Journal of Solid State Chemistry 182 (2009) 3201–3206

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Synthesis of nanosized silicon particles by a rapid metathesis reaction

C.W. Won [a], H.H. Nersisyan [a,*], H.I. Won [a], H.H. Lee [b]

[a] RASOM, Chungnam National University, Yuseong, Daejeon 305-764, South Korea
[b] Korea Research Institute of Chemical Technology, Daejeon 305-600, South Korea

ARTICLE INFO

Article history:
Received 2 July 2009
Received in revised form
3 September 2009
Accepted 12 September 2009
Available online 19 September 2009

Keywords:
Silicon nanoparticles
Combustion synthesis
Sodium silicon tetrafluoride
Sodium azide
Combustion temperature
Sodium fluoride

ABSTRACT

A solid-state rapid metathesis reaction was performed in a bed of sodium silicofluoride (Na_2SiF_6) and sodium azide (NaN_3) powders diluted with sodium fluoride (NaF), to produce silicon nanoparticles. After a local ignition of $Na_2SiF_6+4NaN_3+k$NaF mixture (here k is mole number of NaF), the reaction proceeded in a self-sustaining combustion mode developing high temperatures (950–1000 °C) on very short time scales (a few seconds). Silicon nanoparticles prepared by the combustion process was easily separated from the salt byproducts by simple washing with distilled water. The structural and morphological studies on the nanoparticles were carried out using X-ray diffractometer (XRD) and field emission scanning electron microscope (FESEM). The mean size of silicon particles calculated from the FESEM image was about 37.75 nm. FESEM analysis also shows that the final purified product contains a noticeable amount of silicon fibers, dendrites and blocks, along with nanoparticles. The mechanism of Si nanostructures formation is discussed and a simple model for interpretation of experimental results is proposed.

1. Introduction

Silicon nanopowder is an exciting and relatively new material with potential to revolutionize the electro-optic semiconductor industry, which comprises solid state lighting, lasers, microelectronics and biological tags, etc. [1–3]. Furthermore, nanosized Si which is non-toxic would be an ideal candidate for replacing fluorescent dyes for labeling in vivo cells and may serve as an alternative to other semiconductor-based luminescent tags, like CdSe [4,5]. Although nanostructured silicon displays very high chemical reactivity and is also a promising fuel for highly energetic materials [6,7].

Currently considerable research effort is devoted to the production and engineering of Si nanopowders and numerous synthesis techniques have been developed for Si nanopowders. Among them pulsed laser ablation (PLA) technique [8–15], CO_2 laser pyrolysis of silane [16–18], electron beam evaporation of silicon ingot [19,20] become attractive to produce Si nanopowders. Generally, the synthesis of silicon nanoparticles by PLA technique is made in an ambient gas as argon, helium and thus produced nanoparticles are collected on a filter, substrate, cold plate, etc. Usually this method is appropriate to produce small amount of powder, but the technique of CO_2 laser pyrolysis of silane gas appears as a flexible tool for the production of Si nanoparticles in development quantities [16]. However, this method required precise control of reaction parameters, such as pressure of silane, reaction temperature, etc. to produce homogenous size Si powder. Moreover, silane as a precursor material is expensive and explosive when contacts with air. Electron beam evaporation of silicon usually allows to obtained nanopowders of average particle size 3–4 nm [20]. Similar to previous cases, this method also suffers from low production rate.

In these points of view rapid metathesis reactions (RMR) looks promising for preparation of silicon nanopowders. Rapid metathesis reactions producing nanoscale ceramic materials are well-known in the literature [21,22]. Gillan et al. reported the synthesis of refractory ceramics using exothermic metathesis reaction between metals chloride ($TiCl_3$, $ZrCl_4$, $MoCl_5$, etc.) and Li_3N and/or MgB_2 to produce nitride and boride ceramics (TiN, ZrN, BN, NbB_2, TaB_2, etc.) [21]. The synthesis of Si_3N_4 nanoparticles and nanorods via chemical metathesis route using $SiCl_4$ and NaN_3 precursor materials were reported in [22]. In this process, well-crystallized Si_3N_4 with an average size of 150 nm was obtained at 480 °C in stainless autoclave. To the best of our knowledge, the synthesis of nanostructured silicon via RMR route has not been reported yet.

In this paper, the processing route for the synthesis of nanostructured silicon via rapid metathesis reaction is demonstrated on $Na_2SiF_6+4NaN_3$ precursor mixture. The effect of NaF mole fraction and argon gas pressure on the combustion parameters and the morphology of silicon powder is examined and discussed as well.

2. Experimental

Na_2SiF_6 powder ($<100\,\mu m$, purity 98%), NaN_3 powder ($<200\,\mu m$, purity 99%) and NaF ($\sim 50\,\mu m$, purity 97%) were the

* Corresponding author. Fax: +82 42 822 9401.
E-mail address: haykrasom@hotmail.com (H.H. Nersisyan).

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doi:10.1016/j.jssc.2009.09.007

raw materials used in this study. As shown in Fig. 1, 37.6 g Na_2SiF_6 powder mixed with 52 g NaN_3 was hand compacted into a metallic cup 3.0 cm in diameter and 10 cm in height (a) and then the cup was placed into a combustion reactor (b) under the nickel–chromium ignition wire (c). The reactor was evacuated to 10^{-2} MPa followed by backfilling with Ar gas from 0.5 to 5.0 MPa. The combustion reaction was induced by electrically heated nickel–chromium wire 7 mm in diameter. The temperature profiles during a combustion reaction were monitored by chromel-alumel thermocouples inserted directly into the reaction mixture. The signals of thermocouples were collected by data logger system and recorded on personal computer (d). The combustion parameters examined were the combustion temperature (T_c) and combustion wave propagation velocity (U_c) The combustion velocity was calculated as $U_c=x/t$ (t is the time interval between temperature profiles and x is the distance between thermocouples).

The entire combustion process was accomplished within 10 s. The combustion product was hand grinded, washed by distillated water and dried at 70–80 °C. The mass of the recovered powder

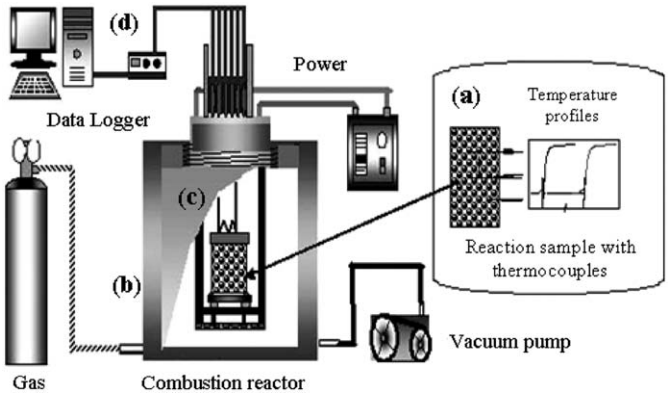

Fig. 1. Schematic representation of the experimental apparatus.

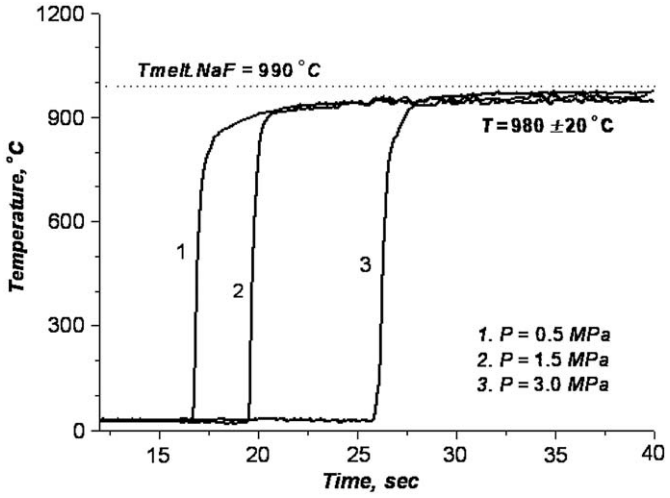

Fig. 2. Temperature profiles of Na_2SiF_6+4NaN_3 system vs inert gas pressure.

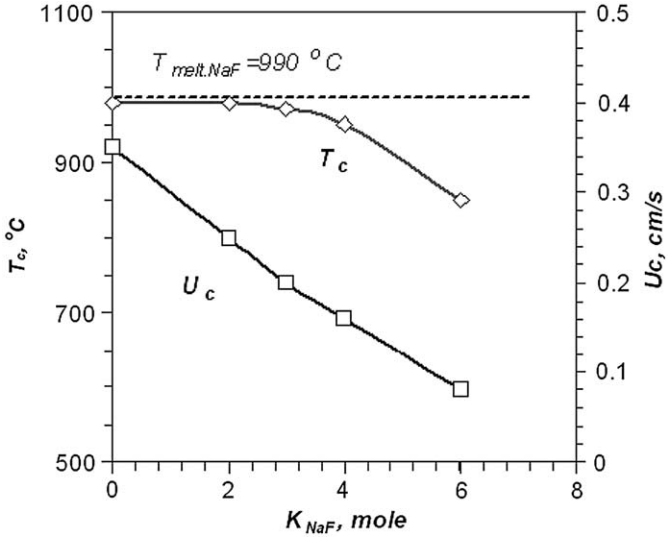

Fig. 3. Combustion temperature (T_c) and velocity (U_c) as a function of NaF mole fraction.

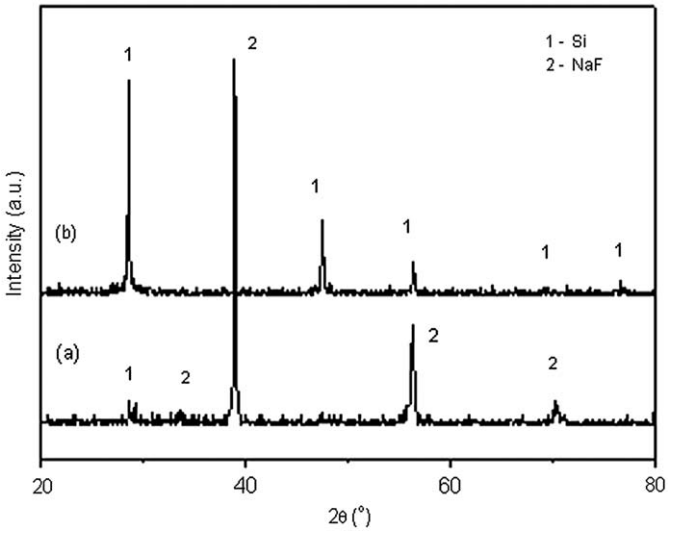

Fig. 4. Adiabatic combustion temperature (T_{ad}) and equilibrium composition of products as a function of NaF mole fraction.

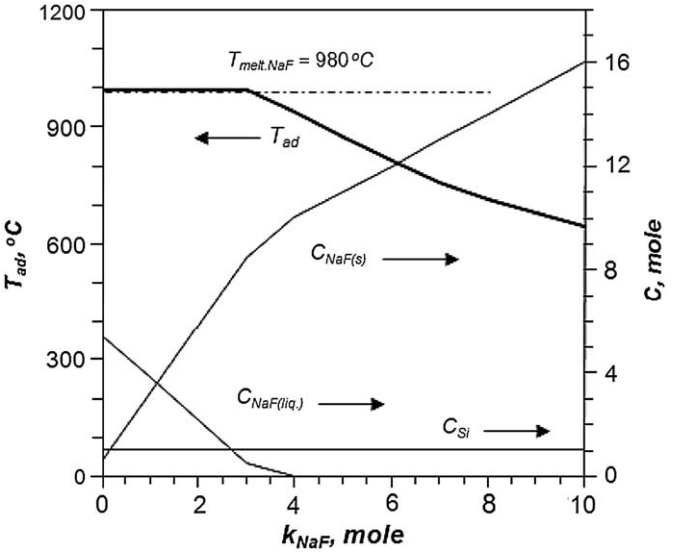

Fig. 5. XRD patterns of combustion products before (a) and after purification (b).