

Si₃N₄ nano-microsphere synthesized by cathode arc plasma and heat treatment

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Abstract: The Si₃N₄ microcrystals with a hollow sphere structure were prepared by using the simple heat treatment of the Si₃N₄ flakes, which were prepared by using the cathode arc plasma. The products were characterized by XRD, SEM and TEM. The photoluminescence (PL) spectrum of the Si₃N₄ nano-microsphere was studied. The obtained Si₃N₄ microcrystals, which show a hollow sphere structure, are up to several nanometers in diameter. During the process, the heat treatment and Ni catalyst play a key role in the forming structure and morphology. This result provides a possibility for mass producing Si₃N₄ microcrystals.

Key words: Si₃N₄ hollow sphere; heat treatment; photoluminescence; cathode arc plasma

1 Introduction

Silicon nitride (Si₃N₄) is an advanced ceramic material, and it has many potential applications due to its good performance in mechanical, chemical, electronic, and thermal applications[1]. Being an important member of the promising semiconductors of nitrides (such as GaN and AlN), Si₃N₄ is also a wide band gap (about 5.3 eV) semiconductor. In addition, the dopant-treating Si₃N₄ compounds are widely used in the microelectronics industry for various applications as the optical devices[2].

As a result, the synthesis of difform Si₃N₄ nanomaterials has received extensive attention in recent years and various synthesis routes have been proposed. Recently, the three kinds of known polymorphs of α -Si₃N₄, β -Si₃N₄ and γ -Si₃N₄ with a spinel structure have been prepared[3–7]. By using ammonia microwave plasma heating, the Si₃N₄ nanoneedles grown on silicon were prepared[8]. And the Si₃N₄ nanorods were synthesized with the mild benzene-thermal route as the template[9]. Si₃N₄ nanowires and Si₃N₄ single-crystalline nanobelts were achieved by a vapor-solid thermal reaction with ammonia and silicon monoxide[10]. The large-scale synthesis of single-crystalline Si₃N₄ nanobelts with high yield via catalyst-assisted pyrolysis of

polymeric precursor. The growth mechanism of the nanobelts was also proposed[11]. The Si₃N₄ whiskers with dendritic and riblike structure were achieved by a chemical vapor deposition technique[12–13]. Branched Si₃N₄ whiskers have been fabricated via catalyst-assisted pyrolysis of polymeric precursors[14]. To date, one-dimensional Si₃N₄ nanostructures have been synthesized via different methods. However, the simple and massive production of Si₃N₄ microcrystals are still not proposed.

In this work, the Si₃N₄ microcrystals with a hollow sphere structure were prepared. A simple and novel route for the preparation of Si₃N₄ nano-microsphere with urchin-like structure by heat treatment was reported. The optical properties of as prepared Si₃N₄ nano-microsphere were discussed.

2 Experimental

Before the preparation of Si₃N₄ nano-microsphere, Si₃N₄ flakes were synthesized by cathode arc plasma, which is one of the most powerful methods because of uniform particles and high efficiency, using Si powder and nickel nanopowder with a molar ratio (100:1) in pure nitrogen atmosphere. The nickel nanopowder acted as the catalyzer in the reaction. The mixture of pure silicon powder and nickel nanopowder served as the anode, and

a tungsten rod served as the cathode. After the vacuum level of the chamber was up to 10 Pa, the pure nitrogen gas was introduced into the chamber as the reaction gas. During the preparing process, the pressure of the chamber was 2.0×10^3 Pa, the arc discharge voltage was 40 V and the current was 40 A. The arc discharge was maintained for 10 min to evaporate the mixture. The black Si_3N_4 flakes powders were obtained. Then, the black Si_3N_4 flakes were calcined in a quartz tube furnace at 500 °C for 5 h in argon atmosphere and the offwhite Si_3N_4 nano-microsphere powders were obtained.

The structure of the sample was measured by X-ray diffraction (XRD) on a Rigaku D/Max-2400 diffractometer with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda=0.154\ 056$ nm) and θ - 2θ scan. Transmission electron microscopy (TEM) examination was carried out by using a Hitachi H-600 transmission electron microscope operated at 100 kV with a nominal point-to-point resolution of 0.23 nm. The morphology observation was performed on field emission scanning electron microscope (FE-SEM, Hitachi S-4800). Photoluminescence (PL) measurements were carried out at the room temperature by using the pulsed (5 ns) RF-5301 laser with the excited wavelength of 280 nm. The experiment with similar conditions was also carried out without the Ni powder additive for comparison.

3 Results and discussion

Fig.1 shows the XRD pattern of the Si_3N_4 nano-microsphere. The diffraction peaks can be indexed to the orthorhombic structure of Si_3N_4 , which exactly accords with the reported values of JCPDS card No. 76-1408. The impurity peaks suggest that the Si powder reacts incompletely with nitrogen.

The structural analysis of the nano-microsphere was performed by using TEM and SEM. Fig.2(a) shows the SEM image of the Si_3N_4 nano-microsphere obtained by

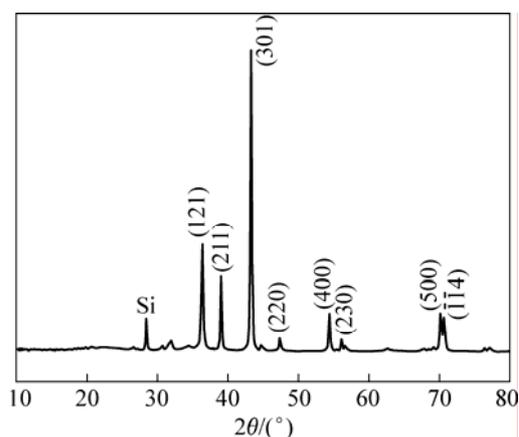


Fig.1 X-ray powder diffraction pattern of Si_3N_4 hollow

heat treatment of Si_3N_4 flakes for 5 h. Fig.2(b) shows the TEM image of the Si_3N_4 nano-microsphere with diameters around 2 μm , and the image also confirms that the Si_3N_4 nano-microsphere is in hollow structure.

Fig.3(a) shows the TEM image of as-prepared Si_3N_4 flakes and the corresponding SAED pattern (inset of Fig.3(a)). It can be seen that Si_3N_4 flakes take on a flake-like morphology, and the SAED pattern of the flake shows that it consists of several layers. It is believed that the special structure of the Si_3N_4 flakes plays an important role in the following transformation.

The heat treatment plays an important role in the structure and morphology of Si_3N_4 nano-microsphere. Fig.3 shows the evolution of morphology during the heat treatment. Fig.3(b) shows that the flakes begin to bend and kink when they are calcined at 500 °C for 1 h. Fig.3(c) shows the TEM image of the product after being calcined for 3 h. It can be seen that the structure is broken down into amorphous aggregations and the amorphous turns into erose nano-microsphere. As shown in Fig.3(d), when the calcination time increases to 5 h, most of the amorphous turn into the nano-microsphere and come to separate from the amorphous.

It is noticed that if the electron beam intensity of TEM is strong enough, the spheres would splittingly fall

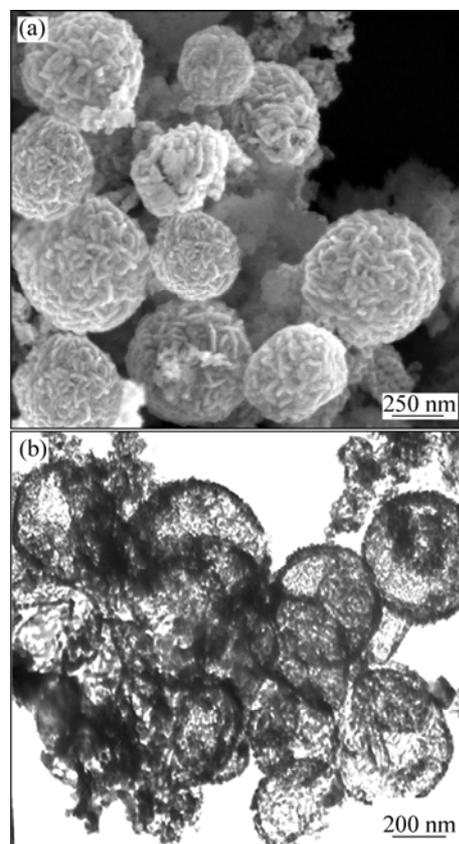


Fig.2 SEM image (a) and TEM image (b) of product calcined for 5 h

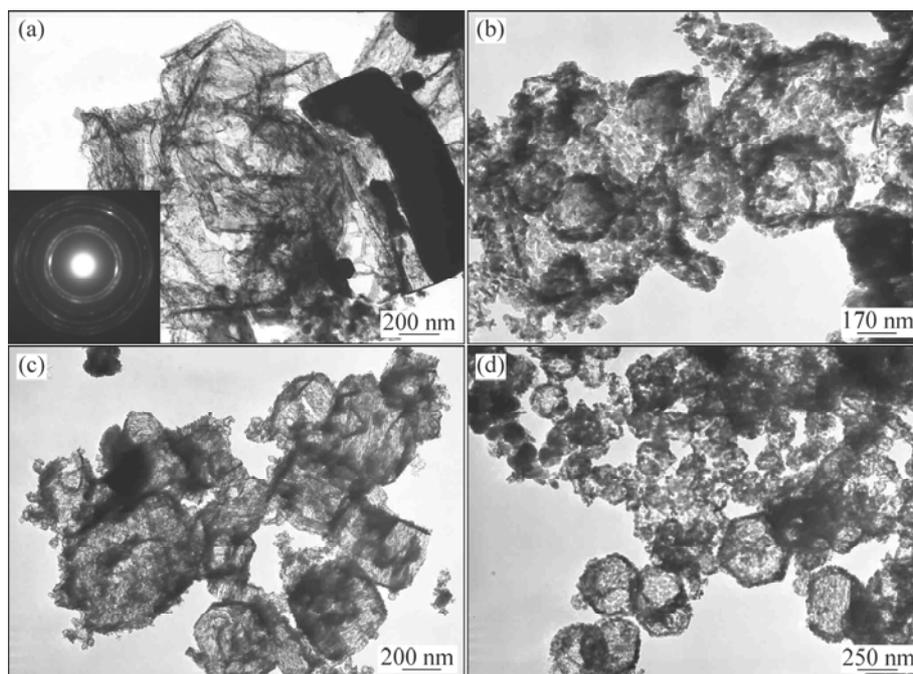


Fig.3 Morphologies of product obtained under heat treatment for different times: (a) As-prepared Si_3N_4 flakes; (b) Product calcined for 1 h; (c) Product calcined for 3 h; (d) Product calcined for 5 h

apart into small nanosheets. When the electron beam intensity of TEM is lower than critical stable value, those small nanosheets would form into new spheres.

From the above experimental results, the formation mechanism of Si_3N_4 hollow spheres is suggested as shown in Fig.4. When the precursors with structure of flakes are obtained by the arc discharge treatment, one side of the flake's surface shows electronegative quality and the other side shows electropositive quality for their structure reason. So several flakes are superposed

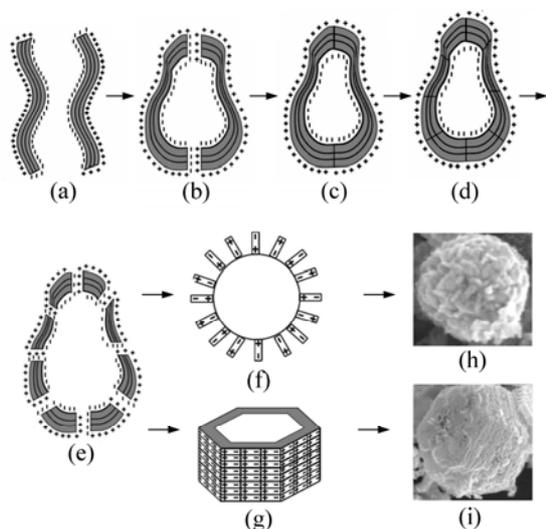


Fig.4 Schematic illustration of hierarchical structure of formation mechanism of Si_3N_4 hollow spheres

(Fig.4(a)). During the annealing, two flakes are connected to form an erose hollow sphere (Figs.4(b) and 4(c)). With the increase of the annealing temperature, the erose hollow spheres break up and recrystallize (Fig.4(d) and 4(f)). As to the minimum surface energy and surface tension of the sphere and hexahedron, the broken flakes are reassembled and turn into sphere and hexahedron (Figs.4(g) and (i)). However, the exact mechanism is still unknown and needs further investigation.

We also studied the PL properties of the Si_3N_4 nano-microsphere obtained in the experiment. Fig.5 shows the PL spectra of the Si_3N_4 nano-microsphere using the excitation line at 280 nm measured at room temperature. The spectra ranging from 300 nm to 600 nm

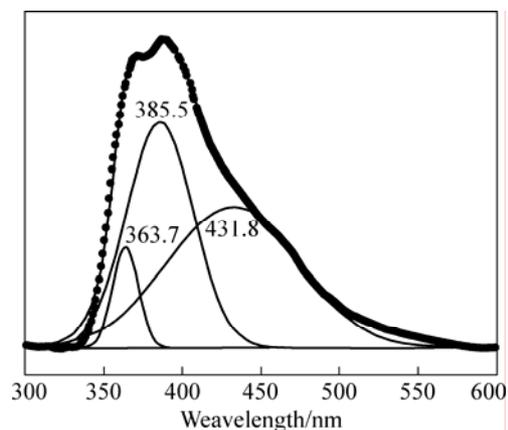


Fig.5 Room-temperature PL spectra of Si_3N_4 hollow spheres

are smoothed and deconvoluted into several Gaussian peaks, as shown in Fig.5. From the PL spectrum of the Si_3N_4 nano-microsphere, a strong violet emission peak centered at 385.5 nm (3.19 eV) is observed, and other strong emission peaks are also observed at 363.7 nm (3.38 eV) and 431.8 nm (2.85 eV).

It is obvious that these intensive light emissions from Si_3N_4 nano-microsphere are not the direct band gap emission, but are generally attributed to the deep-level or trap-level defects. According to Robertson and Powell's report[15], there are four principal defects closely related to its light emission, including the Si and N dangling bonds ($\equiv\text{Si}-$ and $=\text{N}-$), $\equiv\text{Si}-\text{Si}\equiv$, $=\text{N}^0$, $\equiv\text{Si}^0$. There are two nitrogen defective conditions that give rise to the levels within the gap, namely N_4^+ and N_2^0 , which were calculated to close to the conduction and valence band respectively. The presence of the nitrogen dangling bond defect was confirmed by spin resonance measurements. According to Deshpande's report[16], the recombination process at the silicon dangling bond is due to the rise of the broad (2.5 ± 0.1) eV peak, and the (3.0 ± 0.1) eV peak is due to recombination either from the conduction band to the N_2^0 level or the valence band to the N_4^+ level. So the luminescence at 431.8 nm (2.85 eV) is possibly caused by recombination process at the silicon dangling bond. The luminescence at 385.5 nm (3.19 eV) and 363.7 nm (3.38 eV) are possibly caused by the electronic recombination either from the conduction band to the N_2^0 level or the valence band to the N_4^+ level.

4 Conclusions

1) A very simple and scalable pathway towards Si_3N_4 nano-microsphere is achieved. The Si_3N_4 nano-microsphere is prepared via heat treatment of the Si_3N_4 flakes at 500 °C for 5 h in argon atmosphere.

2) The Si_3N_4 flakes are prepared by using the cathode arc plasma. It is found that the heat treatment and Ni catalyst play an important role in the forming of structure and morphology.

3) An intensive broad blue light emission peak at 385.5 nm and other strong broad light emission peak at 363.7 nm and 431.8 nm are observed from the room-temperature PL spectrum. The current results can

lead to a new and simple way for mass production of Si_3N_4 microcrystals.

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