One-Dimensional Nanostructures by Pulsed Laser Ablation

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ABSTRACT

One-dimensional (1D) nanostructures represent a unique system for investigating phenomena at the nanoscale and are also expected to play a critical role as both interconnects and functional components in the fabrication of nanoscale electronic devices. Pulsed laser can provide extremely intense energy in a small spot and it can ablate virtually any materials. Various nanostructures have been investigated and fabricated with pulsed laser ablation, and this technique is not limited by the type of materials or crystal structures. This article focuses on 1D nanostructures and presents an overview of the common growth mechanism of nanowires by pulsed laser ablation. We first introduce a general scheme of the pulsed laser ablation in a tube furnace for the nanowire growth. Subsequently, we discuss various growth mechanisms involved to generate 1D nanostructures from pulsed laser ablation, including vapor–liquid–solid growth, oxide-assistant growth, and vapor–solid growth. Defects can also play an important role and they have been observed in the nanowires from different growth processes.

KEYWORDS: Laser Ablation, Nanostructure, Nanowire, VLS, VS.

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1. INTRODUCTION

One-dimensional (1D) semiconductor nanostructures are of particular interest because of their unique role for the fundamental study as well as their potential applications in nanoscale electronic and optoelectronic devices. To date, various new techniques have been developed to grow 1D nanostructures, such as thermal chemical vapor deposition (CVD),1 molecular beam epitaxy (MBE)2 and chemical beam epitaxy (CBE).3 Among various techniques to synthesize nanomaterials, the laser ablation of solid targets is of particular interest because bulk-quantity nanowires can be readily obtained directly from solid source materials and this growth method is applicable in synthesizing nanowires containing complex chemical compositions.

Since Theodore Maiman made the first ruby laser in 1960,4 pulsed laser ablation (PLA) was soon developed and attracted wide interests because of its great potential in material processing. Pulsed laser was firstly employed for the preparation of thin films in 19655 and then for hole piercing, micro- and nanomachining, and surface cleaning.6 In the past decade, PLA has been intensively investigated for the synthesis of nanostructures. The nanomaterial synthesis with PLA can take place in two distinct conditions: one occurs in a vacuum or gaseous environment, and the other occurs in liquid. The nanomaterials from the solution normally have spherical or roughly spherical shape, except when particles aggregate into fractal structure. Spherical or roughly spherical nanomaterials have been the major materials from the vacuum or diluted gas. Interestingly, 1D nanostructures have also been discovered from laser ablation of solid materials in gaseous environment. Considering the unique property and application brought by those one-dimensional nanostructures, we will discuss different growth processes of 1D materials with PLA technique. Starting with a general description of the PLA method, we will discuss respectively the vapor–liquid–solid process, oxide-assistant growth (OAG), and vapor–solid (VS) growth, and finally conclude with a summary.

2. PULSED LASER ABLATION PROCESS

The laser ablation of solid targets is an effective technique to produce bulk-quantity nanomaterials directly from the
solid source materials, and it has been employed for the synthesis of nanostructures such as fullerenes\(^7\) and carbon nanotubes\(^8\). Pulsed laser can achieve extremely high temperature within extremely short time and it has many advantages in fabricating nanostructures. First, due to the highly intense energy of the laser spot, almost any material can be ablated for the synthesis purpose. In addition, PLA can generally allow better control over stoichiometry of the deposited materials, which will benefit the growth of complex materials. Introducing the pulsed laser into the tube furnace has enabled the growth of many high-quality nanomaterials, which cannot be easily achieved otherwise.

Nanomaterials can be synthesized with ultra-short (picosecond or femtosecond) pulse,\(^9,10\) nanosecond pulse,\(^11,12\) or even continuous-wave conditions,\(^13,14\) although the ablation process is very complicated and can be different. When the laser is focused on the solid target, the intense laser radiation can cause the materials ejection and plasma plume from the solid target. The plasma plume will eventually condense to form thin film or nanostructures. The generation, transformation, and condensation of the plasma plume play important roles in nanomaterials preparation. The nanomaterial growth is determined by both laser parameters (wavelength, pulse length, and fluence) and properties of the ambient medium that can be controlled with the furnace.

When the pulse is ultra-short, the laser energy is mainly transferred to the target instantaneously and the plasma forms right after the laser pulse. The plasma will expand without any further heating process and condense with a short life. Otherwise, the later part of the incident laser pulse continuously irradiates the plasma plume and enhances the excitation and ionization of the species in the plume. Meanwhile, it also irradiates the solid target to ablate more species into the plume. Consequently, the plume can expand further with a longer life. The interface between the ejected plasma plume and the ambient gas provides a path for possible chemical reactions and heat exchange. Plasma will cool down and condense, resulting in the nanostructures either on a substrate or in the cool ambient gas.

Figure 1 is a schematic PLA setup for the growth of nanomaterials in a tube furnace. Tube furnace can achieve well control over the growth temperature at the substrate, flowing gas type and speed, and pressure during the whole growth process. Furnace by itself can be used to grow nanomaterials through a vapor deposition process,\(^15\) while pulsed laser is another unique and localized heating source with extremely high temperature within extremely short time. The integration of PLA with furnace has been widely employed to grow different nanomaterials. PLA can allow better control over stoichiometry of the deposited materials, which will benefit the growth of complex functional materials. The solid target for the laser ablation contains the material, or component materials, for the targeting nanowires. It can also contain impurity metals as the catalyst for the VLS growth. The target is normally located in the middle of the furnace, and a substrate or collecting colder finger is adjacent to the target. Under the laser ablation, the target material will be vaporized and deposited on the substrate or colder finger. With careful control of the parameters for the laser (pulse energy, wavelength, etc.) and the parameters for the furnace (pressure, temperature, carrier gas, etc.), researcher can synthesize novel nanostructures with excellent controllability.

3. GROWTH MECHANISMS OF NANOWIRES

3.1. Vapor–Liquid–Solid Process

Since the VLS growth mechanism was proposed by Wagner and Ellis in 1964 for silicon whiskers,\(^16\) this process has been widely adopted to explain the growth of nanostructures from different methods. The impurity metal is normally induced intentionally to serve as catalyst in liquid state to define and guide the growth of nanowires.\(^17\) However, some source materials can decompose under laser ablation and form liquid droplets to serve as the catalyst assisting the growth of nanowire. Such VLS growth without impurity metal is also called self-catalytic or catalyst-free growth.\(^18,19\) The laser-assisted VLS process has produced nanowires from elementary materials (Si,\(^17\) Ge,\(^17\) and B\(^20\)), binary materials (In\(_2\)O\(_3\),\(^21\) SnO\(_2\),\(^22\) ZnO,\(^23\) SiO\(_2\),\(^24\) Zn\(_3\)P\(_2\),\(^25\) GaN,\(^26\) GaAs,\(^27\) and MgO\(^28\)), ternary materials (GaAs\(_{0.4}\)P\(_{0.4}\), InAs\(_{0.5}\)P\(_{0.5}\), CdS\(_{0.1}\)Se\(_{0.9}\),\(^29\)

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Fig. 1. Schematic setup for the nanowire growth in a tube furnace with the laser ablation of a solid target.

and indium-tin-oxide (ITO), and even more complex materials. In addition, this process has been used for impurity-doped nanowires as well as block-by-block superlattice nanowires.

The VLS growth process is schematically shown in Figure 2(a). The target is composed of mainly the source material for the targeting nanostructure (material M_{source} in the Figure 2) and a small fraction of the catalyst metal (material M_{metal} in the Figure 2). The laser ablation of the target produces the plasma plume containing mainly M_{source} with a small fraction of M_{metal}. The plume quickly cools down and liquid droplets containing M_{metal} and M_{source} start to form. The supersaturation due to the continuous addition of M_{source} into the liquid will result in the precipitation of M_{metal} and the formation of the nanowires, as shown in Figure 2(a).

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Although the exact role or chemical composition of vapor species and their interaction with the liquid droplet are not fully understood, we can still develop certain guidelines to choose the metal as well as the growth condition. The VLS growth method takes advantage of the metal catalyst in liquid state to initiate and guide the growth of the nanowire. Consequently, the selection of the metal material and the growth temperature is critical. The liquid metal should be able to dissolve the nanowire component element. At the same time, they cannot react and form more stable solid phase than the desired nanowire phase. In other words, the metal catalyst should be physically active but chemically stable, which also explains that the noble metal like Au has been successfully used for the growth of many nanomaterials. In addition, the growth condition can also be estimated with the equilibrium phase diagram for the elementary material or pseudobinary phase diagram for more complex materials, as shown schematically in Figure 2(b). For instance, the phase diagram of Si-Au takes the form shown in Figure 2(b), with M_{metal} replaced by Si and M_{source} replaced by Au. In comparison, the phase diagram for the binary and ternary materials can be very complex. However, this complexity can be significantly reduced by a pseudobinary phase diagram for the catalyst material and the targeting nanomaterial. For instance, the pseudobinary phase diagram of Au-GaAs exhibit Au-Ga-As liquid as well as GaAs solid, which will take a similar form as shown in the Figure 2(b). Both cases exhibit a region with both the liquid phase and the M_{source} (Si or GaAs)-rich solid phase. Consequently, Au can be used for the catalyst to grow Si or GaAs at the proper temperature, which is also confirmed experimentally.

Following the similar process, the metal catalyst as well as the growth temperature can be estimated for other nanomaterials with the corresponding phase diagram.

Figure 2(c) shows a ZnSe nanowire terminated with a Au particle at about 800 °C. ZnSe vapor generated by laser ablation was transported by the carrier gas and then dissolved in the Au film to form nanometer-sized liquid droplets. When the concentration of ZnSe in the droplet becomes supersaturated at the substrate temperature, ZnSe crystal will precipitate, leading to the growth of ZnSe nanowires. At the end of the growth the remaining droplet solidifies and forms a particle at the tip of the nanowire, as shown in Figure 2(c).


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nanowires are terminated with the solid catalyst, which is a common phenomenon for the nanowires from the VLS process.

3.2. Oxide-Assistant Growth Process

It’s widely accepted that metal can initiate and guide the growth of the nanowires through the VLS process. In addition, oxide has also been shown to assist the growth of nanowires, following a so-called oxide-assisted growth (OAG).40,41 OAG process is a very versatile method and has been used to grow nanowires from elemental materials (Si,42 Ge),43 binary materials (GaAs,11 GaP,11 GaN),11 and even more complex materials (yttrium–barium–copper–oxygen, YBCO).31

Metal is not necessary for OAG process and no metal droplet is observed at the tip of the nanowire either. In place of the metal catalysts, oxide materials are purposely added to the target with the material of interests. The growth of the nanowire can be significantly enhanced by the oxide. For instance, mixtures of Si and SiO2,42 GaAs and Ga2O3,44 are used for the growth Si nanowire and GaAs nanowire respectively.

The OAG process can be discussed with the growth of silicon nanowire as an example.45 Silicon oxide in the plasma plume is very important for the nucleation and growth of the nanowire. The density-functional calculations indicates the energetically favorable configurations of silicon monoxide clusters (SiO)n for n > 5 contain a sp3 Si core surrounded by a silicon oxide sheath.46 Those very reactive clusters may easily coalesce. The subsequent reconstruction and O migration from the center to the surface result in the crystalline Si core that serves as the nucleus and precursor for the Si nanowires, as shown schematically in Figure 3(a). The Silicon nucleus surrounded by silicon oxide is also confirmed with the transmission electron microscopy (TEM) image of the product at the early stage of the growth, as shown in Figure 3(c). The nanowire nuclei that having their fast growth direction ((112) for silicon in this case) normal to the substrate surface undergo faster growth and forms nanowires. Otherwise, the nucleation with undesirable orientation may stop growing or form Si nanoparticle chains due to the renucleation, as shown in the Figures 3(b) and (d).

3.3. Vapor-Solid Growth

In the absence of metal or oxide catalysts, nanowires have also been grown directly from vapor, which is normally referred as a vapor–solid (VS) process. In this process, the laser ablation of the target containing the materials of interest produces the vapor that condenses and forms the nanowire directly without any catalyst. Nanowires have been grown through VS process from elemental materials (boron),37 binary materials (ZnSe,48 ZnO,49 Al2O3),50 and more complex materials (P-doped Zn1−xMgO).51 Different nanomaterials have been proposed to follow different growth process, such as anisotropic growth, defect-induced growth (e.g., through screw dislocation), or self-catalytic growth.

Fig. 3. Nanowire growth from OAG process. (a) Schematic illustration and (c) corresponding TEM image of Si nanoparticles precipitated from the decomposition of SiO matrix. (b) Schematic illustration and (d) corresponding TEM image of the fast growth and formation of nanowire from the nanoparticles in a preferred orientation. Reprinted with permission from [45], S. T. Lee et al., J. Mater. Res. 14, 4503 (1999). © 1999, Springer.
From the similar or even the same growth condition, different nanostructures can be formed from different processes. For example, the laser ablation of ZnSe target can produce ZnSe nanowire on a Au-coated substrate through a VLS process and ZnSe nanoribbon on bare substrate surface through a VS process. Following the aforementioned VLS process, the nanowires grow from the Au particles, as indicated in Figure 2(c). In order to minimize the interface energy, ZnSe would crystallize with its (001) close-packed plane aligned with the solid-liquid interface, leading to growth along the ⟨001⟩ direction. In comparison, no particle is present in any of the ZnSe nanoribbons, whose growth can be understood in terms of vapor–solid process. The ZnSe nanoribbons tended to nucleate on the bare substrate surface and grow along ⟨120⟩ direction, as shown in Figures 4(a) and (b). The growth of ZnSe nanoribbon most likely originates from the anisotropic growth kinetics along different crystallographic directions as a result of the particular growth conditions. The growth of nanoribbons is normally related to two factors. The surface energy determines the preferential surface that will grow. The growth kinetics determines the final structure. In other words, the crystal planes with lower surface energy tend to be flat and grow larger, forming the enclosure side surfaces of the nanoribbons. The incoming molecules tend to diffuse towards the rougher growth front, resulting in the fast nanoribbon growth along this direction. This anisotropic growth may also explain the formation of many other nanomaterials. 

VS process is also proposed for the growth of amorphous boron nanowire in Figure 4(c) from laser ablation of the target, which indicates a vapor-form agent and material-transporting process. In other words, boron vapor is produced from the laser ablation and transferred with the carrier gas. Because the temperature decreases at the downstream, boron nanoclusters form and serve as the stable sites for the rapid adhesion of additional boron molecules and eventually result in the formation of boron nanowires.

4. SUMMARY

PLA can maintain a good stoichiometry of complex compositions due to its intense energy that is not available in other vapor deposition method. We reviewed the development of various laser assisted methodologies for the growth of 1D nanomaterials in the gaseous environment. The classical VLS process developed in the 1960s is still applicable to many nanowires from PLA. When the target can decompose and form liquid droplet a self-catalytic growth can happen. Oxides are found to be effective to initiate and enhance the growth through an OAG process. In the absence of liquid or oxide, nanowires can grow through a VS process, although the detailed mechanism needs further investigation. In addition, defects can also play an important role during the formation of nanowires and they have been observed in the nanowires grown from VLS process, as well as VS process. The study of the growth mechanism will extend our fundamental understanding of the phenomena in the nanoscale and provide certain prediction on developing novel nanostructures.

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References and Notes