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Hydrogen-assisted spark discharge generation of highly crystalline and surface-passivated silicon nanoparticles

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ABSTRACT

The ability to produce highly pure and crystalline nanoparticles with prescribed surface chemistry is of vital importance as these properties play crucial roles in enhancing the performance of nanoparticle-embedded opto- and nano-electronic devices. In this study, we sought to improve the purity, crystallinity, and surface passivation of silicon nanoparticles as they are produced via spark discharge generation by introducing a hydrogen atmosphere. When pure argon is used as the carrier gas, we find that some particles are oxidized (silicon oxide rather than silicon) due to the trace amounts of oxygen present in the system, and those that are not oxides are often amorphous, as the spark energy is insufficient to produce highly crystalline silicon nanoparticles. When hydrogen is introduced into the chamber, it creates a reducing environment within the spark discharge zone, which effectively reduces the formation of oxide particles. The portion of generated silicon oxide nanoparticles decreases as more hydrogen is introduced into the system. In addition, hydrogen plasma generated from the spark discharge process improved the crystallinity of the produced silicon nanoparticles, and aids passivation of the silicon nanoparticle surface by forming Si-H_x bonds, enhancing their stability during handling in oxygen containing atmosphere. Thus, the presented technique can be used to produce hydrogen-passivated silicon nanoparticles with high purity and crystallinity, and it is expected that these particles can be utilized as quantum dots after size-selection or be incorporated into luminescence devices.

1. Introduction

Spark discharge generation (Schwyn, Garwin, & Schmidt-Ott, 1988) has been well established as a simple and clean technique for generating sub-10 nm nanoparticles among various synthesis methods. The nanoparticles produced by spark discharge generation can be directly incorporated into many electronic and optical devices without the need of any solution-based processing. For instance, spark discharge generated gold nanoparticles were embedded in organic display devices (Sung et al., 2014) to increase the quantum efficiency without appreciable damage of the underlying organic material, and gold seed nanoparticles were used for nanowire growth (Messing, Dick, Wallenberg, & Deppert, 2009). In addition, spark discharge generation has been utilized to fabricate sophisticated three-dimensional nanostructures via ion-assisted aerosol lithography (Jung et al., 2014; Lee et al., 2010; You et al.,

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2010), as well as to enable the positioning of various charged nanoparticles at precise locations on a dielectric surface (Krinke, Fissan, Deppert, Magnusson, & Samuelson, 2001). Furthermore, spark discharge generation is able to produce nanoparticles with complex compositions, such as bimetallic nanoparticles (Byeon, Park, & Hwang, 2008) and composite nanoparticles (Kala, Theissmann, & Kruis, 2013).

Until now, spark discharge generation has been mainly used to produce metallic nanoparticles and the effects of process parameters on the generation process have been well understood. In contrast, spark discharge generation of non-metallic nanoparticles, such as those made of semiconducting materials, have not been widely studied. A recent study regarding silicon nanoparticle generation showed that doped silicon electrodes can be used to enhance the production rate (Vons et al., 2011), but the generated silicon nanoparticles were agglomerated and gradually oxidized in air. Since silicon nanoparticles have unique properties such as large volume change in lithiation and de-lithiation (Ding et al., 2009) and direct bandgap semiconducting behavior (Hirasawa, Orii, & Seto, 2006), they have received much attention and have been used in various applications including Li-ion batteries (Ding et al., 2009), photoluminescence (Hua, Erogbogbo, Swihart, & Ruckenstein, 2006) and photovoltaics (Cabarrocas, Chaabane, Kharchenko, & Tchakarov, 2004). The performance of these devices is greatly affected by the size, crystallinity, purity, and surface chemistry of the nanoparticles. Therefore, it is essential to fine-tune the production process to tightly control these properties.

Silicon nanoparticles have been produced by a variety of physical and/or chemical processes, including laser ablation of bulk silicon (Yoshida, Takeyama, Yamada, & Mutoh, 1996), nucleation in precursor solution (English, Pell, Yu, Barbara, & Korgel, 2002), pyrolysis of gas phase precursor (Huisken, Ledoux, Guillois, & Reynaud, 2002), fracturing of electrochemically etched porous silicon (Lie, Duerdin, Tuite, Houlton, & Horrocks, 2002), or even ball milling of graphite and silicon dioxide (Lam et al., 2000). Generally, gas phase production yields silicon nanoparticles with good size control, yet it is challenging to control their surface chemistry. On the other hand, liquid phase nucleation or electrochemical etching can achieve desired surface chemistry, but suffers from either contamination or irregular shapes of the particles. Production of pure, crystalline, spherical, unagglomerated and surface passivated silicon nanoparticles has not been realized so far to the best of authors' knowledge.

Recently, *Hallberg et al.* have reported that by introducing a small amount of hydrogen into the spark discharge generator, small spherical metal nanoparticles were generated. One possible explanation for the spherical shape may be the absence of oxides acting as diffusion barriers leading to better particle coalescence (Hallberg, Dick, Magnusson, & Messing, 2015). However, it would be also possible that hydrogen addition could influence the discharge characteristics. Hydrogen passivation is a commonly used technique to remove dangling bonds from silicon surfaces to prevent them from forming oxides, and hence the hydrogen-assisted spark discharge generation opens up an opportunity to passivate the silicon nanoparticles in situ as they are produced in the spark discharge chamber. In this study, we sought to produce unagglomerated and surface passivated silicon nanoparticles with improved purity and crystallinity by introducing hydrogen atmosphere into the spark discharge chamber.

2. Experimental methods

The experimental setup consisting of a pin-to-plate spark discharge generator (Han et al., 2012), an electrostatic precipitator, high voltage power supplies and mass flow controllers are shown in Fig. 1(a). The spark discharge generator was constructed using a cylindrical stainless steel chamber, silicon electrodes, electrode holders, and features an inlet and an outlet for carrier gas flow. The spark discharge generator and the electrostatic precipitator were installed in a glove box filled with nitrogen to prevent oxidation of the electrodes and the generated nanoparticles. High purity argon and hydrogen (99.999% purity) were mixed in varying ratios and used as the carrier gas. The gas flows were regulated by mass flow controllers, mixed with a static mixer and injected into the spark discharge generator. The total carrier gas flow was fixed at 3 lpm, and three different mixture ratios were used: pure argon, 1:1 argon and hydrogen, and pure hydrogen. A high-voltage DC power supply was used to apply 6 kV to the pin electrode through the external electric circuit consisting of a capacitor (2 nF) and a resistor (3 MΩ). The electrodes and the circuit were configured to maintain the discharge voltage at 3 kV and the spark frequency at 200 Hz by continuously adjusting the electrode gap distance, and these values were monitored using an oscilloscope (Agilent DSO-X 3014A) and a high voltage probe (Tektronix P6015A). Highly doped n-type silicon (3 ± 0.1 mΩ cm) was used as electrodes. The flow conditions and electrode material were chosen to ensure that the spark current decays by damped harmonic oscillation (Fig. 1(b)), which signifies that the spark energy is mostly used to ablate the electrode material instead of being dissipated in the electrodes, and this results in the increased silicon nanoparticle production rate (Vons et al., 2011).

To characterize the morphology and the size distribution of generated silicon nanoparticles, high resolution transmission electron microscopy (HR-TEM, JEOL ARM 200 F) with energy dispersive X-ray spectroscopy (EDS, X-max^N 80 T) was carried out. Positively charged silicon nanoparticles were collected on a carbon film-coated copper TEM grid using an electrostatic precipitator by applying −3 kV DC bias for 5 min. The particles were collected after several hours of spark discharge operation to ensure that the oxide layers on the silicon electrodes have been ablated away. In addition, the crystallinity, oxidation states and surface chemistry of the nanoparticles were assessed by X-ray diffraction (XRD, Bruker New D8 Advance), Raman spectroscopy (Horiba Jobin-Yvon LabRam ARAMIS), and Fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX 80v) measurements, respectively. These measurements were performed on a porous film of nanoparticles (~8 μm thick after a 12 h deposition) deposited on a silver substrate (99.99% purity, 0.5 mm thick).

3. Results and discussion

HR-TEM images show that the nanoparticles generated in pure argon flow were generally agglomerated (Fig. 2(a) left). The high