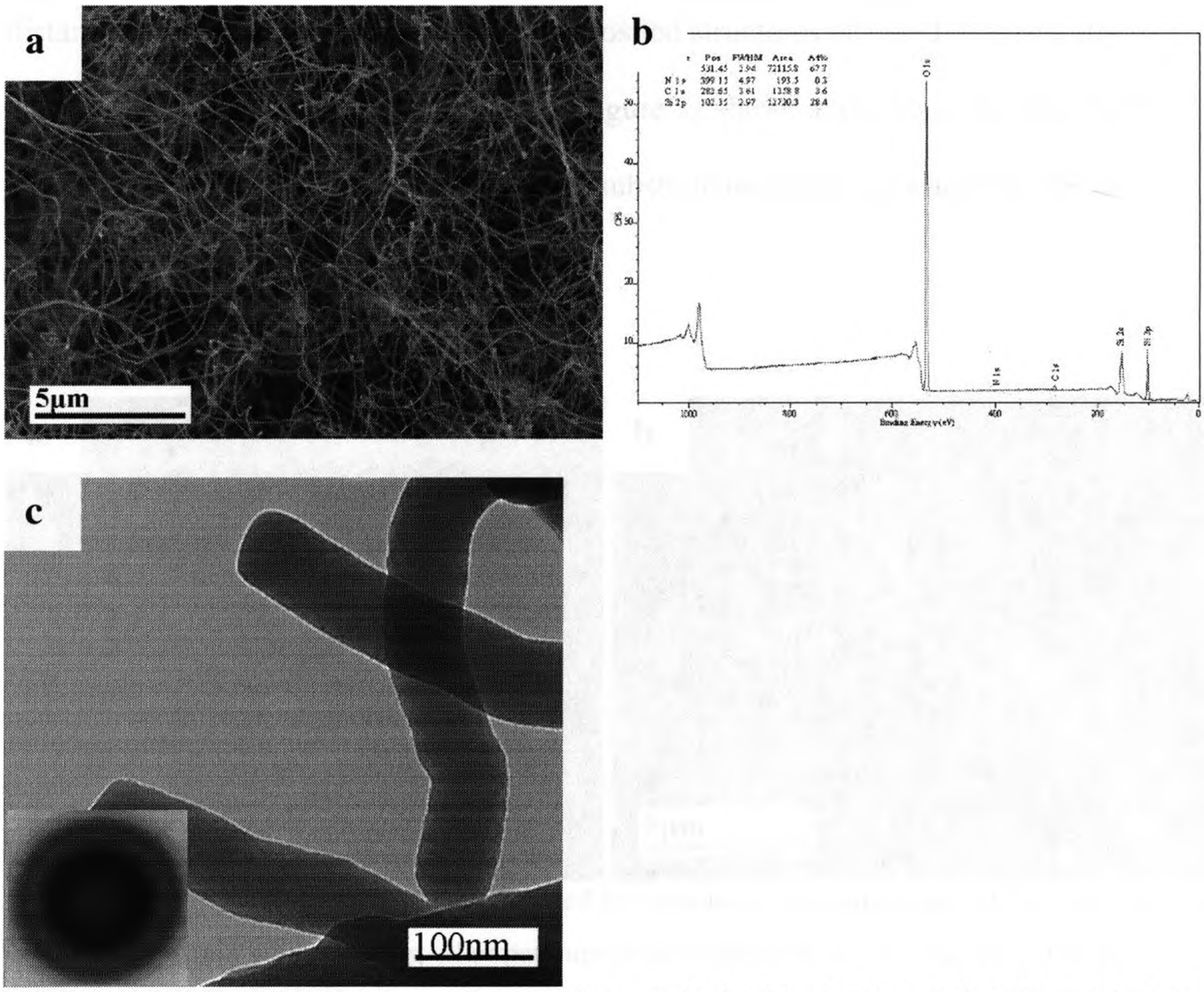

Figure4. SEM images of silicon oxide nanowires synthesized by increasing the distance between manganese powder and silicon substrate to more than 5mm. a) SEM image of silicon oxide nanowires shows that these nanowires have uniform diameters below 100 nm and cover the substrate uniformly. b) XPS results from these nanowires shows that the Si:O ratio is around 1:2 which indicates that these nanowires are mainly SiO_2 nanowires. c) TEM image of silicon oxide nanowires showing smooth surface with narrow diameter range of 70nm. The inset is the SAED pattern of these nanowires taken under TEM reveals that these nanowires have amorphous structure.

2.3 Effect of heating rate

Interestingly, it has been observed that the final composition and structure of the product is considerably dependent on the heating rates of the reaction system. Generally, a low heating rate favored the deposition of manganese oxide nanowires (5°C/min in this case), while keeping other optimized conditions (930°C, 2mm of source/substrate distance) (Figure 1), the morphology of deposited structures changed dramatically by increasing the heating rate of the process. Figure 5a shows a low magnification SEM image of the microstructures that cover the substrate uniformly at a heating rate of 50°C/min. Higher

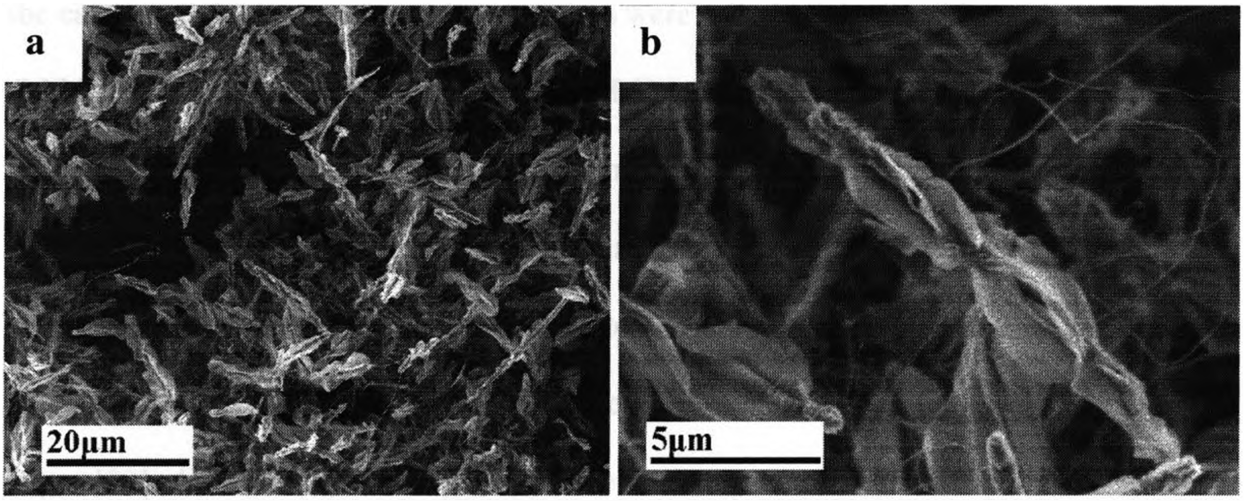

Figure5. SEM images of structures synthesized by increasing the heating rate of the experiment to 50°C/min while keeping other parameters at unchanged. a) low magnification SEM image shows that the composites structures cover the silicon substrate relatively uniformly. b) Higher magnification SEM images shows that these structures are comprised of micro-wires in their core with sheet like structures covering these wires. Initial characterizations via EDX show that the core wire is mainly composed of manganese and oxygen and the sheet covering the wire are mostly silicon oxide as seen in the EDX taken from these structures.

magnification SEM image in Figure 5b reveals that these structures are composed of a microwires covered by epitaxial nanowalls. EDX analysis indicates that the microwires consist of manganese and oxygen elements while only silicon and oxygen were detected on the nanowall-like structure, indicating a composite structure of the product. Our experimental results have shown that increasing the heating rate (5 to 50°C/min) favors the growth of the composite structure and restrains the deposition of manganese oxide nanowires. Further characterization of these structures will be carried out in future.

2.4 Growth mechanism

In the present study, a thin gold layer has been sputtered on the substrates to act as the catalyst and manganese oxide nanowires were failed to obtain without the use of the gold layer. Therefore, vapor-liquid-solid (VLS) mechanism has been proposed here to interpret the growth of manganese oxide nanowires, which is similar to the previous reports [23, 24]. According to this mechanism, Mn and Au form liquid alloy droplets when temperature is around their eutectic point. The liquid surfaces have large accommodation coefficient and are therefore preferred deposition sites for the incoming vapor [25]. After the liquid alloy droplets become supersaturated with Mn, MnO precipitates as nanowires due to residual oxygen in the system. However, catalyst droplets were not observed at the tip of the manganese oxide nanowires during the TEM observations in this study, which is unlike several studies on the synthesis of nanowires following the VLS mechanism. Here we intend to propose two possible reasons: one is due to fragile nature of manganese oxide nanowires which causes the nanowires to break in the TEM sample preparation process. The other is similar to the cases in the previous reports [26-28], in which the manganese oxide nanowires were synthesized following the base growth model of VLS mechanism.

As discussed above, the effect of various parameters on the morphology, composition and structure of the product is supposed to be related to species and pressure of the formed gaseous atoms in the reaction chamber. At a lower temperature (ca. 900°C or below in this case), partial pressure of manganese vapor was low and could not feed the growth of the nanowires. Higher temperatures would increase supersaturation degree of manganese vapor (ca.930°C in this case), which triggered the anisotropic growth of the nanowires. However, exceedingly high supersaturation degree with further increase of the temperature (ca.960°C or higher) might result in radial growth of the nanowires and thicker nanowires were generated.

For the source/substrate distance factor, the distance directly influences the amount of manganese vapor reaching the substrate. At short distances, the substrate is exposed to large amount of manganese vapor enabling the formation of manganese oxide nanowires, while the longer distance makes the amount of manganese deposited on the substrate decrease. In addition, it is possible to synthesize silicon oxide nanowires directly from silicon substrate using gold as catalyst governed by solid-liquid-solid (SLS)[29,30] or VLS [31] mechanism in similar experimental conditions. Under the conditions in the present study, there is a competition between the growth of manganese oxide nanowires and silicon oxide nanowires. Therefore, the density of silicon oxide nanowires increased with increasing the source/substrate distance, and finally only silicon oxide nanowires were synthesized at long distances.

In contrast to the growth of silicon oxide nanowires, which is independent of the heating rate, the achievement of manganese oxide nanowires is determined to a great extent by the control of the heating rate. It is possible that higher heating rate would increase the rate of oxidation of manganese powder inhibiting the partial evaporation of manganese powder, decreasing the amount of manganese vapor in the system. Hence, high heating rate increases the possibility of growth of silicon oxide structures from the substrate along with low density of manganese oxide structures.

In general, the growth parameters have to be carefully controlled to obtain manganese monoxide nanowires with sole phase structure.

3. Conclusions

In summary, high quality crystalline MnO nanowires were successfully synthesized using a simple vapor phase deposition method on silicon substrate with a thin layer of gold as catalyst. SEM observations showed dense and uniform growth of the nanowires with the length up to 100μm. HRTEM image and SAED pattern evidenced single crystalline face centered cubic nature of the MnO nanowires. The systematic study of the growth process indicated that the synthesis of these nanowires was very sensitive to growth parameters such as temperatures, source/substrate distance and heating rate. The controlled growth of manganese oxide nanowires, silicon oxide nanowires and manganese oxide/silicon oxide composite nanostructures could be obtained by modulating the growth parameters. The obtained MnO nanowires in the present study are expected to have great potential in magnetic field applications, catalyst and electrochemical capacitors. In addition, these nanowires provide suitable precursors to synthesize other types of manganese oxides.

Acknowledgments

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Chapter Five: Synthesis and Characterization of One Dimensional Manganese Oxide Nanostructures on Carbon Paper Substrate*

1. Introduction

Over the past decade, one dimensional nanostructures such as nanotubes and nanowires have attracted significant research interests due to their unique properties and potential applications in various fields including electronics, optics and electrochemical applications (e.g. fuel cells and battery technologies). Depending on the needs of various applications, certain criteria are also necessary to evaluate the growth quality of nanostructures. For mechanical applications, it is important to be able to synthesize large amounts of the nanostructures and have good mechanical connection between the nanostructures and the substrate, while for electrochemical applications it is important that the nanostructures are electrically connected to an acceptable electrode.

As far as the electrochemical applications of nanostructures are concerned, careful selection of an appropriate substrate is essential to ensure high electrical connection between the electrodes and the substrate. Among various conductive substrates, carbon paper substrate would be an ideal conductive substrate/electrode for electrochemical applications. Indeed, compared to metallic substrate, carbon paper is a synthetic thin, lightweight matrix with super gas penetration, which has significant advantages over metallic substrates for practical electrochemical based applications. Previously, carbon nanotubes have been proposed as a suitable candidate for producing nanostructured

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*** This paper will be submitted to Journal of Chemical Physics Letter.**

electrodes on carbon paper due to their high electrical conductivity, superior chemical stability [1-4].

Therefore, various techniques have been developed to synthesize carbon nanotubes directly on carbon paper substrates. Recently, Sun et al. [5] reported the synthesis carbon nanotubes network on carbon paper by ohmically heating silane dispersed catalyst site on the substrate. In addition, several researchers [1, 2, 6] have used simple chemical vapor deposition methods (CVD) for the synthesis of carbon nanotubes on carbon paper for the applications in proton exchange membrane fuel cells. These reports indicate that using these structures improves their performance as electrodes in electrochemical applications.

More recently, nanowires have been proposed as electrodes used in fuel cells in a similar way to carbon nanotubes. It has been suggested that direct synthesis of nanowires on carbon paper would greatly improve their electrochemical performance. However, there have been very few reports of synthesizing nanowires on carbon paper. Li et al. [7] reported the synthesis of aligned heterostructures of composite of tin nanowires and amorphous carbon nanotubes with potential electrochemical applications. Further, Saha et al. [8, 9] synthesized SnO_2 nanowires on carbon paper as supports of Pt alloys for fuel cell applications.

In the past few years, nanostructured manganese oxides have attracted considerable research interests due to their superior catalytic properties [10] and their possible applications in fuel cells [11, 12], Li-ion batteries [13], electrochemical capacitors [14] and sensors [15, 16]. Chen et al. [14] showed that manganese oxide nanorods have high specific capacitance and a good reversibility, which makes them an excellent candidate as an electrode material for electrochemical capacitors. It has been reported that MnO nanocrystals have higher oxygen reduction activity compared to bulk MnO in alkaline aqueous solutions [17]. Further, Yang et al. [10] showed that one-dimensional manganese monoxide nanostructures exhibit catalytic function on the oxidation and decomposition of the methylene blue dye with H_2O_2. More recently, Lahann et al. [18] reported that MnO nanowires could separate water and oil. In these reports, nanowires or nanorods generally were synthesized by sol-gel [19] and various hydrothermal methods [10, 14, 20-22] but not many by CVD method [23, 24].

In this study, manganese oxide nanowires and nanobelts have been selectively synthesized on carbon paper substrate by using a catalyst (gold) assisted or catalyst free thermal evaporation of manganese powder under an argon gas atmosphere. Effects of growth parameters such as temperature, catalyst and substrate on morphology and structure of the manganese oxide nanostructures have been systematically investigated. Such structures formed on commercially-used carbon paper are expected to not only improve the performance of manganese based electrodes, but also push the nanostructures towards practical fuel cells and sensors applications.

2. Result and Discussion

After the experiment, the obtained product grown from a gold sputtered carbon paper displayed a light green color. The overall structure of the synthesized product was initially characterized with XRD technique. Figure 1 displays the XRD pattern taken from the products on carbon paper. Miller indices are indicated on each diffraction peak. The diffraction peaks at around 34.86°, 40.46° and 58.56° are assigned to (111), (200) and (220) crystal planes of MnO (PDF No. 07-0230), respectively, indicating that the nanostructures have face centered cubic (fcc) MnO crystal structure. The peaks around 26.3° and 54.3° are assigned to carbon (002) and (004) crystal planes from the carbon paper substrate. Hence, the as-synthesized products can be well determined as pure and well-crystallized MnO.

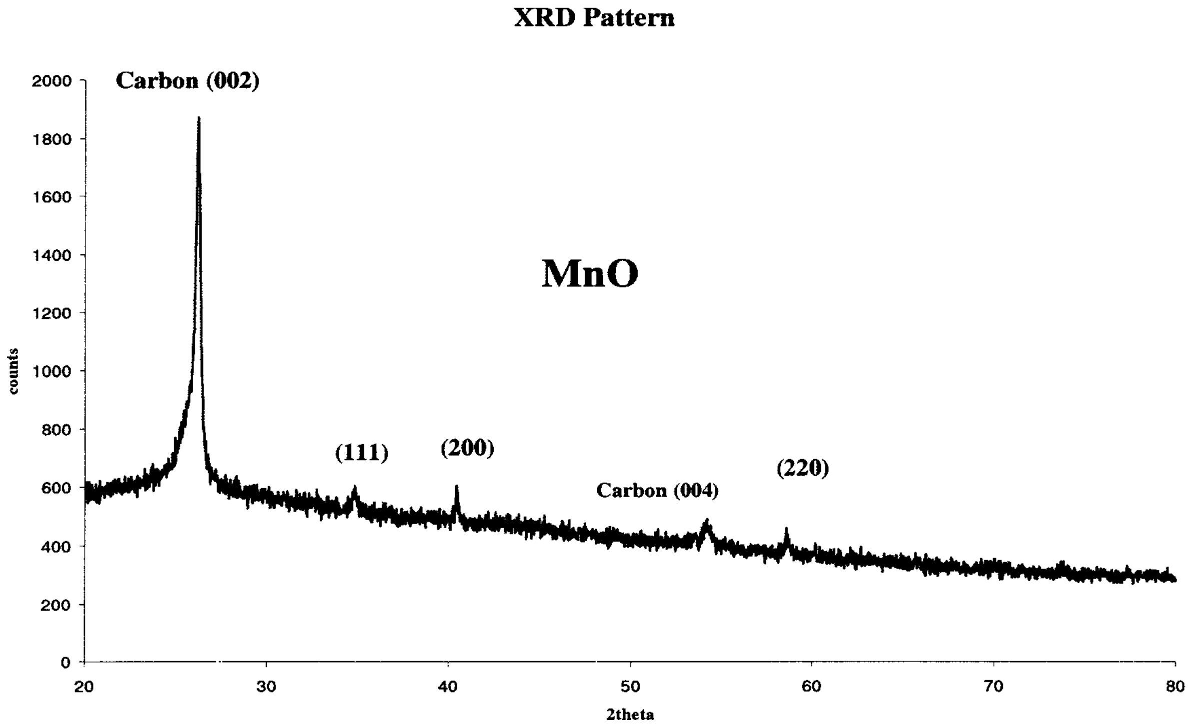

Figure1. XRD pattern from MnO nanowires synthesized on carbon paper with a 15nm thick gold layer.

These MnO nanostructures were synthesized on carbon paper in similar conditions used for the synthesis of MnO nanowires on silicon substrate [25]. However, systematic study on the effects of different growth parameters on the morphology of nanowires synthesized on the carbon substrate indicated many differences compared to the results obtained on the silicon substrate.

It has been found that the optimized values for a number of growth parameters such as synthesis temperature were somewhat different from the optimized conditions for the nanowire growth on silicon substrate. Highest density of manganese oxide nanostructures with small diameters were synthesized at around 970°C (50°C degrees higher than growth temperature used to synthesize MnO nanowires on silicon substrate). In addition, our experimental results indicated that the growth process of MnO nanowires on carbon paper is not very sensitive to some of the growth parameters studied in the synthesis of MnO nanowires on silicon substrate. At higher heating rates and longer substrate (carbon paper)/source (Mn powder) distances, no silicon nanowires or composite structures were deposited on the carbon paper since silicon source was not present in the system, which is different from the growth on silicon substrate. These parameters only influenced the density and length of the nanowires synthesized on carbon paper. Generally, increase of the heating rate or the distance of substrate and Mn powder, the density and length of the nanowires decreased since carbon paper surface was exposed to less Mn vapor.

During the experiments, interestingly, SEM observations revealed that, unlike the MnO nanowires synthesized on silicon substrate, the morphology of nanostructures deposited on carbon paper was dependant on the thickness of the gold layer sputtered on the substrate. Figure 2 illustrates the effect of the gold layer thickness on the morphology of nanowires synthesized on carbon paper. SEM images of the nanowires synthesized on carbon paper with 5nm thick gold layer (fig.2a, 2b) indicate that high-density nanowires grow randomly on the carbon fibers with no preferential directions. Length of the nanowires is up to 20 μm. High magnification image of these nanowires in inset of figure 2b shows that these nanowires show sharper tips compared to MnO nanowires synthesized on silicon substrate. The diameter of these nanowires along their longitudinal axis varies from several hundred nanometers at the base of nanowires to few tens of nanometers at their tip.

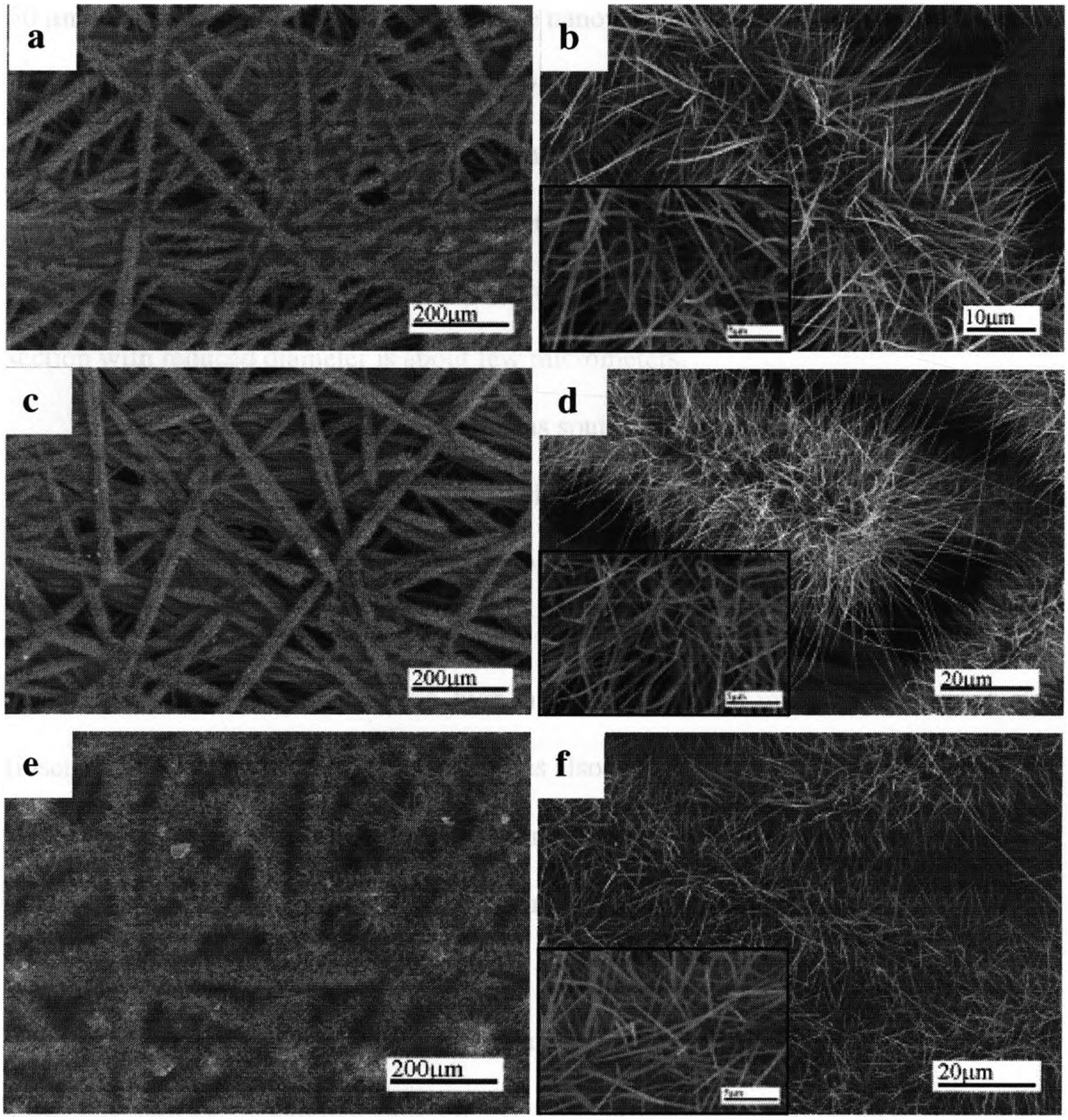

Figure2. SEM images of MnO nanowires synthesized on carbon paper with a thin gold layer of a,b) 5nm, c, d) 10nm and e,f) 15nm showing the change in the morphology of nanowires deposited with the thickness of the catalyst layer.

Compared to the nanowires synthesized on carbon paper with a 5nm thick gold layer, the density of MnO nanowires synthesized on a 10 nm thick gold layer is higher as shown in figure 2c and 2d. SEM images of these nanowires show that the average length of these nanowires is around 30μm and the length of some nanowires even reaches over 50 μm. A high magnification image of these nanowires (inset of fig.2d) shows a similar morphology to the nanowires synthesized with thinner gold layer (inset of fig.2b). However, it can be seen that nanowires with sharp tips are actually composed of two distinct parts. The diameter of the lower parts of these nanowires is around 300-500 nm and near the tip the diameters suddenly decreased to about 100 nm. The length of the section with reduced diameter is about few micrometers.

While a thick gold layer of 15nm was sputtered on the substrate, SEM images of the nanowires in figures 1e and 1f indicate that further increase of gold layer will increase the density of nanowires compared to figure 2c and 1a. However, as seen in figure 1f, thicker gold layer on carbon fibers does not considerably affect the length of nanowires. Similar to the previous two samples, high magnification SEM image of these products (inset of figure 2f) reveals that the nanowires also show sharp and needle-like tips. However, the density of nanowires possessing sudden diameter reductions has been reduced and most of the nanowires show a uniform decrease in their diameter from bottom to tip.

To further study the effect of substrate nature on the growth of the manganese oxide nanostructures, detailed experiments were carried out on carbon paper with different buffer layers including titanium sputtered, tungsten sputtered and bare carbon paper substrate. Optimized growth conditions were applied to deposit manganese oxide nanostructures on these substrates. SEM images of the nanostructures deposited on these three types of substrates are shown in figure 3. It is observed that, in the absence of a gold layer, the morphology of the nanostructures changes dramatically. Similar changes relating to morphological transition of 1D nanostructures have been previously reported by other researchers. Zhang et al. [26] observed a morphological transition between α-Al_2O_3 nanowires and nanobelts due to change in their experimental conditions.

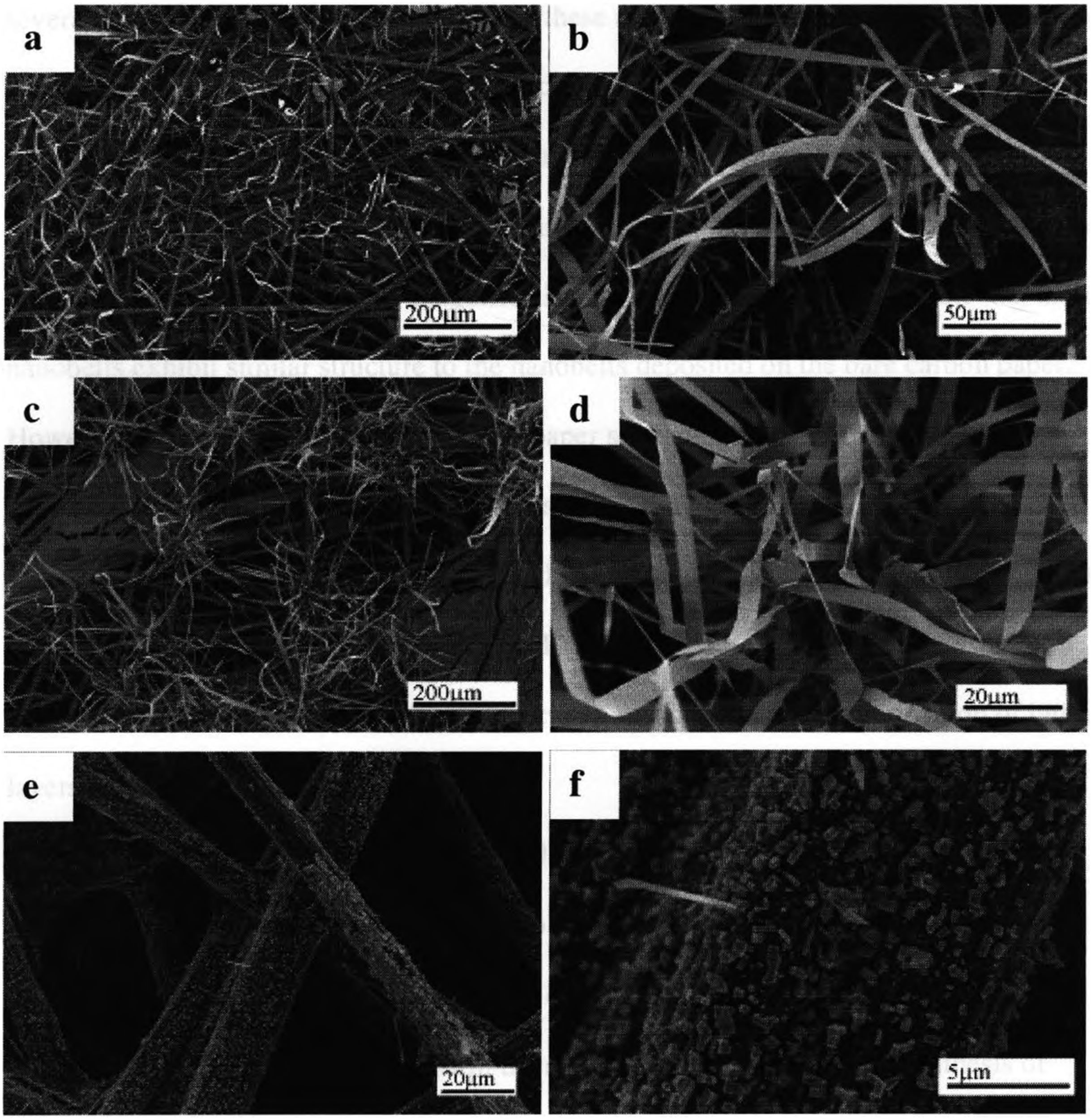

Figure3. SEM images of MnO nanostructures synthesized on a,b) carbon paper, c,d) tungsten sputtered carbon paper, and e,f) titanium sputtered carbon paper in a catalyst free condition, revealing the dependence of the morphology of manganese oxide nanostructures on structure and composition of the substrate.

As shown in figure3a and 3b, SEM images of the product grown on the bare carbon paper (fig.3a, 3b) indicate that manganese oxide nanobelts with very low density were deposited while no catalyst layer was used. The lengths of these nanobelts are up to several hundred micrometers. The width of these nanobelts decreases uniformly from the base (around 6-10 μm) to their tips (few micrometers).

While tungsten sputtered carbon paper substrate was employed, as shown in figure3c and 3d, SEM observations reveal an increase of the nanobelts density compared to the bare carbon paper. Higher magnification image of the nanobelts indicate that these nanobelts exhibit similar structure to the nanobelts deposited on the bare carbon paper. However, when titanium sputtered carbon paper substrate, the density of the1D manganese oxide nanostructures decreased significantly. The microfibers of titanium sputtered carbon paper were mainly covered with manganese oxide microparticles instead of nanobelts, as shown in figure 1e and 1f. These results illustrate that the morphology and structure of manganese oxide nanostructures is sensitive to the composition of buffer layers sputtered on carbon paper.

According to SEM observations and results of synthesizing manganese oxide nanowires on silicon substrate, we intend to propose possible growth mechanism of the synthesis of MnO nanowires and nanobelts on carbon paper, though further characterizations are needed to confirm the synthesis mechanism. In the synthesis of MnO nanowires on silicon substrate with a gold layer, it was concluded that the gold layer acts the catalyst. Vapor-liquid-solid (VLS) mechanism (similar to reports on the synthesis of Mn_3O_4 nanowires [23, 24]) with a base growth model was proposed for the synthesis of these nanowires on silicon substrate. Several other researchers have reported the synthesis of other types of nanowires using this model [27-29]. Based on our experimental results, this mechanism is also suitable for interpreting the synthesis of MnO nanowires on the gold sputtered carbon paper. During the heating process the evaporated manganese vapor from the source (manganese powder) would diffuse into the gold layer making Au-Mn liquid alloy droplets. By further heating the system, the liquid alloy droplets would be supersaturated with Mn species. Then the Mn species with high supersaturation level would precipitate from the droplet as a solid reacting with the trace oxygen in the carrier gas or from air leakage or residue oxygen in the reaction tube and form manganese oxide nanowires.

However, this mechanism is not applicable for explaining the formation of MnO nanobelts on carbon paper due to different substrate conditions. Previously, the VLS process has been employed to interpret the growth of some nanobelts such as SnO [30], ZnO [31], CdS [32] and In_2O_3 [33]. The characteristic of the VLS growth process is the existence of metal nanoparticles which serve as the catalyst between the vapor feed and the solid product. In the current experiments, no catalyst layers were employed. Therefore, we suggest that the formation of MnO nanobelts might be dominated by the vapor-solid (VS) growth mechanism. At high temperatures (900°C – 1000°C), manganese vapor was formed on top of Mn powder, which can react with oxygen in the system and yield small MnO solid particles. The produced MnO particles would deposit on carbon paper substrate and act as the initial nuclei of the MnO nanobelts. With increasing temperatures, the mobility of atoms or molecules is enhanced and the low energy surfaces of a crystal tend to be flat [34, 35], which prevents the accumulation of the newly arrived molecules onto these surfaces and trigger the achievement of the nanobelts. On the other hand, formation of nuclei and aggregation of more MnO species on the growth front during the VS process also depends on the morphology and structure of the substrate as seen in figure 3.

3. Conclusions

In Summary, high density manganese monoxide nanowires and nanobelts were selectively synthesized on carbon paper substrate using a catalyst-assisted or catalyst free growth process, respectively. Vapor-liquid-solid process was proposed for the growth mechanism of the manganese oxide nanowires, while vapor-solid was thought to be the governing mechanism during the nanobelts growth due to the catalyst free condition of synthesizing the nanobelts. In the VLS growth process, it was found that the structure and density of the nanowires were very sensitive to the thickness of gold layer sputtered on carbon paper. For the nanobelt growth governed by the VS mechanism, the density of these nanobelts was found to be dependant on the buffer layer sputtered on carbon paper, which illustrates their growth dependence on the morphology and composition of the substrate. The obtained MnO nanostructures (nanowires and nanobelts) are expected to have great applications in catalyst and electrochemical applications such as fuel cells. In addition, these nanostructures can provide suitable precursors to synthesize other types of manganese oxide nanostructures.

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Chapter Six: Conclusions and Future Work

6.1 General Conclusions

In this study, one dimensional metal oxide nanostructures have been synthesized via simple chemical vapor deposition methods and systematically characterized.

Initially, the growth of silicon oxide nanostructures directly on the substrate was investigated. Silicon oxide nanowire network with diameters of 30-10nm was synthesized by heating the silicon substrate with VO_2 powder at temperatures around 1000°C. According to the detailed microscopic characterization and similar reports of synthesizing silicon oxide nanowires from the substrate, solid-liquid-solid process was proposed as the governing growth mechanism of silicon oxide nanowire. Numerous experiments were carried out to study the effects of various growth parameters. Interestingly, it was found that the mixture of VO_2 and gold as co-catalysts is a critical factor to enhance the network features of the silicon oxide nanowires. Further, the presence of H_2 gas is also important in temperatures below 1000°C for the synthesis of these nanowires while in higher temperatures (~1200°C), a mixture of microfibers and nanowires is synthesized without the use of any metal catalyst or H_2. We proposed that the latter follows a vapor solid mechanism for the growth of silicon oxide nanowires at higher temperatures. This illustrates the temperature dependence of growth mechanism of the silicon oxide nanostructures

In the following part, MnO nanostructures were synthesized on silicon and carbon paper substrates. High quality crystalline MnO nanowires were successfully synthesized using a simple vapor deposition method on silicon substrate with a thin layer of gold as catalyst. SEM observations showed dense and uniform growth of the nanowires with lengths up to 100μm. HRTEM images and SAED pattern evidenced single crystalline face centered cubic nature of the MnO nanowires. The systematic study of the growth process indicated that the growth of MnO nanowires was very sensitive to process parameters such as temperatures, source/substrate distance and heating rate. The controlled growth of manganese oxide nanowires, silicon oxide nanowires and manganese oxide/silicon oxide composite nanostructures could be obtained by modulating the growth parameters.

To my knowledge, high density of MnO nanowires and nanobelts were selectively synthesized, for the first time, on carbon paper substrate using catalyst assisted or catalyst free growth process respectively. Vapor -liquid-solid process was proposed for the growth mechanism of the manganese oxide nanowires while vapor-solid was thought to be the governing mechanism during nanobelts growth due to the catalyst free condition of their synthesis process. In the VLS growth process, it was found that the structure and density of nanowires was very sensitive to the thickness of gold layer sputtered on carbon paper. For the nanobelt growth governed by VS mechanism, the density of these nanobelts was found to be dependant on the buffer layer sputtered on carbon paper which illustrates their growth dependence on the morphology and composition of the substrate.

6.2 Future Work

6.2.1 Silicon Oxide Nanowires on Silicon

Silicon oxide nanowires are very important semiconductors and have found applications in various fields such as electronics, optics and gas sensors. It is predicted that silicon oxide nanowires networks will enhance their performance but research on these nanostructures is still in early stages and a great deal of work needs to be done.

(1) Further experiments and detailed analysis of nanostructures are needed to clarify the role of VO_2 in the synthesis of silicon oxide nanowire networks (HRTEM, IR and Raman spectroscopy).

(2) Various properties of nanowires such as electrical conductivity (using AFM or MEMS based systems, Optical properties (photoluminescence spectroscopy)), and mechanical properties (using AFM) are necessary to be explored.

In addition, studies undertaken in this thesis on the synthesis of silicon oxide nanostructures directly from silicon substrate will help in the synthesis of metal silicides (with high electrical conductivity and oxidation resistance) as promising candidates for electrochemical applications.

6.2.2. MnO Nanostructures on Silicon and Carbon Paper Substrates

The obtained MnO nanostructures are expected to have great applications including magnetic field applications, catalyst and electrochemical applications such as fuel cells. However, some details of synthesis processes of these nanostructures are not very clear and further analysis is required.

(1) Detailed HRTEM analysis of morphology and composition of the manganese oxide nanowires to determine the location of gold catalyst.

(2) Characterization of manganese oxide/silicon oxide composite structure and verify the synthesis mechanism of these structures.

(3) Experiments on the synthesis of manganese oxide nanostructures directly from manganese sputtered substrate for uniform manganese oxide nanostructures.

(4) Further characterization of MnO nanobelts (HRTEM and XRD).

(5) Chemical stability and corrosion resistance testing of MnO nanostructures for fuel cell applications.

(6) Electrochemical characterization of MnO nanostructures such as oxygen reduction of these structures.

(7) Fuel cell performance measurement of MnO nanostructures as catalyst supports in a membrane electrode assembly (MEA).

In addition to characterization of MnO nanostructures, these structures can be used as precursors for the synthesis other types of materials.

(1) Heat treatment of MnO nanostructures for the synthesis of other types of manganese oxides such as MnO_2 which is a promising material for Li-ion batteries.

(2) Doping various elements such as La and Sr in MnO for the synthesis of nanostructures prevoskites such as $La_{1-x}Sr_xMnO3$ for space applications.