



# Mercaptosuccinic acid modified silicon particle inks: Production, structural, and electrical characterizations



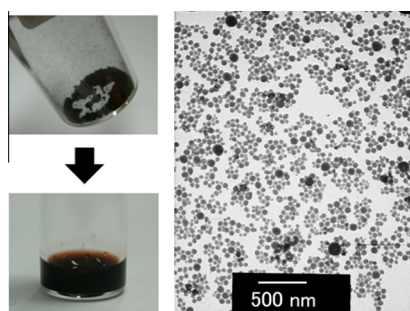
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## HIGHLIGHTS

- We show a simple method for producing highly hydrophilic Si particles.
- Si particle network (i.e. porous-like) films were obtained from the particle inks.
- Surface oxide on the films was hardly grown even after removal of the modifiers.
- The Si films exhibited ohmic  $I$ - $V$  characteristics with resistivities of  $\sim 10^2 \Omega \text{ cm}$ .
- The  $I$ - $V$  curve shapes and slopes changed by changing atmosphere gases.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Water soluble Si particles were produced by modifying the surface with mercaptosuccinic acid (MSA). Using the MSA modified Si particle ink, porous-like Si films with resistivities of  $10^2 \Omega \text{ cm}$  were formed by annealing above  $260^\circ \text{C}$ . Current–voltage ( $I$ - $V$ ) characteristics of the annealed films were ohmic in  $\text{N}_2$ . When the films were exposed to air, the current decreased and the  $I$ - $V$  curve became nonlinear. This nonlinear characteristic could be explained by the Poole–Frenkel model, which indicated that adsorbed gas molecules produced traps for free carriers. The  $I$ - $V$  curve returned to the original shape by changing the atmosphere gas back to  $\text{N}_2$ . The semiconductive porous-like Si films made from the Si particle inks are expected to be applied to a variety of electronic devices such as gas sensors and high capacity anodes for lithium-ion batteries.

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## 1. Introduction

Over the past two decades, porous Si films have attracted considerable interest in fundamental research and potential device applications, e.g., gas sensors to detect toxic and explosive gases [1–3], high capacity anodes for lithium-ion ( $\text{Li}^+$ ) batteries [4,5], multiexciton solar cells [6,7], biosensors [8], drug delivery devices [9,10], and light emitting devices [11,12]. To date, a number of

interesting fundamental properties have been reported; however, applications are not yet sufficiently advanced. The main obstacles that prevent practical applications are difficulties producing good quality films on any surface other than Si, forming ohmic contact with electrodes, and producing films over large areas. In addition, hydrofluoric (HF) acid immersion in the Si etching process is also a practical obstacle. Some attempts to circumvent these problems have been made by chemically synthesizing porous Si [13]. Another possible way is to produce Si particle network films, which can be comparable to porous Si films, from Si particle inks.

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Various Si nanoparticles that stably disperse in organic or aqueous solutions have been reported [14–18]. However, to use Si particles as practical ink particles for making films, the following requirements need to be satisfied: (1) Si particles stably disperse even in dense suspensions (more than at least 0.1 wt%, preferably more than 1 wt% Si ink); (2) Surface covering layers of the Si particles sublime by relatively low-temperature annealing or under weak electron beam to make it possible to form the films on a variety of substrates; and (3) The surface covering layers should be sufficiently thin to produce high-density Si particle network morphology. This report shows that Si particles modified with mercaptosuccinic acid ( $\text{HOOCCH}_2\text{CH}(\text{SH})\text{COOH}$ ; MSA) are promising candidates. MSA is a short chain carboxylic acid, and is known as a surface modifier that makes various particles highly dispersible in water. The reported MSA-modified particles include metal particles (e.g., Au [19], Ag [20], Pt [21]), semiconductor particles (e.g., CdS [22], CdSe [23], CdTe [24],  $\text{TiO}_2$  [25]) and magnetic particles (e.g.,  $\text{Fe}_3\text{O}_4$  [26]). Here, for the first time, we produce MSA-modified Si particles to be used as ink particles, and evaluate their structural and electrical properties. This study will be a first step toward realizing printable porous Si devices.

## 2. Experimental

### 2.1. Materials

Si powders (purity 99.99%, diameter < 0.150 mm) were purchased from Nacalai Tesque (Kyoto, Japan). Super dehydrated methanol (99.8%, water content < 10 ppm), methanol (99.8%), and 2-propanol (99.9%) were purchased from Wako Pure Chemicals (Osaka, Japan) and used as received.

### 2.2. Preparation of Si particle inks

MSA modified Si particles were produced by wet grinding the Si powders in MSA-containing super dehydrated methanol in Ar atmosphere using a Retsch PM100 planetary ball mill with 3-mm tungsten carbide (WC) balls. The obtained colloidal sample was washed by the following processes. First, the WC abraded particles and large Si fragments were precipitated by centrifugation at 400g for 5 min using a Kubota 1720 centrifuge. Then, the supernatant solution in which the Si particles were stably dispersing was collected. To remove unbound MSA molecules from the collected solution, 2-propanol was added to the suspension until the 2-propanol/methanol ratio reached 50% (v/v). Then, the Si particles were precipitated by centrifugation at 14,000g for 30 min, and the supernatant solution in which unbound MSA molecules were dispersing was removed. This removal process was repeated after the precipitated Si particles were redispersed in 50% (v/v) 2-propanol/methanol by sonication. The precipitated particles were then dispersed in distilled water and were freeze-dried for storage. The dried Si particles were redispersed in distilled water prior to being used as the ink.

For transmission electron microscopy (TEM) observation, the specimen was prepared by depositing a droplet of the Si particle ink onto an amorphous carbon-coated Cu grid. For electrical characterization, the ink was deposited on a  $\text{SiO}_2$  film on which Au electrodes separated by a distance of 5  $\mu\text{m}$  were prefabricated.

### 2.3. Instruments

The size distribution of the Si particles dispersing in water was evaluated by dynamic light scattering (DLS) using an Otsuka Electronics ELS-800 with an incident beam from the 633 nm line of a He–Ne laser. For structural observations, TEM with a JEOL

JEM-2010F operating at 200 kV and confocal laser scanning microscopy (CLSM) with a Keyence VK-8510 with an incident beam of 685 nm were used. Chemical analyses of the Si particles were performed using energy-dispersive X-ray (EDX) spectroscopy with a Hitachi S4800 operating at 15 kV, Fourier transform infrared (FTIR) spectroscopy with a Horiba FT-720 to measure absorption, a Bruker VERTEX70 to measure reflection, and X-ray photoelectron spectroscopy (XPS) with Al  $K\alpha$  radiation (1486.6 eV).

## 3. Results and discussion

The appearance of the dried Si particles is shown in Fig. 1(a). By adding distilled water to the dried particles, the particles stably dispersed (Fig. 1(b)). The Si concentration in water could increase to 2 wt%. Fig. 1(c) plots the size distribution of the water-dispersed Si particles measured by DLS. The average diameter obtained from this distribution was 44.2 nm. Fig. 1(d) shows an example of a film made by depositing the Si particle ink. Fig. 2(a) shows the TEM image and the transmission electron diffraction (TED) pattern of the Si particles. No clear diffraction spots or rings were found in the TED pattern, indicating that the Si cores were amorphous. Powder X-ray diffraction (XRD) patterns of the starting Si powders, the precipitates obtained by the slow centrifugation process (400 $\times$ g) and the ink particles are shown in Fig. S1 (Supplementary Material). The figure shows that the starting powders were crystalline Si, and the crystallinity was found in the precipitates but not in the ink particles. This means that the Si particles lost their crystallinities by being milled into the particles small enough to be used as the ink particles. The size distribution obtained from the TEM image (Fig. 2(a)) is shown in Fig. 2(b). The average diameter obtained from this distribution was 41.5 nm. Taking account of the MSA layer thickness (0.6–0.7 nm [27,28]), the average diameter of the particles including the MSA layers is estimated to be approximately 43 nm, which is close to the average diameter measured by DLS. This indicates that the Si particles individually dispersed in water but did not form assemblies. The size distribution obtained from the TEM image (Fig. 2(b)) contains larger particles (especially in the range larger than 60 nm) in comparison with that obtained from DLS (Fig. 1(c)). This is probably because some of the particles were very unstable to electron beam irradiation and were fused together as soon as the TEM observation started. We will show below that the produced Si particles were electron-beam labile. Fig. 2(c) shows a typical EDX spectrum of the Si particles. The Cu peak is from the specimen grid. Impurities such as W were less than the detection limit of the EDX system. The molar ratio of S/Si was estimated to be 0.056. Assuming that all the S atoms locate at the surface of the Si cores, the number of S atoms per one surface Si atom is estimated to be  $\sim 1.7$ . This means that approximately two MSA molecules were bound to one surface Si atom. During the TEM observation, the Si particles were found to gradually connect to adjacent particles under electron beam irradiation as low as 1 pA/cm<sup>2</sup> (Fig. 3). This behavior is preferable for the use of the particles as ink particles to construct the particle network. Close examination of the particles in Fig. 3(b) revealed smaller particles with diameters of 1–3 nm. These particles, which are probably Si nanocrystals, did not exist in the as-prepared particles but emerged after the strong electron beam irradiation required to obtain a higher magnification image.

An FTIR spectrum of the dried Si particles is shown as curve (a) in Fig. 4. For comparison, a spectrum of the poorly dispersible Si particles that were obtained as precipitates by the slow centrifugation process (400 $\times$ g) is shown as curve (b). Although the WC-abraded particles were included in the precipitates, we confirmed in advance that they did not show any FTIR peaks. In the spectrum (a), peaks attributed to carboxy groups, which are in the range

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