

# Growth of Amorphous SiO<sub>2</sub> Net-Like Nanobelts via a Simple Thermal Evaporation of CdS Powder

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**Abstract:** The novel SiO<sub>2</sub> net-like nanobelts have been successfully fabricated on Au-coated Si substrates by a simple thermal evaporation of CdS powder. The as-synthesized SiO<sub>2</sub> nanostructures were characterized by using scanning electron microscope (SEM), transmission electron microscope (TEM) and energy dispersive spectroscopy (EDS), respectively. The as-grown SiO<sub>2</sub> net-like nanobelts are rather uniformly and each nanobelt is about hundreds of micrometers in length and about 1-2 micrometers in width. The important role of CdS in the formation of the SiO<sub>2</sub> net-like nanobelts and the possible growth mechanism of the as-grown nanobelts from the thermodynamic aspect are discussed.

**Keywords:** Nanomaterials, Semiconductors, Net-like, SiO<sub>2</sub> nanobelts, Thermal evaporation.

## 1. INTRODUCTION

Due to their unique optoelectronic properties and potential applications in nanoscale device, the research of one dimensional (1D) nanostructures has attracted much attention [1,2]. In recent years, various 1D nanostructures, including nanowires, nanorods and nanotubes have been synthesized with many materials, such as IV, II-VI, III-V and other group's semiconducting materials [3-5]. As one of the most important semiconductors, SiO<sub>2</sub>, which has a large band-gap energy of 8.8 eV (300K), is a unique functional semiconducting material [6]. Bulk and thin film SiO<sub>2</sub> materials have been extensively investigated owing to their applications for optoelectronic devices such as panel displays and laser emitter [7,8].

Recently, many one dimensional (1D) SiO<sub>2</sub> nanostructures such as nanotubes [9], nanowires [10], and helical fibers [11] have been fabricated by means of various methods, including thermal evaporation [12], solution-phase method [13], and template [14]. The previous researches show that the key factors affect the properties and behaviors of these potential nanodevices are the size, morphology, and crystalline structure of the semiconductor 1D nanostructures [15]. The fabrication of nanostructures with special size and well-defined shape may open new opportunities for exploring unique physical and chemical properties [16]. Thus, further researches are needed to investigate novel morphology.

In this letter, we report on the synthesis of SiO<sub>2</sub> net-like nanobelts, with length about hundreds of micrometers and width on the order of 1-2 micrometers. The important role of CdS in the formation of the SiO<sub>2</sub> net-like nanobelts and the

possible growth mechanism of the as-grown nanobelts from the thermodynamic aspect are discussed.

## 2. EXPERIMENTAL DETAILS

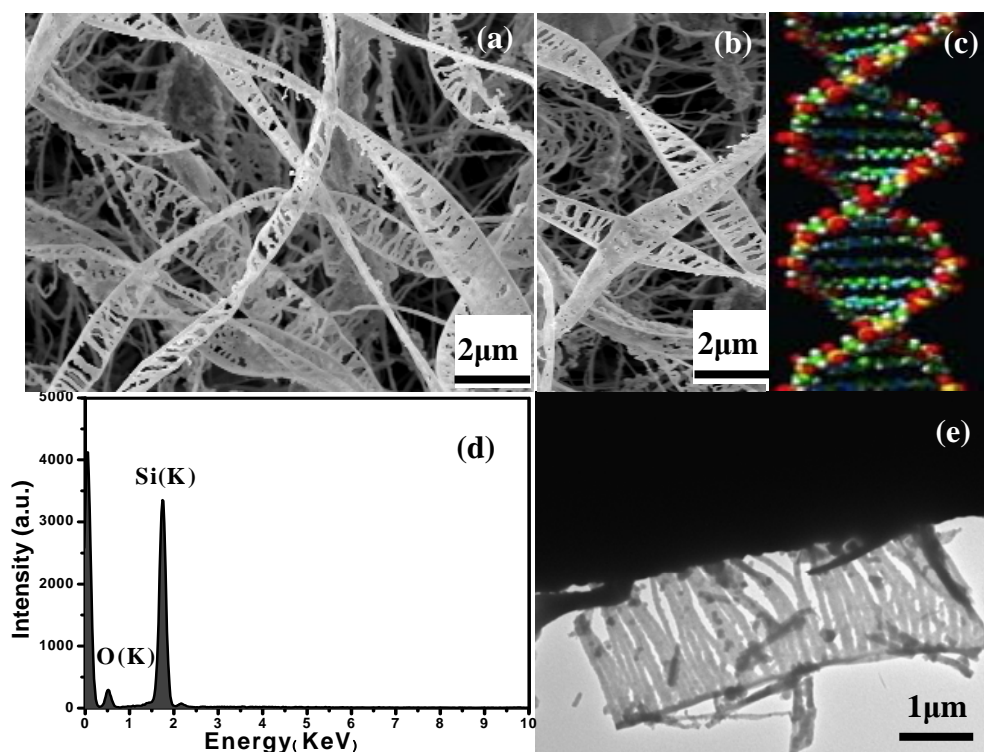
The SiO<sub>2</sub> net-like nanobelts were synthesized using a high-temperature vacuum-tube furnace, as described in detail elsewhere [17]. Briefly, commercial CdS powder was placed on an alumina boat in the center region of a quartz tube. Silicon substrates covered with Au thin film were placed in downstream to collect the products in the quartz tube. The tube was then pumped down to a base pressure of  $\sim 2 \times 10^{-2}$  Torr. Argon gas was introduced into the tube at a constant flow rate of 200sccm (sccm: standard cubic centimeters per minute). The total pressure was kept at  $2 \times 10^{-2}$  Torr during the experimental process. The furnace was maintained at 900°C for two hours before it was cooled to room temperature. A large yield of white product was deposited on the silicon substrates.

The size and morphology of the as-products were examined by SEM (FEI, FEI SIRION 200). The elemental analyses of individual nanostructures were carried out with the EDS (OXFORD, INCA Oxford), an accessory of the SEM. The crystallographic structures of the products were investigated by TEM (Tecnai 20, 200KV, FEG).

## 3. RESULTS AND DISCUSSION

A general morphology of the product shown in SEM images reveal that the net-like nanobelts spread the most area of the Si substrate, as Fig. 1(a) and Fig. 1(b). The nanobelts are rather uniformly and each nanobelt is about hundreds of micrometers in length and about 1-2 micrometers in width. It also shows that the as-grown nanobelts with a novel morphology, two borders jointed by symmetrical nanowires and have a regular helix along the belt, which is similar to the DNA model, as shown in the Fig. 1(c). The EDS profile taken from the SEM, seen in Fig. 1(d), indicates the nanobelt

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**Fig. (1).** (a) SEM image of as-grown Net-like nanobelts. (b) SEM image of the single nanobelts. (c) Image of the DNA molecular structure. (d) EDS pattern of the Net-like nanobelts. (e) TEM image of SiO<sub>2</sub> Net-like nanobelts.

is composed of Si and O, with the atomic rate of  $\approx 1:2$ . No characteristic peak from other elements is detected in the EDS pattern. The SEM and EDS results demonstrate that the as-grown product is SiO<sub>2</sub> net-like nanobelts. The detailed microstructure of the nanobelts is further investigated using TEM. It could be seen from Fig. 1(e) that the SiO<sub>2</sub> nanobelts are amorphous, and the interspaces on the nanobelts are well-proportioned. It also shows that the borders have uniform width about 200nm along their length.

To gain insight regarding the possible growth mechanism of SiO<sub>2</sub> net-like nanobelts, the following factors in the formation of SiO<sub>2</sub> net-like nanobelts were investigated and discussed.

Firstly, CdS plays an important role in the formation of the SiO<sub>2</sub> net-like nanobelts, as supported by the following aspects: a) the only silicon source comes from the Si substrates because there is no extra silicon source provided, and the oxygen is from the residuary O<sub>2</sub> in the tube. Based on thermodynamics [18], the chemical reactions involved in the process may be proposed as follows:



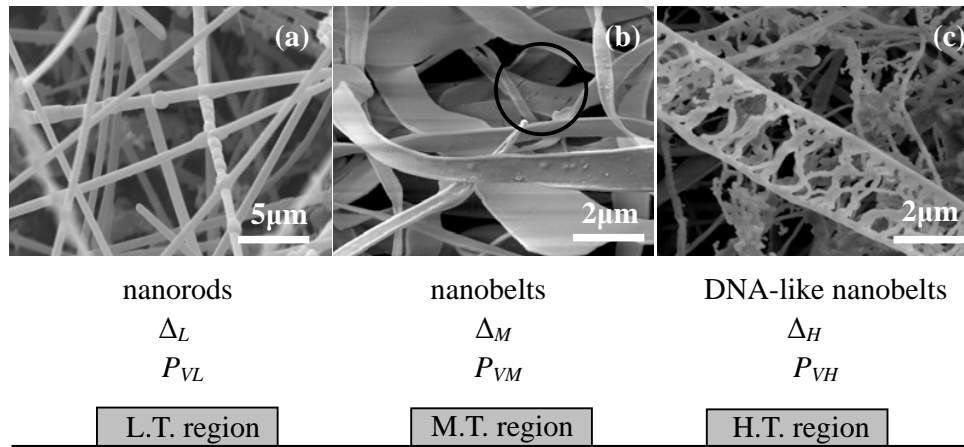
b) solid CdS powders is turned into CdS vapor at the high temperature in the center of the furnace at first, as shown in Eq. (1). Then as the argon flows, CdS vapor can be transported to the downstream region. Furthermore, according to the Au-Si phase diagram, the liquid Au-Si droplet which starts to form on the substrate goes through the temperature

range of 363 to 892 °C [19]. Au-Si alloy droplet, with a higher sticking coefficient, acts as a preferential site for the absorption of vapor CdS, which reacts with Si to produce Cd vapor and SiS, as Eq. (2). c) O<sub>2</sub> vapor has also been absorbed into the alloy droplet, and reacts with SiS for the SiO<sub>2</sub>, as presented in the Eq. (3). d) keeping identical experimental conditions, there is not any morphology of SiO<sub>2</sub> 1D nanostructures on the Si substrates in the absence of CdS powder. e) only amorphous SiO<sub>2</sub> nanowires was obtained on Si substrates in the absence of CdS powder at 1200 °C, with other parameters unchanged.

Secondly, based on the Clapeyron equation, the pressure of supersaturation vapor can be figured approximately as: [20]

$$P_V = P_0 e^{-L(\frac{1}{T} - \frac{1}{T_0})/R} \quad (4)$$

where,  $P_V$  is the pressure of the supersaturation vapor,  $P_0$  and  $T_0$  are the pressure and temperature at the beginning state, respectively.  $L$  is the phase transition thermal energy per mole vapor (appr. as a constant), and  $R$  is the thermodynamics constant. With the increase of temperature ( $T$ ), the supersaturation pressure ( $P_V$ ) is increased rapidly. It can be deduced from Eq. (4) that the relation of the supersaturation pressure at different temperature region is  $P_{VL} < P_{VM} < P_{VH}$  ( $P_{VL}$ ,  $P_{VM}$ ,  $P_{VH}$  stand for the supersaturation pressure at low, middle and high temperature region, respectively).



**Fig. (2).** Schematic diagram of the experimental parameters in the furnace, giving three temperature regions (high temperature (H.T.), medium temperature (M.T.), and low temperature (L.T.)), in which the products have different morphology. SEM image of the as-grown samples: (a) nanorods grown in L.T. region. (b) nanobelts grown in M.T. region. (c) Net-like nanobelts grown in H.T. region.

Furthermore, Gibbs derived a general formula on the basis of the minimization of the Helmholtz free energy during the phase transition to describe the equilibrium crystal growth process [21,22]. The relation is given as

$$P_C - P_V = \sum \delta(J_i \delta S_i) / \delta V_C \quad (5)$$

where,  $P_C$  and  $P_V$  are the pressure of the crystal phase and the vapor phase,  $\sigma_i$  and  $S_i$  are the surface energy and surface area of species  $i$ , respectively, and  $V_C$  is the volume of the crystal phase. It can be seen from the Eq. (5), the higher pressure ( $P_V$ ) results in a decrease in the surface-to-volume ratio ( $(\delta S_i / \delta V_C)$ , marked as  $\Delta$ ), from  $P_{VL} < P_{VM} < P_{VH}$ , that is  $\Delta_H < \Delta_M < \Delta_L$  ( $\Delta_L$ ,  $\Delta_M$ ,  $\Delta_H$  stand for the surface-to-volume ratio at low, middle and high temperature region, respectively). This decreased surface-to-volume ratio ( $\Delta$ ) in the process of the deposition turns to drive the crystal growth to proceed in a growth mode to favor a smaller  $\Delta$  inherent in the nanobelt structure. Therefore, the nanobelts may be grown in the high temperature region, while the nanowires or nanorods are grown in the lower temperature region.

The analysis result mentioned above is proved by a series of experiment. Fig. 2 is the schematic diagram of surface-to-volume ratio  $\Delta$  and the supersaturation pressure at different temperature region vs the as-product grown in different temperature region. Fig. 2(a) is the SEM image of the SiO<sub>2</sub> nanorods growing in low temperature region. The image shows that as-grown SiO<sub>2</sub> nanorods with an average diameter of 1  $\mu\text{m}$  and length of several hundred micrometers. The SEM image of the SiO<sub>2</sub> nanobelts growing in middle temperature region is shown in Fig. 2(b), which indicates that the nanobelts have a typical width of about several micrometers and length of about tens to several hundred micrometers. And the net-like SiO<sub>2</sub> nanobelts, growing in the high temperature region (or high vapor pressure region as mentioned above), is shown in the Fig. 2(c). The higher vapor pressure may result in the formation of split SiO<sub>2</sub> net-like nanobelts.

There are some splits on the surface of ordinary intact nanobelt (indicated by circle) as presented in the Fig. 2(b). The higher vapor pressure, the stronger force. The stronger force might force the surface of the ordinary intact nanobelts which were tore and formed helical shape. The case is just like imposing force onto the surface of ribbon which may result in split and helical shape.

#### 4. CONCLUSION

Amorphous SiO<sub>2</sub> net-like nanobelts were fabricated on Au-coated Si substrates by a simple thermal evaporation of CdS powder. The transportation of CdS plays an important role in the formation of SiO<sub>2</sub> nanobelts. The higher and stronger vapor pressure may result in the formation of the novel morphology of the SiO<sub>2</sub> net-like nanobelts in thermodynamic aspect. The investigation of properties of amorphous SiO<sub>2</sub> net-like nanobelts is in progress. The present results expect to provide a simple process for controllable growth of other semiconducting materials, which will facilitate the understanding of the growth mechanism of 1D nanostructures.

#### ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China under Grant No. 20671018.

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Received: August 27, 2008

Revised: September 26, 2008

Accepted: October 01, 2008

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