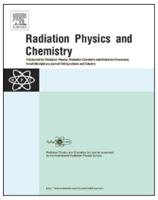
Radiation Physics and Chemistry 103 (2014) 114–118

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Characteristics of pulsed plasma-chemical synthesis of silicon dioxide nanoparticles

Galina Kholodnaya*, Denis Ponomarev, Roman Sazonov, Gennady Remnev

National Research Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk 634050, Russia

HIGHLIGHTS

- We show the fundamental possibility of synthesis of nanosized SiO_2 of required size.
- Decreasing of $SiCl_4$ will decrease geometric size of particle, but not morphology.
- Addition of a buffer gas in the mixture will decrease the average particle size.
- Increasing the action of the electron beam will increase geometric size of the SiO_2.

ARTICLE INFO

Article history:
Received 8 May 2014
Accepted 22 May 2014
Available online 2 June 2014

Keywords:
Plasma chemical synthesis
Pulsed electron beam
Nanoparticles
SiO_2

ABSTRACT

This paper investigates the effect of plasma-chemical synthesis modes of nanosized silicon dioxide initiated by a pulsed electron beam on the geometric size distribution of the product nanoparticles. Findings show that the particles are enlarged following multiple exposures to a pulsed electron beam. Meanwhile, when adding a buffer gas into the initial mixture, the size of the particles decreases.

1. Introduction

Development of energy-efficient, environmental-friendly and wasteless methods for the production of ultradispersed powders of different substances is a topical issue in contemporary science. At present, this fact is mainly explained by the practical necessity to produce nanomaterials, most of which have found numerous applications due to their unique properties. The three most widespread and industrially applied nanopowders are silicon dioxide (SiO_2), titanium dioxide (TiO_2), and argil (Al_2O_3). Each particular kind of oxide is characterized by the set of physicochemical properties defining the sphere of its application. Thus, silicon dioxide is extensively used when manufacturing heat insulators: in the production of optoelectronics; as a component to produce thermostable paints, lacquers, and glues; and as an emulsion stabilizer (Cai and Yang, 2002; Min-Hong et al., 2012; Ye et al., 2007). The currently existing methods for obtaining nanosized silicon dioxide can be arbitrarily classified into two groups: chemical and electrophysical.

Basic chemical methods allow synthesis of nanosized silicon dioxide with an average particle size ranging from 20 to 150 nm (Wei-Fang and Hong-Ru, 2002; Hui and Junling, 2010; Zhang et al., 2003; Kammler et al., 2004); 10–150 nm average particle size of SiO_2 can be obtained by using electrophysical methods (Kalisz and Mroczyński, 2012; Hiroyuki et al., 2009). The main disadvantages of chemical synthesis methods are considerable power inputs caused by high synthesis temperatures and significant consumption of chemical agents, while the drawback of electrophysical methods can be seen as a wide particle size distribution. The nanosized SiO_2 production method based on the plasma-chemical chain reactions initiated by a pulsed electron beam is considered to be promising due to the following set of competitive advantages (Remnev and Pushkarev, 2004a; Sazonov et al., 2011; Ponomarev et al., 2013):

- low specific power inputs;
- capability to perform the reactions in a single stage;
- versatility of the technology and equipment for the production of different oxides;
- potentially high expected specific output of the equipment for a pilot plant (tens of kilograms of the final product per hour);
- capability to produce titanium dioxide, silicon dioxide, and complex composite oxides with specified properties;

---

* Corresponding author. Tel./fax: +73822419158.
E-mail address: galina_holodnaya@mail.ru (G. Kholodnaya).

http://dx.doi.org/10.1016/j.radphyschem.2014.05.048
0969-806X/© 2014 Elsevier Ltd. All rights reserved.

- a wide variety of produced nanosized materials which is made possible by applying several (organic and/or inorganic) initial substances.

The objective of the present paper is to investigate the plasma-chemical synthesis initiated by the action of a pulsed electron beam to a gas-phase mixture of silicon tetrachloride, hydrogen, and oxygen, and the effect of the synthesis modes on the geometric size distribution of silicon dioxide nanoparticles.

2. Experimental

Experiments regarding nanosized silicon dioxide synthesis were performed on a TEA-500 pulsed electron accelerator (Remnev et al., 2004; Pushkarev et al., 2011). To produce silicon dioxide, $SiCl_4$, O_2, and H_2 were used. Most experiments were executed using a plasma-chemical reactor (quartz, 140 mm diameter, 4 l volume). The reactor was equipped with a pressure gauge, a vacuum gauge, a pressure sensor, and a shut-off-and-regulating armature for the initial reagent mixture puffing and gas evacuation. The plasma chemical reactor was heated to a temperature of 350 K, and prior to puffing the gas mixture a pressure of ~1–5 Torr in the reactor was obtained. An electron beam was injected from the end side into the reactor. The beam initiated the hydrogen-burning reaction which was accompanied by the release of a significant amount of energy and by radical formation. It also initiated the dissociation of silicon tetrachloride, forming atomic chlorine (which entered into an exothermic reaction with the hydrogen). Fig. 1 presents a block diagram of the experimental setup.

Under the action of the pulsed electron beam on the silicon tetrachloride, oxygen, and hydrogen mixture, $SiCl_4$ was decomposed by the electron impact in the reactions.

The tetrachloride dissociation:

Low energy electron dissociative attachment is also observed

$$SiCl_4+e^- \rightarrow (SiCl_4)^- \rightarrow Si+2Cl_2+e^-$$

These reactions can refer to the stage of chain initiation. Meanwhile, two parallel chain reactions occur. The first reaction is the interaction of chlorine and hydrogen

$$Cl+H_2=HCl+H+0.05\ \text{eV}$$

$$H+Cl_2=HCl+Cl+2\ \text{eV}$$

$$Cl+Cl+M=Cl_2+M+2.5\ \text{eV}$$

$$H+HCl=H_2+Cl-0.05\ \text{eV}$$

The second reaction is hydrogen oxidation:

$$H_2+O_2=2OH \qquad O+H_2=OH+H$$

$$OH+H_2=H_2O+H \qquad H+O_2=OH+O$$

$$H+O_2+M=HO_2+M \quad HO_2+H_2=H_2O_2+H$$

$$HO_2+H_2O=H_2O_2+OH$$

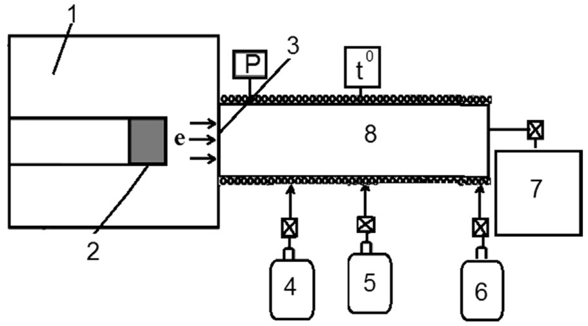


Fig. 1. Block diagram of the experimental setup: 1 – diode chamber of TEA-500 pulsed electron accelerator; 2 – graphite cathode (45 mm diameter); 3 – anode grid and aluminum foil; 4 – $SiCl_4$; 5 – O_2; 6 – H_2; 7 – collection of products; and 8 – plasma-chemical reactor.

Silicon tetrachloride step hydrogenation with silane formation is potentially possible

$$SiCl_4+H_2=SiHCl_3+HCl$$

Dioxide synthesis:

Chain termination reaction is

$$SiCl_4+4H+O_2 \rightarrow SiO_2+4HCl$$

$$SiCl_4+4OH \rightarrow SiO_2+4HCl$$

Table 1 shows the estimated energy balance of the pulsed plasma chemical synthesis of silicon dioxide.

When estimating the energy balance during nanosized oxide synthesis from the tetrachloride, oxygen and hydrogen mixture, it is necessary to consider all energy sources, including not only the beam energy but also the thermal effects of the chemical reactions. For the initial reagent mixture used when obtaining the samples under investigation, the halide was completely decomposed during the action of a single pulse.

3. Results and discussion

Nanosized silicon dioxide with an amorphous structure was produced in the synthesis process. The amorphous structure was analyzed by two duplicating methods: an X-ray phase method (Fig. 2a) and the study of microdiffraction patterns (Fig. 2b) obtained by transmission electron microscopy (TEM).

The composition of the synthesized nanosized silicon dioxide was analyzed via the Rutherford backscattering method, which indicated that it was composed of SiO_x for 99.8% (at%) when $x=1.76$. The element composition of the obtained silicon dioxide is given in Table 2.

The chemical composition of the silicon dioxide was verified by energy dispersive X-ray fluorescence spectrometry (Oxford ED2000 spectrometer). The size of the synthesized nanosized silicon dioxide was calculated using the images obtained by transmission electron microscopy. The total number of the measured particles is no less than 1000 for each image. The particle geometric size distribution is presented as a Gauss distribution on the histograms obtained. The investigation of the plasma-chemical synthesis mode's effect on the geometric size distribution of the SiO_2 nanoparticles was divided into several stages. At first, nanosized silicon dioxide was produced from the initial mixture containing 11.5 mmol O_2+23 mmol H_2+25 mmol $SiCl_4$. The average size of the particles for the obtained sample was 133 nm (Fig. 3a). This sample was used for comparison with all other samples mentioned below under the change of the synthesis modes, i.e. it was taken as the standard sample for the research. The next stage of the experiment was to change the initial amount

Table 1
Estimated energy balance of the silicon dioxide synthesis.

	Energy
Electron beam energy/pulse	100 J
Enthalpy of forming 25 mmol of silicon tetrachloride (638 kJ/mol)	15.95 kJ
Energy release in reaction$H_2+0.5O_2=H_2O+241.8$ kJ/mol	5.56 kJ
Energy release in reaction$Si+O_2=SiO_2+911$ kJ/mol	10.4 kJ