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NOVEL SYNTHESIS TECHNIQUES

FOR NANOSTRUCTURES

By

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B.S., Shahid Beheshti University, Tehran, Iran, 2000

A Thesis

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Louisville, Kentucky

December 2004

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A Thesis approved on

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ABSTRACT

NOVEL SYNTHESIS TECHNIQUE FOR NANOSTRUCTURES

Romaneh Jalilian

December, 2004

Crystalline β -Ga₂O₃ nanowires with two distinct morphologies have been synthesized through simple physical evaporation of Te doped GaAs powder in argon atmosphere. The structure of the nanowires was characterized by SEM, TEM, XRD, EDX, and Raman spectroscopy. Nanowires as long as hundreds of micrometers with diameters in the range of 20-200 nm have been produced with a high yield. Absence of Tellurium in the nanowires indicates that the growth mechanism is not VLS based. The role of Tellurium in the growth process is not clear. Substitution of sulfur in place of tellurium resulted in similar nanostructures. One of the morphologies of the nanowires exhibits herringbone structure and the TEM images show hexagonal crystallites ordered in regular spacing along the nanowire axis. The crystal plane of the nanowire is parallel to one of the facets of the crystallite. The other morphology is essentially platelets and free of hexagonal crystallites.

Laser assisted catalyst growth process has been employed to synthesize various semiconducting nanowires, heterostructural nanowires and single walled carbon nanotubes. Structural characterization and physical properties of individual nanostructures have been explored.

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CHAPTER I

INTRODUCTION

Nanoscience and Nanotechnology

Nanophase and nanostructured materials have attracted a great deal of interest due to their potential applications in different areas such as electronics, optics, catalysis, ceramics, magnetic data storage, and nanocomposites. The unique properties of nanomaterials are determined by their size, surface structures, interparticle interaction and surface to volume ratio.

Nanomaterials are classified into 1) Nanostructured materials, such as nanowires, nanotubes, nanowebs and thin films, and 2) Nanophase materials like nanoparticles and catalysts. To distinguish nanomaterials from bulk it is important to study the unique properties of nanomaterials and their applications in science and technology.

A parameter introduced by nanomaterials is the surface/interface to volume ratio. A high percentage of surface atoms lead to many size dependent phenomena. The finite size of the particle confines the spatial distribution of electrons and causes quantized energy levels due to small size effect. This can provide deep insight into the theory of energy transitions from discrete energy levels for fundamental elements and continuum energy levels for bulk materials. This quantum confinement has applications in semiconductors, optoelectronics and non-linear optics. Another fundamental feature of nanoscience is nucleation. Nucleation and growth are two important parameters for synthesis of thin

films and nanowires resulting in formation of crystalline particles under suitable conditions. Aggregation of these particles leads to nanocrystalline structures.

Nanomaterials have novel mechanical properties. The strength of a solid depends on its size and surface to volume ratio. In a crystalline structure strength is dependent on grain boundary sliding and energy dissipation at interfaces. By decreasing the size of the grain the hardness of the material is increased. The high surface to volume ratio determines the thermodynamic properties of the materials. A structure with less coordinated surface atoms increases the surface energy so that the diffusion of atoms happens at lower temperatures. As a result the melting temperature decreases in nanomaterials. For example, the melting temperature for bulk gold is 1063 °C, but for gold nanoparticles is about 300 °C. Semiconductor nano dots are zero dimensional quantum systems, in which carriers are confined and convert the density of states to a set of discrete quantum levels which is necessary for semiconductor laser function. In nanodevices quantum physics is substituted for classical physics and devices work based on tunneling of the electrons through potential barriers and a single electron can govern the function of a transistor, switch or memory element. The discovery of C₆₀ (Fullerene) is another new field in carbon related nanomaterials. Carbon nanotubes are concentric cylinders of graphite sheets and they appear as single cylinders called single wall carbon nanotubes (SWNT), as two concentric cylinders called double wall carbon nanotubes (DWNT), or multi concentric tubes called multi wall carbon nanotubes (MWNT). The finite dimension of carbon nanotubes and the chirality angle, which determines how the graphite sheet is rolled, result in unique electronic properties; such as ballistic quantum conductance, semiconductor junctions, and electron field emission. The structure of carbon nanotubes

leads to an extraordinary mechanical strength and high elastic strength. There are numerous applications for nanotubes related to their structure and properties. They can be added to a chain of polymer in different ways or used a fine tip for Atomic force microscopy (AFM) or scanning tunneling microscopy (STM). There are a vast number of projects in progress to apply carbon nanotubes for gas sensor or electronic devices and transistors. [1]

There are three important steps in nanotechnology; material preparation, property measurement and device fabrication. Nanomaterials such as nano particles, nanowebs, nanorods, nanowires, nanotubes and more nanostructures have been prepared and some of the nanostructures have been characterized.

Nanoparticles

Nanoparticles are currently made of a wide variety of materials. One of the new generations of materials is ceramics, which are metal oxides such as titanium, zinc, aluminum and iron oxides, as well as metal nanoparticles. Silicate nanoparticles, a kind of ceramic nanoparticle, are flakes about 1 nm thick and 100 to 1000 nm across. The nanoparticles can be incorporated into polymers during polymerization or by melt compounding. Pure metal nanoparticles can be merged into a solid by chemical reaction of a solvent and substrate; these nanoparticles create a thin layer or a film.

Mass production of nanoparticles is important in nanoelectronics, for example, insulating matrices encapsulating metallic nanoparticles exhibit nonlinear optical properties which are size dependent. Any synthesis technique for particles to be used in these applications must produce high quality, individual, nanoparticles with narrow size distributions (mono- dispersed). Spherical, high quality, nanometer sized particles can be made from a

wide variety of materials via laser ablation of micro particles (LAM). The finite volume contained within a target microparticle significantly increases the importance of the breakdown-induced shock wave in nanoparticle formation [2]. The nanoparticles can be obtained via other methods of laser ablation for example in an aqueous solution [3].(Fig.1) There are other techniques for synthesizing nanoparticles. For example; condensation from a vapor, chemical synthesis and solid-state processes such as mechanical milling. Particles can be coated then with hydrophobic or hydrophilic material, depending on the application.

Fig.1 Gold Nanoparticles by laser ablation in aqueous solution of surfactant

The vapor condensation method involves evaporation of a solid metal followed by rapid condensation to form nanosize clusters constituting powder. To obtain metal particles only inert gas is applied, whereas a reactive oxygen atmosphere is applied for metal oxide particles. Another method of the vapor condensation technique is vacuum evaporation on running liquid. This technique utilizes a thin film of viscous material, oil, or a polymer on a rotating plate in a vacuum gauge; the material evaporates or sputters nanoparticles into a vacuum. Another possible method for vapor condensation nanoparticle synthesis is the chemical vapor deposition technique. Both liquid and gas are placed in the reactor and

the reactor is heated for a specific time depending on the desired shape of the particles. The chemical synthesis technique essentially consists of growing nanoparticles in a liquid medium composed of various reactants. This method is also used to create quantum dots. An example of the solid-state method is milling or grinding to create nanoparticles. The milling time and medium affect the resultant nanoparticles [4].

Nanotubes

Carbon nanotubes are unique nanostructures with remarkable electronic and mechanical properties. Nanotubes can behave like one-dimensional quantum wires. The structure of a nanotube is a hexagonal network of carbon atoms that has been rolled up to make a seamless cylinder. The cylinder typically has a diameter of approximately one nanometer and length of tens of microns. Each end is "capped" with half of a fullerene molecule. Single-wall nanotubes can be thought of as the fundamental cylindrical structure, and form the building blocks of both multi-wall nanotubes and ordered bundles of single-wall carbon nanotubes called ropes. Many theoretical studies have predicted the properties of single-wall nanotubes. As shown (Fig.2), three types of nanotubes are possible, called "armchair", "zigzag" and "chiral" nanotubes, depending on how the two-dimensional graphene sheet is "rolled up".

Fig.2 It is shown here a (5, 5) armchair nanotube (Top), a (9, 0) zigzag nanotube (middle) and a (10, 5) chiral nanotube. The diameter of the nanotubes depends on the values of n and m .

The diameter and the chiral angle of the nanotube have been measured with scanning tunneling microscopy (STM) and transmission electron microscopy (TEM). Due to small size of the nanotubes and constant thermal motion of the carbon atoms they have interesting physical properties.

Carbon nanotubes can be prepared by laser vaporization of a carbon target in a tube furnace at 1200 °C. Cobalt and nickel catalyst help the growth of the nanotubes. By use of two laser pulses 50 ns apart, growth conditions can be maintained over a large volume and for a long time. Flowing argon gas sweeps the nanotubes from the furnace to a water-cooled copper collector just outside of the furnace. The result is single wall carbon nanotubes. Recently the carbon-arc method was developed to grow similar arrays of single-wall nanotubes. In this case nanotubes are produced from an ionized carbon plasma, and the heat from the discharge generated by the plasma. At present many international collaborations are working on measuring the properties of single-wall nanotubes. The scanning electron microscopy images of these nanotubes shows ropes of diameters between 10 to 20 nm and lengths of 100 μm . These ropes were examined in a TEM, each rope was found to consist of a bundle of single-wall carbon nanotubes aligned along a single direction. The unique electronic properties of nanotubes result from quantum confinement of electrons within the nanotube. Electrons can only propagate along the nanotube axis and their wave vectors point in this direction. The resulting number of one-dimensional conduction and valence bands effectively depends on the standing waves that are set up around the circumference of the nanotube. These simple ideas can be used to calculate the dispersion relations of the one-dimensional bands.

Calculation of energy dispersion shows that one-third of small nanotubes are metallic and the rest are semiconducting. As the diameter of the nanotube increases there are more wave vectors allowed, thus the band gap decreases. Experiment shows that nanotubes of these different types are stable in pairs. So a metallic carbon nanotube, with semiconducting nanotubes surrounding it can behave like a conducting wire with an insulating shield.

Some of the interesting one-dimensional quantum effects of carbon nanotubes have been observed in Raman spectra, where lattice vibrations are introduced in the material by phonons through the inelastic scattering of light. Dispersion relations have been calculated and shows different vibrational modes coming from carbon atoms; as the nanotube diameter increases more phonon modes appear. Graphite, carbon fibers and carbon nanotubes are expected to be very strong and to resist fracture under extension. Thomas Ebbeson estimated Young's modulus of a carbon nanotube by measuring the vibrations of the free end of a nanotube that was clamped at the other end. Their estimates were consistent with the values of Young's modulus already measured for a graphene sheet. Efforts applying CNTs in electronic devices have been done, for example carbon nanotube field-effect transistors (CNFET) (Fig.3 &4); CNFET performs with

Fig.3 Schematic diagrams of the modeled, single wall carbon field effect transistor[8]

Fig.4 AFM image of CNT in a carbon-nanotube field-effect transistor (CNTFET). bridging 1 μm gap between source and drain [9]

comparable characteristics of silicon field-effect transistors. CNFETs are Schottky barrier transistors [6]. A composite of SWNT and Polyvinylcarbazole can create a light emitting diode [7]. Research on carbon nanotubes is one of the most popular fields at present and scientists are still characterizing CNTs and trying to use them to make devices. Carbon nanotubes are produced by catalyst driven synthesis by different methods; like arc discharge, Chemical Vapor Deposition (CVD), Pulse Laser Vaporization (PLV) and microwave plasma Chemical Vapor Deposition (PECVD). Catalyst samples prepared in different ways depend on catalyst support, the growth method and on the pH of the solution. Cobalt and iron were found to be essential in formation of acetylene and other carbon compounds. Iron leads to higher yield and cobalt enhances the quality of CNTs. The resulting CNTs can be SWNTs and MWNTs, grown as bundles or individually [10]. There are reports of carbon nanotubes made from silica, alumina, silicon and metals in a non-crystal structures; they are synthesized by using carbon nanotubes and porous membranes as templates, or by thin-film rolling. These nanotubes, however, are either amorphous or polycrystalline. There are reports about other types of nanotubes. For example single-crystal GaN nanotubes have been synthesized using hexagonal ZnO nanowires.

Nanowires (NW)

Development of nanotechnology and nanoscience has introduced new types of nanostructures called nanowires. NWs appear as semiconductors, carbides, nitrides, oxides, metals and metal oxides. For example GaAs, GaN, GaP, Si and Ge nanowires are semiconductor nanosize wire structures, while GeO_2 , SiO_2 and Ga_2O_3 produce oxide NWs and gold, silver and other type of metals make metallic nanowires. Due to their

small structures they have different properties than material in bulk and have many possible applications. Semiconductor nanowires, like GaAs can be used in FET or metallic NW can be used as tips for scanning tunneling microscopy. Various novel methods have been employed to create NWs.

Scientists have proposed three different approaches for NW growth; *Vapor Liquid Solid* (VLS), *Vapor-Solid* (VS), and *Solution-Liquid-Solid* (SLS) mechanisms. The principle of VLS growth is that the catalyst particle participating in the growth changes to liquid and the vapor phase atoms of the NW-base material saturates the liquid phase (Fig.5). Thus the temperature should not be less than the melting point of the catalyst. Nanowires can grow without a catalyst, for example, in GeO_2 nanowire growth. In Vapor-Solid epitaxy the vapor atoms adsorbed to the initial crystalline whisker are only temporarily adsorbed and then diffuse along the lateral surface and reach the tip of the wire to continue the growth. If the vapor atoms don't diffuse and get to the tip they evaporate again.

Fig.5 VLS mechanism of Si Nanowire synthesizes using Fe as catalyst nanoparticle

There are other ways to synthesize nanowires at lower temperatures (~around 200°C). An example is the *Solution-Liquid-Solid* (SLS) method. In this electrochemical approach, a solution containing the nanowire constituent is used with the catalyst on the electrode. The difference between SLS and VLS is, instead of a being in the vapor phase, the atoms

for nanowires growth contains in the chemical solution. The catalyst remains at the tip of the wire.

Chemical vapor deposition (CVD) applied for thin film growth has been extended to nanowire synthesis. Many types of nanowires have been grown by CVD, for example Si, Ge, GaAs and InP. The growth mechanism can be VLS or VS. In VLS growth the catalyst is attached to the tip of the wire.

Another method for nanowires synthesis is *Pulsed Laser Vaporization (PLV)*. In this technique a hot oven, a pulse laser and a vacuum system are used. This technique is also called *Laser Assisted Growth (LAG)*. The pulsed laser can be either a Nd:Yag, CO₂ or an excimer laser to vaporize the target and produce a plume while the growth mechanism can be VLS or VS. The catalyst can be on the target or on the substrate. The laser beam provides two dominant effects in laser ablation; collisional sputtering and thermal sputtering. Collisional sputtering employs the momentum transfer from the incident laser beam to the target material and thermal sputtering is the evaporation of the target by reaching a temperature higher than the melting point of the target.

Vapor Phase Evaporation has been used to synthesize metal and oxide whiskers and then extended to nanowire synthesis. The nanostructures are prepared by physical sublimation of a source material or through reduction of a variety of volatile metal halides. For example Si, Ge, GeO₂, Ga₂O₃, GaSe can be synthesized using vapor phase evaporation. The reactor gets heated up and the evaporated or reduced atoms transport in the vapor phase toward the lower temperature gradient and nucleation happen in a random thermal or concentration fluctuation. In Table1 the growth of some nanowires is summarized (there are more possible growth methods for some of these nanowires).

Electrochemical Deposition or *Template Approach* is a production method of metallic nanowires synthesis. The synthesis is based on electrochemical deposition on a porous membrane (e.g. polycarbonate membrane). The pores of the membrane get filled with the nanowires so the next step is lift-off and etching of the membrane to release the nanowires [12].

Another remarkable method for nanowires synthesis is *Oxide Assisted Growth (OAG)*. It is a VLS growth using no metal catalyst. Oxygen plays an important role in nucleation and growth of nanowires. The OAG technique allows large quantities of pure nanowires to be produced [13].

Types of	Growth conditions				Average D of NWs
	Source Materials (at%)	Temp	Atmosphere	Pressure(Torr)	
Si	Si (95) + Fe (5)	1200	Ar	100	~12
	Zn (50) + Se (50)	800	Ar + H ₂	200	60
	Ga	1000	Ar + H ₂	100	20~90
SiO ₂	Si (10) + SiO ₂ (85)+Fe	1250	Ar	150	~ 15
	Ge + Fe	900	Ar	150	15 ~ 80
	Ga + SiO ₂	350	Ar + H ₂	100	60
ZnO	Zn + Se	200	Ar + H ₂	200	40

Table1

The nanowire diameter ranged from 5 nm to 500 nm depending on the material and the length varies between 1 μm to 100 μm . The morphology of NWs can be crystalline, poly

crystalline and amorphous. Semiconductor nanowires can be made from one element, for example from group IV (Si, Ge) or it can be a multi compound, for example binary group III - V (GaAs, GaP, InAs and InP), binary group II - VI (ZnS, ZnSe, CdS and CdSe) on ternary III - V (GaAs/P, InAs/P) [14]. Superlattice nanostructures in the form of *heterostructures* have been synthesized from group III - V and group VI in a uniform, crystalline structure.

The results of the VLS growth process for synthesizing varieties of semiconductor nanowires depend on the Pseudobinary phase diagram of the reactant chemicals (Fig.6). The percentage of the catalyst to the material is thereby defined. For example for GaAs laser assisted growth using Au as the catalyst, it is revealed that the atomic percentage of GaAs to Au should be $(\text{GaAs})_{0.95} \text{Au}_{0.05}$. Also, phase diagram helps to approximately determine the synthesis temperature range.

Fig. 6 Pseudobinary phase diagram for Au and Ga As

The resulting NWs synthesized by the LAG method can be as small as 3 nm in diameter and about 10 μm long. High resolution microscopic images from a SEM or TEM reveal that the catalyst particle is attached to the tip of the NW and Scanning Tunneling

Microscopy (STM) or Field Effect TEM (FETEM) show the crystalline structure of the nanowires and the uniformity of the atoms in the structure. (Fig.7)

Super-lattice nanowires are essentially heterostructures of two types of semiconducting crystalline structures. Composition of modulated superlattices of GaAs/GaP nanowires

Fig.7 (a) Low resolution TEM image of GaAs Nanowires, the catalyst particle is attached to the tip of the NW, (b) FETEM image of the crystalline structure of GaAs Nanowire growth by VLS method

have been synthesized (Fig.8). Furthermore, In As/InP, n-Si/p-Si nanowires and n-InP/p-InP have been synthesized. The growth happens by alternating the vaporization between two different materials and changing the vapor-phase reactant material in a specific period of time. These novel structures composed of nanowires can have unique photonic and electronic properties and the potential applications includes nanosize LEDs and nano-barcode.

Fig.8 (a)GaAs/GaP nanowire TEM image and the diffraction pattern (b),(c),(d) and (e) EDS result for NW , the border of the chemicals is very clear and sharp

There are other types of nanostructures such as nanoribbons, nanorods and nanobelts, which are subgroups of nanowires and we will be covering later in chapter III.

Nucleation

Nucleation is an important concept in the growth process to produce new particles from solution. There are three kinds of nucleation; homogenous nucleation, heterogeneous nucleation, and secondary nucleation.

Homogenous nucleation happens in the absence of a solid-phase. The “Lamer’s Model” describes the nucleation process of sulfur sols and can be applied to other chemicals as well. In this model, when a solution gets supersaturated a new phase nucleates out of it. The particles grow by molecular addition and decrease the solution concentration, when the concentration drops below a critical level nucleation stops and particles continue to grow by molecular addition until reaching the equilibrium concentration of the participant species. In a short period of nucleation all particles reorganize through a self-sharpening process in which the bigger particles do not grow and the smaller ones grow faster. The particles aggregate with other particles and produce bigger particles when the solute is deposited on the solid surface.

Fig.9 Schematic of the formation of mono-dispersive spherical particles by nucleation and aggregation

In the aggregation model the primary particles grown are unaware of the presence of other particles then the particles aggregate and produce bigger particles and decrease the suspended particles in the solution. The aggregated particle grows bigger by combining with the unstable smaller particles. (Fig.9) Nucleation on the solid is heterogeneous. In the nucleation process a critical cluster is formed for a stable crystal growth.

Chemical Vapor Deposition

In chemical vapor deposition (CVD) the precursor is introduced to the reactor in the vapor phase and the molecules adsorb onto a substrate held at higher temperature. These adsorbed molecules thermally decompose or react with other gases (vapors). The grown materials can be metals, semiconductors, or ceramics and can be in amorphous, polycrystalline or crystalline form.

Thermodynamically, the CVD process requires high temperatures and low pressure. In principle, CVD consist of three steps, (1) diffusion of reactant to the growth surface through a boundary layer (2) chemical reaction on the growth surface and (3) removal of the gases produced by the reaction at the growth surface. The concept of boundary layer and diffusion resistance depends on time and distance and is defined by the mass-transfer coefficient. If the mass- flow coefficient of the reactants is less than the product, it is a kinetically controlled system, otherwise it is diffusion controlled. Diffusion mostly happens at high temperature when a homogenous nucleation occurs and kinetic effects occur at low temperature and high flow rate. Homogenous nucleation happens when the

reactor is highly heated and the reactant material is in the gas-phase and it diffuses onto the surface as small solid particles and growth occurs. The growth rate depends on the diffusion coefficient of the solid particles. Pressure is another parameter of growth rate; it does not affect the mass transfer rate but higher pressure increase reaction rate.

Chemical vapor deposition can be carried out at atmospheric or low pressures. Low pressure CVD is used to reduce the gas-phase nucleation and leads to a thin film of the desired material. Nucleation in the gas phase can lead to unwanted particles in the synthesis. However, particle formation in the gas phase can be used to synthesize nanoparticles under some special conditions. So controlling particle formation in the gas phase and controlling the pressure according to the particles' size are key steps for the growth of nanostructures.

Three different growth modes result from nucleation on a substrate. If the substrate and deposited film have a little mismatch (less than 0.2%) a layer-by-layer growth results because of the higher surface energy of the film than the substrate. But at lower film surface energy, the result is partly layers of crystalline planes and partly clusters- looking islands. At lower energy the growth looks like the clusters of material.

There are different types of CVD, for example Plasma enhanced CVD (PECVD) or Low Pressure CVD (LPCVD) or Filament CVD. A CVD apparatus consist of three parts. The precursor sources can be solid or liquid with a bubbler and a carrier gas or it can be a gas source. The gas flow is controlled with a gas flow controller. Next is a heat source like an internal resistance heater or external heater.

Physical Vapor Deposition

Deposition of films by condensation of the vapor phase is commonly called physical vapor deposition (PVD). Some examples of PVD are sputtering, electron-beam evaporation, thermal evaporation, arc-plasma deposition, pulse laser deposition and more. These techniques have been using for deposition of different layers for electronic purposes. Recently they have been used for nanostructure synthesis, especially for thin films.

Sputtering is a method used to get multilayer structures of different types of materials. The sputtering system consists of a vacuum chamber (between 1 – 100 mtorr), an inert gas supplied to the chamber and a RF or DC voltage applied between cathode and anode. The gas gets ionized, producing plasma that bombards the target with the sputtered particles. Some types of sputtering systems have a magnetron to direct the plasma to the substrate. Pulsed laser deposition is another known method for PVD which is used for thin film deposition, nanowires synthesis and more. Various materials can be deposited as thin films such as metals, semiconductors, nitrides, oxides and organic/polymer compounds. Pulsed laser deposition is a process which directs a high-power laser onto a solid target and directs the vaporized material toward the substrate in a vacuum chamber.

Laser Ablation (Pulse laser Vaporization)

The laser ablation method is a promising technique used to synthesize nanostructures mostly in the crystalline phase. Laser ablation has many advantages compared to other methods: the high energy laser beam can be operated in pulsed, continuous mode and different wavelengths of laser (depending on the laser type) may be obtained by using some simple optics. Ablation creates a large plume of evaporated material that can be a

mix of different chemicals from a multi-component target. Ablation can be controlled by the spot size, laser energy and wavelength. In Fig.10 the schematic of a laser ablation system is depicted.

Fig.10 Laser ablation system

The laser beam affects the target in three possible ways, photo thermal ablation, plasma-assisted ablation and photochemical ablation, depending on wavelength, energy and pulse duration of the laser. In the thermal process the photons' energy is absorbed by electrons in the target and converts it to an oscillating energy and increase in temperature. The target is cooled by evaporation. In the second path, plasma-assisted ablation, high peak power in the laser pulse produces plasma next to target. High-energy ionized gas bombards the target, then target atoms are heated and ejected from the target. Photochemical ablation is a quantum phenomenon. If the laser energy is of the same

order as the bonding energy of the molecules it is absorbed and stored by molecule. This leads to breaking the bonding and ejecting the material.

The physical model of laser ablation consists of a high-energy laser beam impacting the target converted to heat, and vaporizing the target. The vapor is partially ionized. This plasma condenses and produces clusters that migrate to the cool part of the reactor and are collected there. Synthesis results can be thin films, particles or wire-like structures in crystalline or amorphous structural form. [15]

Pulsed laser vaporization (PLV) is a combination of the laser ablation method and vapor-liquid-solid (VLS) growth mechanism (also called Laser Catalyst Growth, LCG) . A PLV system consists of a laser, tube furnace, vacuum pumps and gas introduction system. Fig.11 depicts a schematic of a PLV system.

Fig.11 PLV system

In this method catalytic particles play an important role in the growth mechanism. In VLS growth a liquid metal cluster or catalyst acts as the energetically favored site for absorption of gas-phase reactants. The cluster supersaturates and grows one-dimensional structure of the material. The approach results in single crystalline wirelike structures with diameters ranging 5nm-100nm and of tens of micrometers length. [16] A key feature

in VLS growth from LCG procedure is the equilibrium diagram (or Pseudobinary phase diagram), which predicts catalysts and growth conditions. Single and multi-component semiconductors, oxides and carbon nanotubes have been synthesized using the PLV method. Nanowires of the binary group III-V materials (GaAs, GaP, InAs) and binary II-VI compounds (ZnS, ZnSe, CdS) have been produced [17]. Fig.12.a shows silicon nanowires grown by the LAG method, using a KrF excimer laser and target of SiC/ SiO₂ [18].

Fig.12 Laser assisted growth result of Si nanowires

Transmission Electron Microscopy (TEM)

TEM is a powerful technique for structure characterization with real space imaging and resolution of 1 Å and can provide quantitative information as well as chemical analysis. . The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. What you can see with a light microscope is limited by the wavelength of light. TEM uses electrons as the light source and their much shorter wavelength provides resolution of thousand times better than that with a light microscope. The electron transmits through the sample and reveals the finest structures. Electrons have advantages as do X-ray, because they can be focused easily and are more flexible for imaging. In high-resolution transmission electron microscopy

(HRTEM) the phase of the diffracted electron wave is preserved and interferes with the phase of the transmitted wave. An electron gun at the top of the microscope emits electrons that travel through vacuum in the column of the microscope. Instead of glass lenses focusing the light in a microscope, the TEM uses electromagnetic lenses to focus the electrons into a very thin beam. The electron beam then travels through the specimen. Depending on the density of the material present, some of the electrons are scattered and disappear. At the bottom of the microscope the unscattered electrons hit a fluorescent screen, which gives rise to a "shadow image" of the specimen with its different parts displayed in varied darkness according to their flux density [19]. A schematic of a TEM is shown in Fig.13.

Fig.13 Schematic of optical and Imaging of the TEM system

TEM operate based on electron scattering. The electron beam illuminates a thin specimen and according to the atom-electron interaction, different features happen which can be measured. High-energy electrons (~ 20 KeV) impact single atoms elastically or inelastically. Elastic scattering conveys the image and inelastic interaction results in X-ray or Auger electron emission which can give additional information. The electron beam is converged and controlled by electromagnetic lenses. The image can be recorded on

film or CCD detector. Fig.14.b shows some images taken by TEM [20]. High resolution TEM images are good for studying crystalline features in a material, determining the defects in a crystal, imaging the atomic arrangement at interfaces and investigating the crystalline arrangement of an unknown material.

Fig.14 TEM image of some dispersive Boron NWs. (a) the corresponding SAED pattern of the arrowed boron nanowire. (b) HRTEM image of the arrowed boron nanowires

Selective area diffraction (SAD) is another feature used in TEM. The region of interest is determined by imaging the specimen and a SAD aperture is used to image only that region. A diffraction pattern of elastically scattered electrons appears on the viewing screen. Convergent beam electron diffraction is an enhanced mode of SAD, which confines the electrons zoned area to approximately two nanometers for nano-diffraction. The result appears as bright spots for crystals and eccentric bright rings for poly-crystals. The separation of diffraction spots on the viewing screen determines the interplanar spacing of the crystal. Fig.14.a shows a SAD pattern for boron nanowires.

Scanning Electron Microscopy

Scanning electron microscopy is another technique used for imaging small structures. In the SEM, the image is formed by a very converged and high-energy electron beam, which is focused on the surface of the specimen. The beam is scanned over the specimen in a series of lines and frames called a raster. The raster movement is accomplished by means of small coils of wire carrying the controlling current, causing electromagnetic deflection. A schematic drawing of an electron microscope is shown in Fig.15. The specimen is bombarded with electrons over a very small area. The electrons may be elastically reflected from the specimen, with no loss of energy. They may be absorbed by the specimen producing secondary electrons of very low energy, together with X- rays. They may be absorbed and give rise to the emission of visible light (an effect known as cathodoluminescence). And they may give rise to electric currents within the specimen. All these effects can be used to produce an image. By far the most common, however, is image formation by means of the low-energy secondary electrons [21].

Fig.1.15 Schematic drawing of a scanning electron microscope

equally applicable to elastically scattered electrons, X-rays, or photons of visible light -

except that the detection systems are different in each case. Secondary electron imaging is the most common because it can be used with almost any conducting specimen. X-ray analysis equipment as a bolt-on accessory is possible as well. A Secondary electron is an electron that is weakly bound to the sample and is ejected with at most tens of electron volts and can travel a short distance through the material (less than 100 Å), Therefore

Fig.15 Scanning electron microscope schematic

secondary electrons come from near the surface and they are highly interesting for surface topography, being more likely to emerge from the peaks rather than valleys.

X-Ray Powder Diffraction

A conventional x-ray tube consists of a vacuum tube diode (Mo, Co, Cu, Fe...) and a high voltage filament for energetic electron emission used to excite the material for powerful x-ray production [22]. The emitted x-ray is characterized as a $K\alpha$ x-ray for transition of electrons from shell $L \rightarrow K$ and $K\beta$ for transition from $M \rightarrow K$ shell, (x-ray

emission happens when an energetic electron impacts the material and excites inner shell electrons, then outer shell relax and fill the vacancy, releasing an x-ray), (Fig.16).

In a diffraction experiment, the incident wavelength must be comparable to the spacing between the atoms. Bragg's law (Eq.1) explains the diffraction pattern and predicts the lattice spacing of incoming waves to two crystalline planes in sequence, with lattice

Fig.16 Schematic of x-ray emission in K_α and K_β mode in an atom

spacing d , incident angle θ and x-ray wavelength λ .

$$2d \sin \theta = n\lambda \quad (\text{Eq. 1})$$

The interference pattern of the scattered beams is detected. The diffraction pattern from a material contains many distinct peaks, each corresponding to a different interplanar spacing d , which varies according to the particular crystalline structure. In XRD data a constructive interference pattern forms a corresponding peak (Fig.17). The intensity of the peak varies for different interplanar spacing and each diffraction angle has corresponding Miller indices (hkl).

There are many individual crystals of random orientation in a XRD sample, so all possible Bragg's diffractions can be observed in the powder pattern. For simple crystals, it is usually possible to guess the structure from XRD books; more complicated XRD systems require use of computer to investigate the structures. If the material has a composition of more than one crystalline phase, it can be indexed using phase diagram handbooks. Strain effects in the crystals can shift the x-ray diffraction peaks, and these shifts can be calculated. A distribution of strain and inhomogeneous chemical composition causes broadening of the peaks [19].

Fig.17 XRD spectrum for GaAs nanowires[23].

Energy Dispersive X-ray spectroscopy

Inelastic high-energy electron scattering can cause the emission of x-rays from the specimen, which is called energy dispersive x-ray spectroscopy (EDS). EDS is a chemical microanalysis technique performed in conjunction with SEM or TEM, with microscopes fitted with an x-ray detector and photo-multiplier. When the sample is bombarded with electron beam, electrons are ejected from the core level of the atom and leave a vacancy. Electrons from higher shells fill the electron vacancy and release x-rays.

The EDS x-ray detector measures the number of emitted x-ray versus their energy. The x-ray energy characterizes the emitting element, (Fig.18).

X-ray detection of elements from beryllium to uranium is possible, with an accuracy of 0.1 weight percent. The electron beam scans the selected area and x-rays are detected for discrete positions along the line, which is called a line profile analysis. It is possible to map the elemental distribution at a specific area; the map is recorded using image density.

Fig.18 TEM image of the end of GaAs nanowires (the dark part at tip of wire is gold as catalyst) and EDS spectrum for two white spots on the image [25]

Raman Spectroscopy

Raman spectroscopy is used to study vibrational, rotational, electronic, and other frequency phonon modes in a material. It relies on inelastic scattering of an optical phonon from the lattice structure of the material and creates or annihilates optical photons. Usually a monochromatic laser in the visible, UV or IR range illuminates the sample, resulting in emission or absorption of a phonon shifting the frequency of the

outgoing laser beam. The shift in energy gives information about the phonon modes in the system; a phonon is the quantized vibration in a crystal structure. The Raman scattering is weak and it is important to separate it from the laser scattered light. The spectrometer of a Raman system consists of a holographic diffraction grating and multiple dispersion stage to obtain a high rejection of the laser.

A photo-multiplier (PMT) or a CCD detector detects the scattered photons. In (Fig.19) the principle of Raman spectroscopy is shown.

Fig.19 Raman scattering

The photons are scattered by the emission or absorption of phonons, shifting photon energy which is measured by the interferometric technique. One phonon contributes to the scattering of a photon and changes the photon frequency to $\omega_s(k)$. The process is called “Brillouin scattering” when the photon emitted or absorbed is acoustic, and Raman scattering when it is optical. The Raman signal gives information on the population of a given phonon mode in the ratio between the Stokes (down-shifted) intensity and anti-Stokes (up-shifted) intensity. When a photon is scattered elastically from a molecular

system and the emitted photon has the same wavelength as the absorbing photon it is called “Rayleigh” scattering. In Raman scattering the energy of the incident and scattered photons are different. The energy of the scattered radiation is less than the incident radiation for the “Stokes” line and the energy of the scattered radiation is more than the incident radiation for the “anti-Stokes” line (Fig.20) The intensity of anti-stokes scattering is much less than stokes.

Fig.20 (a) Raman excitation (b) Stokes and anti-stokes and Rayleigh Radiation

CHAPTER II

EXPERIMENT

Synthesis

In this chapter two different synthesis methods and the growth result will be discussed. CVD and PLV are the approaches that have been tried for growth of various structures of different materials in the lab. The growth process is very sensitive so small changes of any parameter can produce a new type of nanostructure. Following are details of the experimental methods and results:

Design and set-up of the chemical vapor deposition system

As mentioned in “chapter I”, a chemical vapor deposition is a versatile way of producing nanostructures. The body of the CVD consists of four parts; the reactant chemical inlet, reactor, furnace and exhaust. The chemical was introduced in gas phase through a valve to the five-channel mass flow controller (EDWARDS, Model 825).

Mass flow controller is a combination of flow transducer and flow controller, which measures the mass flow rate of the gas flowing through the hose and controls the gas flow with an internal servo amplifier and proportional control valve. Depending on the reacting materials, up to five gases can be mixed and introduced to the reactor simultaneously. The reactor is a quartz tube, with 3.80 cm outer diameter and 61 cm length, and is attached at both sides with QF quick connectors, which is connected to QF

flange with five swagelok gas inlet from one side and one swagelok for outlet on the other side for the exhausts. One zone tube furnace (Barnstead International, model F79300) used for heating the reactor The furnace power and the set point is controllable and provides enough flexibility of temperature ramping for any set point up to 1200 °C. The last part is the exhaust, which starts from the outlet swagelok to a tygon tube with its end immersed in a beaker of water. This provides backpressure, which helps to control the reaction pressure easier.

Fig. 21 CVD schematic

Fig. 22 CVD set up in the laboratory

The bubbles of the gas coming out of the tube into the water helps to make sure the gas is flowing with a glance. In Fig. 21 the schematic of the CVD is shown and in Fig.22 the actual set up is depicted.

CVD growth of Gallium oxide

In this section the synthesis process of gallium oxide (Ga_2O_3) using CVD system is presented. An unsuccessful attempt to grow gallium arsenide nanowires produced unique Ga_2O_3 nanostructures. This reaction was done in CVD system but by physical vapor decomposition (PVD) method.

The raw material was a GaAs n-type wafer, doped with Tellurium, (University wafer Inc.), which was ground carefully and mixed with gold (atomic percentage GaAs: Au was 0.95: 0.05). The mixture was placed in a quartz boat in the middle of the tube furnace inside the quartz reactor; argon gas was passed through the reactor during the process and the flow rate was kept at 100 sccm (standard cubic centimeters per minutes). The furnace temperature was adjusted to 900-1000 °C and heated up uniformly from room temperature. After 1-2 hours the system was cooled down. The resulting material was a white colored material around the inner walls of the quartz boat. The experiment was repeated for the n-type GaAs without gold and similar white colored wool shaped material was observed around the boat in addition to some long glass needle shaped structures sticking out of the boat. Also undoped GaAs (Aldrich, 99.99%) with/without gold was tried as initial material, interestingly it didn't grow any structure, although the same powder mixed with sulfur (with weight percent of (0.999: 0.001) has resulted in Gallium oxide synthesis (in chapter III we discuss more about the structures of the above

growth conditions). In all the trial processes discussed above, the same temperature and gas flow condition have been applied.

Design and set-up of the pulse laser vaporization system

Pulse laser vaporization is a versatile method for nanowire, nanoparticles and nanostructures synthesis. The basic function and capability of PLV has been covered in “Chapter I”. Now the design and details of the PLV system built in the lab will be described. Figure 23 shows the schematic of PLV has been designed and manufactured.

Fig.23 Schematic of Pulse laser vaporization system

The PLV has several important features and accessories as follow: high power pulse laser, optics, reactor, furnace, target holder, stepping motor, pressure controller and gas flow controller. The laser is a Q-switched Nd: Yag laser, which operates in pulse mode with two possible frequencies, 10 Hz and 20 Hz. The output beam includes the first, second and third harmonic of the laser, wavelengths of 1064 nm, 532 nm and 355 nm, separable with an optics setting (it is optional choice). Pulse width is 5-7 ns for the first

harmonic and 4-6 ns for the other harmonics. Its power is 4.6 watts for 1064 nm, 2.1 watts for 532 nm and 1.4 watts for 355 nm. The laser beam is reflected from four mirrors (purchased from RMI) to direct the beam into the converging lens and focused into the reactor toward the target. The mirrors are reflective for wavelengths between 550 nm to 1200 nm, and are transparent for the rest of the wavelengths. In Figure 24 the reflectivity versus wavelength of the mirrors is depicted. The reason for the use of four mirrors is to save space on the optical table, where PLV is mounted on.

Fig. 24 Graph of reflectivity of mirrors vs. the wavelength

The reflected beam is directed through a converging lens (RMI, convex lens) with a focal length of 76 cm (for $\lambda=1064$ nm). The lens has a high transmission coefficient for the primary and second harmonic of the laser beam.

The reactor is a 3.8 cm quartz tube concentrically mounted inside a 5.08 cm quartz tube. The inner tube resides on two half circle poco graphite pieces, purchased (Pocostore) and machined carefully to make the tubes concentric. The outer tube sits in the hinged tube furnace and connected to a stainless steel head housing a “fused silica” window. This head has provisions to a stainless steel QF flange (Kurt J. Lesker) to support a

capacitance manometer. The quartz tube is connected at the other side to a QF quick connector (Kurt. J. Lesker), which in turn connects to a QF cross with three other sides connected to gas inlet, turbo pump and to the outlet of the system (a servo-valve and a mechanical pump). This arrangement of the tubes allows the gas to uniformly heat up in the space between the outer and inner tubes before entering the inner tube, where the reaction takes place, this provides equally heated inert media and all the catalyst particles and reactant materials get heated to the same condition for more homogenous growth.

For controlling the vacuum the PLV apparatus is equipped with two pumps, a turbo pump (Edwards) is used for initial pumping of the reactor down to 0.5 torr, through a stainless steel valve. Then the turbo pump is isolated from the system by closing the angle valve and a mechanical pump is opened to the reactor through a manual valve (Kurt J. Lesker) and a servo-valve (or control valve, Edwards, model DM20). The pressure is controlled with the servo-valve, which opens the outlet according to the pressure setting at the pressure controller box (Edward, model 1501C) and the pressure monitored with a capacitance manometer (Edward, model 600 Barocel). In this configuration the servo-valve is placed downstream on the system, which is a better way to control the pressure of the reactor while some gas is flowing and the pump is operating through the servo-valve down stream. The servo-valve is a solenoid controlled compact device.

The fluidic part of the PLV system is a mass flow controller (MKS, model 1179A), which transport gas from the source through a small manual gas valve and the 1/4 inch stainless steel tubing to one side of the QF cross that has been discussed before. The mass flow controller is connected to a controller (MKS, type 247), which can access four different channels and set the flow rate with an accuracy of 0.1 sccm.

The furnace is a one-zone furnace (Barnstead International, model 97300), equipped with a programmable temperature controller. It can be programmed for three ramps, ramping to the first set point and dwell time and second ramping (which in our experiment is usually cooling down to room temperature).

The converging lens is mounted to a support on the top of a stepping motor (Velmex, Inc. Series MA2500) and (VXM) controller, and operated via computer with “Lab View”. The reason for use of the stepping motor is to raster the laser beam on the target. Since the laser spot is very sharp after focusing with the converging lens (0.5 mm^2), for easy penetration. In order to have more material ablated, it is better to scan the target horizontally and vertically.

The target holder is a poco graphite piece (Pocostore, 10381 AXM-5Q ground plate 0.63 cm) machined according to the size of the target; it is made of two similar pieces with four legs to sit inside the inner tube reactor and screwed with molybdenum screws and nuts (molybdenum has a higher melting temperature than the PLV temperature).

Fig.25 Schematic of graphite target holder

The schematic of target holder is shown at Figure 25. The pcco graphite is a high temperature material especially in inert media. The target is a mixture of reactant materials, sometimes mixed with catalyst, pressed in a stainless steel pellet maker with a diameter of 1.27 cm (Fig.26.b). It has two cartridge heaters to heat up the powders mixture, and a thermocouple to read the temperature. The heaters and the thermocouple are connected to a temperature controller (Eurotherm controls, model 808/847), which is programmable for set point, ramp rate, and dwell times for two segments.

In Figure 26 a picture of the PLV apparatus is shown and its accessories and details.

Fig.26 (a) PLV set up in the lab in the lab (b) pellet maker (c) target

PLV growth of some nanowires

Several successful syntheses have been accomplished with PLV. The advantage of this method is that the growth procedure is very clean and the nanowires or nanotubes are relatively pure and long. For all growth procedures in our experiments the laser beam was

maintained at 10 Hz frequency and consisted of the first and second harmonic ($\lambda=1064$ nm and 532 nm).

GaAs nanowires were grown by PLV; GaAs powder (Aldrich, 99.99%) was mixed with gold powder (Alfa Aesar, spherical, 0.8-1.5 micron) with atomic percentage of GaAs: Au (0.95:0.05), uniformly mixed, and hot pressed in the stainless steel pellet maker at a hydraulic presser of 6000 psi and temperature of 200 °C for about five hours, then cooled to room temperature resulting a coin shape pellet (Fig.27 shows the figure of the target holder). Then the target was placed in the target holder inside the inner tube at the focal point of the lens, and the system evacuated down a pressure of at most 0.5 torr with the turbo pump. Then the valve was opened and flow was started, while controlling the flow by means of mass flow controller at flow rate of 100 sccm.

Fig.27 POCO graphite target holder target holder

The pressure controller was set up for 300 torr with the servo-valve in auto mode for automatic pressure control according to the set point (Notice that the second pump, mechanical pump, was pumping through the servo valve). While the inert gas was flowing, the furnace was slowly heated at a rate of 10 °C/min high as 950 °C, and maintained at that temperature for 4 hours and then cooled down to room temperature (10°C/min).

When the furnace temperature reached 900-950 °C, the laser and the stepping motor were turned on. The stepping motor used in the lab sweeps only in the x-direction (horizontally); so the knob on the adjusting frame of the reflecting mirror was used to manually scan the beam in y-direction (vertically). The laser was turned off before the furnace started to cool. Essentially PLV produces plasma of GaAs and LAG and VLS growth methods result in nanowires/nanotubes synthesis. After the system was cooled down, gray- black ashes were observed around the inner tube outside of the furnace, where it was cool enough for nanowires to collect on. More information about the growth result will be presented in chapter III. It is important to accurately scan only the target area but not the graphite holder to avoid too much carbon residue on the collected materials.

GaP nanowires have been grown under similar conditions. GaP crystalline pieces (Aldrich, 99.99%0 were ground and mixed with gold powders (Alfa Aesar, spherical 0.8-1.5 micron) with atomic percentage GaP: Au (0.95:0.05). Then the mixture of powders was loaded in the pellet maker and heated up to 200 °C. The target was then attached to the target holder inside the reactor and the furnace was heated up to 850-950 °C at a ramp rate of 15 °C while the argon gas was flowing, and held at that temperature for 3 hours. The pressure was kept at 300 torr and the flow was 50 sccm. Material collected at the cold part of the inner tube had a light brown color. (More information in chapter III)

Silicon nanowires were synthesized using flat pieces of silicon, and gold/iron nanoparticles (catalyst), and deposited on a silicon wafer substrate. By immersing the Si substrate in iron solution (iron nitride, $\text{Fe}(\text{NO}_3)_3$) and then washing with hexane the iron particles replaced with some atoms on the substrate. To obtain gold nanoparticles the

substrate was immersed in gold colloidal solution for less than a minute. The substrates with iron/gold catalyst placed in other side of the target. Argon gas was applied as an inert gas flowing at a rate of 50 sccm, and the temperature of the furnace was increased to 1200 °C. The laser ablation of the target lasted for 3 hours at this temperature. The nanowires were grown on the substrate from the catalyst particles. The growth result will be discussed more in chapter III. Also Silicon nanowires were grown using a pellet of Si mixed with Au micro particles. The pellet was a mixture of (Si:Au) with molecular ratio of (0.95:0.05), hot pressed at 200 °C for 4 hours under 5000 psi pressure. The PLV method was applied and the pressure kept at 300 torr while argon gas was flowing with rate of 100 sccm at temperature of 1200 °C for one hour. The growth was successful and nanowires were collected on the wall of the PLV quartz tube at the cool part.

Another successful attempt was heterostructure **GaAs/GaP nanowires**. The target was half GaAs and half GaP fixed in the graphite holders. The temperature was kept at 850°C. The catalysts particles used were iron/gold and the same method mentioned in last paragraph was used to disperse particles on the substrate. The stepping motor was programmed differently than in the previous case (Fig.28); the laser beam raster each half of the target for a short time (30 sec.) and then switched to the other half.

Fig.28 LabView
screenshot for scanning
the GaP/GaAs target

The growth was successful mostly from the substrate, which was at the side of the target. The flow rate was 80 sccm and pressure was 300 torr. The scanning path of the laser is shown in Fig.29.

Fig.29
Scanning path
of the laser on
GaP/GaAs
target

SWNTs were synthesized using the PLV method. The target was made of a mixture of carbon, nickel and cobalt, as transition metal catalysts. The molecular ratio of the three elements was as follow, C: Ni: Co (91%: 4.5%: 4.5%) and they were mixed thoroughly and hot pressed under 5000 psi pressure at 200 °C. The target was secured in the graphite target holder, placed in the PLV system, and heated up to 1200 °C. The pressure was kept at 500 torr with argon gas 150 sccm flow rate, and the ablation lasted for 5 hours.

CHAPTER III

CHARACTERIZATION

Results and discussion

This chapter is mainly focused on the results of nanowire synthesis including structure analysis and chemical and physical properties. Several surface science techniques were employed to ascertain the identity, shape, crystal structure and chemical composition of the synthesized material. Analysis has been done on each material with more thorough study on certain materials and less analysis on others due to unavailability of some facilities in the period of time this thesis project progressed. SEM, AFM, TEM, XRD, EDS and Raman studies on some of the samples are presented in the following sections.

Ga₂O₃ nanowires and herringbone structures

Gallium oxide synthesis was one the most interesting and unexpected experimental results achieved. PVD growth of gallium oxide covered in the last chapter, and we observed Te doped gallium arsenide powder with or without Au results in growth of Ga₂O₃. The same result was observed for undoped GaAs powder mixed with S and it is expected that the same growth would happen for the mixture of GaAs and Se (S, Te, Se belongs to group V, chalcogenide). A summary of Ga₂O₃ growth result is presented in table2.

The final growth product was a white woolly substance covering the inner side of the boat. Some crystalline needles were pointing out of the edge of the boat. Some of the

	Au	S	Nothing
GaAs /Te (doped)	Yes	NR	Yes
GaAs (undoped)	No	Yes	No

Table 2

structures were larger enough to be visible optical microscope. To see smaller structures with more details, scanning electron microscope “LEO 1430” was used. The images showed the same morphology as the big structures. Fig.30 (a, b and c) shows the images of the results for the three experimental approaches: GaAs doped with Te, undoped GaAs mixed with S and GaAs doped with Au. The growth structure slightly changed for each synthesis. However the resulting material was beta-gallium oxide for all three experiments. Presence of tellurium (a chalcogenide) in gallium arsenide results in nanowires and herringbone structures. GaAs/Te mixed with gold resulted in nanowires

Fig.30 Ga_2O_3 nanostructures,
PVD growth form (a) GaAs/Te
(b) From GaAs/S (c) GaAs/Te and Au

with smaller diameter. The nanowires produced from GaAs/Te looked like ribbons and wires from GaAs/Te and Au have a cylindrical cross section more like rods.

GaAs/S produced nanowires and herringbone structures and most of the nanowires looks like sheets and ribbons. The structures were grouped as ribbon structures with sharp edges, cylindrical needle structures with sharp tips, sheet-like structures with right angles, and herringbone structures with steps. The ribbons and needles resulting from GaAs/Te mixed with Au result in the smallest structures, ranging between 10-200 nm in diameter. The sheets and rods resulting from GaAs/S had bigger structures to about 50-500 nm.

The width of the herringbone structures was found to range from 20 to 10 μm . Fig.31.a, b and c shows the ribbons, sheet and herringbone structures of gallium oxide.

Fig.31 Ga₂O₃ (a) ribbons, (b) sheets and (c) herringbone structures

The growth mechanism was assumed to be physical evaporation of Te doped GaAs powder. Ga get oxide with the oxygen in the reactor after decomposition, and arsenide leaves the reactor, and Te and S promote the reaction.

Fig.32.b shows the selective area diffraction (SAD) of nanowires (ribbons and sheets). The diffraction pattern reveals a single crystalline structure for Ga_2O_3 . The high resolution TEM (HRTEM) image of nanowires, Fig.32.a, shows that the structure has a rectangular shape with 50 nm width and very small thickness.

Fig.32 Ga_2O_3 nanoribbons (a) HRTEM image (b) SAD pattern

Fig.33.a shows a HRTEM image of the herringbone structure of gallium oxide and it exhibits some hexagonal crystalline facets located in the middle of the structure, with similar sequential spacing. The rest of the nanostructure was a single crystal, and the crystalline planes were grown parallel to two edges of the hexagon facet. In the HRTEM images, the hexagons look darker than the rest of the structure which indicates for different crystallinity of them. Measurement of the interplanar spacing of the herringbone

structure (the bright and dark regions of structure, shown in Fig.33.b) was done and the spacing for the hexagonal region was found to be about 0.58 Å and for the rest of the structure about 0.29 Å.

The SAD pattern, Fig.33.a, shows the crystallinity of the herringbone structure. In this pattern two of the closest neighbors to the central spot were indexed, ($\bar{2}02$) and (002). Using these two planes and the measured lattice spacing from HRTEM image the growth

Fig.33 (a) SAD diffraction pattern of nanostructure (b) TEM image of herringbone structure (c) another HRTEM image (consider the distances of hexagons) (d) ribbons HRETM images and it shows that the ribbon is not flatten on the surface

direction was determined. The growth direction for herringbone structure made 35° with [002] direction. For this diffraction pattern the zone axis assumed to be along [010].

The electron beam spot size of the TEM was about 80 nm, so it can be seen that the diffraction resulted from both crystalline structures. According to calculation, the diffraction pattern from herringbone structure didn't show the diffracted spots from the hexagon facets. It is because hexagons are a small part of the herringbone structure.

There are some debates about the crystal growth of these structures. It has been said that tellurium didn't participate in the growth, and it was not a VLS growth; but the presence of Te is essential as seen in the experiment. Arsenide exhausted from the reaction. A critical amount of oxygen was necessary in order to form gallium oxide. The nano-sized gallium oxide structures were initiated and the growth continued depending on the condition of the growth. Lattice mismatch and disorder in nanocrystals resulted in different final structures like nanowires (nanoribbons, nanorods and nanosheets) or herringbone structures. Hexagon facets behave like the initial seeds for the growth of herringbone structures and the lattice mismatches result in growth of crystalline parallel planes and this get repeated by new seeds, as in a nucleation process.

The XRD spectrum, Fig.34, was achieved by using a "Rigaku" diffractometer with a copper- $K\alpha$ x-ray tube, $\lambda=1.54 \text{ \AA}$. The sample was a bunch of nanostructures scraped off of the white layer deposited on the quartz boat, and taped to a frame, which was placed vertically in the goniometer of the XRD system. The peaks of the spectrum identified the nanostructures as beta-gallium oxide. Beta Gallium oxide is a monoclinic crystal, with space-group $C2/m$ and lattice parameters, $a=1.2214 \text{ nm}$, $b=0.30371 \text{ nm}$, $c=0.57981 \text{ nm}$,

$\beta=103.7^\circ$, $\alpha=\gamma=90^\circ$. Each diffraction angle of the XRD spectrum belongs to a specific lattice spacing and each lattice spacing, d , represents a lattice plane.

The XRD spreadsheet data was plotted in “Igor-Pro”. Using Bragg’s law (Eq.1), d (the lattice spacing) was calculated for corresponding θ . Allowed lattice index regarding to each d for a beta- Ga_2O_3 was checked from EMS on line [26]. Finally all peaks of XRD spectrum were indexed.

Fig.34 X-ray powder diffraction of the Ga_2O_3 nanostructures

Energy dispersive x-ray spectroscopy (EDS) has been used to investigate the Ga_2O_3 nanostructures, and the resulting spectrum showed that they were composed of Ga, O and C; No trace of As, Te, S or Au has been observed for three different approaches. The atomic ratio of Ga/O was 2/3 for most of the measurement. The spectrum of Fig.35

exhibits peaks of oxygen at 0.5 KeV, gallium at 1.1, 9.3 and 10.2 KeV, and finally carbon at 0.3 KeV.

Fig.35 EDS
spectrum of
Gallium oxide
nanostructures

The EDS spectrum was acquired in the SEM system with an electron beam diameter of $1\mu\text{m}$, which meant that the detection spot included a number of ribbons and the resolution of the instrument was limited to bigger structures. However the EDS done with the TEM system has higher resolution, using a smaller electron beam spot size (80 nm). It shows the same composition of the nanostructure, Ga, O and some C. Some Cu was detected corresponding to TEM copper grid. (see Fig.36)

Fig.36 EDS spectrum
of Ga_2O_3 smaller
nanostructures taken
with TEM

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Raman spectroscopy of the gallium oxide nanostructures, Fig.37, was investigated and the result was identical with the spectrum of known gallium oxide nanostructures. Most of the peaks narrowed compared to the bulk gallium oxide Raman spectrum [23].

A Renishaw Micro-Raman “T64000” was applied to obtain the spectrum. The laser has 514.5 nm wavelength, 3 mW power, the exposure time of 900 seconds for 2 accumulations of spectrum, slit width 200 μm and 3 cm^{-1} resolution of the CCD detector. The same features have been observed in the spectrum attained with a 488 nm excitation laser (2 mW), macro Raman “HR460” spectrometer. Both data were identical with known $\beta\text{-Ga}_2\text{O}_3$ Raman spectrums. This means the structure is high-quality gallium oxide nanostructures.

Fig.37
Macro-Raman
spectroscopy of Ga_2O_3
nanoribbons, 514.5 nm
laser excitation

The AFM image, Fig.38, of the Gallium oxide nanoribbons dispersed on a substrate shows straight and rectangular structures of some ribbons. The width of the ribbons

varies between 20 nm and 2 μm , in length between 1 μm and 50 μm , and thickness of 5 nm to 50 nm.

Fig. 38 AFM image of Ga_2O_3 nanoribbons. (the scale for vertical and horizontal axis is nm)

Gallium Arsenide nanowires

Gallium Arsenide nanowires are very important binary compound semiconductor materials with many potential applications in electronics and optics. GaAs synthesis was done applying laser assisted catalyst growth (LCG) method. Gold was used as catalyst for growth and after laser ablation it changed to a cluster of nanosize gold catalytic particles. The laser ablation provides plasma of reactant material while the furnace is at the set point. At this point the VLS growth of GaAs begins.

SEM images of GaAs nanowires, Fig.39, indicated wire-shaped structures of final product on a silicon substrate. This substrate had been placed in the inner tube of the PLV system for easier collection of synthesis product. The diameter of the wires ranged between 20nm-80 nm and length varies from 1 μm to 10 μm . Most of the wires had straight structures with smooth surfaces, but some of the wires have curly structure. In both cases the catalyst was attached at the tip of the nanowires.

Fig.39 (a) GaAs collected on the silicon substrate (b) GaAs dispersed on the silicon; straight shape (c) dispersed curly nanowires of GaAs

EDS data determined, Fig.40, the composition of nanowires to be Ga and As (equal atomic ratio) with some carbon and oxygen as impurities. Because of the limit of the resolution of EDS system, the gold wasn't detected and energy Dispersive x-ray spectroscopy of the nanowires showed mainly Ga and As.

Fig.40 EDS of GaAs
nanowires

Gallium phosphate nanowires

The synthesis process explained in the previous chapter resulted in GaP nanostructure. SEM images, Fig.41, have shown nanowires of GaP. The structures looked thicker than GaAs; the reason might be because of the initial source of GaP, which was ground powder of gallium phosphate crystalline pieces. As the initial powder was ground for longer time the growth product was straighter, longer and directional, otherwise they became thicker with a curled surface [24]. The diameter of the nanowires varied between 80 nm – 300 nm and length between 5 μm - 20 μm . The growth product collected on the tube's wall. SEM images show that GaP nanowires grow out of some bigger clusters of gold and some of them grow directionally out of the clusters.

Fig.41 SEM images of GaP nanowires (a) deposited on a piece of silicon (b) dispersed on silicon

The EDS data, Fig.42, verified that the nanowires are composed of Ga and P. The wires were big enough to be characterized by EDS system. After dispersing a solution of nanowires on Si, the sample was taken to the SEM system and one wire was selected and EDS spectroscopy and mapping were done. The EDS spectrum shows the presence of Si, O, and even some Al resulting of the precursor stage.

Fig.42 EDS spectrum of GaP nanowires

The EDS mapping shows that the nanowires are pure Ga and P and the substrate is Silicon as depicted at Fig.43.

Fig.43 (a) The SEM image of GAP NW and EDS mapping of (b) Ga (c) P and (d) Si substrate with nanowires on the surface

GaP-GaAs nanowires

Attempts have been made to synthesize super-lattice nanowires composed of crystalline GaAs and GaP. The SEM images indicated that the material collected on the tube's wall was nanowires. The exact growth mechanism is ambiguous, since the catalyst particles were deposited on silicon substrate before synthesis and it was expected the growth would happen mainly on the substrate (LCG growth mechanism). But the majority of the collected nanowires were on the wall of the inner tube and fewr wires were found on the substrate (as shown in Fig.44.a and b); Thus explanation of the growth mechanism of the

wires collected on the tube's wall could be as follow; The floating catalytic particles, which separated from the substrates transported away with argon gas flow, and through VLS growth nanowires synthesized and collected on the tube's wall; or it could be an oxygen assisted growth, OAG, mechanism caused by minute amounts of oxygen leaked into the system. The synthesis succeeded for both types of catalyst particles, iron and gold; but iron catalyst seemed more promising for high yield growth on the substrate. Fig. 44 shows different structures from the three growth processes.)

Fig.44 SEM images of GaAs-GAP hetero-structures (a) collected on the walls (b) Dispersed GaP/GaAs NW on Si substrate with gold path (c) Fe as catalyst (d) Au catalyst

The nanowires grown on substrate are larger with diameter ~ 100 nm and length ~ 15 μm . The collected materials on the tube's wall have smaller structures with diameter ~ 30 nm and length ~ 5 μm . (It was hard to image clearly these small nanowires with the limited SEM resolution.

Energy dispersive x-ray spectroscopy of GaP-GaAs nanowires, Fig.45, revealed the presence of Ga, As and P as constituent elements for NWs and some C and O as impurities. The EDS data on the materials collected from tube's wall indicates more oxygen identifying the growth be OAG. It is possible to extract information about the growth mechanism, using advance TEM and EDS on a very small area of the nanostructure, but lack of time and facility made it not possible to be completed during this project).

Fig.45 EDS data of GaP/GaAs NWs

Fig.46 shows the Raman spectrum of GaAs/GaP structures taken by HR460 spectrometer with 488 nm laser excitation. The intense peak ~ 266 cm^{-1} corresponds to GaAs like peak

with a downshift. The broadened peak $\sim 355 \text{ cm}^{-1}$ corresponds to a GaP-like peak. The shoulder peak $\sim 279 \text{ cm}^{-1}$ could be due to the compound of GaAs/GaP.

Fig.46
Macro Raman
spectrum of
GaAs-GaP
NWs.

As shown in Fig.44.b, a nanowire has been dispersed on Si substrate and gold contacts were placed at both ends of it (using electron beam lithography and microfabrication), then IV measurement practiced in a probe station applying a DC voltage.

Fig.47. IV measurement of GaP/GaAs nanowires

The result of the measurement is shown at Fig.47. The sample displays a nonlinear, rectifying behavior, and strong temperature dependence.

Silicon nanowires

The experimental details of the synthesis of Si nanowires were explained in last chapter. The SEM images, Fig.48, are indicative of VLS growth with Fe or Au as catalyst particles. The growth essentially has been observed on the substrate and Ga did not act as catalyst. The Si nanowires grown with Au catalyst have diameters in the range of 20 nm-100nm and lengths in the range of 5 μm -20 μm . Si nanowires grown with Fe catalyst have larger diameters about 100-500 nm and lengths about 20 μm -200 μm . However with a closer look it shows that larger clusters of catalyst nanoparticles resulted in uncontrolled growth at some locations of the substrate. This has to be optimized in the future by uniform distribution of catalysts.

Fig.48 SEM images of Si NWs (a) with Au catalyst (b) with Fe catalyst

The other method for silicon nanowire growth, from Si and iron target (explained in chapter II), was successful and SEM images show the growth product collected from the tube's wall has many nanowires. The average diameter of these nanowires was small and they were long. Gold catalyst particles observed at the tips of wires (Fig.49).

Fig.49 SEM images of Si NWs with gold catalyst

EDS showed the composition of nanowires was mainly Si, oxygen and carbon was present as impurities. It is expected that the nanowires had an oxide layer on the surfaces since Si is very interactive with oxygen.

Single wall carbon nanotubes

The last part of this thesis is the result of PLV synthesis of SWNTs. After the synthesis process black colored materials covered the wall of the inner tube of the PLV system, and they could be scraped off easily. The material looked like some fluffy black soot.

One of the non-destructive techniques to prove the presence of SWNTs is Raman spectroscopy. Micro-Raman (Renishaw Raman microscope) was performed on several

nanotubes, with a red laser, wavelength of 632.8 nm and power of 16-17 mW. Two well separated peaks appearing $\sim 1555\text{ cm}^{-1}$ correspond to the tangential modes for metallic and semiconductor nanotubes. Low frequency modes $\sim 160\text{ cm}^{-1}$ correspond to radial breathing modes, which is radius dependent. Second order Raman peaks appear $\sim 2615\text{ cm}^{-1}$. (Fig.50)

Fig.50
Raman
spectrum of
SWNT

CHAPTER IV

CONCLUSION

Ga₂O₃ nanowires with herringbone and ribbon structures and Ga₂O₃ nanosheets were synthesized using three different methods. Te doped GaAs powder in argon inert atmosphere at 900 °C resulted in white color gallium oxide after physical vapor decomposition of GaAs and oxidation of Ga in the reactor. GaAs and Te mixed with gold powder produced gallium oxide nanostructures under similar experimental conditions. Also undoped GaAs mixed with S resulted in gallium oxide nanostructures. Ga₂O₃ nanostructures were characterized with SEM and TEM. The presence of Au reduces the diameter of the nanowires while S increases it. Some changes were observed in nanowires morphology for these methods as follow; Te/GaAs results nanoribbons, adding some Au produced nanorods and S results in sheets. Herringbone structure observed for all methods and they are unique. AFM, EDS, XRD and Raman spectroscopy were done for more chemical and physical characterization of the synthesis products.

GaAs nanowires were synthesized through VLS growth in the PLV system using Au as catalyst. The diameter of the nanowires was small ~30 nm in diameter and ~10 µm long. SEM and EDS were used to study the nanowires and provided more information.

GaP nanowires were grown in the PLV using Au as catalytic particles. Experiment showed, if the initial GaP crystalline pieces were ground for longer time, the diameter of the nanowires decreased and the length increased. SEM and EDS revealed more information about the appearance and constituent elements of the nanowires.

GaP/GaAs nanowires were synthesized by applying the pulse laser vaporization method. The structure of the nanowires was superlattice of crystalline GaP and GaAs. High resolution TEM is needed to observe the superlattice structure. Au and Fe used as catalytic particles dispersed on the Si substrate. Nanowires were grown on the substrates and the walls of the quartz tube. SEM, EDS, Raman spectroscopy were used for structure characterization. Some broadening and shifting were observed for GaAs and GaP peaks in the Raman spectroscopy result.

Si nanowires were grown using PLV, with Au and Fe catalysts. The catalysts used in two different ways; micropowder mixed with Si powder in the target, and catalyst nanoparticles were dispersed on the substrate.

SWNTs were synthesized by the vapor liquid solid (VLS) method in the PLV system. Raman spectroscopy showed peaks corresponding to tangential and radial breathing modes of metallic and semiconducting SWNTs.

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