Nanoscience and Nanotechnology (2017)

ORIGINAL RESEARCH ARTICLE

Experimental Progress of Semiconductor Nanomaterials

Weiqing Guan,Bing Han,Xiaoxia Yang

Department of Materials Engineering and Applied Chemistry, Sanya University of Science and Technology, Hainan, China

ABSTRACT

The research of semiconductor nanomaterials is the forefront of contemporary science and technology. Because of its optical nonlinearity and luminescent properties different from the bulk materials, it has great application prospect in the future optical switch, optical storage, light fast conversion and ultra-high speed processing. By arranging the commonly used low-dimensional semiconductor nanomaterials preparation methods and methods of characterization, then compare them, it can helps to open up ideas and aids for in-depth thinking. In this paper, the preparation methods of laser ablation, carbon nanotube template, molten salt, solution-liquid-solid method and template electrochemical method are introduced. The characterization method is analyzed from particle size and morphology, composition and structure analysis, surface interface analysis and several other aspects.

KEYWORDS: semiconductor nanomaterials; preparation method; characterization method;

Citation: Weiqing Guan, *et al.* Experimental Progress of Semiconductor Nanomaterials. (2017); 1(1): 6–11.

Correspondence to: Xiaoxia Yang, Department of Materials Engineering and Applied Chemistry, Sanya University of Science and Technology, Hainan, China. zxx3897113418@163.com

Nanoscience is a new scientific field that has risen and prevailed in the last century. The field of nanoscience research is a non-macroscopic middle field in which human beings have never been involved, thus opening up a new level of human understanding of the world and allowing people to transform nature directly to molecules and atomic levels. Human science and technology has entered a new era, that is, the nanotechnology era. The new technological revolution, centered on nanotechnology, will become an important research direction in the 21st century. Nano-technology mainly studies the motion laws and interactions between the material composition systems with sizes between 0.1 and 100 nm and its possible practical applications. When the bulk material is gradually refined into nano-scale particles, although the composition of the material without any change, but the performance of nanoparticles with the original block of material completely different behavior, such as surface area increases, the electronic state of particles mutations and so on, thus showing a unique volume effect, surface effect, quantum size effect and macro quantum tunneling effect, showing a special light, electricity, magnetic, thermal and chemical properties. And these unique performances not only has a wide range of applications in the information storage, optical communications, computers and sensors, metallurgy, chemical and other engineering technology [1], but also opened up some new research and application areas.

Because of its optical non-linearity and luminescent properties, the semiconductor nanomaterials have great application prospect in the future optical switch, optical storage, light fast conversion and ultra-high speed processing. In this paper, the main preparation methods and characterization methods of semiconductor nanomaterials are summarized.

1. The preparation of semiconductor nanomaterials

(A) Laser ablation

At present, in many nano-powder preparation methods, the laser used as the heat source of the preparation process due to the availability of high purity, small particle size and narrow distribution of ultra-fine powder, so occupy a particularly important position [2]. According to the different characteristics of the process, the laser preparation of nano-powder can be divided into three kinds, including the laser chemical vapor phase synthesis (LICVD), laser thermal evaporation (LTE) and laser ablation (PLA).

Laser ablation (abbreviated as PLA) preparation of nanoparticles is by the use of pulsed laser beam to target the target in the moment (<10ms) then heated to the gasification temperature and above, resulting in the target atoms, ions

and clusters of vapor plume (plumes). The latter in the course of flight with the collision of environmental gas atoms deceleration, then collide with each other, and nucleation to form nanoparticles.

Compared with other nanoparticle preparation methods, the laser ablation method has the following characteristics: (1) Using a very narrow pulse width of the YAG laser or excimer laser, the peak power is high. (2) Laser to make the target gasification time is very short, less than 10ms, more than 103 times faster than the thermal evaporation of the laser, is directly from the solid to the gaseous phase transition process. (3) Nano-powders suitable for the preparation of any solid target, including metals, ceramics, macromolecules and composites, especially for multicomponent alloys or ceramic powders, which do not result in differences in the physical properties of the nanomaterials And the target is very different. (4) Because the laser will target the explosive evaporation of atoms, ions or clusters (clusters), which can be obtained particle size less than 10nm nanoparticles. This small size particle is useful in some special applications, such as catalysts, sensitive components in gas sensors.

In January 1998, Morales and Lieber of Harvard University had reported the use of laser ablation and gas-liquid-solid growth mechanism to prepare Si and Ge single crystal nanowires.

In this method, the effect of laser ablation is to overcome the limitation of the size of the clusters in the equilibrium state, and to form a liquid-phase catalyst cluster that has a smaller diameter than the minimum size of the clusters in the equilibrium state. The size of the phase catalyst clusters defines the diameter of the linear product that is subsequently grown as a VLS mechanism.

The laser light is emitted from the laser source 1 through the lens 2 to focus on the sample 3, the sample is vaporized in the heating furnace 4, and the nanotubes are also precipitated during the transfer to the condensing device 5 , Forming a nanowire solid at the condensing unit.

Lieber et al. used Si0.9Fe0.1, Si0.9Ni0.1 and Si0.99Au0.01 as the target, and the single crystal Si nanowires with diameter of 3 - 9 nm and length of 1 - 30μm were prepared by this method. At the same time, the single crystal Ge nanowires with diameter of 3 - 9 nm and length of 1 - 30 μm were synthesized by Ge0.9Fe0.1 as the target. Now, other people have been successfully prepared GaAs, SiO2 and other substances in the nanowires by using this technology.

(B) Carbon nanotube template method

Since the discovery of carbon nanotubes in 1991 [3], carbon nanotubes has many potential application value in the future high-tech field with their unique high tensile strength, high elasticity, from metal to semiconductor electronic properties, high current load and high thermal conductivity and unique quasi-one-dimensional tubular molecular structure. It has also quickly caught the attention of scientists in the chemical, physical and materials science field.

In February 1994, the University of Arizona Department of Materials Science and Engineering students such as Zhou had used carbon nanotubes as a precursor for the first time in the flow of argon (Ar) gas protection and SiO gas under 1700 ℃ reaction, and had synthesize a solid with the length and diameter as similar with nanatube, 'needle-like' silicon carbide (SiC) whisker of an order of magnitude larger than the carbon nanotubes. The total reaction in the process is:

$$2C\ (S) + SiO\ (V) \rightarrow SiC\ (S) + CO\ (V)$$

Where S is a solid; V is the steam. It has pointed out that the solid SiC whiskers can be synthesized by the carbon nanotube precursor in the absence of gold catalyst because of the high activity of the carbon nanotubes and its geometrical configuration for the formation and growth of whiskers has a decisive role.

After a lapse of one year (March 1995), HJ Dai, a professor of chemistry at Harvard University, successfully reacted the carbon nanotubes with oxides or halides under higher vapor pressures and had successfully synthesize a diameters of 2 to 30 (TiC, SiC, NbC, Fe3C and BCx) with a length of 20 μm.

In 1997, SiC, Si3N4 and GaN nanowires were successfully prepared by carbon nanotube template method, such as Fan Shou-shan from Department of Physics in Tsinghua University, China. They had made an in-depth theoretical analysis of the formation mechanism. The most likely growth mechanism of this method is that the nano-space of the precursor carbon nanotubes provides a special environment for the gas phase chemical reaction in the above synthesis process, as well as the growth of the nuclear which provides a superior condition. The role of carbon nanotubes is like a special 'test tube', on the one hand it provides the required carbon source in the process of reaction and consumes itself, on the other hand, it provides a nucleation site, while limiting the growth direction of the product.

(C) Molten salt method

Molten salt method is a new method to prepare inorganic powder materials. It has the characteristics of low synthesis temperature, short reaction time, has simple process, high purity of synthetic products, controllable crystal shape and morphology of powder particles, showing a potential advantage in the synthesis of inorganic non-metallic materials.

(NP-9) and flux (NaCl) were used to grind the precursor again after a certain time, and then the precursor was prepared by solid-phase chemical reaction at room temperature by simple grinding. The oxide nanowires were prepared by thermally decomposing the precursors at temperature. A variety of oxide nanowires can be synthesized by this method. The method was successfully used to prepare oxide nanowires such as Mn3O4, SnO2 and NiO.

Reaction mechanism:

Grinding

A (solid) + B (solid) C (solid) (precursor nano particles) + D (solid, liquid or gas) (by-product)

Surfactant & u0026 molten salt

C (solid) (precursor nanoparticles) E (oxide nanowires) + F (gas) (by-product)

Thermal decomposition

The following method of preparing α-Al2O3 powder by molten salt method is introduced as an example.

Use the pure Al2 (SO4) 3 · 18H2O as raw material, NaCl and KCl as the composite molten salt, according to n (molten salt): n (raw material) for the four materials and mixed in the agate tank, with anhydrous ethanol as the medium ball 6 hours, mixed evenly in a vacuum oven at 80 ℃ drying. The dried powder was placed in an alumina crucible and fired separately at different temperatures. The resulting powder was cooled and washed repeatedly with deionized water until the filtrate was tested with AgNO3 without Cl-. Then, dry it in a vacuum box to obtain the desired α-Al2O3 powder.

The advantage of the molten salt method is that it does not require a certain pressure, catalyst, and excitation element. It does not require complex high temperature reaction equipment and experimental technology, and can prepare a variety of oxide (binary or multiple oxides) nanowires.

Its growth mechanism is Ostwald ripening; Ostwald ripening was discovered by Wilhelm Ostwald in 1896, a description of the solid solution in the multi-phase structure changes over time with a phenomenon. When a phase precipitates from a solid, some of the high energy factors cause large precipitates to grow and the small precipitates shrink. So that the material in the composition close to the balance of the matrix phase a desalination of the competitive growth of particles.

(D) Solution - liquid - solid (SLS) method

In order to obtain a highly crystallized semiconductor or nanowires at low temperatures, Buhro et al. had proposed the SLS method at the University of Washington, USA, and fabricated III-V nanowires such as InP, InAs and GaAs at low temperature (165 to 203 ° C) [4]. This method can be considered as a generalization of the VLS method in solution. The typical SLS preparation process is as follows: The low melting point metal (In, Sn, Bi) is dispersed as a catalyst in the solution and the component ME of the material to be prepared is produced by the decomposition of the corresponding organometallic precursor (R3M + EH3-ME + 3RH), the ME nanowires are gradually formed in the solution as the ME continuously incorporates the catalytic droplets and reaches saturation. Using a similar method, Korgel et al. had used supercritical fluids as solvents to produce single-crystal Si nanowires successfully with very uniform diameter (4.5 nm) [5].

The nanowires grown by this method are polycrystalline or nearly single crystal, and the nanowires have a wide range of sizes. Its diameter is 20 - 200 nm and length is about 10 μm. The analysis shows that the mechanism of this low temperature SLS growth method is similar to the VLS mechanism described above, and the growth process is shown in Fig. The difference with the VLS mechanism is that the raw materials required are supplied by the gas phase during the growth process according to the VLS mechanism, and the raw materials required for the growth process according to the SLS mechanism are provided from the solution.

(E) Template electrochemical method

Electrochemical deposition method is simple, cheap and fast, while most of the synthesis at room temperature, etc., it is considered to be the most ideal preparation of super-lattice nanowires and most commonly used method. The most important is that the electrochemical deposition method can precisely control the potential of each electrode [6], by controlling its potential to control the deposition of different materials, by changing the deposition time to adjust the length of each section of the super-lattice nanowires, that is, electrochemical deposition method can be a good regulation and control of the synthesis of materials. In 1987 Martin et al. By using electrochemical and template synthesis methods to combine polycarbonate filters as templates to fabricate Pt nanowire arrays successfully. Ge / Sb superlattice nanowires were prepared by electrochemical deposition method in Hefei physical solid, and Bi2Te3 / Sb superlattice nanowires were successfully prepared in the unit. The United States Yoo Research Group has prepared Bi2Te3 / (Bi0.3Sb0.7) 2Te3 superlattice nanowires [16], which can control the length of each section by controlling the deposition voltage and time.

Template electrochemical synthesis method is to select a porous material with nano-pore diameter as the cathode, the use of substances in the cathode electrochemical reduction reaction to the material into the nano-pore channel, the template wall will limit the shape and size of the synthesized material, one-dimensional nanomaterials. The flow chart is shown in Figure 1.

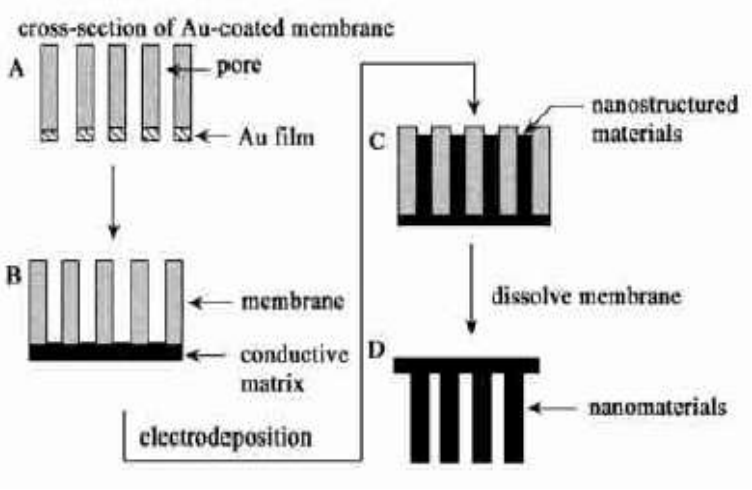

Figure 1. Flowchart of template electrochemical method

The electrochemical method opens up a new world for the preparation of nanomaterials. Compared with other methods, this method has the advantages of simple equipment, convenient operation and low energy consumption, and can obtain different shapes and sizes of nanomaterials through the pore size of the template and changing the electrochemical parameters. Furthermore, this method is widely used, and in principle, the particles deposited on the electrode can be prepared by the method of nanoparticles, and can also be used in combination with other methods. However, the electrochemical synthesis of nano-materials research methods started late, some of the reaction process mechanism is unclear. In addition, it cannot be used in large quantities of synthetic nano-materials, so we still need to study further.

Besides, there are some other methods with their own characteristics, such as ion implantation preparation III-V semiconductor nanocomposite film, co-sputtering III-V / SiO2 nanocomposite film, solid-state replacement reaction, metal organic chemical vapor deposition, molecular beam epitaxy technology, pyrolysis method, organic solvent thermal method, hydrothermal method, gel method, etc., are not described in detail here.

2. The means of characterization

(A) Particle size analysis of nanomaterials

Most of the solid materials are constructed from a variety of different shapes of particles, so the shape and size of fine particles have an important effect on the structure and properties of the material. Especially for nanomaterials, the particle size and shape play a decisive role in the properties of the material. Therefore, it is important to characterize and control the particle size and shape of nanomaterials. General solid material particle size can be expressed in terms of particle size concept.

Because the particle size distribution of the powder material is wide, it can be from nanometer to millimeter, so when the particle size of the material is described, the particles can be divided into nanoparticles, fine particles and coarse grains by size. In recent years, with the rapid development of nanoscience and technology, the particle size distribution and particle size of nanomaterials have become one of the important indexes of nanometer material characterization. The particle size distribution is mainly in the range of 1 - 500nm, 20nm between the size of the nanomaterials is the most concerned about the size range.

Microscopy is a commonly used method for the determination of particle size. Optical microscopy range of 0.8 - 150μm, less than 0.8μm must be observed with an electron microscope. Scanning electron microscopy and transmission electron microscopy are often used to directly observe the size of particles in the range of 5 m, suitable for nanomaterial size and morphology analysis. Image analysis technology is recognized as the best test technique for measuring the results and the actual size distribution due to the randomness, statistics and intuition of the measurement. The advantage is that direct observation of particle shape; you can directly observe whether the particles are reunited. The disadvantage is that the sampling representative is poor, the experimental reproducibility is poor and the measurement speed is slow. At present, the method of granularity analysis for nanomaterials is mainly laser dynamic light scattering particle size

analysis and photon correlation spectroscopy, the smallest particle size can be measured to achieve 20nm and lnm. For the particle size analysis of nanomaterials, it is necessary to distinguish between the primary particle size and the secondary particle size. (SEM), transmission electron microscopy (TEM), scanning tunneling electron microscopy (STM) and atomic force microscopy (AFM) were used to observe the particle size range of the samples, the original particle size and morphology of individual particles. As the electron microscopy is the observation of the local area, so in the analysis of particle size distribution, the need for multiple photos of the observation is obtained by software analysis of the statistical size distribution. The results of the primary particle size analysis obtained by the electron microscopy are generally difficult to represent the distribution of the actual sample particles. The secondary particle size statistical analysis method of nanometer material particle system is divided into three advanced methods according to the principle, which is the high-speed centrifugal sedimentation method, laser particle size analysis method and electric ultrasonic particle size analysis method.

(B) The morphology of nanomaterials analysis

1. The importance of morphological analysis

The morphology of the material, especially the morphology of the nanomaterials, is an important part of the material analysis. Many of the physical and chemical properties of the materials are determined by their morphological characteristics. For nanomaterials, its properties are not only related to the size of the material particles but also to the morphology of the material. Therefore, the morphological analysis of nanomaterials is an important research content of nanomaterials. The main content of the morphological analysis is to analyze the geometrical morphology of the material, the particle size of the material, the distribution of the particles and the composition and phase structure of the microstructure.

2. The main method of morphological analysis

Nano-materials commonly used morphology analysis methods are scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM) method. Scanning electron microscopy and transmission electron microscopy not only use to analyze nanomaterials, but also use to analyze the morphology of bulk materials. The information provided mainly includes the geometrical shape of the material, the dispersion state of the powder, the size of the nanoparticles, the distribution of the elements and the phase structure of the specific morphological area. Scanning electron microscopy analysis can provide morphological images from a few nanometers to millimeters. Transmission electron microscopy has a high spatial resolution, especially for powder material analysis. It is characterized by the small amount of sample used, not only able to get the sample morphology, particle size, distribution, but also able to get a specific area of the element composition and phase structure information. Transmission electron microscopy is more suitable for nano-powder sample morphology analysis, but the particle size should be less than 300 nm, otherwise the electron beam cannot penetrate. For the analysis of block samples, transmission electron microscopy generally requires thinning of the sample. The scanning tunneling microscope is mainly used for the analysis of the morphology of some special conductive solid samples, which can reach the resolution of atomic level. It is only suitable for the analysis of surface morphology and the analysis of surface atomic structure, so it is not suitable to analyze nano-powder materials. Scanning atomic force microscopy can analyze the morphology of nano-films with a resolution of several tens of nanometers, which is worse than scanning tunneling microscopy, but suitable for conductor and non-conductor samples, and is not suitable for nano-powder morphology analysis. In conclusion, these four morphological methods have their own characteristics, and the electron microscopic analysis has more advantages, but scanning tunneling microscopy and atomic force microscopy have the characteristics of in situ morphological analysis.

3. Analysis of the composition of nanomaterials

The physical properties of nanomaterials such as light, electricity, sound, heat, magnetic and so on are closely related to the chemical composition and structure of nanomaterials. Therefore, to determine the composition of nanomaterials, nanomaterials in the determination of the type and concentration of impurities, nanomaterial analysis is one of the important elements.

Analysis of nanomaterials according to the analysis object, it can be divided into two types which is the trace sample analysis and trace component analysis. Micro-sample analysis is in terms of sampling volume. The trace component analysis is based on the content of the component to be measured in the nanomaterial. Since the content of impurities or dopant is very low, as low as one part per million or even lower, the analysis is called trace component analysis. The compositional analysis method of nanomaterials is divided into body element analysis, surface composition analysis and microanalysis analysis according to the purpose of analysis.

The elemental composition of the nanomaterials and the analysis methods of their impurity components include atomic absorption, atomic emission, ICP mass spectrometry and X-ray fluorescence and diffraction analysis. The first three analytical methods need to be dissolved after the sample and then measured, therefore, they are belong to the

destructive sample analysis method, while X-ray fluorescence and diffraction analysis method can directly use on the solid sample determination, hence known as non-destructive elemental analysis

4. Structural analysis of nanomaterials

Material structure characterization method is quite large, suitable for nanomaterial structure analysis of the instrument and the new character is also emerging, such as high-resolution electron microscopy has been able to show atomic arrangement and atomic composition at atomic resolution. The tunnel scanning microscope can measure the surface and near-surface atomic arrangement and electronic structure of the material. Low-energy electron microscopy can be used to show surface defects.

With the continuous development of analytical instruments and technologies, the Institute of Nanomaterial Structures can use more and more test instruments, including high resolution transmission electron microscopy (HRTEM), scanning probe microscopy (SPM), scanning tunneling microscopy (STM), atomic force (AFM), field ion microscopy (FIM), X-ray diffracto-meter (XRD), extended X-ray absorption fine structure analyzer (ExAFs), Mossbauer spectroscopy (Ms) and Raman Scattering Wait. It can be argued that the research methods of nanostructures have almost all of the instruments involved in all material structural analysis tests.

5. Surface and interface analysis of nanomaterials

The surface and interface analysis of solid materials has been developed as an important part of nano-thin film materials research, especially for elemental chemical analysis of elements, three-dimensional analysis of elements and micro-area analysis. At present, commonly used surface and interface analysis methods are X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), static secondary ion mass spectrometry (SIMS) and ion scattering spectroscopy (ISS). XPS accounted for 50% of the entire surface composition analysis, AES accounted for 4O% while SIMS accounted for 8%. In these surface and interface analysis methods, XPS is the most widely used. It is suitable for the analysis of various materials, especially for the analysis of chemical state of materials, more suitable for the field of chemical information related to the study.

At present, the commercial surface analysis shows the highest vacuum level of spectrometer is up to 1O-8Pa. X-ray photoelectron spectrometer and Auger electron spectrometer must be used in ultra-high vacuum system, mainly for two reasons. First, XPS and AES are surface analysis technology. Secondly, if the analysis room of the vacuum is poor, the cleaning surface may be covered by residual gas in the vacuum in a very short time. It is impossible to obtain real surface information without super high vacuum conditions.

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