Research Article

Characteristics of Silicon Dioxide Particles in PCVD Synthesizing Silica Glass Process

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SiO₂ nanoparticles in PCVD process were investigated by SEM, TEM, and optical emission spectra (OES). There are large spherical SiO₂ particles with diameter of 50–200 nm and more small particles about 10–50 nm in PCVD process. Size of SiO₂ particles is influenced by distance and feeding speed but not electron temperature. The amount of large spherical SiO₂ particles decreases with the increase of distance and decrease of feeding speed due to lower concentration. In addition, the evolution of SiO₂ particles was inferred from the experimental results.

1. Introduction

The technology of plasma chemical vapor deposition (PCVD) [1] synthesizing silica glass uses atmospheric pressure high frequency induction plasma as heat source and high purity silicon tetrachloride as raw material. Silica glass synthesized by this method is the purest man-made bulk silica glass [2] (metallic impurities < 1 ppm, OH-groups < 1 ppm) due to unpolluted and water-free heat source and raw material. It is the key material in inertial navigation and optical field due to its high purity and unbroken structural network.

Quality of silica glass is mostly decided by the preparation process. The stage of SiO₂ nanoparticles forming, colliding, aggregating, and depositing onto substrate is the key step in PCVD process, and size and morphology of the particles ultimately influence quality of silica glass [3]. So investigation of SiO₂ particles in PCVD process can help us to improve quality of silica glass and depositing efficiency and reduce consumption of energy and raw materials. However, little research on it has been reported until now. Many studies have been carried out on SiO₂ nanoparticles in other flames. Ulrich and coworkers [4–7] studied synthesis of SiO₂ nanopowders in hydrocarbon flames and related particle size to residence time and precursor concentration and process temperature. Wang et al. [8] studied SiO₂ particles in oxyhydrogen flame CVD synthesizing silica glass and observed shrinkage of

particle along the flame at low precursor concentration, which they attributed to evaporation, and few changes on its characteristics at high concentration. Tandon and Boek [9] presented models to estimate SiO₂ soot number density and mean size at different locations in oxyhydrogen flame.

The objective of the present study is to investigate characteristics of SiO₂ particles in PCVD and understand evolution of SiO₂ particles in plasma flame. Input power of plasma generator has been changed to get different flame temperature and feeding speed has been changed to get different concentration. Characteristics of SiO₂ particles at different distance from exit of plasma torch have been discussed to investigate evolution of SiO₂ particles. At last, the evolution of SiO₂ particles in PCVD process will be discussed.

2. Experimental

Plasma flame was generated by high frequency generator with rated power of 100 kW and frequency of 4.6 MHz. Ionizing gas and protecting gas were both filtered dry air. Optical emission spectra of the plasma flame in the region of 200–1077 nm were recorded by 7 channels' AvaSpec-ULS-3648 fiber spectrometer with best resolution of 0.05 nm. Electron temperature T_e was calculated by Boltzmann plot method using N spectra [10, 11]. Pure oxygen carried silicon tetrachloride was injected into the plasma flame and formed

SiO₂ particles. Silica glass sampler was swept past the flame quickly and SiO₂ particles deposited onto the sampler. Morphology of the SiO₂ particles was investigated by Hitachi SU8010 scanning electron microscope and Hitachi H-800 transmission electron microscope.

3. Results and Discussions

3.1. Formation of SiO₂ Particles. Because feeding gas in PCVD process is oxygen and ionization gas of plasma is air, only oxidation reaction of silicon tetrachloride takes place in the plasma flame. The chemical reaction equation is as follows:

Silicon tetrachloride is ionized immediately when it goes into plasma flame carried by oxygen. The change of state of plasma results in the change of optical emission spectrum. Figure 1 shows the optical emission spectra of the plasma flame at the distance of 9 cm before and after feeding, when the input power of plasma generator was 80 kW and feeding speed of silicon tetrachloride was 10 g/min. It can be seen that strong Si and Cl lines appear after feeding. Particularly, the region of 540–665 nm containing Si, Cl, O, and N lines has significant difference after feeding. As a result, optical emission spectrum of this region will be mainly discussed. Electron temperature T_e decreased from 15245 K to 9666 K after feeding, which demonstrates that heavy ions of silicon tetrachloride and oxygen absorb quantity energy of electrons. Even so, the temperature is much higher than melting point of SiO₂ and enough to melt it. So SiO₂ particles are in liquid state in plasma flame.

SiO₂ particles at 9 cm were sampled, and SEM and TEM morphology were observed, which are shown in Figures 2 and 3. The SEM morphology shows that most SiO₂ particles are “tiny” spherical ones with diameter of 10–50 nm, and few abnormal “large” spherical particles about 50–200 nm in diameter (encircled), which are less than 1 percent in quantity. The TEM morphology of Figure 3(a) also shows that most particles are smaller than 50 nm and some of them are larger than 50 nm. Figure 3(b) shows particles with diameter of about 200 nm, but it takes effort to find them through TEM. In addition, it is hard to observe the surface morphology of SiO₂ particles by TEM. As a result, morphology of SiO₂ particles will be characterized by SEM in the following study.

3.2. Influence of Input Power. State of plasma is influenced greatly by input power of plasma generator, and higher input power results in higher electron temperature. SiO₂ particles were investigated when input power is 80 kW, 85 kW, and 90 kW, respectively, when the feeding speed of silicon tetrachloride was 10 g/min and sampling distance was 9 cm. Optical emission spectra of the plasma flame at different input power are shown in Figure 4. It can be seen that the spectrum is stronger slightly when input power increases. Electron temperatures T_e calculated are 9666 K, 10054 K, and 12875 K at 80 kW, 85 kW, and 90 kW, respectively. The electron temperature increases dramatically when input power increases.

Figure 5 shows the SEM morphology of SiO₂ particles at 85 kW and 90 kW. Compared with Figure 2, which was at the condition of 80 kW, most SiO₂ particles in the three conditions are smaller than 50 nm, and only several particles larger than 50 nm can be observed (encircled), which are less than 1 percent in quantity. Therefore, electron temperature does not affect the size of SiO₂ particles.

3.3. Influence of Distance. In order to investigate evolution of SiO₂ particles in plasma flame, SiO₂ particles at distances of 8 cm, 9 cm, and 10 cm from exit of plasma torch were sampled when input power was 80 kW and feeding speed of silicon tetrachloride was 10 g/min. SEM morphologies of SiO₂ particles at the distances of 8 cm and 10 cm are shown in Figure 6, and that of 9 cm can be seen in Figure 2. Figure 6(a) shows that about 50 percent of SiO₂ particles are larger than 50 nm at 8 cm, and near 10 percent of them are larger than 100 nm. When the distance increases to 9 cm (Figure 2), less than 1 percent of the particles are larger than 50 nm. While at the distance of 10 cm showed in Figure 6(b), no SiO₂ particles larger than 50 nm can be observed. Therefore, the amount of large SiO₂ particles decreases with the increase of distance.

Optical emission spectra of the plasma flame at different distance are shown in Figure 7. It can be seen that optical emission spectrum at 9 cm is the strongest, and spectrum at 10 cm is stronger slightly than that of 8 cm. And electron temperature T_e at the distance of 8 cm, 9 cm, and 10 cm is 7904 K, 9666 K, and 9445 K, respectively. Because inductively coupled plasma has a hollow structure and the distance of 8 cm is near core of plasma, the temperature at 9 cm is higher than that of 8 cm. Temperature decreases at the tail of plasma flame, so the temperature at 10 cm is lower than that of 9 cm.

The results show that when the distance increases, the electron temperature first increases and then decreases, while the diameter of SiO₂ particles always decreases. So the diameter of SiO₂ particles is influenced by distance, but not electron temperature, which confirms the conclusion of former part.

3.4. Influence of Feeding Speed. Feeding speeds of silicon tetrachloride were set as 10 g/min, 12 g/min, and 14 g/min, respectively, and SiO₂ particles at distance of 9 cm were sampled. SEM morphology of 12 g/min and 14 g/min is shown in Figure 8, and Figure 2 shows the SEM morphology at the speed of 10 g/min. It is clear that with the increase of feeding speed SiO₂ particles become bigger, and the amount of large spherical SiO₂ particles increases. Few large spherical SiO₂ particles can be seen at 10 g/min. When the feeding speed increases to 12 g/min, about 30 percent of the particles are larger than 50 nm, while at the feeding speed of 14 g/min, most SiO₂ particles are larger than 50 nm. Optical emission spectra of the plasma flame at the three conditions are shown in Figure 9, which shows that optical emission lines decrease slightly with increase of feeding speed. Electron temperature T_e at the feeding speed of 10 g/min, 12 g/min, and 14 g/min is 9666 K, 9648 K, and 9616 K, respectively. T_e decreases slightly with the increase of feeding speed.

Now we can infer the evolution of SiO₂ particles from the experimental results. Si is dissociated immediately by plasma after silicon tetrachloride was injected into it. Free Si

FIGURE 1: Continued.

FIGURE 1: Optical emission spectra of the plasma flame before and after feeding.

FIGURE 2: SEM morphology of SiO_2 particles (80 kW, 10 g/min, and 9 cm; encircled particle is particle larger than 50 nm).

(a) Common morphology

(b) Large particles hard to find

FIGURE 3: TEM morphology of SiO_2 particles (80 kW, 10 g/min, and 9 cm).

atoms will be combined with O to form a large amount of tiny SiO_2 particles, which are in liquid state and moving in high speed due to high temperature of plasma. The tiny SiO_2 particles can collide and aggregate with each other to form larger particles. At the same time, large SiO_2 particles can get smaller due to evaporation. SiO_2 particles have stronger

probability to form large ones when the concentration is high. As a result, there are more large SiO_2 particles at higher feeding speed. In addition, when the distance from exit of plasma torch is longer, SiO_2 will be mixed with fluid of plasma and the concentration will decrease, so the amount of large SiO_2 particles will decrease.

FIGURE 4: Optical emission spectra of the plasma flame at different input power.

FIGURE 5: SEM morphology of SiO_2 particles at different input power (10 g/min, 9 cm; encircled particles are particles larger than 50 nm).

FIGURE 6: SEM morphology of SiO_2 particles at different distance (80 kW, 10 g/min).

FIGURE 7: Optical emission spectra of the plasma flame at different distance.

4. Conclusions

There are large spherical SiO_2 particles with diameter of 50–200 nm and more small particles about 10–50 nm in PCVD

process. Size of SiO_2 particles is decided by SiO_2 concentration, which influences aggregation and division of particles. The amount of large spherical SiO_2 particles decreases with the increase of distance and decrease of feeding speed due to lower concentration. Electron temperature is high enough for melting of SiO_2 particle and has no effect on its size. It is generally accepted that larger SiO_2 particles have larger momentum and have more chance to pass through sheath and deposit on substrate in PCVD. Therefore, increasing feeding speed and shortening the distance of plasma torch and substrate can improve depositing efficiency, while changing input power of plasma generator has no effect on it. But higher temperature is beneficial for melting SiO_2 particles deposited on substrate. In order to produce high quality silica glass, further studies should be carried on to find optimal

FIGURE 8: SEM morphology of SiO_2 particles at different feeding speed (80 kW, 9 cm).

FIGURE 9: Optical emission spectra of the plasma flame at different feeding speed.

combination of input power and depositing distance and feeding speed.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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