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Thermal CVD synthesis and photoluminescence of SiC/SiO_2 core–shell structure nanoparticles

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ABSTRACT

SiC/SiO_2 core–shell nanoparticles were firstly successfully synthesized by using a novel route of thermal CVD and thermal annealing process. The properties of the nanoparticles were characterized by scanning electron microscope, Transmission electron microscope, and X-ray diffraction. A possible growth mechanism was proposed for the nanoparticles according to the characterization results. The photoluminescence spectrum of the untreated nanoparticles revealed broad visible luminescence emission band. After the annealing treatment, the nanoparticles showed good blue emission, indicating potential applications in blue-light optoelectronic devices.

1. Introduction

As an important wide band gap semiconductor, silicon carbide appears as most promising applications for blue and ultraviolet light emitting devices [1], high power and high frequency electronic devices, which can be operated at high temperature and in harsh environment [2]. However, the applications of SiC in optoelectronic devices are limited due to its indirect band gap structure, which results in very low light emission efficiency [3]. Recently, the two-dimension SiC/SiO_2 film and quasi-one-dimension SiC/SiO_x nanocables can greatly enhance the emission intensity of the SiC as reported [4,5]. Little work has been done on how to realize the zero-dimension SiC/SiO_2 core–shell nanoparticles and whether it can enhance the luminescence efficiency. So far, quasi-one dimensions SiC core–shell has been synthesized by several techniques, including carbothermal reduction of sol–gel-derived silica xerogel [6], physical vapor deposition (PVD) [7], arc discharge process, and so on [5,8]. Compared with these methods, the thermal chemical vapor deposition (T-CVD) is greatly effective for synthesizing the one- and zero-dimensional nanomaterials [9,10]. The CVD system is very simple and inexpensive to construct. The materials grown by CVD can be achieved with high purity and high yield. In particular, the CVD is a common technique for growing optoelectronic device structure materials and the nanoparticles grown by CVD may easy to fabricate devices.

In this paper, a two steps growth method is developed for synthesis of SiC/SiO_2 core–shell nanoparticles by low-pressure thermal CVD and thermal annealing process. The SiC/SiO_2 core–shell nanoparticles have been achieved successfully. The experimental results indicate that the thermal annealing process at appropriate temperature can effectively enhance their blue-light emission intensity. The SiC/SiO_2 core–shell nanoparticles may have potential applications in blue-light optoelectronic devices.

2. Experimental

Thermal chemical vapor deposition was employed for growing SiC/SiO_2 core–shell nanoparticles by two steps. It contained: fabricating SiC core nanoparticles covered with Si shell firstly and then oxidizing the Si to form amorphous SiO_2 shell. The growth process can be described below. The reactor of the T-CVD system was heated to 1100 °C in a stream of 300 sccm of argon. After the constant temperature zone reached to the desired temperature, methane (purity 99.99%), silicane (5% SiH_4 diluted by H_2) and hydrogen (purity 99.999%), as C, Si precursors and pushing gas to grow the SiC core and Si shell, were fed into the reactor with a gas flow 20 sccm, 200 sccm, and 300 sccm, respectively. The growth time is about 1 h and the pressure is kept at about 560 Torr. After the growth completed, the argon gas was fed at a flow rate of 300 sccm (purity 99.999%) into the reactor to maintain an inert atmosphere while the temperature of the furnace was down to room temperature. The product was a type of thin deep yellow powder. The powder strongly depended on the temperature and only be synthesized on the inner wall of downstream end of the quartz tube with water-cooling. In order to achieve steady SiO_2 shell and improve the crystal quality of the nanoparticles, the deep yellow powder was scraped off and annealed in argon and oxygen mixture gas atmosphere with a flow rate of 500 sccm, and 1 sccm at an alumina tube for 1 h at temperature 1300 °C.

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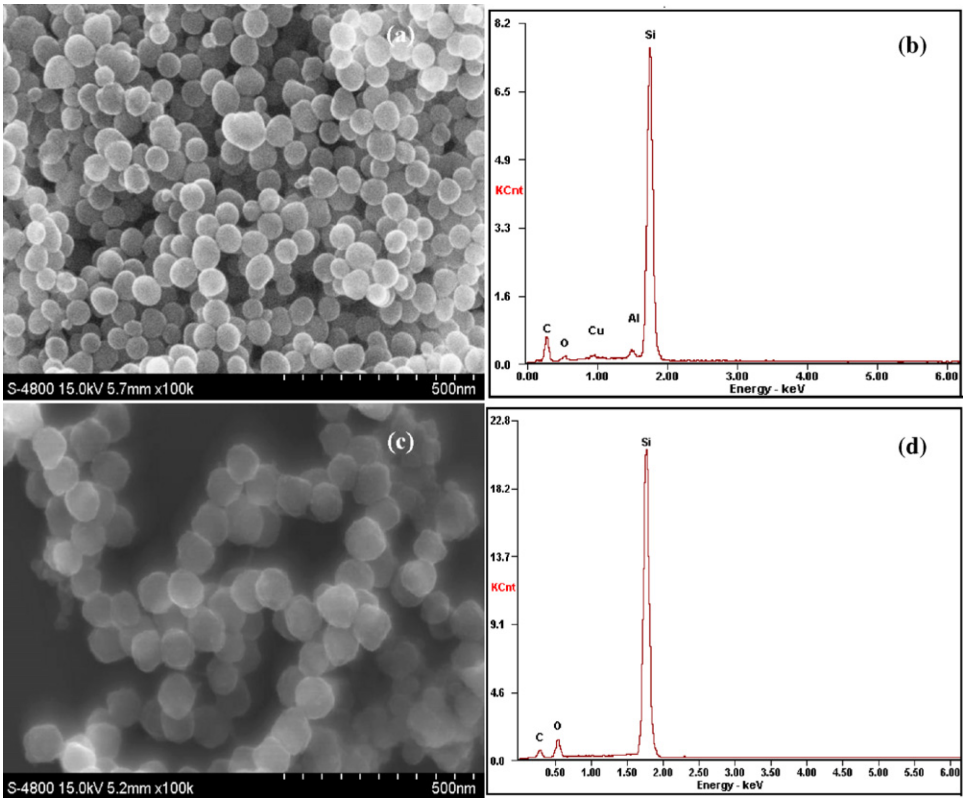

Fig. 1. (a) SEM image of the sample A and (b) is the corresponding EDX spectroscopy; (c) typical SEM image of sample B and (d) shows the corresponding EDX spectroscopy. (For characterization, the as-fabricated powder is spread on clean sheet copper substrate, the weak copper and aluminium peaks coming from substrate and sample frame.)

The powder became gray-white in color after the annealing treatment. We named the powder without annealing and thermal annealing at 1300 °C as sample A and sample B, respectively.

The general morphologies of the nanoparticles were investigated by scanning electron microscopy (SEM, Hitachi S-4800) equipped with energy dispersive X-ray (EDX) spectrometer. The detailed structure properties were examined by transmission electron microscopy (TEM, JEM-2010). The crystalline structures of the powder were analysed by X-ray diffraction (XRD, Ricoh). The room-temperature photoluminescence (PL, LABRAM-UV, Jobin Yvon) of the SiC/SiO_2 core–shell nanoparticles was excited by a He–Cd laser as the excitation source. The laser had a photon energy of 3.82 eV (325 nm).

3. Results and discussion

The typical SEM image of the powder is shown in Fig. 1. It can be seen that the powder is composed of nanoparticles. Fig. 1(a) is the SEM image of the sample A, without thermal annealing treatment, and (b) is the corresponding EDX spectroscopy. The nanoparticles of sample A have diameters of 75–85 nm. The EDX spectroscopy of samples A shows that the powder contains only C, Si, and O. The quantitative analysis demonstrates the C:Si:O atomic ratio of sample A is 57.6:40.4:2. The little oxygen element may come form the remnant air in quartz tube during the growth process. A typical SEM image and the corresponding EDX spectroscopy of sample B are shown in Fig. 1(c) and (d). After the thermal annealing treatment, the sizes of nanoparticles have some increase, and the corresponding C:Si:O atomic ratio is become 37.2:46.1:16.7. The three elements coexisting strongly suggest that the thermal annealing treatment sample may be formed SiC/SiO_2 core–shell nanoparticles, which is also proved by later TEM and XRD observations.

In order to investigate the microstructure of the powders, the TEM is employed. Fig. 2(a) and (b) are the TEM micrographs of the nanoparticles which are optionally taken from the as-grown and annealed powder, respectively. The inner cores have a uniform diameter about 70 nm and the outer shell has a thickness about 5–15 nm.

According to the EDX and TEM results, the mechanism of our two steps growth of SiC/SiO_2 core–shell nanoparticles should be as follows. At first SiC covered with Si shell has been grown by CVD. And then, the Si is oxidated to form SiO_2 shell during the annealing process. The deposition temperature of SiC and Si by CVD system is about 1050 °C [11] and 650 °C [12]. Considering the growth temperature of SiC is higher than Si, the two matters will be formed at different temperature zones. So, we choose the thermal CVD system, because the system can give an intrinsic temperature-gradient from the constant temperature zone to water-cooling zone. The SiC cores are formed at high temperature zone. And the Si atoms

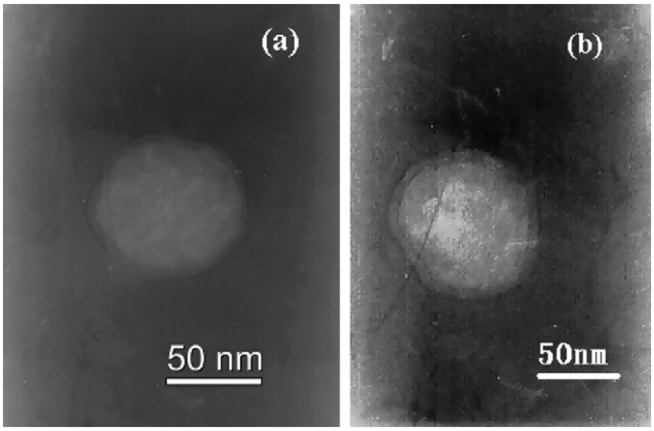

Fig. 2. TEM micrographs of the nanoparticles which are optionally taken from the samples A and B: (a) SiC/Si core–shell structure with a diameter about 85 nm and (b) typical images of thermal annealing treat at 1300 °C.

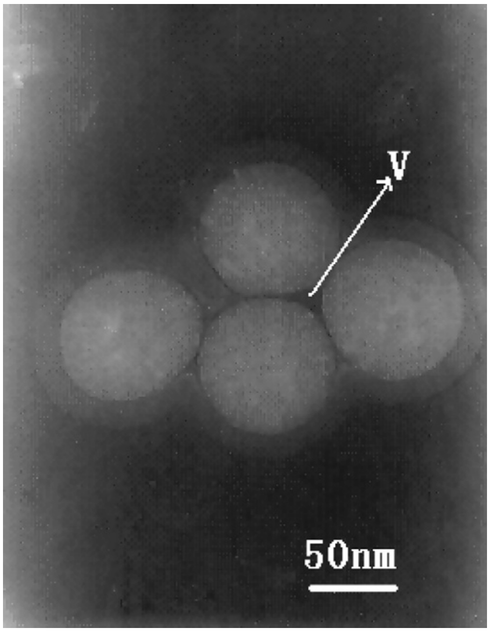

Fig. 3. TEM micrographs of four cores over-coating with one shell structure SiC/SiO_2 nanoparticles.

adsorb and deposit on the surface of SiC core at appropriate temperature zone to form a thin Si shell, while the SiC nanoparticles move to the cooling water zone being driven by the pushing gas and deposited there. The SiC/Si core–shell powder is annealed at argon and oxygen mixture gas atmosphere, and the Si will be completely oxidized to form the SiC/SiO_2 core–shell nanoparticles successfully. As an evidence of the two steps growth mechanism, the structure that four gathered cores over-coating with one shell has been found, as shown in Fig. 3. Because the nanoparticles tend to assemble to reduce their free energy, the vacant region (marked as V) within three cores arranged in a triangle is formed. The process of conglomerating may occur during the nanoparticles transportation process and then is coved by one Si shell at appropriate temperature zone. As the growth process is complicated, more work need to be done to get more detailed information.

To confirm the core–shell structure and give an evidence of this growth mechanism, powder X-ray diffraction (XRD) is carried out. Fig. 4 shows the XRD result of samples A and B. The XRD spectrum of sample A shows three 6H-SiC [13] diffraction peaks at 35.6°, 41.4° and 60°, respectively. In addition, two Si [13] diffraction peaks at 28.4° and 56.3° have been observed. Meanwhile, a series of diffraction peaks at 44.3°, 47.3° and 50.1°, corresponding to carbon [13] are also detected. The excessive C elements of samples A may come from the graphite particles and amorphous carbon, which are deposited at the same time in the nanoparticles fabricated process. After annealed at 1300 °C, the silicon and carbon diffraction peaks disappeared, but the SiO_2 amorphous diffraction band around 22° is observed [14]. The excessive C must be reacted with the oxygen and exhausted by the mechanical pump during the thermal annealing process.

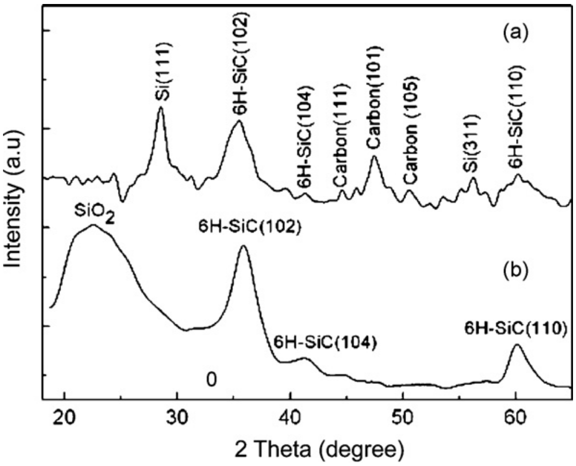

Fig. 4. XRD pattern: (a) of sample A and (b) of sample B.

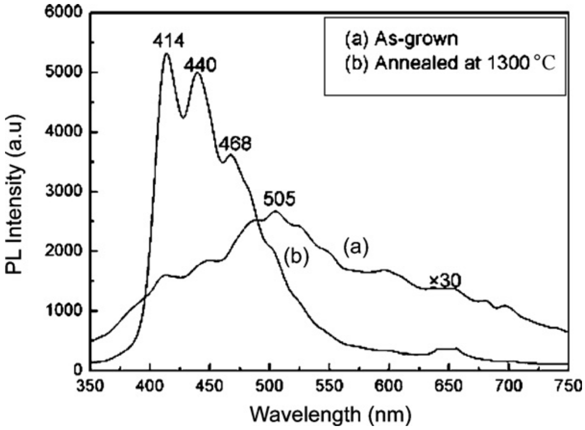

Fig. 5. Photoluminescence spectra: (a) of sample A and (b) of sample B. (For comparison, the relative spectra intensity of (a) was enlarged to 30 times.)

The room-temperature PL of the as-grown samples A and annealed samples B are carried out, as shown in Fig. 5. Curve (a) shows the PL spectrum of sample A. A weak and broadband luminescence from 400 nm to 700 nm with the maximum peak around 505 nm is present. The broadband luminescence is similar with that generally observed in silica containing SiC nanostructures. The luminescence around 505 nm is usually attributed to various carbon element related SiC surface defect nanostructures [4].

The PL spectrum of sample B is shown in Fig. 5 curves (b). This spectrum shows that the luminescence of the SiC/SiO_2 core–shell nanoparticles after annealed becomes narrow and locates only in the blue-green region. Three emission peaks, which exist weakly in as-grown samples A, became obvious. The positions of each peak are at 414 nm (3.0 eV), 440 nm (2.82 eV) and 468 nm (2.65 eV), respectively. The emission at 414 nm is due to the band gap luminescence of the 6H-SiC (with band-gap energy 3.0 eV). The peak of 468 nm may be caused by oxygen vacancy defects in the SiO_2 shell [15]. With increasing the crystallization degree of SiC, the local stress must be released and large numbers of defect states (such as –O–Si–O–, –O–Si–C–O, and oxygen vacancy defects) will be present at the interface between the core and shell. So the corresponding interface defect states recombination emission may be the origin of the blue emission at 440 nm [16]. Furthermore, the luminescence integrated intensity of sample B is more than 70 times as strong as that of sample A and the emission around 505 nm disappear. The decreasing of excessive C may cause C-related PL around 505 nm of sample A to decrease even to disappear. It is also consistent with the experimental results of XRD.

4. Conclusions

In summary, we have synthesized SiC/SiO_2 core–shell nanoparticles successfully in two steps by T-CVD and thermal annealing process. The nanoparticles synthesized have obviously temperature dependence. According to the TEM results, a new growth mechanism was proposed. Furthermore, the synthetic approach presented here opens a new route to fabricate other high pure core–shell structure nanoparticles materials. After the annealing treatment, the SiC/SiO_2 core–shell structure materials reveals good blue emission with a main peak at 440 nm. These particles may be applied in full-color display and related optoelectronic devices.

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