Thin Solid Films 587 (2015) 142–149

Contents lists available at ScienceDirect

Thin Solid Films

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

Effects of phosphorous incorporation on the microstructure of Si nanoparticles as an anode material for lithium-ion battery

Chun-young Jung [a,b], Jeong-boon Koo [a,b], Bo-yun Jang [a,*], Joon-soo Kim [a], Jin-seok Lee [a], Sung-soo Kim [b], Moon-hee Han [b,*]

[a] Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 304-343, Republic of Korea
[b] Graduate School of Energy Science and Technology, Chungnam National University, 99 Deahak-ro Yuseong-gu, Daejeon 305-764, Republic of Korea

ARTICLE INFO

Available online 7 February 2015

Keywords:
Silicon
Nanoparticles
Phosphorous
Doping
Lithium ion batteries

ABSTRACT

Si nanoparticles were synthesized by inductively coupled plasma and a specially designed double tube reactor. By injection of large amount of PH_3 during the synthesis, the effects of phosphorous incorporation on their microstructures and chemical binding environments were investigated. Injection of PH_3 gas during the synthesis resulted in a change from crystalline to amorphous phase, a reduction of particle size as well as a process yield. All of the above results were attributed to a lower plasma density when higher amount of PH_3 was injected. From energy-dispersive X-ray spectroscopy, secondary ion mass spectrometry, and X-ray photoelectron spectroscopy analysis, it was revealed that P was doped in Si nanoparticles. However, secondary phases such as P_4 and P_2O_5 were formed as amorphous ones in nano-scale when a relatively large amount of PH_3 was injected. In addition, those nanoparticles were applied as an active material in the lithium-ion battery's anode. Unexpectedly, amorphous Si nanoparticles with secondary phases showed improved electrochemical properties. P-doping in Si nanoparticles could not directly advance cycling performance by improvement of electrical conductivity of Si nanoparticles. It was rather assumed that a secondary phase influenced and enhanced electrochemical properties by additional capacity due to a formation of Li_3P and forming an effective buffer against large volumetric change of Si nanoparticles during the charge/discharge. The initial reversible capacity of amorphous Si nanoparticles synthesized with 100 sccm of PH_3 flow rate was 2113 mAh g^{-1}, and that at the 100th cycle was still about 1000 mAh g^{-1}, which was twice as high as that of Si nanoparticles synthesized without PH_3 injection.

1. Introduction

Semiconducting nanoparticles have gained much attention due to their exclusive characteristics that are different from those of the bulk one [1–3]. Semiconductor nanoparticles embedded in a dielectric matrix have generated our interest due to the fact that they possess numerous potential applications in fields such as photovoltaics [4–6], data storage [7], and optoelectronics [8]. Among semiconducting nanoparticles, Si is a principal candidate applicable to the above fields due to its eco-friendly characteristics and abundance in the Earth. The existence of widespread infrastructure for Si-based electronics is another benefit in favor of developing Si nanoparticles. Therefore, there has been enormous research on synthesis and characterizations of Si nanoparticles [9–11].

Plasma was known to be an effective approach for a synthesis of nanoparticles. Among various plasma syntheses of nanoparticles, non-thermal plasma enables us to gain monodispersed particle sizes without agglomeration of nanoparticles [12,13]. The studies on nanoparticle synthesis by using non-thermal plasma fall into two categories: capacitively coupled plasma (CCP) and inductively coupled plasma (ICP) [12]. Mangolini et al. reported a synthesis of Si nanoparticles with average sizes smaller than 10 nm and an evaluation of application for luminescence source using CCP [13]. Jang et al. proposed ICP synthesis method with efficient plasma controllability to obtain monodispersed crystalline Si nanoparticles [14].

Doping with phosphorous (P) or boron (B), which introduces a donor or an acceptor level in the energy band gap of Si, is a key process to realize a Si-based diode. Generally, dopant concentration and profile determine the final energy band structure that is tightly related to the device performance. In addition, Si exhibits electrically semiconducting or almost insulating properties. Doping can also be a solution for some applications in which a relatively high electrical conductivity of Si is needed. Accordingly, P- or B-doping of Si nanoparticles is also a primary process that can broaden the applications of these materials for various devices. For instance, P-doping of Si nanoparticles enhances visible photoluminescence intensity due to donor level acting as a trap center of excitation in the Si nanoparticles [15,16]. Kim et al. has also reported that P-doped Si nanowires exhibited an enhanced initial discharge capacity due to significant reduction of charge transfer resistance [17].

---

* Corresponding authors. Tel.: +82 42 860 3476; fax: +82 42 860 3133.
E-mail address: byjang@kier.re.kr (B. Jang).

http://dx.doi.org/10.1016/j.tsf.2015.01.068
0040-6090/© 2015 Elsevier B.V. All rights reserved.

According to microstructural analysis and impedance measurement, doped-P existed in surface of nanowires and reduced interfacial resistance.

A number of synthesis processes for P- or B-doped Si nanoparticles have been reported. Scriba et al. produced B-doped Si nanoparticles using hot wire thermal catalytic pyrolysis [18]. Fukata investigated doping effects of B in Si nanowires synthesized by laser ablation [19]. Song et al. used plasma enhanced chemical vapor deposition to synthesize P- or B-doped Si nanoparticles, and reported the increasing electrical conductivity of Si nanoparticles by doping [20]. Fujii et al. doped P or B into Si nanoparticles embedded in SiO_2 via co-sputtering of Si and phosphosilicate glass [21]. Gupta et al. synthesized P-doped Si nanoparticles by using low-pressure microwave plasma and characterized optical properties of doped Si nanoparticles [16].

As mentioned above in P-doped Si nanostructures such as nanowires and nanoparticles, P-doping was known to enhance the electrical conductivity of Si nanostructures, which could also lead to better cyclic performance of anode if they were used as active materials for lithium-ion battery. Typical doping concentration in previous researches ranged from 10^{17} to 10^{18} atoms/cm^3 to obtain sufficient electrical conductivity. It was thought that the higher doping concentration might result in the better cyclic performance. In this study, we synthesized Si nanoparticles with large amount of PH_3 gas injection to have even higher P concentration than solubility limit (10^{21} atoms/cm^3) in Si nanoparticles using ICP and a double tube reactor. Homogeneous and high doping concentration could be obtained by injection of PH_3 during the synthesis of Si nanoparticles. We investigated the effects of large amount of P on the microstructures and chemical binding environments of synthesized Si nanoparticles by using various analyses. Also, the synthesized Si nanoparticles with high concentrations of PH_3 were applied as active materials in the lithium-ion battery's anode, and we observed the feasibility of using these materials in such a manner.

2. Experimental procedures

A schematic diagram of the double tube reactor with an ICP coil is shown in Fig. 1. The system consisted of gas-injection, plasma-reaction, cooling, and gathering zones. The gas-injection part consisted of five inner tubes and four holes on the cap of reactor as shown in Fig. 1(b). The role of the inner tube was to concentrate plasma, and details of the procedure were given in our previous report [22]. A mixture gas of monosilane (SiH_4), phosphine (PH_3), and argon (Ar1) was injected into the inner tubes. And another argon (Ar2) was injected through holes on the cap of the outer tube to reduce the deposition of Si nanoparticles on the quartz reactor. The plasma reaction part consisted of a quartz tube wrapped with an ICP coil. As shown, plasma formed only from the end of inner tube to the bottom of plasma reaction part. We defined a plasma volume as total volume of the visibly-emitting portion of plasma. Additional argon (Ar3) was introduced via ceramic nozzles into the cooling region along the side tube. This Ar3 cooled the synthesized nanoparticles to prevent agglomeration. The flow rates of all the gases were precisely controlled by the mass flow controllers, and the synthesized nanoparticles were collected by using steel mesh in the bottom of reactor [see Fig. 1(c)]. This gathering part was directly connected to a glove box to prevent the contamination of Si nanoparticles during gathering and weighing. To study the effects of P in Si nanoparticles, we prepared samples under the same process conditions except for an introduction of PH_3 flow rate during the synthesis. When a high vacuum state of less than 1.33 Pa was achieved in the reactor, and 500 sccm of Ar1, 300 sccm of Ar2, and 300 sccm of Ar3 were injected into the inner tubes, outer tube, and cooling region, respectively. The typical working pressure was 133.33 Pa, and it was controlled with precision by an auto-throat valve. A radio frequency (RF) power of 300 W at 13.56 MHz was applied to the reaction region through the ICP coil. When the plasma was stable, a mixture gas of 20 sccm SiH_4 and 0–100 sccm PH_3 with Ar1 was additionally injected into the inner tubes. After synthesis for 2 h, plasma power was turned off and the residual gas was removed inside the ICP reactor. The samples were collected from the steel mesh with atmospheric pressure in the glove box.

X-ray diffraction (XRD; Rigaku, HPC-2500) was measured to identify crystal structures with theta-2 theta configuration at a voltage of 40 kV and a current of 100 mA, using Cu-K$_{\alpha 1}$ radiation (λ = 0.15406 nm). Scanning electron microscope (SEM; Hitachi, S-4800) was used to investigate the microstructures of synthesized nanoparticles at operating voltage of 5.0 kV. X-ray photoelectron spectroscopy (XPS; Thermo, MultiLab 2000) analysis was also carried out to define the chemical binding environment of Si and P in each sample at passing energy of 20 eV using Al K$_\alpha$ source. The binding energy scale was calibrated using the C1s peak. The amount of P in Si nanoparticles was measured by using secondary ion mass spectroscope (SIMS; CAMECA, IMS-6f), and Cs$^+$ ion gun was used with a proton impact energy of 15 keV and a current of 100 nA. Elemental concentrations were obtained by using energy dispersive spectroscope (EDS; HORIBA, X-MAX 50) with an operating voltage of 15.0 kV and a collection time of 0.5 min.

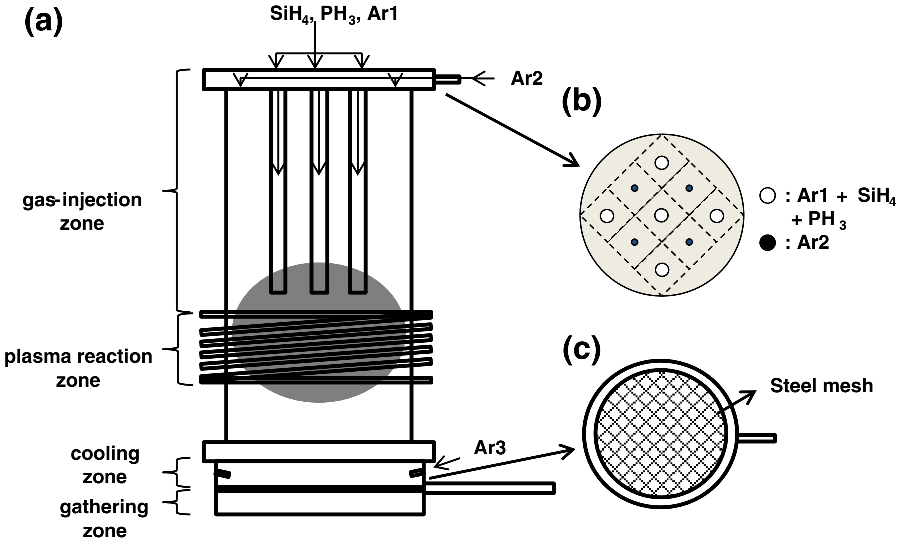

Fig. 1. Schematic diagram of the double tube reactor with an inductively coupled plasma coil.