Controlled growth of antimony based nanostructured materials by chemical vapor deposition

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CONTROLLED GROWTH OF ANTIMONY BASED
NANOSTRUCTURED MATERIALS BY
CHEMICAL VAPOR DEPOSITION**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Sb-based materials have attracted intense attention for a wide range of applications. As demonstrated, Sb-based nanomaterials can achieve enhanced performance, especially in thermoelectric and lithium ion batteries[1-3]. Thus, the controlled growth of Sb based nanomaterials is a major concern in this research field. The attempt of this work was to fabricate Sb-based nanomaterials with tunable sizes by the catalyst-free chemical vapor deposition approach. The study of their growth mechanisms and the effect of growth parameters revealed the effectiveness of this method to prepare nanostructures with controllable sizes. Further measurements on the properties of the as-grown Sb based nanomaterials were conducted to verify the structure-performance relationship.

At first, regarding that elements Sb and Te have similar melting points and boiling points, the fabrication of Sb_2Te_3 nanomaterial through a catalyst-free chemical vapor deposition technique was presented. The obtained Sb_2Te_3 nanoparticle thin films followed the island growth mechanism. By changing the substrate distance, Sb_2Te_3 samples varied from micron-sized plates to ~10 nm nanoparticles, which was due to the large difference in substrate temperatures and concentration of precursors.

Besides the nanoparticle thin film growth, the catalyst-free chemical vapor deposition could also be applied in the nanowire growth. Based on the consideration that In of low melting point could act as a catalyst during the process to induce one-dimensional growth, the self-catalyzed chemical vapor deposition growth of InSb

nanowires was introduced. The vapor-liquid-solid growth process of InSb nanowires was discussed in detail.

Due to the difficulty caused by the large condensation temperature gradient between Sb and Cu, it was of special interest to extend the catalyst-free CVD process in growing Cu-Sb alloys. By using copper foils as substrates and the Cu source, Cu-Sb nanostructures were prepared. Simply controlling the substrate distances, Sb-Cu alloy nanostructures, e.g. $\text{Cu}_{11}\text{Sb}_3$ nanowires, Cu_2Sb nanoparticles, or pure Sb nanoplates, were obtained. Such growth strategy could be extended to other Sb alloys, e.g. Co-Sb, Fe-Sb.

After fabrication, the property measurement of the as-grown samples was carried out. The as-prepared Sb_2Te_3 nanoparticle thin film samples showed 100-150% higher Seebeck coefficients and 100-400% lower thermal conductivities as compared with those of bulk Sb_2Te_3 with similar charge carrier concentration. The maximum power factor of above $1.1 \times 10^{-3} \text{ W/mK}^2$ was realized in the annealed 20-nm Sb_2Te_3 particle film. The InSb nanowires and the Cu_2Sb nanoparticle thin film had discharging capacities of ~280 and 278 mAh/g after 50 cycles with 100% and 50% enhancement, as compared with the same materials prepared by other methods. The improved cyclability and reversibility shown in the InSb nanowires and the Cu_2Sb nanoparticle thin film was due to the enhanced bonding between active materials and current collectors by the CVD growth. All these results demonstrated that CVD was a promising route to achieve Sb based nanomaterials with enhanced properties.

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Chapter 1 Introduction

1.1 Background and motivation

Sb-based materials have attracted attention for a wide range of applications, such as InSb in infrared image[4], CoSb₃[5, 6] and Zn₄Sb₃[7] as good thermoelectric materials, Fe₂Sb[8] and Mn₂Sb[9] in magnetic field. Besides these applications, Sb-based alloys are also promising anode materials in lithium ion batteries [10-13]. As demonstrated, Sb-based materials with desired shapes and nano-dimension can achieve enhanced performance in thermoelectric and lithium ion battery as compared with bulk materials[1-3, 14]. Thus, the synthesis of Sb-based nanomaterials is the main concern of the work.

As Sb₂Te₃, InSb and Cu-Sb alloys are synthesized in this work, the fabrication of these materials through different approaches, e.g. electrochemical deposition[12, 15], chemical reduction route[16, 17], ball milling[18, 19], and pulsed laser deposition (PLD)[20] is reviewed. For Sb₂Te₃, different morphologies, such as nanosheets[21], nanoplates[22], nanoforks[23] and nanobelts[24] were synthesized through the solvothermal or hydrothermal method with the assistant of surfactants. The growth of Sb₂Te₃ nanowires was reported through the Au-induced CVD process[25] and the electrochemical deposition using anodic aluminum oxide (AAO) templates[26]. Sb₂Te₃ thin films were prepared by electrochemical deposition[27] and other methods[28]. Gonvalve et al. reported the thermal co-evaporation of Sb₂Te₃ polycrystalline thin films with 1 μm thick under a high vacuum [29]. Fan et al. used

ion beam sputtering deposition to prepare Sb_2Te_3 with easily controlling composition at a high deposition rate[30]. For InSb, most of the reported nanowires were fabricated through the vapor-liquid-solid growth[31-33]. Au evaporated on Si substrates was used as the catalyst to incur the nanowire growth. By changing the size of Au catalyst, the diameter of InSb nanowires could be varied. The ultra thin InSb nanowires with diameter of 4.5 nm were reported[34]. Electrochemical deposition[35] was also applied in the InSb nanowires growth via AAO templates. For Cu-Sb, the study on the preparation of nanomaterials was less than that of Sb_2Te_3 and InSb. It has been reported that Cu_2Sb nanoparticles were synthesized by ball milling[36] and the solution route[16] and that Cu_2Sb thin films were prepared by PLD[20] and electrochemical deposition[12].

These approaches mentioned above have their advantages and disadvantages. Electrochemical deposition is able to synthesize nanowire arrays through AAO templates, but the removal of AAO templates before sample testing is required [37]. The thin film samples can also be synthesized by electrochemical deposition and need to be dried in the vacuum to avoid the absorption of water and oxygen on the surface. For chemical reduction process, the production of Sb and Sb-based alloys with controlled sizes remains a great challenge. Since Sb has high diffusivity and low surface energy [38, 39], it is difficult to control the particle size without effective functional groups to prohibit continuous growth, which in the end leads to the non-uniform size and agglomeration. Ball milling can not control the particle size and agglomeration always occurs during the process. PLD is preferred in growing thin

film samples. Although this method is convenient and the quality of the films is relatively good, the production cost is high due to its requirement of high vacuum.

As a result, CVD approach is a good alternative to grow Sb based nanomaterials with controlled morphologies and sizes. Right now only Au catalyzed Sb based nanowires through CVD growth have been reported [14, 25]. Considering the high cost of Au and the contamination effect of foreign catalysts, the catalyst-free CVD growth is more preferable. Hence, it is of great meaning to study the growth of Sb-based nanomaterials through the non-catalyst chemical vapor deposition and to investigate the effect of experimental parameters on sizes and compositions. Additionally, the samples obtained through this method can be directly used for further property measurements without any treatment.

So far, there is no report on the catalyst-free CVD growth of Sb based nanomaterials. The innovation of the project is to use the non-catalyst CVD method to fabricate Sb based nanostructures. Sb_2Te_3 thin films with different particle sizes can be obtained by changing the substrate distance. InSb nanowires are grown with In itself acting as the catalyst. The growth of Cu-Sb nanostructures is achieved by using Cu foils as substrates and the Cu source. The as-prepared samples through such growth can be directly used for property measurement. The good adhesion between samples and substrates, the small particle size as well as good electrical conductivities contribute to the enhancement of performance in thermoelectric and lithium ion batteries.

1.2 Objectives

The objective of this work is to grow Sb-based nanomaterials, particularly Sb_2Te_3 , InSb and Cu_2Sb by the catalyst-free chemical vapor deposition. The morphologies, sizes and compositions of these three materials are controlled under different growth conditions. On the other hand, investigation on the dependence of morphology and phase on different reaction parameters is conducted to provide insight into the growth mechanism of the as-prepared samples.

Firstly, nanostructured Sb_2Te_3 , a traditional thermoelectric material is grown via a CVD synthetic route and the systematic study of the CVD mechanistic growth of Sb_2Te_3 nanoparticle thin films is conducted. The effect of flow rate and substrate temperature is studied to achieve the right composition and the smaller particle size. To demonstrate the possibility of catalyst-free CVD growth of nanowires, the next work focuses on the self-catalyzed VLS growth of InSb nanowires due to the consideration that In is a low melting point metal and can act as catalyst during growth. Both the growth mechanism of InSb nanowires and the effect of different growth parameters on morphologies and sizes are investigated. Besides Sb_2Te_3 and InSb , the growth of Cu_2Sb by chemical vapor deposition has not yet been reported due to the high melting point and boiling point of Cu . Thus, attempt is made on performing CVD growth of Cu-Sb intermetallic compound by using Cu foil as both the substrate and Cu source. The formation mechanisms of Cu-Sb intermetallic compounds with different morphologies and compositions are studied. In addition, the effect of different growth parameters, such as substrate temperature, surface roughness of Cu foils and flow rate

of the carrier gas on the structures and morphologies of Cu-Sb intermetallic compounds is discussed in depth.

1.3 Organization of the thesis

The thesis is composed of 8 chapters. The present chapter, Chapter 1 introduces the motivation, objectives and organization of the thesis.

In Chapter 2, the introduction of CVD route and the thermoelectric and lithium ion battery applications are covered. The literature review on the fundamental study of chemical vapor deposition process includes the typical growth process of traditional chemical vapor deposition, introduction of different types of chemical vapor deposition developed in recent years, control step during process as well as the growth mechanisms of whiskers and thin films.

Chapter 3 provides the experimental procedures of the CVD growth of Sb-based compounds. The set up of CVD system, growth parameters as well as techniques used in determining material structures, thermoelectric properties and electrochemical properties are presented in details.

Chapter 4 presents the fabrication of assembled Sb_2Te_3 nanoparticle films by a simple vapor transport process without the assistance of any catalyst. The island growth mode was proposed to explain the growth mechanism of Sb_2Te_3 nanoparticle. The size of the Sb_2Te_3 particles can be tuned by varying the growth parameters, i.e., the Ar/ H_2 flow rate and the substrate temperature/substrate position.

Chapter 5 presents the self-catalyzed chemical vapor deposition growth of InSb nanowires. The growth process follows self-catalyzed vapor-liquid-solid growth

mechanism. To optimize the morphology and phase of InSb, various parameters such as substrates, heating temperatures, flow rates and substrate temperatures are studied to achieve stoichiometric InSb nanowires with desired size.

In Chapter 6, catalyst-free chemical vapor deposition process to fabricate Cu-Sb nanostructures, e.g. $\text{Cu}_{11}\text{Sb}_3$ nanowires or Cu_2Sb nanoparticles thin film is introduced. The vapor-solid growth mechanism and island growth mode are proposed to describe the growth process of $\text{Cu}_{11}\text{Sb}_3$ nanowires and Cu_2Sb nanoparticles thin film, respectively. The morphologies, phases and sizes of the nanostructures could be controlled through the variation of substrate distance, surface roughness of substrate and Ar/H₂ gas flow rate.

Chapter 7 provides the performance of as-grown Sb based nanomaterials, e.g. the thermoelectric properties of Sb_2Te_3 nanoparticle films, electrochemical properties of InSb nanowires and Cu_2Sb nanoparticle thin film. The size effect on the performance is investigated.

In Chapter 8, a summary of the whole project and some recommendations for continuous work based on present topic are presented.

Chapter 2 Literature Review

2.1 Application of Sb based materials

In the twenty-first century, energy challenge is undoubtedly an urgent matter in the world. In response to the depleting non-renewable energy, such as coal and petroleum, it is essential to study the systems of energy conversion and storage. Regarding the huge amount of waste heat produced every year, converting waste heat to electricity through thermoelectric devices provides a good approach to reuse the waste heat. The produced energy need to be stored in devices for satisfying the usage in daily lives. Lithium ion battery, with the highest energy density and the smallest size among batteries, occupies a large part of the energy storage market. To fulfill the daily usage, devices of energy conversion and storage are of rapid development, but still not completely meet the needs. Therefore, improving the performance of devices is the key concern of the research, which depends on the properties of materials composing devices.

Sb-based materials have attracted attention for their wide range of applications, such as InSb in the infrared image[4], CoSb₃[5, 6] and Zn₄Sb₃[7] as good thermoelectric materials, Fe₂Sb[8] and Mn₂Sb[9] in the magnetic field. Besides these applications, Sb-based alloys are also promising anode materials in lithium ion batteries [10-13]. In this work, as-grown Sb-based nanomaterials are considered to be applied in thermoelectric and lithium ion battery regarding their unique properties.

The basic introduction of thermoelectric and lithium ion battery will be given in the following part.

2.1.1 Thermoelectric materials

(1) Introduction of Thermoelectric (TE) phenomena

When two sides of any isolated conducting material have a temperature gradient, mobile charge carriers tend to diffuse from the hot side to the cold side and then the different concentration of charge carriers at two sides causes an electrical potential inside the material. Such phenomenon is known as the Seebeck effect. Recovery of waste heat through the Seebeck effect is a promising approach to generate electricity. The realization of a high-efficiency thermoelectric (TE) module for solid state energy conversion requires the development of TE semiconductors with high figure of merit ZT [40], a dimensionless factor expressed as

$$ZT = (S^2\sigma/\kappa) T \quad (2.1)$$

where T is the temperature in Kelvin, S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity.

In order to maximize ZT , materials with high values of the Seebeck coefficient S and the electrical conductivity σ , and a low value of the thermal conductivity κ are ideal for the thermoelectric application. Three parameters (S , σ and κ) are all as a function of the carrier concentration (n). However, effects of the carrier concentration on these three parameters are different as shown in the following equations.

The electrical conductivity is expressed as

$$\sigma = ne\mu, \quad (2.2)$$

where μ is the carrier mobility and e is the electron charge. Indicated from equation 2.2, the electrical conductivity is proportional to the charge carrier concentration.

The Seebeck coefficient can be expressed as

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (2.3)$$

where n is the charge carrier concentration, m^* is the effective mass of the charge carrier, and k_B is the Boltzmann constant. The equation 2.3 shows that the Seebeck coefficient is inversely proportional to the charge carrier concentration.

From the equation 2.4a, the thermal conductivity consists of two sources: (1) charge carrier transporting and (2) phonons travelling through lattice. The lattice contribution K_l is related with the properties of the material lattice, which is independent of the carrier concentration. The part of charge carrier contribution K_e depends on the electrical conductivity according to the equation 2.4b.

$$K = K_e + K_l, \quad (2.4a)$$

$$K_e = LT\sigma = ne\mu LT, \quad (2.4b)$$

where, L is the Lorenz number, equal to $2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$. As the K_e is proportional to the charge carrier concentration, the total thermal conductivity will increase with the raising of the charge carrier concentration.

The variation of figure-of-merit ZT , Seebeck coefficient α , electrical conductivity σ , and total thermal conductivity κ values as the function of the carrier concentration is shown in Fig. 2-1[41]. It is noted that the highest ZT value can be achieved when the carrier concentration is in the range of 10^{19} cm^{-3} and 10^{20} cm^{-3} .

Figure 2-1. Dependence of figure-of-merit ZT , Seebeck coefficient, electrical conductivity, and thermal conductivity on carrier concentration[41].

(2) Thermoelectric materials

Among all TE semiconductors, Bi_2Te_3 , Sb_2Te_3 and their alloys have been extensively studied due to their high ZT values in the temperature range of 300~500 K [42-44]. Group-IV telluride-based materials, such as PbTe and SnTe , are often used in

the mid-temperature (500~900K). Si and Ge alloys with various atomic ratios are applied in high-temperature thermoelectric generators. Shown in Fig.2-2[45], the state-of-art bulk materials reported have maximum ZT values around 1.7. The nano or doped materials have higher ZT values, which are still less than 3. As shown in Fig. 2-3, only thermoelectric generators with ZT value of 4 or above are comparable to other commercialized energy generators[46]. Therefore, the aim of the research in the thermoelectric area is to improve the ZT value.

Figure 2-2. ZT value of state-of-art materials as function of temperature[45].

Figure 2-3. Efficiency of best practice engines compared with an optimistic thermoelectric estimate[46].

To present, several methods have been proposed to achieve higher ZT values. One is to explore new materials with complex structures[41, 47]. Thallium-based TE materials such as Ag_9TlTe_5 [48] have high ZT values because of their low lattice thermal conductivities. Zintl compounds such as $\text{Yb}_{11}\text{MnSb}_{11}$ [49] and $\text{Ca}_x\text{Yb}_{1-x}\text{Zn}_2\text{Sb}_2$ [50] have complex structures in which two different sub-structures perform different functions. The phonon-glass region, used to house dopants, can reduce the lattice contribution. The electron crystal regions are thin enough to induce the quantum confinement effect for the enhancement of Seebeck coefficient. Although the quantum confinement effect also causes the reduction of the electrical conductivity, the power factor $S^2\sigma$ is still slightly increased. The second approach is to fabricate nanostructured semiconductors[51-54]. With the sizes of nanostructured

semiconductors smaller or comparable to their de Broglie wavelength, the quantum size effect can be incurred[55], leading to the increasing density of state (DOS) near the Fermi level and the enhancement of S [56, 57]. In addition, the increased interfaces and surfaces scatter phonons and charge carriers, leading to the reduced thermal conductivity and electrical conductivity [41, 44, 56-58]. With the enhanced Seebeck coefficient and the decreased thermal conductivity and electrical conductivity, the net ZT value is increased. Such nanoscale approach has been proved by the 2D $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices[43] and 1D Si nanowires[56]. Other approaches are introducing dopants or defects into the matrix[47, 59]. Dopants can change DOS near the Fermi level and then enhance the Seebeck coefficient. Defects can effectively scatter phonons, which results in decreasing thermal conductivity and increasing the net ZT value.

2.1.2 Anode materials for lithium ion battery

(1) Introduction of lithium ion batteries

Lithium ion battery is a kind of commercial rechargeable batteries used in our daily life. Compared with other batteries (see Fig.2-4), e.g. lead-acid battery and Ni-Cd battery, lithium ion battery has the higher energy density (210 Wh/kg or 560 Wh/dm⁻³) and the lower self-discharge rate (about 5% or less per month), so it is popularly used in commercial small portable devices. In addition, lithium ion battery with the flexible shape and size is easier to be fitted into different devices. These unique properties make lithium ion battery applicable in a variety of electronic devices, such as notebooks, mobile phones and electric vehicles. Therefore, in these years,

lithium ion battery dominates the battery market and the demand is expected to grow in the future.

Figure 2-4. Comparison of gravimetric and volumetric energy density between the rechargeable batteries[13].

The basic components of lithium ion battery are shown in Fig 2-5. There are negative electrode (anode), positive electrode (cathode), electrolyte, separator and current collectors inside a typical lithium ion battery.

Figure 2-5. Schematic structure of a typical rechargeable lithium ion battery[13].

i. Electrodes

Anode and cathode are very important components in lithium ion batteries. In a battery system, the electrode material containing Li and having the higher positive standard reduction potential (normally > 3.0 V) is regarded as cathode. The other electrode with the relatively low positive standard reduction potential (average value: 0.0-1.0 V) is referred as anode. During charging, Li atoms are extruded from the cathode material and intercalated to the anode material. This behavior can not occur automatically, which requires energy from the external system to activate the reaction. Therefore, the electrical energy is transferred to the chemical energy in the charge process and then stored inside the electrode materials. Reversely, Li ions are extracted from the anode material during discharging with the chemical energy consumed and transferred to the electrical energy.

To find out whether a material is suitable as an electrode, the high theoretical capacity is the first concern. During the chemical reaction, the total amount of charge Q can be expressed by the equation:

$$Q = znF \quad (2.4)$$

where n is the number of moles of the electrode material (assumed as a single component) consumed in the chemical reaction, z is the number of electrons produced when 1 mole of the electrode material is consumed, and F is the Faraday constant, 96500 C/mol. As Q is the total electricity produced during charging or discharging and m is the total mass of the electrode material involved in the reaction, the specific capacity C can be expressed as:

$$C = Q/m = zF/M \quad (2.6)$$

where M is the molecular weight of the electrode material.

Besides the high theoretical capacity, the high operating voltage is also favored, which equals the theoretical standard cell voltage minus the lost voltage caused by the overpotential and the resistance inside the battery. As the internal resistance of the battery is partly contributed from the resistance of electrode materials, well conducting of electrode materials are required. The theoretical standard cell voltage can be expressed by the equation:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad (2.7)$$

where E_{cathode} and E_{anode} are the standard electrode potential of cathode and anode materials, respectively. From the equation 2.7, it is better to choose cathode material with higher standard electrode potential and anode material with lower standard electrode potential to obtain higher operating voltage.

ii. Electrolyte

The electrolyte in lithium ion battery should have good stability and ion conductivity in the working environment as well as the desired potential range. The potential range should be larger than the working voltage window of lithium ion battery. Now the commercially available electrolyte in lithium ion battery is a mixture of ethylene carbonate (EC)-dimethylcarbonate (DMC) that contains LiPF_6 . The advantages of this electrolyte are the good electrochemical stability and ionic conductivity (10 mS/cm).

iii. Separator

The separator used in lithium ion battery is an electrical insulator that can physically separate anode and cathode to prevent the internal short-circuit of the battery. The separator membrane is only permeable for Li ions while electrons are not allowed to pass through the insulating separator in the charge and discharge processes. The driving force for the diffusion of Li ions inside the electrolyte is the concentration gradient of Li ions between two sides of the separator.

iv. Current collector

The current collector serves as a conductor to ensure the electric contact between the battery system and the external circuit. The current collectors for anode and cathode materials are different, usually aluminum foils for cathode and copper foils for anode.

(2) Types of anode materials in lithium ion batteries

In commercial lithium ion batteries, graphite serves as the anode materials. Although graphite was suggested as the anode material in 1973, it was commercialized in the battery system in 1990. Graphite has the excellent reversible insertion capability, thermodynamic stability and compatibility with the electrolyte. In addition, carbon is naturally abundant, so the production cost is low. However, the theoretic capacity and volumetric capacity of graphite are relatively low, which are 372 mAh/g and 820 mAh/cm³ respectively. The lower packing density of graphite results in the low energy density of cell. Besides, the state-of-the-art graphite anode still poses some safety issues. As seen from Table 2-1, the potential of Carbon vs. Li is about 0.05 V. Although carbon is safer than Li, the safety issue still exists as the

precipitation of Li dendrite on the anode surface remains unsolved. Continuous growth of dendrites may impale the separator and subsequently cause the direct electrical contact between anode and cathode. Therefore, non-carbon-based anode materials with slightly higher potentials, such as Si, Sn and Sb are considered as the alternatives.

Table 2-1. Comparison of different anode materials in the theoretical specific capacity, charge density, volume change and onset potential [60].

Materials	Li	C	Si	Sn	Sb
Density (g/cm^3)	0.53	2.25	2.33	7.29	6.7
Lithiated phase	Li	LiC_6	$\text{Li}_{4.4}\text{Si}$	$\text{Li}_{4.4}\text{Sn}$	Li_3Sb
Theoretical specific capacity (mAh g^{-1})	3862	372	4200	994	660
Theoretical charge density (mAh cm^{-3})	2047	837	9786	7246	4422
Volume change (%)	100	12	320	260	200
Potential vs. Li (~V)	0	0.05	0.4	0.6	0.9

Compared with graphite, Si, Sn and Sb based anode materials have higher energy capacities and are safer to use. Nevertheless, the large volume change ($> 200\%$) arising from Li trapping in the host during cycling leads to the severe cracking and pulverization. The accompanied loss of active materials and the decreased electrical conductivity are the main cause of their poor cycling performance. The high irreversible capacity at the initial cycle and the low cycle life limit the commercialization of these materials. One desirable approach is to develop nanostructured materials[61-64]. The large specific surface area of nanomaterials

provides larger electrode-electrolyte contact area, which causes the higher charge/discharge rate. The nanomaterials have superplasticity due to their small sizes, leading to better accommodation of volume expansion during the lithium insertion. Additionally, the smaller size attributes to the shorter diffusion path distance for electrons and Li ions[63]. The above advantages contribute to the good cyclability and reversibility of nanomaterials in lithium ion batteries.

2.2 Chemical vapor deposition process

It has been demonstrated that Sb-based materials synthesized with nano-dimension can achieve enhanced performance in thermoelectric and lithium ion batteries [1-3]. The fabrication of nanostructured Sb-based materials is the major concern of the research. In this work, Sb-based nanomaterials with controlled phases and sizes are fabricated by the catalyst-free chemical vapor deposition method. The detailed information of the CVD process will be introduced in the following.

2.2.1 Introduction

Chemical vapor deposition, like other techniques, is developed to meet the industrial requirements. For example, the production of materials with high purity and coating films on insulating substrates of large areas are not easy by using traditional methods before the invention of CVD. The first report on CVD was the deposition of the high melting point metal W by using WCl_6 as the precursor in 1855[65]. Nowadays, CVD has been widely used in the purification process, the thin film coating as well as the fabrication of single crystals and polycrystalline materials including oxides, sulfides, and group III-V compounds.

In a typical CVD process, a chemical reaction occurs among precursors in the gas phase and then the thin film product is deposited on a solid substrate material. A detailed CVD process is shown in Figure 2-6. The following are the main steps. (1) The initiation of volatile precursors by the thermal energy from the surrounding environment. (2) The gaseous reactants are transported to the solid substrates by the carrier gas and then adsorbed on the surface. (3) The chemical reaction occurs during the transportation and deposition. (4) The solid product is obtained on the substrate, while the gaseous by-products diffuse to the surrounding medium and then are exhausted by the pump.

Figure 2-6. Sequence of a typical chemical vapor deposition growth process[66].

As a manufacturing technique, CVD has the following advantages:

(1) The solidification processes of CVD, simply driven by reactions are different from other techniques used for thin film coating. During the deposition, the film is condensed on the substrate with smooth surface as the formation of product at the atomic level. In addition, the occurring chemical reaction leads to the strong bonding

between the adatom and the substrate. Thus, the coating film is not easy to peel off the substrate.

(2) CVD shows the excellent performance in coating uneven and irregular substrates. Unlike physical vapor deposition (PVD), which is a line of sight process, the CVD process guarantees each point of the substrate contacting with the precursor gas and the deposition rate is not various with different locating distances. Thus, CVD can effectively produce homogeneous thickness films.

(3) The crystal structures, compositions and morphologies of samples are controllable in the CVD process by changing the experimental parameters, such as the flow rate and the substrate temperature. The flow rate can influence the residence time of precursors. The increased residence time by decreasing flow rate may accelerate the particle growth rate, so samples with larger sizes are expected at a low flow rate. The substrate temperature is related with the energy providing for the occurring of chemical reactions. Appropriate substrate temperature ensures the formation of desirable materials. Additionally, the low diffusion rate of adatoms at the low substrate temperature may greatly decelerate the growth process.

(4) There is a wide range of choice in the chemical precursors for CVD. Unlike the sputtering machine requiring metal targets with high purity, only some of the elements are used in CVD, which have the high vapor pressure at the relatively low temperature. For those elements with high melting point and boiling point, halides, nitrides and organo-metallic compounds are considered as precursors. As a result, the deposition temperature is relatively low compared with those of pure elements, which

makes CVD an effective manufacturing technique for the fabrication of refractory materials.

(5) CVD system usually works in a medium vacuum. Compared with some other techniques, e.g. PVD, which require ultra high vacuum, CVD equipment is relatively simple and of low-cost.

Although the CVD process has many advantages, four criteria have to be satisfied to obtain the desired product. (1) At the heating temperature, the vapor pressure of reactants should be high enough to guarantee the formation of desired products at a certain deposition rate. (2) The by-products should be volatile to prevent the impurity remaining inside the products. (3) The deposited product and substrate should have low vapor pressure at the substrate temperature, which permits the solidification process and the production of samples with desired compositions. (4) The safety issue should be seriously considered as sometimes the chemical precursors used in the CVD system are quite toxic, corrosive and explosive.

2.2.2 Variation of chemical vapor deposition

The CVD process can be divided into low pressure CVD, plasma enhanced CVD, laser enhanced CVD and metal organic CVD due to their characteristics. The following is the introduction of each process.

(1) Low pressure CVD (LPCVD)

For LPCVD (shown in Fig. 2-7), the process is conducted under the low pressure rather than the atmospheric pressure. Materials are easier to evaporate under low pressure, so the reaction can occur at lower temperature. In addition, the low pressure environment induces the increased diffusion constant, which leads to the

enhanced diffusion of gas reactants and by-products. As a result, the fast deposition and growth rates can be achieved at the low pressure condition.

Although the reaction temperature can be lowered in the low pressure condition, LPCVD has its limitation in the growth of materials with higher formation energies. Thus, plasma and laser are introduced into the CVD system, which utilizes the plasma and laser energy to excite the movement of atoms and decrease the reaction temperature. Another process, metal organic CVD is also used to solve this problem, due to much lower boiling points of metal organic precursors.

Figure 2-7. Schematic of typical LPCVD setup[67].

(2) Metal organic CVD (MOCVD)

Metal organic CVD uses metal organic materials as precursors, which is different from the normal CVD. A typical MOCVD setup is shown in Fig. 2-8. The metal organic precursors should meet three requirements: (1) stable at room temperature and easily synthesized (2) of the high vapor pressure at the low temperature (3) with easy removed by-products. Hence, MOCVD shows pros and cons in precursors compared with the normal CVD. During the deposition, there is no etching effect on the substrate and the deposition rate can be controlled by diluting the metal organic vapor. Because of the lower activation energies of chemical reactions, the lower substrate temperature is enough for the formation of products, as compared with the normal CVD. However, vapors of many metal organic compounds are toxic and flammable and hence, are difficult to prepare, store and use. Therefore, the usage of MOCVD is sometimes confined due to the safety reason and the high production cost.

Figure 2-8. Schematic of typical MOCVD setup[67].

(3) Laser assisted CVD and plasma-enhanced CVD (PECVD)

The conventional CVD and MOCVD use the thermal energy to initiate the chemical reaction during the deposition process, so it requires the moderate and even high substrate temperature to guarantee a certain growth rate. When the substrate temperature is low, the growth rate is slow as it is limited by the kinetics of chemical reactions. Owing to this limitation, laser-assisted CVD and plasma enhanced CVD, developed from normal thermal CVD, which use the electrical energy to activate the

precursor molecules and enhance the deposition rate under a low substrate temperature. In spite of that, the thermal activation process still play an important part in both laser-assisted CVD and plasma-enhanced CVD, and electrical energy can be regarded as a supplement to lower the activation energies of chemical reactions.

Laser-assisted CVD, as shown in Fig.2-9, uses a focused laser beam to scan across the substrate surface and then provides energy for the growth of samples. The most efficient way of using laser energy is to maintain the temperature increment on the substrate surface without changing the temperature of the surrounding gas and the inner part of the substrate. Thus, the wavelength of the laser beam has to be carefully selected to prevent the adsorption and reflection of laser from the substrate as well as the surrounding gas. As the laser scanning area is selective, this unique property permits the growth of rods, nanowires and thin films with designed patterns.

Figure 2-9. Schematic of a laser-assisted CVD setup[67].

In the PECVD (see Fig. 2-10), plasma can (1) ionize the gas molecules with high chemical potentials, which will decrease the reaction temperature, (2) increase the diffusion and the deposition rate of reactants, (3) enhance the adsorption of precursors on the substrate by lowering bonding energies of particles. Due to the merits of plasma, PECVD has the following advantages.

- i. The reaction temperature is low, e.g. 573-623 K.
- ii. The film obtained from PECVD has the uniform composition, less inside stress and pores, and strong adsorption.
- iii. PECVD can be used in the different substrates and deposited materials without considering the lattice misfit.

Figure 2-10. Schematic of a PECVD setup[67].

2.2.3 Reaction rate and rate controlling step

The deposition of chemical reactants during the CVD process includes 5 steps.

(1) The chemical vapor is transported to the upper atmosphere of the substrate with the formation of the boundary layer due to the gas concentration gradient. The boundary layer is a layer region where the reactant gas velocity decreases from the bulk gas flow rate to zero (at the substrate surface). (2) The reactant vapor diffuses through the boundary layer and then reaches the substrate surface. (3) The reactant adatoms are adsorbed on the substrate, which changes the surface energy of the substrate. (4) The chemical reaction occurs among reactants, such as the decomposition of the reactant and the recombination reaction. (5) The by-products, if there are any, evaporate and then diffuse through the boundary layer. The removal of by-products is very important in CVD process, as the by-products will form impurity, non-uniform coating and even crack in the film product. The rates of above steps are different, so the deposition rate, or the growth rate, are determined by the slowest step among the above 5 steps. Usually, step 2 or step 4 is the rate determining step.

(1) The reaction is controlled by the surface reaction kinetics (step 4).

The reaction rate increases with the increased substrate temperature, until the substrate temperature reaches to a certain value, indicated from the Arrhenius equation

2.8:

$$k = Ae^{-E_a/RT} \quad (2.8)$$

where k is the reaction rate constant, A is the pre-exponential constant in the Arrhenius equation, E_a is the activation energy of the reaction, R is the universal gas constant, T is the temperature..

(2) The reaction is controlled by the diffusion rate (step 2).

When the reaction temperature is higher than a critical point, the reaction rate is no longer the slowest step and then the CVD process is under the diffusion control. In the boundary layer, the driving force for the gas diffusion is the difference of the gas concentration. With the thinner boundary layer, the duration of the diffusion step can be shortened, which enhances the growth rate.

According to the fluid mechanics, the precursor gas inside the tube is transported to the substrate surface by the laminar gas flow. Reynolds number R_e , a dimensionless parameter is used to characterize the laminar gas flow during the CVD process. The thickness of boundary layer δ is related to R_e from the equation 2.9.

$$\delta = \frac{4.91x}{\sqrt{R_e}} \quad (2.9)$$

where x is the distance between the substrate and the inlet of the tube. As the gas flows in a tube, the Reynolds number can be expressed by the equation 2.10:

$$R_e = \frac{QD_H}{Av} \quad (2.10)$$

where, D_H is the inner diameter of the tube, Q is the volumetric flow rate, A is the cross-sectional area of the tube, ν is the kinematic viscosity. For a certain CVD process, the size of the tube is constant, so only the flow rate is variable. With increasing flow rate, the thickness of the boundary layer decreases, and the CVD reaction rate can be increased.

The other parameter affecting the diffusion step is the diffusion coefficient of the precursor in the transporting gas. Empirically, diffusion coefficients are generally proportional to the inverse of the pressure, indicating that the diffusion coefficient increases with decreasing the chamber pressure below the atmospheric value[65]. Thus, with the chamber pressure decreasing from the atmosphere to intermediate pressure, the diffusion coefficient increases. However, the diffusion rate is still not fast enough. At that condition, the growth rate is controlled by the gas diffusion and the reaction kinetics. When the pressure is below 1Torr, the large enhancement of the diffusion coefficient leads to the disappearance of the boundary layer and then the reaction kinetics become the dominant process.

2.2.4 Whisker growth mechanism

(1) Vapor liquid solid (VLS) growth

In 1964, Wagner and Ellis first suggested the vapor-liquid-solid (VLS) growth to explain the Si nanowires growth process[68]. Now VLS growth is widely applied in the growth of most semiconductor nanowires and heterostructure nanowires. Since the VLS growth of Si nanowires has been fully studied, it can be used as a reference to explain the VLS growth mechanism. Fig. 2-11a is the scheme of vapor-liquid-solid growth mechanism. At first, Au clusters are deposited on the substrates. When the

substrate is heated to a certain temperature, silane gas is transported and decomposed with the formation of Si vapor. It is assumed that the Au catalyst decreases the activation energy required for the decomposition of silane. Meanwhile, Si vapor adsorbs onto the Au droplet surface and subsequently diffuses from the surface to the inner part of the droplet. The Au-Si liquid alloys are formed as the substrate temperature is higher than T_E , the eutectic temperature of alloy. The composition of Si in Au-Si liquid alloys continuously increases, until it reaches the maximum value, which can be inferred from the eutectic point of the Au-Si binary phase diagram. As shown in the Au-Si binary phase diagram (see Fig. 2-11b), the eutectic point of Au-Si alloy with 18.6 at. % Si is at 636 K, which is much lower than the melting points of Si (1687 K) and Au (1337 K). At this point, slow cooling process will cause the precipitation of Si and Au from the liquid alloy. Further adsorption of Si vapor leads to the supersaturation state, which requires high surrounding temperature to maintain the liquid phase. Therefore, Si will extrude from Au-Si liquid alloys to keep them stable. With the guide of Au catalyst, the one-dimensional growth of Si is preferred at the liquid solid interface. This is because the dissolving process at the liquid-solid interface requires less energy than the formation of secondary nucleation sites. After the system cools down and the supply of Si precursors is discontinued, the catalyst changes from the liquid to solid phase, while the Si concentration remains unchanged.

Figure 2-11. (a) Scheme of vapor-liquid-solid growth mechanism[69]. (b) Au-Si binary phase diagram[70].

The VLS growth has been proved by the in situ TEM observation of the Ge nanowire growth with Au as the catalyst[71]. Meanwhile, it is found out that the size of Au nanoclusters greatly affects the diameter of nanowires. Increasing the Au particle size, the diameter of nanowires also increases and is always larger than the Au particle size.

(2) Vapor solid solid (VSS) growth

As we know, Au is widely used in VLS growth as the catalyst due to its unique property, e.g. stable at the high temperature and nonreactive with precursors. However, Au greatly affects the performance of semiconductor nanowires, especially in optical and electronic applications. For example, Si nanowires grown by the CVD process with Au as the catalyst show inferior properties as Au forms deep level electronic states in the bandgap of Si [72]. As a result, new catalysts that form solid alloys with Si are investigated to initiate the growth of Si nanowires[73, 74]. The vapor-solid-solid process is firstly proposed by Tatsumi for the growth of Si nanowires with Cu as the catalyst[75]. The VSS growth is similar as the VLS process, except that the formed alloy is not liquid but solid during the adsorption of precursors. The Cu-Si phase diagram (see Fig. 2-12) shows that the liquid Cu-Si alloy only appears in the growth process when the substrate temperature is above 975 K. However, their experiment was carried out at the temperature below 975 K[75], which indicates the generation of the solid Cu-Si alloy at that substrate temperature. During the growth process, the silane gas is transported to the substrate by the carrier gas. Owing to the Cu catalyst, silane is decomposed at a lower temperature and then the product Si diffuses through the Cu droplet with the formation of the solid Cu-Si alloy. When the concentration of Si in the Cu-Si alloy reaches the limit, the nucleation of Si will occur from Cu-Si solid particle. The continuous extrusion of Si from solid catalysts finally causes the formation of Si nanowires.

Figure 2-12. Cu-Si binary phase diagram[70].

The reaction rate of the VSS growth mechanism is greatly affected by the substrate temperature. As we know, Cu serves as the catalyst to reduce the activation energy of the chemical reaction, so the decomposition of silane into Si can occur at lower surrounding temperature. Inferred from the Cu-Si binary phase diagram, the Cu-Si alloy is in the solid phase, which hinders the diffusion of Si and the diffusion rate of Si inside solid phase is quite low. As a result, the limiting step is not the decomposition of silane but the diffusion of Si inside Cu-Si solid alloys.

Although the diffusion step is the rate-determining step, the substrate temperature can indirectly affect the growth rate through a incubation period. The incubation time is defined as the time required for the catalyst to reach super-

saturation, which induces the growth of nanowires. The incubation time can be expressed by the following equation:

$$\tau \approx \frac{h^2}{D_{so} \exp(-E_a/KT)} \quad (2.11)$$

where h is the height of the catalyst nanoparticle, D_{so} is related to the pre-factor of the diffusion coefficient of Si through Cu_3Si , and E_a corresponds to its activation energy. Decreasing the substrate temperature, the incubation time will increase, causing the delay of the whole process. From the equation, it also can be concluded that the VSS growth requires more incubation time than the VLS growth, since the diffusion coefficient of Si through solid catalysts is much smaller than that of Si through liquid catalysts. Therefore, the growth rate of Si nanowires by the VSS growth is slower than that of the VLS growth, which has been evidenced by the Al catalyzed Si nanowire growth [72].

(3) Vapor solid (VS) growth

The VLS and VSS growth need to introduce catalysts to initiate the one-dimensional growth of materials without the preferential orientation. The existence of foreign catalysts may cause the processing difficulty of fabricating devices. The vapor solid growth, a direct nanowire growth, does not require any catalyst for the nanowire growth. From this viewpoint, pure VS-grown nanowires can meet the requirements of the semiconductor device fabrication.

The initiation of nanowire growth can be explained by the VS mechanism, which is due to the various interfacial free energies of different crystal planes. Hence, the growth rates of crystal planes are different and the plane with the lowest interfacial free energy[76] has the fastest growth rate. In other words, the VS growth can only be applied in the growth of materials with anisotropic structures. During the CVD process, the plane with low interfacial energy nucleates first and grows faster than other planes, resulting in one-dimensional growth. Taking Fe_2O_3 as an example, the $\alpha\text{-Fe}_2\text{O}_3$ is a close-packed rhombohedral structure (space group $R3c$) with lattice constants $a=0.503$ nm and $c=1.375$ nm. The obtained Fe_2O_3 nanowires are confirmed to grow along (110) direction because of the minimum energy barrier needed to be overcome for growing along this direction. Takagi [77] proposed that the substrate had various defects on the surface, which can also lower the energy barrier of the reaction and the initial nucleation of nanowires preferably occurs on these surface defects[78]. After the extrusion of Fe_2O_3 nanoparticles from the Fe substrate, Fe atoms beneath the surface can constantly diffuse to the surface as an iron source reservoir. When the substrate temperature is high enough, the reaction kinetics no longer delay the growth process [79]. Therefore, the growth of Fe_2O_3 nanowires is mainly limited by the diffusion of iron atoms from the bottom to the surface of the Fe substrate as well as from the base to the tip inside the Fe_2O_3 nanowires.

Other than the substrate temperature, the mass flow rate is also an important parameter that affects the concentrations of precursor vapors and the resident time. With the low mass flow rate, the growth of nanowires is not preferred due to the low oxygen concentration. On the other hand, the gas flow rate also has impacts on the

size and shape of the nanowires. The reason is that the gas flow rate is related to the gas resident time. The gas resident time is defined by the following equation [78]:

$$\tau = \frac{P \times V}{Q} \quad (2.12)$$

where P is the pressure inside the reaction chamber, V is the volume of the reaction chamber, and Q is the flow rate of carrier gas, respectively. At a constant pressure and chamber volume, the long resident time of gas leads to high consumption of precursors. This may cause non-homogeneous gas concentration gradient at different regions of the substrate, leading to non-uniform growth of nanowires.

2.2.5 Thin film growth mechanism

Besides the whisker growth, CVD technique is also frequently used in the thin film growth. There are three thin film growth modes, namely Volmer-Weber (3D island formation), Frank-van der Merwe (2D layer by layer) and Stranski-Krastanov (layer-plus-island) growth modes.

In a typical thin film growth, material A is deposited on a foreign material B. Here, material A can be considered as the adsorbate, while material B is the solid substrate. During the CVD growth process, material A in the gas phase is transported to the surface of material B by the carrier gas. The mix gas of vapor A and the carrier gas can be regarded as the surrounding medium. After the adsorption of A on B, the interfacial energy of the system changes from the bare substrate-medium interface energy to the adsorbate-medium and the adsorbate-substrate interface energy. The

difference of the surface energy, $\Delta\sigma$ before and after the deposition is related with the growth mode which can be expressed by the following formula:

$$\Delta\sigma = \sigma_A + \sigma_i - \sigma_B \quad (2.13)$$

where, σ_B is the interfacial energy between the substrate B and the surrounding medium, σ_i is the interfacial energy between the substrate B and the adsorbate A, σ_A is the interfacial energy between the adsorbate A and the surrounding medium.

(1) When $\Delta\sigma$ is positive ($\Delta\sigma > 0$), the chemical potential μ increases during the deposition of adsorbate atoms on the substrate surface. The chemical potential μ is referred as the partial molar Gibbs energy G , so the Gibbs free energy will increase when material A is adsorbed on the substrate surface. From the thermodynamic point of view, the reaction will occur towards the direction of decreasing Gibbs free energy or chemical potential. Therefore, after A atoms deposit on the substrate surface, the subsequent gas atoms will preferably deposit on the adatoms of the same material rather than on the substrate of the foreign materials to minimize the Gibbs free energy. The continuous deposition leads to the formation of island. Thus such growth is termed as the island growth, or the Volmer-Weber growth, as shown in Fig. 2-12a.

Figure 2-12. Three thin film growth modes including (a) Volmer-Weber (VW: island formation), (b) Frank-van der Merwe (FM: layer-by-layer), and (c) Stranski-Krastanov (SK: layer-plus-island) growth modes[80-82].

(2) When $\Delta\sigma$ is negative ($\Delta\sigma < 0$), the chemical potential or Gibbs free energy decrease during the deposition of material A on the substrate. Thus, the deposition of adsorbate atoms A on the substrate B is more favorable. Then a smooth layer is obtained on the substrate. This kind of phenomenon is similar to a perfect wetting effect of material A on substrate B. Such growth, as shown in Fig. 2-12b is termed as the layer growth or the Frank-van der Merwe growth, which can be used to explain the formation of a smooth layer on the substrate.

(3) When $\Delta\sigma$ equals to 0, the thin film growth is an intermediary process between VW growth and FM growth. At first, the deposition follows the layer growth until the thickness reaches to a critical value. The critical value is related with surface energies and lattice parameters of both substrate B and material A. After reaching to the critical value, the growth switches from the thin film growth to the island growth.

Such growth is termed as the Stranski-Krastanov growth. As shown in Fig. 2-12c, the samples grown under the Stranski-Krastanov growth mode shows a combination of the thin film and islands.

Chapter 3 Experimental procedures

3.1 Synthesis of Sb₂Te₃ nanoparticle thin film

3.1.1 Materials

Tellurium powder (Aldrich, 99.8%, 200 mesh) and Antimony powder (Sigma-Aldrich, 99.5%, 100 mesh) were used as received.

3.1.2 Growth procedure

The experiment was conducted in a CVD system, which consisted of a tube furnace, a mechanical pump, a flow meter controller as well as some connections and tubing (see Figure 3-1). Sb powder in a crucible was kept at the middle of the tube furnace, which was regarded as the origin point. Te powder was placed at 15 cm upstream side of Sb powder. Ten pieces of glass substrates (1.5×1 cm) were washed with deionized water and dried in the oven. After that, glass substrates were placed at 20~30 cm downstream side of Sb source (see Figure 3-1). Before the growth, the quartz tube was first evacuated to low pressure ($\sim 10^{-3}$ mbar) and refushed with forming gas (95%Ar+5%H₂) to reduce the possibility of oxidation. Before heating, the flow rate of forming gas was set at 200 standard cubic centimeters per minute (sccm). The pressure of quartz tube for the growth was controlled at 2.6 mbar. After the above steps, the growth began. The temperature at the middle of furnace was increased from 348 K to 853 K at the rate of 30 K/min and then the temperature was kept at 853 K for 3 hours.

Figure 3-1. Schematic of the tube furnace used for synthesizing nanoparticle thin film growth

3.2 Synthesis of InSb nanowires

3.2.1 Materials

Indium shot (Sigma-Aldrich, 99.9%, 2-5 mm diameter), Antimony powder (Sigma-Aldrich, 99.5%, 100 mesh), Copper foils (20 μm in thickness), Nickel foils (0.5 mm in thickness) and stainless steel foils (1 mm in thickness)

3.2.2 Growth procedure

The growth of InSb nanowires was carried out in the same CVD set-up system. Sb powder and In shot were used as received. 1×1 cm stainless steel foils were carefully washed by deionized water and finally dried in a vacuum oven. In shot in a crucible was placed at the middle of the tube furnace and Sb powder was placed at 18 cm upstream side of Sb powder. Three pieces of stainless steel foils were placed from 16 to 18 cm in the downstream zone. Before the growth, the quartz tube was first evacuated to low pressure and refilled with forming gas to enhance the vacuum

inside the quartz tube. Before heating, the flow rate of forming gas was set at 100 sccm and the pressure of quartz tube for the growth was controlled at 1.5 mbar. After the above steps, the growth began. The temperature at the middle of furnace was increased from 348 K to 1223 K at the rate of 30 K/min and then the temperature was kept at 1223 K for 1 hour. The InSb nanowires were obtained on the stainless steel foil placed at $d_{\text{sub}} = 17$ cm, which could be directly used for cell assembling.

To examine the effect of substrate, heating temperature and flow rate, control experiments were carried out by replacing stainless steel foils with copper foils and nickel foils, changing heating temperature from 1073 K to 1223 K and flow rate of carrier gas from 50 to 150 sccm.

3.3 Synthesis of nanostructured Cu-Sb compounds

3.3.1 Materials

Antimony powder (Sigma-Aldrich, 99.5%, 100 mesh) and two types of Copper foils with different roughness (20 μm in thickness)

3.3.2 Growth procedure

The experiment was carried out in the same CVD system. Sb powder and Cu foil was used as received. 1×1 cm Copper foils were treated by dilute acid (1M HCl) to remove the oxidized layer, then carefully washed by deionized water and finally dried in a vacuum oven. Sb powder in a crucible was kept at the middle of the tube furnace. Several pieces of Copper foils were placed from 14 to 30 cm in the downstream zone. Before the growth, the quartz tube was first evacuated to low

pressure and refushed with forming gas to reduce the concentration of oxygen inside the quartz tube. After the above steps, the growth began. The temperature at the middle of furnace was increased from 348 K to 1223 K at the rate of 30 K/min and then the temperature was kept at 1223 K for 1 hour. For the control experiments, the flow rate of forming gas was set at 50, 100 and 200 sccm to study the effect of mass flow rate on the size of as-grown materials.

3.4 Sample Characterization

3.4.1 Material and structure characterization

The as-prepared samples were directly used for SEM and XRD measurements. The X-ray diffractograms were obtained by using a monochromatic Cu K α radiation with wavelength (λ) of 1.5406 Å under V = 40 kV and I = 40 mA. The XRD data were collected over the 2 θ range of 20 °~60 ° at the scanning speed of 1 °/min with the step kept at 0.02 °. The determination of the phase was done by using the Match software. The SEM images of the as-grown samples were obtained by using a field-emission SEM (JEOL JSM7600F) operating at 5 kV. To further determine the phase of materials and the grain size, transmission electron microscopy (TEM) characterization was used. The preparation of TEM samples was carried out as follows. The samples together with substrates were put inside 5 ml ampoules. Ethanol was then added to cover the samples. After ultrasonication for 2 hours, the samples were dispersed in ethanol and formed uniform solutions, which were then dropped cast onto Cu grids or Ni grids (for Cu-Sb nanostructures). TEM images, selected-area electron

diffraction (SAED) patterns and high-resolution transmission electron microscopy (HRTEM) were taken by using a JEOL 2100 system operating at 200 kV. To confirm the element and composition of nanosized samples, energy-dispersive X-ray spectroscopy (EDS or EDX) spectra were obtained under the transmission electron microscopy (STEM) mode with the electron beam size about 1~1.3 nm.

3.4.2 Thermoelectric properties characterization

The thickness of the films, used to calculate the electric resistivity, was measured using a surface profile scanning system (Alpha-step IQ Surface Profile) and confirmed by the cross-section SEM images. Before the growth, approximately half of glass slides were pasted with thermal tapes. After growth, the thermal tapes were removed and the edges were scanned by surface profile. The average thicknesses of samples were obtained from five different points of the samples.

The resistivity and Seebeck coefficient were measured from 323K to 598K using a commercial available ZEM-3 Seebeck meter under helium environment. The working principle of ZEM-3 is shown in Fig. 3-2. The effective charge carrier concentration of samples were measured using a typical S7-500-1-0.55T probe station with Keithley 4200 semiconductor characterization, adjustable pole electromagnet (Model 1607037) and hall effect gauss meter (Model GM-700).

Figure 3-2. Working principles of ZEM-3 in the vacuum heating chamber for measuring electrical resistivity and Seebeck coefficient.

The thermal conductivity of 20-nm nanoparticle thin film was measured by pulsed photothermal reflectance (PPR)[83-85]. For the PPR technique, the measurement on thin film samples was carried out in the perpendicular direction to the surface as previous reported[83]. Before the measurement, the thin film sample deposited on the high-resistivity silicon substrate was coated with a gold film layer of 1 μm thickness. Gold was preferred as a light absorption element because it is not susceptible to oxidation at room temperature and can reflect light differently at different wavelengths. Before the measurement, the system was calibrated by measuring sputtered AlN thin films on Si substrates with thickness of 400 nm, 800 nm and 1 μm . The values of thermal conductivity of AlN thin films were 1.6, 3.7 and 4.4 W/mK, which agreed to the reported values[86]. This result indicated the reliable PPR system. The experiment began with the gold film irradiated by a Nd:YAG laser pulse

(see Fig. 3-3). After the excitation of the laser pulse, the surface temperature of samples increased sharply and then slowly relaxed to room temperature. The relaxation time was determined by the thermal properties of the films. To obtain the temperature excursion profile, a He-Ne probe laser was continuously focused on the gold film with occurrence of reflection. Then a fast speed photodetector was used to capture the reflected light signal. Since the reflectivity is inversely proportional to the surface temperature, the acquired signal was inverted to obtain a temperature excursion profile. For the $\text{Au/Sb}_2\text{Te}_3$ nanostructures thin film/Si structure, the temperature profile was curve fitted using the three-layer heat conduction model in which the silicon substrate was regarded as an infinite medium. In the end, the thermal conductivities of Sb_2Te_3 nanostructures thin films were obtained from the result of curve fitting.

Figure 3-3. Scheme illustrating the set up of pulse photothermal reflectance (PPR) measurements.

3.4.3 Property Measurement of Lithium ion battery

The anode materials obtained on current collectors through CVD method could be directly used for battery packing and testing without the electrode preparation step. The coin-type battery cell was assembled in a glove box, which was filled with argon gas and the concentration of moisture and oxygen was less than 1 ppm. The Li foil, separators (two pieces), anode (as-prepared samples on current collectors), spacer and spring were stacked by the order in the coin cell case. Li foil was used as the counter electrode and the reference electrode material. 50 μ L electrolyte was then filled into the case. The electrolyte was 1M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume). After that, the coin cell was sealed by the crimping machine. Cyclic voltammetry of InSb or Cu_2Sb electrodes in coin-type cells was performed with the Solartron analytical equipment (model 1470E) at the scan rate of 0.5 mV/s. The cycling performance of InSb or Cu_2Sb electrodes in coin-type cells was tested on a NEWARE multi-channel battery test system. The voltage window range was between 0.5V and 1.2 V or 0.01 V and 1.2 V for InSb and between 0.01 V and 1.2 V for Cu_2Sb . The current density was set at 0.2 C.

Figure 3-4. Scheme illustrating the composition of the coin-type cell. The discs are stacked by the order in the coin cell case: negative case + Li foil + separator (two pieces) + anode (as-prepared samples on current collectors) + spacer + spring + positive case.

Chapter 4 Catalyst-free CVD growth of Sb₂Te₃ nanoparticle films with controlled sizes

4.1 Introduction

Because of similar melting point and boiling point of elements Sb and Te, the catalyst-free CVD growth of nanostructured Sb₂Te₃ is chosen as the starting work. Sb₂Te₃ has been extensively studied among all the TE semiconductors, due to their promising performance in thermoelectric [42-44]. The realization of high-efficiency thermoelectric (TE) module for solid state energy conversion requires the development of TE semiconductors with high figure of merit[40], which is a dimensionless factor expressed as $ZT = (S^2\sigma/\kappa)T$, where T is the temperature in Kelvin, S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. Right now, bulk Sb₂Te₃ still can not meet the requirement of $ZT > 3$. Further enhancement of ZT is expected by nanostructuring these semiconductors[3] due to the occurrence of quantum size effect leading to the enhancement of S [87, 88] and increased interface scattering of phonons to reduce the thermal conductivity[44, 56-58].

Sb₂Te₃ nanostructures have been prepared by various methods including the solvothermal process [89, 90], electrochemical deposition [91], and the Au-catalyzed vapor-liquid-solid (VLS) growth [25, 92]. These methods all have many advantages and some disadvantages. For example, the solvothermal process can easily produce nanocrystals with uniform sizes, shapes and compositions with the possible scale-up

production yield. But the shape and size control may require insulating capping ligands that needs to be removed to achieve the appropriate electrical conductivity. Electrochemical deposition can synthesize nanocrystals with pre-defined shape, size and uniformity. But it may require the removal of anodic aluminum oxide (AAO) templates. Au-catalyzed vapor-liquid-solid growth can deposit single crystalline nanowires with excellent control of the structural orientation, sizes and the aspect ratio. But the yield of the growth may not be high enough for thermoelectric module integration. Currently, the fabrication of nanocrystalline TE modules still largely depends on ball milling combined with hot pressing[57], or nanostructuring of bulk materials[93-95], which does not give adequate control over the crystal size and the excessive crystal growth is inevitable during the process.

In this study, Sb_2Te_3 nanoparticle films are fabricated by a simple vapor transport process without the assistance of any catalysts. The Sb_2Te_3 particle size can be tuned in the range of 10~100 nm by varying the growth parameters, i.e., the Ar/ H_2 flow rate and the substrate temperature/substrate position. The as-prepared nanoparticle films show reduced electrical resistivity while high electrical resistivity is an important issue related to applications of TE nanocrystals prepared by wet-chemistry process[88, 96] (e.g. tedious chemical processes are not required to remove surface capping ligands as in the wet chemical processes[96-98]). To our best knowledge, such close-packed nanoparticle films with controllable particle size by the simple vapor transport growth process have not been reported before. This growth process is promising for producing two-element nanocrystal samples for

nanoelectronics with good electrical conductivity, defined nanoparticle/grain size and well-crystallized phases, which are keys to induce many performance enhancements.

As the doped Sb_2Te_3 has the higher ZT value than the pure Sb_2Te_3 [99, 100], the growth of doped Sb_2Te_3 thin films through CVD is pursued. The common dopants introduced into Sb_2Te_3 are Pb, Ag, In, Bi, Se and S. Pb and Ag are not chosen because of the toxic Pb vapor and because that the evaporation temperature of Ag exceeds the working temperature of the tube furnace. Then the growth of Sb_2Te_3 thin films doped with In, Bi, Se and S is tried to be carried out. As In and Bi with high evaporation temperatures (>1023 K) largely deposit at $d_{\text{sub}} < 16$ cm, obtained samples are of micron-size and the atomic ratios of dopants are not easy to control. Se and S with much lower evaporation temperatures (<423 K) condense at $d_{\text{sub}} > 25$ cm in a large amount. The as-prepared thin films with smaller particle sizes have very high concentrations of Se or S (> 50 %). Therefore, the doped Sb_2Te_3 nanoparticle thin films are not easy to be prepared through CVD. The following work will still focus on the CVD growth of two-element systems.

4.2 Phase analysis and morphology characterization of as-grown samples

A typical synthesis is conducted in a CVD system. Two crucibles containing Te powder and Sb powder, respectively, are placed inside the quartz tube. At 200 sccm forming gas flow, the Sb and Te vapors are deposited on glass substrates in the downstream zone. Figure 4-1 (a)-(c) show the SEM images of the as-prepared nanoparticles by the vapor transport growth process. Analysis on the SEM images

reveals that the average particles size of the films is highly dependent on the substrate position/temperature. Films with average particle sizes of 100, 50 and 20 nm are obtained on substrates placed at distance of $d_{\text{sub}} = 20, 25$ and 30 cm away from center of the furnace with the substrate temperature of 347, 313 and 309 K, respectively. The substrate temperature is judged from the temperature profile of the furnace at 853 K (see Fig. 4-2). These nanoparticles closely pack onto the substrates, which show moderate size distribution (see Fig. 4-3).

Figure 4-1. (a)-(c) SEM images of Sb_2Te_3 nanoparticles obtained at $d_{\text{sub}} = 20$ cm, 25 cm and 30 cm, respectively[101].

Figure 4-2. Temperature profile of the furnace at 853 K.

Figure 4-3. Particle size distribution of Sb_2Te_3 particle films grown at $d_{\text{sub}} =$ (a) 30 cm, (b) 25 cm and (c) 20 cm.

The Sb_2Te_3 nanoparticle films on the glass substrates are dipped into ethanol solution and subjected to sonication for the preparation of TEM samples. The resulting solution is drop cast onto Cu grids for TEM observation. Energy dispersive x-ray (EDX) analysis (see Fig. 4-4) confirms that the ratio of Sb : Te is close to 2: 3. Here, the carbon peak is mainly from the carbon film in the Cu grid. TEM images (Fig. 4-5a-c) reveal the faceting of 100-nm particles while samples of other sizes are relative spherical. High resolution TEM (HRTEM) images (Fig. 4-5d-f) indicate the polycrystalline nature of these nanoparticles. Selected area electron diffraction (SAED) pattern (Fig. 4-5g) on the nanoparticle films exhibits rings corresponding to the rhombohedral Sb_2Te_3 .

Element	Wt%	At%
Sb	39.49	38.37
Te	60.51	61.63

Figure 4-4. Representing EDX spectroscopy of Sb_2Te_3 nanoparticle films grown at $d_{\text{sub}} = 30$ cm. The copper peaks and carbon peaks are from the carbon coated Cu grid[101].

Figure 4-5. (a) TEM and (d) HRTEM micrographs of 100-nm Sb_2Te_3 nanoparticles obtained at $d_{\text{sub}} = 20$ cm. (b) TEM and (e) HRTEM micrographs of 50-nm Sb_2Te_3 nanoparticles obtained at $d_{\text{sub}} = 25$ cm. (c) TEM and (f) HRTEM micrographs of 20-

nm Sb_2Te_3 nanoparticles obtained at $d_{\text{sub}} = 30$ cm. (g) SAED pattern of the 20-nm Sb_2Te_3 nanoparticles[101].

To investigate the crystal structure as well as estimate the grain sizes of the samples, x-ray diffraction (XRD) studies are carried out. The XRD patterns (Fig. 4-6) obtained for the as-prepared particle films confirm the existence of only the rhombohedral Sb_2Te_3 phase (JCPDS-ICDD card 15-0874), which is consistent with the SAED analysis (see Fig. 4-5g) in the TEM characterization. Based on the analysis of the full width at half maximum using the Scherrer equation[102], the grain sizes are estimated to be about 6, 11, 15 nm for the 20-, 50- and 100-nm particle films respectively. The result is consistent with the HRTEM observations. Here, it is noticed that the grain size of the samples is much smaller than that of Sb_2Te_3 nanocrystals made by wet-chemical approaches[103] and is smaller/comparable to the de Broglie wavelength of Sb_2Te_3 , e.g. 18 nm (estimated from the equation $\lambda_D = h/(2mk_B T)^{1/2}$)[104, 105], which is important to induce the quantum size effect[3]. Actually, based on the previous experiments[38], Sb or its compound nanoparticles are very difficult to be synthesized with the uniform shape and small size, e.g. <20 nm, mainly due to lack of effective capping ligands interacting effectively with Sb.

Figure 4-6. XRD patterns obtained from as-grown Sb_2Te_3 nanoparticles with different sizes[101].

4.3 Study of the growth process

4.3.1 Growth mechanism of Sb_2Te_3 nanoparticle thin films

The growth of Sb_2Te_3 nanoparticle thin films through the CVD process contains two main steps: (1) the evaporation and transportation of precursors and (2) the reaction and deposition of precursor vapors on substrates. The evaporation rates of Sb and Te powders are determined by their surrounding temperatures and the total pressure inside the quartz tube. The high surrounding temperature and the low inside pressure facilitate the fast evaporation. During the experiment, the total pressure is set at a constant value by controlling the pump valve, so only changing the place of crucibles can vary the evaporation rate. From Sb-Te binary phase diagram (in Fig. 4-7), the melting points of Sb and Te elements are 903.7 K and 722.6 K, respectively. When the Sb and Te sources are placed in one crucible at the centre of the furnace, Te

powder evaporates first. When Te evaporates completely, most Sb powder remains in the solid phase, which leads to the multi-phase and non-uniform composition of thin film samples. To grow uniform Sb_2Te_3 nanoparticle thin films, two crucibles containing Sb powder and Te powder respectively, should be placed at different places in the quartz tube. Inferred from the temperature profile of the tube furnace, Sb powder is placed at the centre of the tube furnace, while Te powder is placed at 14 cm away from Sb powder in the upstream zone.

According to the growth scheme shown in Fig. 4-8, Sb and Te vapors are firstly transported to the substrate surface by the carrier gas. Due to the high surrounding temperature, the reaction occurs with the formation of Sb_2Te_3 . The chemical reaction formula is:

The condensation of Sb_2Te_3 gas on substrates begins from the distance of 16 cm, because the substrate temperature is too low to sustain the gas phase of Sb_2Te_3 . At substrate distances of 20, 25 and 30 cm, the substrate temperatures, below 373 K, lead to the fast nucleation and the slow surface diffusion. As a result, the nanoparticle thin films with the particle size of 100, 50, 20 nm are obtained. The island-like morphologies indicate that the Sb_2Te_3 vapor favors to deposit on the adatoms rather than the substrate surface. The preferable deposition sites of adatoms also can be inferred from the sticking probability S_L of precursors on substrates. As indicated by the following equation[106], S_L is determined by the substrate temperature.

$$S_L = \exp\left(-\frac{E_{AS}}{k_B T}\right) \quad (4.2)$$

where E_{AS} is the activation energy per adsorption, T is the substrate temperature, k_B is the Boltzmann constant. The thermal energy provided by the substrate should exceed the activation energy per adsorption E_{AS} , otherwise, the adsorption on the substrate is not thermodynamically feasible. At the low substrate temperatures at d_{sub} of 20, 25, 30 cm, the deposition is preferable on the adatoms rather than substrates, which indicates the growth following the island growth mode. The deposition of Sb_2Te_3 in the island growth process is not necessary epitaxially attached to the glass substrates, although in some cases, such growth may require epitaxial lattice mismatch between the substrates and the growth species, e.g. Ge on Si (100) surface[107]. This is because that amorphous glass slides are used as substrates and that the low substrate temperatures permit the fast deposition and nucleation.

Figure 4-7. Sb-Te binary phase diagram[70]

Figure 4-8. Scheme suggests the possible growth process. The competence of surface diffusion and nucleation determines the morphology of the as-grown Sb_2Te_3 . Slow surface diffusion with high nucleation favors nanoparticle formation while slow nucleation and fast surface diffusion induce continuous films.

4.3.2 Effect of substrate temperature on the size of as-grown samples

Control experiments are carried out to investigate the influence of substrate temperature on the size of as-grown materials with glass slides placed from 16 to 36 cm. The FESEM image in Fig.4-9a shows that large Sb_2Te_3 crystals are obtained at the shorter distance, 16 cm. These Sb_2Te_3 are plate-shaped with the diameter around a few microns and the thickness around 100 nm (see Fig.4-9b). The diffraction pattern (see Fig. 4-9c) indicates that the plate-like Sb_2Te_3 is single crystalline.

Figure 4-9. (a) A SEM image, (b) TEM image and (c) HRTEM image of Sb_2Te_3 plates grown at $d_{\text{sub}} = 16$ cm.

At $d_{\text{sub}} = 16$ cm, the substrate temperature is 533 K, which causes the formation of the micron-sized Sb_2Te_3 . When the gas reaches to the surface, it is first adsorbed on the previous deposited Sb_2Te_3 particle. The high substrate temperature leads to the fast diffusion and crystal growth rate, which contribute to the formation of Sb_2Te_3 micron-sized plates. Concluded from the experimental results, the samples with larger particle size favor to grow at the high substrate temperature, owing to the annealing.

Increasing d_{sub} to 20, 25 and 30 cm, the substrate temperatures are 347, 313 and 309 K, respectively. Films with average particle sizes of 100, 50 and 20 nm are obtained on substrates, which are much smaller than Sb_2Te_3 micron-sized plates. Further increasing d_{sub} to 36 cm leads to the formation of the nanoparticle film with even smaller average particle size, e.g. ~ 10 nm (see Fig. 4-10). However, due to the low concentration of precursor vapors and the slow growth rate at $d_{\text{sub}} = 36$ cm, it requires very long growth time, e.g. >6 hours, to form a relatively continuous film with a thickness of ~ 150 nm. The different substrate temperatures and concentration of precursors contribute to the decreased sizes from 16 to 25 cm. Since the substrate temperatures at 25, 30 and 36 cm are all close to the room temperature, the reduced particle size is mainly caused by the decreased concentration of precursor vapors.

Figure 4-10. (a) SEM of Sb_2Te_3 nanoparticle films grown at $d_{\text{sub}} = 36$ cm with an average size of ~ 10 nm. (b) A TEM image of Sb_2Te_3 nanoparticles from the film in (a) [101].

4.3.3 Effect of flow rate on the composition of as-grown samples

The flow rate of the carrier gas affects the composition of thin films through the gas resident time. The gas resident time is defined by the Equation 2.12:

$$\tau = \frac{P \times V}{Q}$$

where P is the pressure inside the reaction chamber, V is the volume of the reaction chamber, and Q is the flow rate of carrier gas, respectively. In the experiment, the pressure inside the quartz tube and the volume of the quartz tube are constant, so the resident time is proportional to the reverse of the gas flow rate. The resident time is longer with the slower mass flow rate. With different flow rates, the compositions of obtained thin films are various at different distances. For example, at a flow rate of 50 sccm, the composition of the as-prepared sample is Sb-rich Sb_2Te_3 even pure Sb at $d_{\text{sub}} < 16$ cm, while for $d_{\text{sub}} > 16$ cm, the composition is first right close to Sb_2Te_3 , then Te-rich Sb_2Te_3 , and finally pure Te. At the fast flow rate (e.g. 200 sccm), Sb_2Te_3 vapor does not have enough residence time. Two phases, Sb and Sb_2Te_3 are obtained on substrates at $d_{\text{sub}} < 16$ cm, due to the evaporation of Te from unstable Sb_2Te_3 at the high substrate temperature. At the distance from 16 to 36 cm, pure Sb_2Te_3 phase is obtained, because the relatively low substrate temperature (< 373 K) does not cause the decomposition of Sb_2Te_3 . The rest Te vapor is deposited at $d_{\text{sub}} > 36$ cm. From the results, it is concluded that at the fast flow rate, the deposition zone with the formation of Sb_2Te_3 is longer. Therefore, the flow rate should be fast enough to achieve the uniform compositions of samples. From the experiment result, the optimized flow rate

is 200 sccm. Further enhancement of the flow rate has no obvious impact on the composition.

4.4 Concluding Remarks

In this chapter, the work demonstrated a new facile process to grow Sb_2Te_3 nanoparticle films with controlled particle sizes using a catalyst-free vapor transport growth technique. The island-like nanoparticle thin films suggested that the growth followed the island growth mechanism. The low substrate temperature (below 373 K) attributed to the slow diffusion rate and the fast nucleation rate, which resulted in the preferable adsorption on adatoms and the small particle size. The effect of carrier gas flow rate on the composition and morphology of samples were studied from the control experiments. The fast flow rate permitted the sufficient supply and the co-deposition of precursors, which caused the uniform composition of thin film samples on each substrate. Such growth process allowed the realization of nanocrystal films with tunable crystal size, e.g. 5~15 nm, comparable to the de Broglie wave length of Sb_2Te_3 , which may result in good thermoelectric properties.

Chapter 5 Self-catalyzed VLS growth of InSb nanowires

5.1 Introduction

Besides the nanoparticle thin film growth, the catalyst-free chemical vapor deposition can also be applied in nanowire growth. Based on the consideration that In is a low melting point metal and can act as catalyst during the process to induce one-dimensional growth, the growth of InSb nanowires will be the next work. InSb is an intermetallic compound with zinc-blend type structure. The low band gap of InSb (0.18 eV) and high electron mobility ($7.8 \times 10^4 \text{ cm}^2/\text{Vs}$) make InSb a promising material for investigation in thermoelectrics[108, 109], lithium ion batteries[110], field effect transistor (FET) devices [111] and optoelectronic devices [112].

The fabrication of InSb nanostructure is mainly through ball mill[110], solution method[113, 114], pulsed electrochemical deposition with AAO template[111, 115] and Au catalyzed VLS growth[116]. Ball milling is the most commonly used method to synthesize InSb nanoparticles for lithium ion battery application. In is a soft metal with good ductibility due to its low melting point. Hence, it may attach onto the surface of the milling container or ball, which leads to the loss of indium during the milling process and the formation of Sb-riched phase. In addition, the ball and container that made of different materials may introduce some impurity into InSb. The reported InSb nanowires growth by electrochemical deposition on AAO template requires further etching of the AAO template before the on-going properties testing.

However, the etching process may cause the deformation in lattice[117]. The formation of bundling nanowires instead of the maintaining the free-standing film-like morphology after etching is another problem not solved right now. The difficulty in controlling the size and morphology of InSb is a big concern in the solution method. For Au-catalyzed VLS growth, the use of noble metal Au increases the production cost and the scaling-up is difficult through this method.

Here, the self catalyzed VLS growth of InSb nanowires on stainless steel substrates is introduced. Different anode current collectors, Cu foils, Ni foils and stainless steel foils are used as substrate to examine their effects on the compositions and morphologies of the samples. Due to easily spoiled Cu foil at high temperature and reactions between Ni foil and precursor vapors, only stainless steel foils are suitable for the growth of InSb nanowires. The growth mechanism of InSb nanowires is discussed in detail. Then the control experiments with different heating temperatures, substrate temperatures and flow rates are carried out. As these parameters significantly affect the structures, morphologies and sizes of the as-grown samples, they are optimized to obtain the InSb nanowires with desired composition and size.

5.2 Phase analysis and morphology characterization of InSb nanowires

It is observed from the SEM and TEM images (see Fig. 5-1 a-b) that nanowires are obtained on the stainless steel substrates at $d_{\text{sub}} = 17$ cm in the downstream zone. The substrate temperature, inferred from Fig. 5-2 is approximate 785 K. These nanowires are 200 nm in diameter and about 5 μm in length. The EDX result (see Fig. 5-3) on these NWs shows that the atomic ratio of In : Sb in single InSb nanowire is close to 1 : 1, while the tip of the InSb nanowire is a little In-riched. The spot diffraction pattern in the selected area electron diffraction (SAED) (shown in Fig. 5-1c) reveals that the nanowires are single crystalline cubic InSb phase (JCPDS card 006-1896). The high resolution TEM image (see Fig. 5-1d) shows a lattice spacing of 0.174 nm along the long axis of the nanowire, which corresponds to the (222) lattice direction of InSb. The XRD pattern of these nanowires (see Fig. 5-1e) indicates only peaks of the cubic InSb and stainless steel foil.

Figure 5-1. (a) SEM image, (b) TEM image (c) SAED pattern, (d) HRTEM image and (e) XRD pattern of InSb nanowire grown on the stainless steel foil of $d_{\text{sub}} = 17 \text{ cm}$ at the substrate temperature of 785 K under 100 sccm flow rate.

Figure 5-2. Temperature profile of the furnace at 1223 K.

	InSb nanowire		Tip of InSb nanowire	
Element	Wt%	At%	Wt%	At%
Sb	49.19	47.74	42.53	41.09
In	50.81	52.26	57.47	58.91

Figure 5-3. Representing EDX spectroscopy of (a) an InSb nanowire and (b) the tip of

the InSb nanowire. The tip shows higher In atomic ratio than the whole InSb nanowire. The copper peaks are from the Cu grid.

5.3 Study of the InSb nanowire growth process

5.3.1 Self-catalyzed VLS growth of InSb nanowires

The InSb nanowires are grown on the stainless steel substrate at $d_{\text{sub}} = 17$ cm. TEM image (see Fig.5-1b) shows the single InSb nanowire with a catalyst at the tip. Proved by the EDX analysis (see Fig. 5-3), the catalyst, without foreign elements, is of higher In atomic ratio than the nanowire. According to the high substrate temperature, the In riched catalysts is liquid, which leads to the supposition that the InSb nanowires follow the self-catalyzed VLS growth mechanism. The growth consists of four processes: (1) the evaporation and transportation of precursors to substrates; (2) the chemical reaction during the transportation and deposition; (3) the adsorption of precursor vapors by the liquid droplets at the vapor-liquid interface; (4) the precipitation of atoms and the continuous nanowire growth at the liquid-solid interface.

The beginning of evaporation is at the heating temperature below 1223 K, although the concentration of precursor vapors in the carrier gas is very low. The condensation of In and Sb on the substrate leads to the nucleation of InSb nanoparticles, which are unstable and intend to decompose at the substrate temperature. The evaporation of Sb causes the decomposition of InSb nanoparticles and the formation of In-riched nuclei. Inferred from In-Sb binary phase diagram (see Fig. 5-4), these In-riched nuclei are in liquid phase. The re-evaporated Sb vapor is preferably deposited on the distance > 17 cm, so Sb-riched InSb nanoparticles

nucleates at 18 cm in the downstream zone. Then the heating temperature reaches 1223 K, which results in the enhanced concentration of precursor vapor. The incoming In and Sb vapor are gradually adsorbed by liquid nuclei at the vapor-liquid interface, followed by the increased particle size and Sb atomic ratio. The liquid nuclei change from In-riched InSb to stoichiometric InSb with largely increased melting point of the compound (from 429.6 K of pure In to 798.7 K of InSb). As the substrate temperature at 17 cm is ~ 785 K, the liquid catalysts should convert to solid phase. To maintain the liquid phase of catalysts, solid InSb extrudes from the liquid catalyst at the liquid-solid interface, which guarantees the liquid In-riched nuclei. In such tip-led growth, with the guide of catalyst, the continuous supply of In and Sb vapor during the growth promotes the further growth of InSb nanowires.

Figure 5-4. In-Sb binary phase diagram[70].

5.3.2 Effect of Substrate

One of the advantages of the CVD growth is that as-grown samples can be directly used to test their performance without the electrode preparation step. This can be attributed to the in-situ growth of the InSb nanowires on the current collector that can provide strong adhesion and intimate electrical contact. In this regard, the commonly used current collectors, Cu foil, Ni foil and stainless steel foil, are considered as substrates to grow InSb. To investigate the effect of substrate, the CVD growth of Sb-based materials is carried out on three different substrates under the same growth condition, 1223 K heating temperature, 100 sccm flow rate and d_{sub} from 16 to 18 cm.

Cu foil with thickness of 20 μm is the most frequently used anode current collector in lithium ion batteries due to its good conductivity and flexibility. However, Cu foil is easily spoiled at the substrate temperature higher than 673 K due to its thinness. Therefore, Cu foil is not a suitable substrate for the growth of InSb. This phenomenon does not occur in the cases of Ni foil and stainless steel foils with thickness of 0.5 mm and 1 mm respectively.

Fig. 5-5 are the SEM images and XRD results of the samples grown on Ni foils with different substrate distances. From the SEM images (see Fig. 5-5 a, c, e), these thin film samples have reduced particle sizes from $d_{\text{sub}} = 16$ cm to 18 cm. The XRD result (see Fig. 5-5b) shows that two phases InSb and Ni_3In co-exist at $d_{\text{sub}} = 16$ cm and the peak intensities of InSb and Ni_3In are similar. At $d_{\text{sub}} = 17$ cm, Ni_3Sb and InSb are obtained, as shown in Fig. 5-5d. When increasing d_{sub} to 18 cm, only NiSb phase (see Fig. 5-5f) is observed. The formation of Ni-Sb and Ni-In intermetallic compounds

indicates that Ni foils react with In or Sb vapor during the growth. At $d_{\text{sub}} = 16$ cm, the excess In vapor is adsorbed and reacts with the Ni foil. With the substrate temperature of 918 K, the high diffusion rate of Ni atoms and the large condensation of In vapor lead to the growth of Ni_3In . From the InSb binary phase diagram (see Fig. 5-4) InSb is in liquid phase at that substrate temperature. The diffusion of liquid InSb among Ni_3In particles causes the formation of the smooth film after cooling down. Increasing the substrate distance to 17 cm, the XRD diffraction peaks of InSb and Ni_3Sb (see Fig. 5-5d) emerge. Because a considerable amount of In vapor is consumed due to the reaction with the Ni foil at 16 cm, the vapor is rich in Sb and Ni-Sb instead of Ni-In alloy is obtained. Since the substrate temperature at 17 cm is around 855 K, the diffusion rate of Ni atoms in Ni foil and Ni-Sb intermetallic compound is still fast enough to facilitate the formation of Ni_3Sb . Further increasing the substrate distance to 18 cm, there is only NiSb phase, as shown in Fig.5-5f. It is noted that all In vapor in the carrier gas is consumed before 18 cm and only Sb vapor is left to react with Ni foil. At $d_{\text{sub}} = 18$ cm, Sb vapor begins to condense largely and the diffusion rate of Ni atoms cannot keep pace with the deposition rate of Sb vapor, leading to the formation of NiSb.

Figure 5-5. (a), (c) and (e) are SEM images of samples obtained at nickel foils with $d_{\text{sub}} = 16$ cm, 17 cm and 18 cm, respectively. (b), (d) and (f) are corresponding XRD patterns at $d_{\text{sub}} = 16$ cm, 17 cm and 18 cm, respectively.

Due to the formation of Ni alloys, Ni foils are not considered as substrates for the growth of InSb. Then the experiment is carried out on stainless steel foils. The XRD results show that except for Fe peak from substrates, there are In and InSb at $d_{\text{sub}} = 16$ cm (see Fig. 5-6a,b), pure InSb phase at $d_{\text{sub}} = 17$ cm (see Fig. 5-1e) as well as Sb and InSb at $d_{\text{sub}} = 18$ cm (see Fig. 5-6c,d) without the observation of Fe-Sb intermetallic compounds. This means that unlike Ni foils, there is no reaction between stainless steel foils and precursor vapors.

Figure 5-6. (a) and (c) are SEM images of materials obtained at stainless steel foils with $d_{\text{sub}} = 16$ cm and 18 cm, respectively. (b) and (d) are corresponding XRD patterns at $d_{\text{sub}} = 16$ cm, and 18 cm, respectively.

From Ni-Sb and Fe-Sb binary phase diagrams[70] (see Fig. 5-7), the stable solid regions of Ni-Sb and Fe-Sb alloys are in the similar temperature range. Because the formation energies of Ni-Sb and Fe-Sb alloys are not of large difference, it is supposed that owing to the strong bonding between Fe and carbon, stainless steel foils are not reactive under the same growth condition.

The different compositions and structures of the as-grown samples at the same substrate distance obtained on Ni foils and stainless steel foils lead to their different morphologies. At $d_{\text{sub}} = 16$ cm, micron-sized In spheres are obtained on the InSb nanoparticle film (see Fig. 5-6a). The high substrate temperature decelerates the deposition rate of Sb vapor, so the amount of condensed In are more than Sb. Besides the formation of InSb nanoparticles, extra In vapor is deposited on the stainless steel foil. Unlike the occurring reaction between extra In vapor and Ni foils, In vapor only adsorbs on stainless steel foils but not reacts with them. The liquid In clusters on stainless steel foils diffuse and migrate together with raised particle sizes. The contact angle (θ) of In liquid cluster, the angle at which the liquid–vapor interface meets the solid–liquid interface, is larger than 90° . This indicates that the interaction between liquid In clusters and the solid substrate is weak. Thus, the liquid In clusters prefer to form liquid droplets rather than the smooth wetting on the substrate surface. Compared with thin film (InSb and Ni_3Sb multiphase) grown on the Ni foil at $d_{\text{sub}} = 17$ cm, the sample obtained on the stainless steel foil at $d_{\text{sub}} = 17$ cm is InSb nanowires with diameter of 200 nm and length above 5 μm . It is obvious that at the same substrate distance, more Sb vapor is adsorbed on Ni foil than on stainless steel foil. The difference might be caused by the consumption of excess In vapor by Ni foil at

$d_{\text{sub}} = 16$ cm and the reaction between Sb vapor and the Ni foil at $d_{\text{sub}} = 17$ cm. Therefore, two phases, InSb and Ni_3Sb are formed on Ni foil while only InSb phase is formed on stainless steel substrate.

Figure 5-7. The binary phase diagram of (a) Fe-Sb[70] and (b) Ni-Sb[70]

5.3.3 Effect of heating temperature

The heating temperature is an important parameter for tuning morphologies and compositions of desired products in the CVD growth. Although the melting point of In (429 K) is low, its boiling point is much higher than that of Sb. Thus, In slots should be placed at the center of the tube furnace and the heating temperature should be high enough to permit the required concentration of In vapor for the nanowire growth. To find out the suitable heating temperature, control experiments are carried out at 1073 K, 1173 K, 1223 K and 1273K. From the experiment results, it is noted that no In volatilizes during the growth with the heating temperature at 1073 K. At 1173 K, In evaporates in a small amount, which leads to the formation of Sb-rich samples. When the heating temperature is set at 1223 K, InSb nanowires are obtained at $d_{\text{sub}} = 17$ cm. Further increasing the heating temperature to 1273 K, all the samples are composed of large In spheres owing to the high In vapor concentration. Thus, the optimized heating temperature is 1223 K.

The determination of the distance between In and Sb sources is through the temperature profile of the tube furnace (see Fig. 5-2). The surrounding temperature at 15 cm of the upstream zone is 934 K. Sb powder placed at 15 cm evaporates very fast and may completely volatilize in the middle of the growth process, which leads to non-uniform composition of samples. Increasing the distance to 16 or 17 cm, the surrounding temperature decreases with a little improvement in the uniformity. When placed at the distance of 18 cm, the suitable evaporation rate of Sb leads to the formation of InSb at $d_{\text{sub}} = 17$ cm. Further increasing the distance of Sb source, the crucible is located outside the tube furnace. In this situation, the surrounding

temperature drops steeply, which causes the slow evaporation of Sb powder and the generation of In spheres. Besides the difficulty of co-evaporation, the different evaporation temperatures also confine the co-condensing region of In and Sb. The Sb vapor mainly deposits at $d_{\text{sub}} > 17$ cm of the downstream zone, while the In vapor mainly deposits at $d_{\text{sub}} < 18$ cm of the downstream zone. That is why only at $d_{\text{sub}} = 17$ cm, the stoichiometric InSb is obtained.

5.3.4 Effect of gas flow rate on the nanowires growth

As following the self-catalyzed vapor-liquid-solid growth mechanism, the growth of InSb nanowires is achieved only when the residence time is longer than the incubation time. The incubation time required for the VLS growth is mainly determined by the surrounding temperature from Equation 2.11. The growth of InSb nanowires is achieved at the substrate distance of 17 cm, where the substrate temperature and the incubation time are constant at the same substrate temperature. Inferred from Equation 2.12, the residence time of precursor gas is in inverse proportion of the flow rate. When the flow rate is higher, e.g. 150 sccm, the residence time is short for the incubation of InSb nanowires and therefore, nanowires are not obtained (see Fig. 5.8a). Additionally, the short residence time of In vapor leads to the reduced deposition amount of In at $d_{\text{sub}} < 17$ cm, which allows the condensation of In vapor at $d_{\text{sub}} = 17$ cm in a large amount. Thus, non-uniform In spheres are formed on the surface when cooling down to the room temperature, as shown in Fig. 5.8a. When the flow rate is set at 100 sccm, the as-grown sample is InSb nanowires (shown in Fig.5-1a). Further decreasing the flow rate to 50 sccm, the residence time is long enough for the nanowire growth. As adatoms have enough time to diffuse along the

surface of the substrate, diameters of liquid catalysts increase. Catalysts on the top of the nanowires, clearly shown in Fig. 5-8b, are larger than those in Fig. 5-1a, which is consistent with the speculation. It is proven by the VLS growth of Si nanowires that the diameters of nanowires are determined by the sizes of catalysts[71]. In Fig. 5-8b, nanowires are of larger diameter and shorter length as compared with those obtained at 100 sccm. Therefore, the flow rate of 100 sccm is suitable for obtaining smaller InSb nanowires.

Figure 5-8. SEM images of materials obtained on stain steel substrates with the flow rate of (a) 150 sccm and (b) 50 sccm, respectively.

5.3.5 Effect of substrate temperature

The substrate temperature is another important parameter influencing the CVD process. As the surrounding temperature can provide thermal energy to activate the chemical reaction, the structures and morphologies of the as-grown samples are varied at the different substrate temperatures. Inferred from the temperature profile of the tube furnace (see Fig.5-2), the substrate temperatures of 16, 17 and 18 cm are 858 K, 785 K and 703 K respectively, which leads to different deposition rates and compositions (excess In and InSb at 16 cm, pure InSb at 17 cm as well as Sb and InSb

at 18 cm). It is noted that InSb nanowires are grown only at $d_{\text{sub}} = 17$ cm while the other two are thin films. At $d_{\text{sub}} = 16$ cm, the substrate temperature causes the unstable InSb phase. The decomposition of InSb leads to the evaporation of Sb with excess In left in the sample. When cooling down to the room temperature, the solidification results in the formation of In micron-sized spheres together with the smooth InSb thin film. The substrate temperature at 18 cm is lower than those at 16 and 17 cm, so the nucleation rate is faster and there is not enough time for incubation. As a result, InSb nanowires growth is favored at the substrate temperature at $d_{\text{sub}} = 17$ cm.

5.4 Concluding Remarks

In summary, the self catalyzed VLS growth was introduced to fabricate InSb nanowires. The detailed growth process and mechanism were deduced from the growth results. As the as-grown InSb nanowires were directly used for battery assembling, different anode current collectors, Cu foils, Ni foils and stainless steel foils were used as substrate to examine their effects on the compositions and morphologies of the samples. Due to easily spoiled Cu foil at the high temperature and reactions between Ni foil and precursor vapors, only stainless steel foils were suitable for the growth of InSb nanowires. Then the control experiments with different heating temperatures, substrate temperatures as well as flow rates were carried out. As these parameters significantly affected the structures, morphologies and sizes of the as-grown samples, they were optimized to obtain the InSb nanowires with desired composition and size.

Chapter 6 Controlled growth of Cu-Sb nanostructures

6.1 Introduction

After the growth of InSb nanowires, it is proposed to further extend the catalyst-free CVD growth process in the fabrication of Cu-Sb nanostructures. Several methods have been introduced in the synthesis of Cu-Sb nanostructures, e.g. ball milling [18, 19], electrochemical deposition [12, 118] and chemical reduction process [16, 17, 119]. The advantages and disadvantages of above approaches have been discussed in the previous chapters. Until now, there is no report on the CVD growth of Cu-Sb alloy, because the large difference of the evaporation and condensing temperatures between Cu and Sb.

According to unexpected result of Ni-In and Ni-Sb alloys obtained on Ni foils during the fabrication of InSb, it reminds the usage of substrates as the Cu source. As a result, a flexible non-catalyst CVD process is proposed to synthesize Cu-Sb nanostructures, e.g. $\text{Cu}_{11}\text{Sb}_3$ nanowires and Cu_2Sb nanoparticles. In such growth process, Cu foils as substrates, are also used as the Cu source, which react with the Sb vapor and form Cu-Sb alloys. The various morphologies and compositions of Cu-Sb alloy are able to obtain by varying the substrate distances.

6.2 Phase analysis and morphology characterization of nanostructured Cu-Sb alloy

A typical growth is conducted in the tube furnace at 773 K. Sb powder in a crucible is placed at the middle of the tube furnace and Sb vapor is transported by continuous Ar/H₂ gas flow to Cu foils in the downstream zone. The substrate temperature can be inferred from the temperature profile of the tube furnace at 773 K, shown in the Fig. 6-1.

Figure 6-1. Temperature profile of the tube furnace at 773 K.

As shown in the SEM and TEM images (see Fig. 6-2 a-b) that nanowires are obtained on the Cu foils at $d_{\text{sub}} = 14$ cm in the downstream zone. The EDX result in the TEM (see Fig. 6-3) on nanowires reveals that the atomic ratio of Cu : Sb is around 11 : 3. Here, nickel grids instead of Cu grids are used for the TEM observation to avoid the interference from Cu grids. The spot diffraction pattern (shown in Fig. 6-2c)

corresponds to the orthorhombic $\text{Cu}_{11}\text{Sb}_3$ phase (JCPDS card 042-0823) and also indicates that the as-grown nanowire is single crystalline. The high resolution TEM image (Fig. 6-2d) shows a lattice spacing of 0.216 nm, which indicates the nanowire grow along the (002) lattice direction. The XRD pattern of the sample (see Fig. 6-2e) reveals only existence of the orthorhombic $\text{Cu}_{11}\text{Sb}_3$ and Cu foils.

Figure 6-2. (a) SEM image, (b) TEM image (c) SAED pattern, (d) HRTEM and (e) XRD pattern of $\text{Cu}_{11}\text{Sb}_3$ nanowire grown on copper foil of $d_{\text{sub}} = 14$ cm at substrate temperature of 563 K under 200 sccm flow rate[120].

Figure 6-3. Representing EDX spectroscopy of $\text{Cu}_{11}\text{Sb}_3$ nanowire. The nickel peaks and carbon peaks are from the carbon coated Ni grid.

Increasing d_{sub} to 16 cm leads to the growth of nanoparticles (NPs) rather than nanowires, as indicated in the SEM and TEM images (see Fig. 6-4a-b). The spot pattern shown in the SAED (see Fig. 6-4c) indicates that the NPs are single-crystalline. The XRD pattern of the sample (see Fig. 6-4e) confirms that the nanoparticles are tetragonal Cu_2Sb (JCPDS card 003-1023), which is consistent with the result of SAED (see Fig. 6-4c) and HRTEM image (see Fig. 6-4d). Except for the Cu peak from the Cu foil, there is no other impurity peaks in the XRD pattern.

Figure 6-4. (a) SEM image, (b) TEM image, (c) SAED pattern, (d) HRTEM and (e) XRD patterns of the as-grown Cu_2Sb nanoparticles at $d_{\text{sub}} = 16$ cm under an Ar/H_2 gas flow rate of 200 sccm[120].

Further increasing d_{sub} to 20 cm results in the decreased substrate temperature (353 K) and the growth of nanoplates (see Fig. 6-5a-b). These nanoplates are 150~200 nm in diameter and 8-15 nm in thickness. The EDX results (see Fig. 6-6) confirms only the existence of Sb. The SAED result (see Fig. 6-5c) reveals that these are single crystalline Sb nanoplates. The HRTEM observation indicates (110) facets along the

surface (see Fig. 6-5d). The XRD pattern also confirms that there is only the rhombohedral Sb phase (JCPDS card 035-0732) except for the Cu peak from the Cu foil(see Fig. 6-5e).

Figure 6-5. (a) SEM image, (b) TEM image, (c) SAED pattern, (d) HRTEM and (e) XRD pattern of the as-grown Sb nanoplates at $d_{\text{sub}} = 20$ cm under an Ar/H₂ flow rate of 200 sccm[120].

Figure 6-6. Representing EDX spectroscopy of Sb nanoparticle. The nickel peaks and carbon peaks are from the carbon coated Ni grid[120].

From the above discussion, $\text{Cu}_{11}\text{Sb}_3$ nanowires, Cu_2Sb nanoparticle thin film and Sb nanoplates are obtained at the substrate distance of 14, 16, 20 cm, respectively. Three substrates are not far from each other, but their substrate temperatures are quite different, inferred from Fig. 6-1. The fast declining of the substrate temperature is one factor contributing to various structures and morphologies. It is noted that there is a temperature gradient within 1 cm at $d_{\text{sub}} > 14$ cm. Since Cu foils with size of 1x1 cm are used as the substrates, the large temperature gradient on one Cu foil may cause the non-uniformity in the as-grown sample. Due to the fast heat transfer of Cu, the large temperature gradient on the Cu foil is avoided, which ensures the formation of uniform samples.

6.3 The study of growth mechanisms of Cu-Sb nanostructures

6.3.1 The study of formation of different Cu-Sb alloys

From Cu-Sb binary phase diagram (see Fig. 6-7), there are many intermetallic compounds, e.g. Cu_2Sb , $\text{Cu}_{11}\text{Sb}_3$, Cu_9Sb_2 and $\text{Cu}_{11}\text{Sb}_2$. Among all the Cu-Sb intermetallic compounds, the formation free energy of Cu_2Sb is lowest, -4.23 kJ/mol[121]. As a result, the favorable Cu-Sb alloy synthesized at low temperature is Cu_2Sb . The Cu_2Sb thin film was reported to be prepared by annealing Cu and Sb films at the temperature range of $423 \sim 573$ K[121]. Increasing temperature to above 573 K, Cu_2Sb phase was not stable and switched to other intermetallic compounds with high Cu atomic ratio, e.g. Cu_9Sb_2 at $623 \sim 873$ K[121].. It is supposed that at a high temperature, Cu_2Sb begins to decompose with the evaporation of Sb and then transfers to other intermetallic compounds, which are more stable at high temperatures.

For Cu-Sb intermetallic compounds, the phase with higher molar ratio of Cu to Sb requires more energy for the growth. During the CVD growth process, the energy to initiate the reaction is provided by the surrounding substrate temperature. As a result, Cu_2Sb is obtained at 16 cm, while $\text{Cu}_{11}\text{Sb}_3$ is obtained at 14 cm. Cu_9Sb_2 phase could only grow at the substrate distance less than 13 cm. The higher substrate temperature is required for the occurrence of chemical reactions and to speed up the diffusion rate of Cu atoms to complement enough Cu atoms for the formation of Cu_9Sb_2 . Since the used copper foil is of $20\text{ }\mu\text{m}$ in thickness and can not sustain the

temperature higher than 673 K, Cu-Sb alloy with high Cu molar ratio, e.g. Cu_9Sb_2 and $\text{Cu}_{11}\text{Sb}_2$ may not be obtained through this method.

Figure 6-7. Cu-Sb binary phase diagram[70].

6.3.2 Study of the $\text{Cu}_{11}\text{Sb}_3$ nanowires growth

(1) Growth mechanism of $\text{Cu}_{11}\text{Sb}_3$ nanowires

Since no foreign materials are introduced during the growth process, the initiation of the $\text{Cu}_{11}\text{Sb}_3$ nanowires without catalysts suggests that the growth follows the vapor solid growth mechanism. The $\text{Cu}_{11}\text{Sb}_3$ nanowires are obtained at $d_{\text{sub}} = 14$ cm, where the substrate temperature is too high for the condensation of Sb vapor. If there is no reaction between Sb vapor and Cu foil, no samples will be obtained at $d_{\text{sub}} = 14$ cm. To prove that, the control experiment is carried out with a glass slide placed

at 14 cm. No deposition is observed at the glass slide. When Cu foils are used as substrates, the occurring reaction facilitates the deposition of Sb vapor due to the formation of the stable $\text{Cu}_{11}\text{Sb}_3$ phase at that substrate temperature. The chemical reaction happening on Cu foil is:

The product $\text{Cu}_{11}\text{Sb}_3$ is stable at the substrate temperature, which hinders the decomposition of $\text{Cu}_{11}\text{Sb}_3$ and further evaporation of Sb.

The initial adsorption of Sb vapor is supposed at those extrusion sites, which have high surface energy and require less energy for the occurrence of adsorption and reaction. Then formed $\text{Cu}_{11}\text{Sb}_3$ nuclei are favorable sites for the adsorption of incoming Sb vapor. At the $d_{\text{sub}} = 14$ cm with the substrate temperature of 563K, the fast surface diffusion rate of Cu atoms encourages the continuous growth of $\text{Cu}_{11}\text{Sb}_3$ nuclei rather than the new nucleation. The orthorhombic $\text{Cu}_{11}\text{Sb}_3$ phase is of anisotropic structure with lattice constants: $a = 19.080 \text{ \AA}$, $b = 4.724 \text{ \AA}$ and $c = 4.324 \text{ \AA}$. The growth along c axis direction requires the lowest formation energy, inferred from the smallest c value. In the view point of thermodynamic, both the nucleation and the continuous growth of $\text{Cu}_{11}\text{Sb}_3$ are preferred to occur at the crystal plane with the lowest formation energy, which is along c axis and consistent with the HRTEM result (see Fig. 6-2d).

The nanowire growth on the extrusion sites of Cu foil need the continuous supply of Cu atoms. At the beginning, the source of Cu atoms comes from the nuclei surrounding. After the surrounding surface atoms deplete, Cu atoms inside Cu foil

diffuse from beneath to the surface as the replenishment. Since the diffusion coefficient is in proportion to the surrounding temperature, the substrate temperature at $d_{\text{sub}} = 14 \text{ cm}$ is high enough for the fast diffusion and to permit the $\text{Cu}_{11}\text{Sb}_3$ nanowires growth.

(2) Effect of substrate surface roughness

From the detailed discussion of $\text{Cu}_{11}\text{Sb}_3$ nanowire growth process, the surface extrusion on the substrate surface, acting like the catalyst, can lower the energy barrier of the reaction and initiate the nanowire growth. In order to understand the effect of substrate surface roughness on the growth process, the control experiments are carried out on different Cu substrates. As examined from the SEM image (see Fig. 6-8a), the Cu foils used for the above NWs growth are relatively rough. The average surface roughness (R_a) is around 154 nm (see Fig. 6-8b). Substituting the rough substrates with a relatively smooth Cu foils (see Fig. 6-8c), the average surface roughness (R_a) decreases to 66 nm (see Fig. 6-8d), which causes the formation of clustered particles (see Fig. 6-9a) rather than nanowires. The size of these clustered particles ranges from 0.5 to 2 μm without changing the composition and phase (see Fig. 6-10).

The above two types of Cu foils are used as-received. To further confirm the effect of surface roughness on the nanowires growth, the smooth Cu foils are etched to increase their surface roughness. The smooth Cu foils are polished with P800 sand paper and then annealed at 563 K under Ar atmosphere for 30 minutes. After such treatment, the smooth Cu foils become rougher, which can be proved by the increased R_a of 212 nm (see Fig. 6-8 e-f). Then, nanowires are successfully obtained on the

treated Cu foil (see Fig.6-9b). The XRD result (see Fig.6-10) confirms that these as-grown nanowires are the orthorhombic $\text{Cu}_{11}\text{Sb}_3$.

Figure 6-8. (a) SEM image and (b) surface roughness profile of the rough Cu foil used for $\text{Cu}_{11}\text{Sb}_3$ nanowires growth. (c) SEM image and (d) surface roughness profile

of smooth Cu foil. (e) SEM image and (f) surface roughness profile of processed smooth copper foil[120].

Figure 6-9. SEM images of $\text{Cu}_{11}\text{Sb}_3$ obtained on (a) the smooth Cu foil and (b) the treated smooth Cu foil. The treatment includes polishing with sand paper and annealing at 563 K under Ar atmosphere for half an hour[120].

Figure 6-10. XRD pattern of $\text{Cu}_{11}\text{Sb}_3$ particles obtained from smooth copper foils of $d_{\text{sub}} = 14 \text{ cm}$ [120].

Although the $\text{Cu}_{11}\text{Sb}_3$ nanowires are successfully obtained by roughing the smooth Cu foil, the nanowires grown on the sand paper treated Cu foil (roughness 212 nm) have lost uniform orientation comparing to the Cu foil with a roughness of 154 nm. The reason can be revealed by the low magnification SEM images of these two Cu foils. As shown in Fig. 6-11, the convexity of the rough copper foil is parallel while that of the processed copper foil is of different orientations. Since the convex area on the surface serves as the seed to initiate the nanowire growth, the non-uniform convex area on the sand paper treated Cu foil leads to the obtained nanowires with various orientations. It is proved that the surface of Cu foil can be treated to initiate the nanowires growth. However, the roughing treatment method is not able to achieve Cu foil with desirable roughness. Without Cu foils with roughness ranging from 66 nm to 154 nm, the morphologies of samples obtained on such Cu foils are unknown. Therefore, it can be only concluded that the nanowire growth is achieved on Cu foil with roughness above 154 nm and the thin film growth on Copper foil with roughness below 66 nm.

Figure 6-11. Low magnification SEM images of (a) rough Cu foil and (b) sand paper polished Cu foil[120].

(3) Effect of the gas flow rate on the size of nanowires

The effect of different flow rates on the as-grown $\text{Cu}_{11}\text{Sb}_3$ nanowires under is also investigated by carrying out experiments with varied flow rates at 50, 100, 200 sccm. As shown in Fig. 6-12a, decreasing $F_{\text{Ar/H}_2}$ from 200 sccm to 100 sccm attributes to the growth of nanowires with shorter length ($\sim 1.5 \mu\text{m}$) and larger diameter ($\sim 500 \text{ nm}$) for the growth time $t_g = 1$ hour. Further decreasing $F_{\text{Ar/H}_2}$ to 50 sccm, the as-grown nanowires with length of $1 \mu\text{m}$ and diameter of $> 1 \mu\text{m}$, begin to agglomerate (see Fig. 6-12b). It can be concluded from the observation that decreasing $F_{\text{Ar/H}_2}$ leads to the growth of nanowires with shorter lengths and larger diameters at the same t_g . The reason can be inferred from the growth process. The growth of the nanowires is regarded as a competition between the diffusion of adatom on the surface and the nucleation of Cu-Sb alloy. Lower gas flow rates cause the slow transportation of Sb vapor and the increased resident time of Sb vapor, which in the end enhance the diffusion process and the growth rate. Thus, the diffusion of as-deposited atoms along the substrate surface is sufficient before the deposition of the next layer of atoms, which causes the increased diameter.

Figure 6-12. SEM images of $\text{Cu}_{11}\text{Sb}_3$ obtained on rough Cu foil under Ar/ H_2 gas flow rates of (a) 100 sccm and (b) 50 sccm[120].

6.3.3 Study of the Cu_2Sb nanoparticle thin film growth

(1) The growth mechanism of Cu_2Sb nanoparticle thin film

The Cu_2Sb nanoparticle thin film obtained at $d_{\text{sub}} = 16$ cm follows the island growth. As discussed before, the substrate temperature at $d_{\text{sub}} = 16$ cm only allows the formation of Cu_2Sb , which is grown and stable at the low temperature. After transported and adsorbed to the substrate, the Sb vapor reacts with the Cu foil. The following is the chemical reaction formula, which occurs during the growth process.

In this chemical reaction, 2 mole Cu is consumed by 1 mole deposited Sb. Because of the higher atomic ratio of Sb in Cu_2Sb , the growth needs more deposition of Sb vapor than that in the $\text{Cu}_{11}\text{Sb}_3$ nanowire growth. At $d_{\text{sub}} = 16$ cm, the decreased substrate temperature (503 K) and the formation of Cu_2Sb encourage more Sb vapor condensing on the Cu foil, as compared with the deposition at $d_{\text{sub}} = 14$ cm. Additionally, the

diffusion rate of Cu atoms decreases at the low substrate temperature, so Cu atoms are not replenished promptly for the growth of the high Cu atomic ratio Cu-Sb alloy. After the nucleation, the continuous deposition on the Cu₂Sb nuclei can depress the increasing interfacial energy of the system. Cu₂Sb has the tetragonal structure with lattice constants: $a = b = 4.000 \text{ \AA}$ and $c = 6.103 \text{ \AA}$, so the difference in formation energies of crystal planes is not large. The growth rate along each direction is close, which allows the formation of Cu₂Sb nanoparticles along different directions. Thus, the Cu₂Sb nanoparticle thin film is obtained.

(2) Effect of the flow rate on the Cu₂Sb particle size

Due to the island growth mode, the low substrate temperature allows the easy deposition of Sb and the particle growth of Cu₂Sb. Such growth does not require the initiation from extrusion sites on the Cu foil surface, so the growth of nanoparticles is independent on the roughness of Cu foil. The size of the particles is tunable through adjusting the flow rate F_{Ar/H_2} . The average sizes are ~200 nm (see Fig. 6-13a) and 1 μm (see Fig. 6-13b) for $F_{Ar/H_2} = 200$ and 50 sccm, respectively. It is observed that the nanoparticles of larger size are grown at low gas flow rates. The main reason is that low gas flow rates provide the sufficient time for the surface diffusion of adsorbed atoms and the continuous particle growth.

Figure 6-13. SEM images of Cu_2Sb nanoparticles obtained at = 16 cm under an Ar/H_2 gas flow rate of (a) 200 sccm and (b) 50 sccm[120].

6.3.4 Study of the Sb nanoplate growth

The island growth is also applicable in the growth of Sb nanoplates at the distance of 20 and 25 cm. Due to even low substrate temperatures, the reaction between Sb and Cu foil does not occur. The obtained nanoplates on the Cu foil are merely single crystalline rhombohedral Sb nanoplates. From the rhombohedral structure of Sb with lattice constants: $a = b = 4.307 \text{ \AA}$ and $c = 11.273 \text{ \AA}$, it is noted that the growth along (0001) direction is not preferable because of the high formation energy required by (0001) direction. Thus, the deposited Sb grows towards (100) and (010) directions, which leads to the nanoplate morphology of Sb.

The size of the as-grown Sb nanoplates is also tunable through adjusting the substrate distance. For example, at $d_{\text{sub}} = 20 \text{ cm}$, nanoplates are 150~200 nm in diameters and 8-15 nm in thickness (see Fig. 6-5a), while at $d_{\text{sub}} = 25 \text{ cm}$, the as-grown sample has the similar morphology with smaller diameters (80-100 nm) and

thinner thicknesses (~ 6 nm) (see Fig. 6-14). The increased substrate distance leads to the lower substrate temperature and Sb vapor concentration. With lower Sb vapor concentration, both the nucleation rate and the crystal growth rate decrease. At the lower substrate temperature, the crystal growth rate is slower than the nucleation rate. Thus, the obtained Sb nanoplates are smaller and more uniform with increasing the substrate distance.

Figure 6-14. SEM image of Sb nanoplates obtained on copper foils at $d_{\text{sub}} = 25$ cm with a substrate temperature of 313 K[120].

6.4 Concluding Remarks

In summary, a simple catalyst-free chemical vapor deposition process was reported to grow nanostructured Cu-Sb alloys. At such growth, Cu foils acted both as the substrates and the Cu source, which offered an alternatively flexible route to synthesize Sb alloys with elements of high evaporation temperatures. By simply controlling the substrate distances, different nanomaterials, e.g. $\text{Cu}_{11}\text{Sb}_3$

nanowires, Cu_2Sb nanoparticles, or Sb nanoplates, were achieved. In the regard of anisotropic $\text{Cu}_{11}\text{Sb}_3$, $\text{Cu}_{11}\text{Sb}_3$ nanowires in such catalyst-free process were initiated by the convex areas on the substrate surface and assumed to follow vapor-solid growth. As the growth of Cu_2Sb nanoparticle thin film was based on the island growth, the surface roughness of Cu foil did not affect the morphology of Cu_2Sb . The size of the as-grown Cu-Sb nanostructures could be tuned by the flow rate of the carrier gas. Such growth strategy could be extended to other Sb alloys, e.g. Co-Sb and Fe-Sb.

Chapter 7 The performance of the as-grown

Sb based nanostructures

7.1 Thermoelectric property of the as-grown and annealed Sb₂Te₃ nanoparticle thin films

After the fabrication of the Sb₂Te₃ particle films with different particle sizes, their thermoelectric properties will be measured to further demonstrate the nanostructuring effect on the enhancement of ZT through increasing Seebeck coefficient and lowering thermal conductivity.

7.1.1 Electrical property of the as-grown samples

The as-prepared Sb₂Te₃ particle films have smooth surfaces (as shown in Fig. 7-1a) and their thicknesses are highly uniform. This means that they can be used directly for the electrical and thermoelectric characterization without further processing. The surface profiler is used for the measurement of thickness. A typical cross-section scan across a large distance ~1mm is shown in Fig. 7-1b. It is expected that there is ~10% error. The thicknesses of samples are double checked with SEM (see Fig. 7-1c).

The four-point-probe measurements in the temperature range of 325-600 K performed in the commercial ZEM 3 system reveal that three films of different particle sizes have very low electrical resistivity in the range of $10^{-4} \Omega \text{ m}$ (see Fig. 7-1d), which is about 2-3 orders lower than that of Sb₂Te₃ nanocrystals prepared by wet-chemical methods [122]. For thermoelectric semiconductors, low electrical resistivity

is essential to achieve high ZT values. For all three types of samples, the electrical resistivity decreases with temperature. Although this trend indicates a typical semiconductor behavior [123], other factors may also affect the electrical resistivity of these samples, e.g. the annealing effect at higher measuring temperature leads to partial agglomeration and hence enhances the contact among the particles to decrease the electrical resistance. Thus, the measurement on the annealed samples is used to assess the intrinsic trend of the electrical resistance vs. temperature.

Figure 7-1. (a) An optical image of the Sb₂Te₃ particle film grown at $d_{\text{sub}} = 30$ cm. (b)

A low magnification SEM micrograph show the cross section of the sample with

uniform thickness. A crack is generated during the preparation of the cross-section sample. (c) A typical cross-section scanned by the surface profiler. (d) Electrical resistivity of the as-grown nanoparticle films[101].

7.1.2 Phase analysis and morphology characterization of annealed samples

The samples are annealed at 523 K for 60 minutes, which is a useful process to reduce the electrical resistivity. The partial agglomeration, evidenced from the SEM observations (see Fig. 7-2a-c) enhances the contact between the particles in all three types of samples after such annealing process. No obvious grain coarsening is observed as indicated by the HRTEM results (see Fig. 7-2d-f), e.g. grain sizes of 7, 13 and 19 nm are obtained for the annealed 20-, 50- and 100-nm particle films respectively, which is consistent with the analysis of the peak width of the XRD patterns of the annealed samples (see Fig. 7-2g).

Figure 7-2. SEM micrographs of (a) 100-nm, (b) 50-nm and (c) 20-nm nanoparticle films after annealing at 523 K for 60 minutes. The dotted square frames are to illustrate areas with partial particle agglomeration that can enhance the electrical contact. HRTEM micrographs of (d) 100-nm, (e) 50-nm and (f) 20-nm annealed

nanoparticle films. (g) XRD patterns obtained from annealed Sb_2Te_3 nanoparticles with different sizes[101].

7.1.3 Comparison of the thermoelectric properties of the as-grown and annealed samples

The measurement on the annealed samples is used to assess the intrinsic trend of the electrical resistance vs. temperature. The electrical resistivity of the annealed samples shows reduced values (see Fig. 7-3) as compared to their corresponding as-prepared ones. In addition, their values are enhanced at higher temperature range, which is expected in metals or heavily doped semiconductors. For either as-prepared or annealed samples, the lower electrical resistivity shown in the larger sized particle films is anticipated as the quantum size effect increases the band gap, E_g , of the semiconductor particles [3, 88].

Figure 7-3. Electrical resistivity of the as-grown and annealed nanoparticle films[101].

The effective charge carrier concentration, n , at room temperature has been investigated by the Hall Effect measurement system[124] (Fig. 7-4a-b). For the as-prepared samples, the effective charge carrier concentration is in the range $3\sim 8\times 10^{19} \text{ cm}^{-3}$, which is an ideal concentration range to achieve optimized ZT values [41]. The effective charge carrier concentration increases slightly, e.g. $6\sim 10\times 10^{19} \text{ cm}^{-3}$ after annealing at 523 K for 60 minutes for all three types of samples. The higher effective charge carrier concentration obtained in larger sized particle films is expected as increasing the band gap due to the quantum confinement may decrease the value of n [57]. Based on the charge carrier concentration data, we can estimate the effective hole mobility μ of particle films using $\sigma = ne\mu$ (Fig. 7-4c-d). The estimated effective hole mobility of the samples increases by 5~7 times after the heat treatment. This suggests that the enhanced contact among the particles after annealing can effectively reduce the interface scattering of the charge carriers.

Figure 7-4. Room-temperature effective charge carrier concentration, n , of (a) as-prepared and (b) annealed samples with different particle sizes. Hole mobility of (c) as-prepared and (d) annealed samples with different particle sizes.

Thermoelectric characterization with the ZEM 3 system shows that all three sized Sb_2Te_3 particle films are p-type with high maximum Seebeck coefficients, e.g. $>200 \mu\text{V/K}$, $>180 \mu\text{V/K}$, and $>160 \mu\text{V/K}$ for 20-nm, 50-nm and 100-nm particle films, respectively (see Fig. 7-5a). These values are 100-150% higher than that of bulk Sb_2Te_3 crystals ($79 \mu\text{V/K}$) with similar charge carrier concentrations [125] and are

also higher than that of Sb_2Te_3 nanoplates ($125 \mu\text{V/K}$) synthesized by wet-chemical approach[103]. The enhanced Seebeck coefficient is mainly attributed to the quantum confinement effect. When the particle/grain sizes decrease to the quantum scale, the difference between the Fermi level and the average mobile carrier energy is increased [57], which results in the higher S values. As the quantum confinement effect attributes to the enhancement of Seebeck coefficient, the enhancement should be directly related to the change of the band gap. The band gap of the semiconductor is related to the feature size as

$$E_g = \frac{A h^2}{8 m L^2} \quad (7.1)$$

where h is the Plank constant, A is the constant related to the orbital numbers, m is the charge carrier mass and L is the feature size of the semiconductor. Thus, smaller L leads to larger band gap, which means the confinement effect is stronger. In addition, the enhancement is also related to energy filtering effect. Smaller grains induce more grain boundaries to filter the low energy charge carriers and in the end result in higher Seebeck values.

Besides, all three sized particle films show increased Seebeck values at higher temperature range. For heavily doped semiconductors or metals, the electron contribution to Seebeck is proportional to the absolute temperature. The values of Seebeck for the annealed samples are comparable to those of the as-prepared ones (see Fig. 7-5b), although their electrical resistivities are significantly lower.

Figure 7-5. (a)-(b) Seebeck coefficient of the as-grown and annealed nanoparticle films[101].

The plots of power factor (see Fig. 7-6a-b) defined as $S^2\sigma$ of the as-prepared samples show values $> 3 \times 10^{-4} \text{ W/mK}^2$ at $T > 550 \text{ K}$. The power factors for the annealed samples are significantly improved by 2-3 times. A maximum power factor $> 1.1 \times 10^{-3} \text{ W/mK}^2$ is measured in the 20-nm particle films at $T=500 \text{ K}$. The smaller sized particle films show the higher power factor, which is mainly due to the contribution of their higher values of Seebeck coefficients.

Figure 7-6. (a)-(b) Power factors of the as-grown and annealed nanoparticle films[101].

The measurement of κ for nanostructures or even thin films is very difficult [56, 126] because of the small feature size. The pulsed photothermal reflectance (PPR) [83, 84] process is carried out to evaluate the thermal conductivity of the samples. It is noted that the PPR measurements can only test the thermal conductivity along the vertical plane of the particle film while the previous discussion on Seebeck coefficient and electrical conductivity is along the surface of the samples. Although these nanoparticle-assembled films are expected to be isotropic because of their unique build-up structures, we can only estimate ZT values based on these measurements. For PPR method as discussed in detail in the experimental session (also see Fig. 3-3), the thermal conductivity, κ , is obtained by curve fitting the time dependence surface temperature profile of the Au film coated sample with the three-layer heat conduction model.

Although the PPR measurements have the advantage that do not require the known values of density and specific heat of the samples, only room-temperature thermal conductivity of as-prepared and annealed samples could be obtained (see Table 7-1) due to the limitation of our instrumental set up. The PPR measurement indicates that the 20-nm Sb_2Te_3 nanoparticle films show much reduced values of κ at room temperature, e.g. 0.23 W/mK for as-prepared samples and 0.33 W/mK for annealed samples, which are much lower than that reported for compact bulk Sb_2Te_3 , e.g. ~ 1 W/mK [127]. The values of the thermal conductivity for Sb_2Te_3 samples with different particles sizes, e.g. 0.2~0.5 W/mK for as-prepared particles and 0.3~0.8 W/mK for annealed particles, are comparable to those recently reported values for Bi_2Te_3 nanoparticles[128, 129].

Table 7-1. Room temperature thermal conductivity of Sb_2Te_3 nanoparticle samples[101].

Thermal conductivity measured by PPR	As-prepared Samples (W/mK)			Annealed Samples(W/mK)		
	100 nm	50 nm	20 nm	100 nm	50 nm	20 nm
	0.5	0.38	0.23	0.78	0.55	0.33

As we know, the heat inside materials is transported by two sources, charge carriers and phonons. The charge carrier contribution is proportional to the electrical conductivity and the measuring temperature through the Wiedemann-Franz law. The phonons transport heat through lattice. The lattice contribution depends on the

properties of the material lattice, which can be seen as independent of the carrier concentration. Here, the carrier thermal conductivity of samples at room temperature can be calculated, which is not high, e.g. 0.012~0.04 W/mK for as-prepared samples and 0.17~0.26 W/mK for annealed samples from the calculation using Wiedemann–Franz’s law [130, 131] (Equation 2.4b):

$$\kappa_{\text{carrier}} = LT/\rho$$

where L is the Lorenz number, e.g. $2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$, ρ is the electrical resistivity, and T is the temperature in Kelvin. Then the phonon contribution is obtained by subtracting the charge carrier contribution from the total thermal conductivity, which is larger than the electron contribution. The small grain sizes in the Sb_2Te_3 nanoparticle samples with more interfaces can scatter phonon effectively and reduce the total thermal conductivity of samples. Therefore, thin film samples with smaller grain size have lower thermal conductivity.

7.2 Electrochemical properties of InSb nanowires

From the published references [14, 108, 132], the thermoelectric performance on the InSb single nanowire and InSb thin film samples were intensively investigated both theoretically and experimentally. As a result, the continuous study of InSb synthesized by CVD in thermoelectric application is not of great innovation. InSb, a promising anode material in lithium ion batteries, has the theoretical capacity of 300 mAh/g[110], but its volumetric capacity, $1710 \text{ mAh}/\text{cm}^3$, is twice of graphite (820

mAh/cm³). The good electrical conductivity of InSb can contribute to the low cell resistance. The relatively small volume expansion of InSb leads to the good capacity retention during charge/discharge cycling. These features make InSb a good candidate as anode to replace graphite. Therefore, in this section the measurement of electrochemical property of InSb nanowires will be carried out.

The as-grown InSb nanowires on the stainless steel substrate can directly be assembled and tested in the coin-type cell with Li foil as the reference electrode. The schematic in Fig. 3-4 shows the structure of the coin-type cell. The assembling process is described in Chapter 3. Fig.7-7 is a cyclic voltammogram (CV) curve of InSb nanowires cycling cathodically and anodically. The voltage window is between 0.0 and 2.6 V with scan rate of 0.5 mV/s. The broad peak of the first cathodic sweep is visible from approximately 0.7 V. The reported lithiation process of InSb nanowires includes three steps [110, 133], but there are no expected three peaks representing each step at the initial discharge of CV curve. Such change may be caused by the possible oxidation of InSb nanowires surface and slight altering of the InSb structure at the first intercalation. The attribution to the broad peak is termed as the conditioning reaction, reported by Johnson and Vaughey[110, 133]. At the first step, Li atoms are inserted into interstitial sites of InSb zinc blend structure with the extrusion of In atoms. In this reduction, two Li atoms incorporate with InSb and Li₂InSb is formed as shown in the following[110, 134].

In the subsequent step, more Li atoms insert into Li_2InSb structure with the replacement of the In sites. The following is the insertion reaction formula of second step [110, 134].

The formation of $\text{Li}_{2+x}\text{In}_{1-x}\text{Sb}$ indicates that not all In atoms are extruded in this step.

Sweeping from 0.5 to 0.0 V, the remaining In atoms are further replaced by Li atoms. Besides, Li reacts with the extruded In and the product is Li_xIn phase e.g. LiIn , Li_5In_4 , Li_3In_2 , Li_2In and $\text{Li}_{13}\text{In}_3$. The reaction formulae of this step are shown in the following [110, 134].

For the initial anodic sweep, the peak near 0.5 V can be attributed to the delithiation from Li_xIn phase. Then, three subsequent peaks exist between 0.5 V to 2.6 V. The first peak at about 0.7 V is attributed to the further removal of Li from Li_xIn phase. The second peak at about 1.0 V represents the Li extraction from Li_3Sb and In partially reincorporated into $\text{Li}_{2+x}\text{In}_{1-x}\text{Sb}$ framework. The third peak at about 1.2 V is due to further reincorporation of In with the formation of InSb [110, 134].

On the second sweep, there are clearly two peaks at around 0.8 V and 0.5 V, compared with the first sweep. The first peak owes to the first step of Li intercalation into InSb framework. The second peak is composed of two split peaks, which represent the further insertion of Li and the reaction of Li with In, respectively. The

peaks in the second anodic sweep are similar as the initial sweep, which means the occurrence of same delithiation process.

Figure 7-7. Cyclic Voltammogram of InSb nanowires with scan rate of 0.5 mV/s.

The cycling performance of InSb nanowires is tested in the coin-type cell. Fig. 7-8 shows the cycling performance of InSb nanowires obtained at 100 and 50 sccm with a voltage window of 0.01-1.2 V at a current density of 0.2 C, which depicts the discharging capacities of their first cycles are ~750 and ~680 mAh/g, respectively. The large irreversible capacities between the first and second cycle are observed in two samples, which are mainly due to the decomposition of electrolyte and the formation of SEI layer on the electrode surface. The SEI layer consists of Li₂CO₃, various Li alkylcarbonates (ROCO₂Li), LiF, Li₂O and nonconductive polymers. After the first cycle, the discharging capacities of InSb nanowires decrease gradually, remaining ~ 400 and 330 mAh/g at the 50th cycle for InSb nanowires obtained at 100

and 50 sccm. The reason for observing such unstable cyclability is due to the further reaction of Li with extracted In atom from InSb. During this process, several strategies lead to the permanently trap of Li ions in the alloys, such as the slow Li ion diffusion and release as well as the production of highly stable Li-In alloys. Additionally, the large variation of volume and complex structural transformation during the formation of Li-In alloys cause the formation of defects or grain boundaries in alloy particles. As a result, a large amount of In atoms remain outside of the InSb structure, which also leads to the gradual loss of capacity during cycling.

Observed from Fig. 7-8, the better cycling performance of InSb nanowires is obtained at 100 sccm in spite of the larger irreversible capacity. As the smaller size of InSb nanowires obtained at 100 sccm leads to the larger electrode/electrolyte contact area, more Li atoms are consumed through the formation of SEI, which causes the larger irreversible capacity. Due to their smaller size, the better accommodation of the volume expansion and the shorter diffusion path distance for Li ions and electrons contribute to the better cyclability of InSb nanowires obtained at 100 sccm. The performance of InSb nanowires obtained at 100 sccm is better than that of micron-sized InSb particles, which had a capacity of 270 mAh/g after 10 cycles[113] and comparable to the reported 10 nm InSb nanoparticles, which maintained a capacity of 480 mAh/g after 30 cycles[114].

Figure 7-8. Cycling performance of InSb nanowires obtained at 50 and 100 sccm with a voltage window of 0.01-1.2 V at a current density of 0.2 C.

As discussed above, the performance of InSb nanowires can be improved by narrowing the potential window to avoid the lithiation of In. Thus, the voltage window is set at 0.5 -1.2 V. As shown in Fig. 7-9, the performance of InSb nanowires at the current rate of 0.2 C is more stable as compared with that in Fig. 7-8. The initial discharging capacity is 368 mAh/g and the irreversible capacity is 63 mAh/g. The capacity is ~280 mAh/g after 50 cycles. The reduced irreversible capacity is due to the confined lithiation of In. The voltage window, set at 0.5-1.2 V, yields the theoretical specific capacity of InSb is 340 mAh/g compared to 679 mAh/g at the voltage window of 0.01-1.2 V. Although the capacity is lower at the voltage window of 0.5-1.2 V, the cycling performance is much better.

Figure 7-9. Cycling performance of InSb nanowires with a voltage window of 0.5 - 1.2 V at a current density of 0.2C.

7.3 Electrochemical properties of Cu₂Sb nanoparticle thin films

Besides InSb, Cu₂Sb as an anode material in Li ion batteries also shows less volume changes and better reversibility among Sb alloys. The nanosized Cu₂Sb with enhanced tolerance of volume expansion is expected to have better performance than bulk Cu₂Sb. In addition, the growth of Cu₂Sb with Cu foil as the source of precursor improves bonding between the active materials Cu₂Sb and Cu foils, which may prevent the loss of active materials during cycling. To reveal the above effects on the performance of Cu₂Sb nanoparticle thin film, the measurement of electrochemical property of Cu₂Sb nanoparticle thin film is carried out in the same way as InSb nanowires.

Fig. 7-10 is the cyclic voltammogram curve of the Cu₂Sb nanoparticle thin film cycling cathodically and anodically. The voltage window is between 0.0 and 3.0 V with the scan rate of 0.5 mV/s. A broad peak with two separated peaks is evidenced at the initial cathodic sweep. The potential of peak is not consistent with the reported reduction potential of Cu₂Sb[20]. It is supposed that the reason is similar as InSb. At the initial break-in cycle, the conditioning reaction occurs, which indicates that the lithiation process of Cu₂Sb, the reduction of electrolyte and the formation of SEI layer associating with the possible surface oxidization on the surface of active materials contribute to part of the broad peak.

For the initial anodic sweep, the peak near 1.1 V can be attributed to the reformation of Cu₂Sb from Li₃Sb phase. The delithiation process includes two steps. The first step is the formation of Li₂CuSb at 0.93 V and the second step is at 1.05 V[20]. The overpotential and the quick scan rate lead to the formation of one broad peak, shown in the anodic sweep of the first cycle.

At the second cathodic sweep, there are two peaks, which represent two stages of the lithiation process of Cu₂Sb. The peak, starting from approximately 1.0 V with the maximum potential at 0.8 V, attributes to the intercalation of Li atoms into interstitial sites of Cu₂Sb framework with the product of Li₂CuSb[18]. The chemical formula is shown in the following[18].

From the formula, it is noted that the first lithiation stage is to place every one Cu atom with two Li atoms. Cu₂Sb is of tetragonal structure with lattice parameters a=b=

4.03 Å, $c = 6.01$ Å, while Li_2CuSb is the cubic structure with lattice parameters $a=b=c = 6.28$ Å. After this phase transition, the volume expansion is about 25.2 % [18].

The subsequent peak is at ~ 0.6 V. During this stage, the left Cu atoms are all extruded from Li_2CuSb and the Li_3Sb phase is finally obtained. The following is the chemical formula of the reaction [18]:

Here, every one Cu atom is replaced with one Li atom. Li_3Sb is also a cubic structure with the lattice parameter of 6.55 Å, a little larger than that of Li_2CuSb , so the increasing volume is smaller than the first stage, only 13.3 % [18].

The second anodic sweep is similar as the first sweep, but the broad peak in the anodic sweep is clearly composed of two split peaks, which indicates two steps of the delithiation process.

Figure 7-10. Cyclic voltammogram for Cu_2Sb nanoparticle thin film from 3.0 V to 0.01 V vs. Li/Li^+ with the scan rate of 0.5 mV/s. The first two cycles are shown.

Fig. 7-11 is the cycling performance of Cu_2Sb nanoparticle thin films obtained at 50 and 200 sccm at a current density of 0.2 C with a voltage window of 0.01-1.2 V. The initial specific capacities of Cu_2Sb nanoparticle thin films are ~545 and 466 mAh/g, respectively. The large irreversible capacities of these two Cu_2Sb nanoparticle thin films are due to the decomposition of electrolyte and the formation of SEI layer on the electrode surface. The capacity of the sample obtained at 50 sccm is lower than that obtained at 200 sccm, due to its larger particle size. After the first cycle, a capacity of 278 mAh/g at the 50th cycle is achieved at the Cu_2Sb thin film obtained at 200 sccm, which is ~86% of the theoretical capacity of Cu_2Sb . The steady performance within 50 cycles indicates the good reversibility after the first cycle. The reason for the good cyclability is the instinct property of Cu_2Sb and the increased bonding between active materials and current collectors. As mentioned before, the volume expansion of Cu_2Sb during Li insertion and extrusion is small. In addition, the good electric conductivity and ionic conductivity of Cu_2Sb compared with other semiconductor anode materials permit the fast diffusion of electrons and Li ions. Although the nanostructure can further depress the volume expansion and the pulverization, the reported Cu_2Sb thin film fabricated by pulsed laser deposition showed the severe capacity fading[20] and the Cu_2Sb nanoparticles with particle size of 50-70 nm had a capacity of 200 mAh/g within 25 cycles. The loss of active materials and the low matrix conductivity due to the loss contact between the active materials still existed in the reported samples. As a result, it is supposed that the CVD growth of Cu_2Sb with Cu foil as the precursor improves the bonding between the

Cu₂Sb nanoparticle thin film and Cu foil, which can increase the electrical conductivity and effectively avoid the loss of active materials.

Figure 7-11. Cycling performance of Cu₂Sb nanoparticles thin films obtained at 50 and 200 sccm with a voltage window of 0.01-1.2 V at a current density of 0.2C.

7.4 Concluding Remarks

In this chapter, the work demonstrated the expected improved performance of the as-grown Sb based nanomaterials through CVD process. The measurement of thermoelectric properties of Sb₂Te₃ particle samples with tunable crystal size, e.g. 5~15 nm showed a 100~150% raising in the Seebeck coefficients as compared to that of bulk Sb₂Te₃ due to the quantum confinement effect. The power factor of above $1.1 \times 10^{-3} \text{ W/mK}^2$ was realized in the 20-nm Sb₂Te₃ particle films and the thermal

conductivity of 20-nm Sb_2Te_3 particle sample was much lower than that of bulk Sb_2Te_3 , which owed to the dropped κ_{lattice} from increased phonon scattering.

As promising anode material for lithium ion battery, the electrochemical properties of InSb nanowires and Cu_2Sb nanoparticle thin film were also investigated. The cycling performance of InSb nanowires under the current density of 0.2 C at the potential window of 0.5-1.2 V showed the specific capacity was ~ 280 mAh/g after 50 cycles. The cycling performance of Cu_2Sb nanoparticle thin film at the current density of 0.2 C was carried out. The specific capacity of Cu_2Sb nanoparticle thin film was ~ 278 mAh/g after 50 cycles. The nanostructuring effect and the enhanced bonding between active materials and substrates (also as current collectors) through the CVD growth attributed to good reversibility and cyclability of both InSb nanowires and Cu_2Sb nanoparticle thin film.

Chapter 8 Conclusions and Future work

8.1 Conclusions

This thesis investigated the processes and mechanisms of the catalyst-free chemical vapor deposition growth of Sb based nanomaterials, e.g. Sb_2Te_3 , InSb and Cu_2Sb . The measurements of thermoelectric properties of Sb_2Te_3 nanoparticle films as well as electrochemical properties of InSb nanowires and Cu_2Sb nanoparticle films were carried out to evaluate their performance. The ultimate goal of the study was to understand the non foreign catalysts induced CVD growth mechanism of Sb based compounds and to verify the size-performance relationship caused by such growth.

The present work started from the growth of Sb_2Te_3 nanoparticle films with the controlled particle size using a catalyst-free vapor transport growth technique. Films with average particle sizes of 100, 50 and 20 nm were obtained on substrates placed at $d_{\text{sub}} = 20, 25$ and 30 cm away from the center of the tube furnace with the substrate temperature of 347, 313 and 309 K, respectively. Due to the low substrate temperature (below 373 K), the slow diffusion rate and the fast nucleation rate resulted in the preferable adsorption on previous adsorbed adatoms and the small particle size. Thus, the nanoparticle thin films followed an island growth mechanism. The effect of carrier gas flow rate on the compositions and morphologies of samples was studied from control experiments. The fast flow rate permitted the sufficient supply of precursors, so the compositions of thin film samples on each substrate were uniform. Such growth

process allowed the realization of nanocrystal films with tunable crystal size, e.g. 5~15 nm, which may result in good thermoelectric properties.

Most reported nanowire growth by CVD was induced by foreign catalysts. To carry out the nanowires growth through the catalyst-free CVD process, InSb was chosen, due to the consideration that In has a relatively low melting point and can act as catalysts to initiate oriented nanowire growth. Therefore, a simple self-catalyzed chemical vapor deposition process was introduced to grow InSb nanowires on stainless steel substrates. Deduced from the experimental results, the growth of InSb nanowires occurred under the VLS growth mechanism. Control experiments with varying parameters were carried out to study the effect of substrate materials, the flow rate of carrier gas, the heating temperature and the substrate temperature on the structures and morphologies of as-grown materials. These parameters were optimized to achieve stoichiometric InSb nanowires.

The third part of this work was to use the catalyst-free chemical vapor deposition process to grow Cu-Sb nanostructures. In this growth, Cu foils served as the substrates as well as the Cu source, which offered a simple and flexible route to prepare different Cu-Sb alloy nanostructures. By simply controlling the substrate distance, different nanomaterials, e.g. $\text{Cu}_{11}\text{Sb}_3$ nanowires, Cu_2Sb nanoparticles, or pure Sb nanoplates, were obtained. In the regard of anisotropic $\text{Cu}_{11}\text{Sb}_3$, $\text{Cu}_{11}\text{Sb}_3$ nanowires in such catalyst-free chemical vapor deposition process followed vapor-solid growth and was dependent on the substrate surface roughness. As the growth of Cu_2Sb nanoparticle thin film was based on the island growth, the surface roughness of Cu foil did not affect the morphology of Cu_2Sb . Besides, the size of as-grown Cu-

Sb nanostructures could be tuned by the flow rate of carrier gas. Such growth strategy could be extended to other Sb alloys, e.g. Co-Sb, Fe-Sb.

After fabrication, the performance of the as-grown nanomaterials in thermoelectric and lithium ion battery was studied. The measurement of thermoelectric properties of the Sb_2Te_3 particle samples with tunable crystal size, e.g. 5~15 nm showed a 100~150% rise in the Seebeck coefficients as compared to that of bulk Sb_2Te_3 due to the quantum confinement effect. The power factor of above $1.1 \times 10^{-3} \text{ W/mK}^2$ was realized in the annealed 20-nm Sb_2Te_3 particle films and the thermal conductivity of 20-nm Sb_2Te_3 particle sample is much lower than that of bulk Sb_2Te_3 , because of the reduced κ_{lattice} from increased phonon scattering.

As promising anode materials for lithium ion battery, the electrochemical properties of InSb nanowires and Cu_2Sb nanoparticle thin films were investigated. The cycling performance of InSb nanowires under the current density of 0.2 C at the potential window of 0.5-1.2 V showed the specific capacity was ~ 280 mAh/g after 50 cycles. The cycling performance of Cu_2Sb nanoparticle thin films at the current density of 0.2 C were carried out. The discharging capacity of Cu_2Sb nanoparticle thin films was ~ 278 mAh/g after 50 cycles. The nanostructuring effect and enhanced bonding between active materials and current collectors (also as substrates) through the CVD growth were credited for the good reversibility and cyclability of both InSb nanowires and Cu_2Sb nanoparticle thin films.

The above results demonstrated that CVD was a promising route to achieve Sb based nanomaterials as interesting TE semiconductors and battery anode materials with good cyclability.

8.2 Future work

Based on the results of the present work on the controlled chemical vapor deposition growth of Sb based compounds, following work can be inspiring.

8.2.1 Study of the growth process of other Sb based intermetallic compounds

The Sb based materials synthesized in the present work are Sb_2Te_3 , InSb and Cu-Sb nanostructures. Other intermetallic compounds, such as Sn-Sb, Co-Sb, Fe-Sb and Mn-Sb also exhibit good performance in lithium ion batteries[135-137] and thermoelectric[138-140]. Inspired by the fabrication of Cu-Sb by using Cu foil as substrates and the Cu source, it is tempting to grow Sn-Sb and transition metal antimonides by the same process. Based on the experimental results, the growth process and the experimental parameters will be investigated. Then, their performance in thermoelectric or lithium ion battery will be studied to achieve expected good properties.

Sn-Sb alloy is regarded as a promising anode material to replace graphite in lithium ion battery, because both Sn and Sb can alloy with Li to form $\text{Li}_{22}\text{Sn}_5$ (specific capacity: 994 mAh/g) and Li_3Sb (specific capacity: 660 mAh/g). The theoretical specific capacity of Sn-Sb alloy varies due to the different weight ratios of Sn and Sb, but it is still higher than other antimonides alloying with inactive materials (not reactive with Li at the potential window of 0-3.0 V). The fabrication methods reported are the co-reduction method from aqueous solution[141], electrochemical deposition[142] and carbothermal reduction of SnO_2 and Sb_2O_3 powders[143]. Shown in these references, the fabricated SnSb particles were of large size or aggregated

nanoparticles. Their cycling performance showed that the first irreversible capacities were large and the capacity retention was relatively low[136, 141, 143]. The large volume expansion of Sn and Sb during cycling causes the lost contact between active materials and current collectors. Such volume expansion and even pulverization lead to the severe capacity fading. Decreasing the particle size of SnSb may of great help in improving the cyclability. Smaller particles show good tolerance to the volume expansion, so the loss of active materials during charging and discharging is much less than that of larger particles. Therefore, the study of the catalyst-free chemical vapor deposition growth of nanosized SnSb is of great meaning to achieve separated SnSb nanostructure and improve its performance in lithium ion batteries.

Transition metal antimonides, e.g. Co-Sb, Fe-Sb, Mn-Sb, show good performance in both thermoelectric and lithium ion batteries. Unlike Sn-Sb, transition metal antimonides are inactive materials [136] alloyed with Sb, so their specific capacities are lower than that of SnSb. During cycling, the transition metals (Co, Fe and Mn) are extruded as the buffering matrix. The matrix can increase the electronic conductivity and prevent the large volume expansion at the same time. Besides the application in lithium ion batteries, their performance in thermoelectric[138, 139] also deserves investigation.

8.2.2 Synthesis of Si coated Sb based alloys through two-step CVD growth

Although Sb based alloys are of high volumetric specific capacities (in mAh/cm³) and high working potentials, their mass capacities (in mAh/g) are low. Both high volumetric and mass specific capacities are required in lithium ion batteries to achieve high energy density. The total capacities of lithium ion batteries are mainly

determined by the capacities of electrodes. It is noted that when the capacities of anode materials reach 1200 mAh/g, the increasing in the total capacities is negligible [144]. Thus, one aim in this field is to synthesize anode materials with capacities ~1200 mAh/g. As far as we know, the reported material of the highest specific capacity is Si. During the lithiation, Li-Si alloys such as $\text{Li}_{12}\text{Si}_7$, $\text{Li}_{14}\text{Si}_6$, $\text{Li}_{13}\text{Si}_{14}$ and $\text{Li}_{22}\text{Si}_5$ are formed at different potentials. The formation of $\text{Li}_{22}\text{Si}_5$ phase means that one Si atoms can alloy with 4.4 Li atoms, so theoretical specific capacity of Si is 4200 mAh/g. Introduction of Si into single-phase Sb based nanomaterials is interesting to enhance the specific capacities of Sb based nanocomposites. The growth of Si by CVD is full studied. The typical Si precursor is silane and the decomposition temperature is not high, ~ 673 K. Therefore, coating crystalline or amorphous Si layers on the surface of nanostructured Sb alloys with improved specific capacities is expected to pursue.

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