Pure Silicon Nanoparticle Synthesis using Tandem Type of Induction Thermal Plasmas with Simultaneous Controlled Modulation of Upper- and Lower-Coil Current

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Abstract: A tandem type of modulated induction thermal plasma with an upper coil and a lower coil was adopted to synthesize silicon nanoparticles. The upper-coil current was modulated weakly, whereas the lower-coil current was modulated largely. This modulation effect was investigated on size and constituents of synthesized particles experimentally. Results suggests that larger modulation of two coil current offers smaller Si nanoparticles.

Keywords: Thermal plasma, Modulated induction plasma, Silicon, Nanoparticle

1. Introduction

Induction Thermal Plasma (ITP) is widely utilized in materials processing such as nanomaterial synthesis, thin film deposition, surface modification, and so on. The ITP has an advantage of high gas-temperature around 10000 K and high enthalpy. From these features, the ITP can heat solid feedstock rapidly, resulting in its vaporization to produce high density atoms. Additionally, the ITP forms clean chemical reactive field with molecular gases without contamination because of electrodeless discharge. To control the thermofluid field in the ITP in time-domain, we have developed Pulse-Modulated Induction Thermal Plasma (PMITP) [1]. In the PMITP, amplitude-modulated coil-current can generate time-varying temperature field. Higher gas temperature field is obtained during the timing of higher input power, while lower temperature field is provided during lower input power timing. Taking advantages of these features of PMITP, we have successfully synthesized nanoparticles with a high production rate ~ 400 g/h at 20 kW [2]. In nanoparticle synthesis using the PMITP, feedstock powder is supplied in higher temperature plasma by higher input power, then more efficient evaporation of the feedstock is obtained. Conversely, vaporized feedstock is rapidly cooled to nucleate during low input power timing. In addition, grain growth to μm order is avoided by quench from the modulation. However, the PMITP becomes unstable for too high modulation degree. It is thus not easy to obtain larger fluctuated temperature field. In other words, the thermal plasma can hardly recover from lower-temperature state to higher-temperature state.

To enhance the stability of PMITP, we have further developed a tandem type of modulated induction thermal plasma (tandem-MITP) system [3]. A tandem type of induction plasma, which is also called an RF-RF hybrid plasma or a dual RF plasma using two independent induction coils, is already known to have its high stability compared with a conventional single-coil induction plasma, and to be an effective reactor for materials processing [4,5]. Here, we have developed a tandem ITP with coil current modulation as well. The tandem-MITP has higher robustness because of two coils compared to the single-coil MITP. For example, the one coil current can be used to sustain thermal plasma stably in the torch, while another coil current can be used to control high temperature field. Moreover, tandem-MITPs has following advantages except its higher stability. One is that tandem coil arrangement generates a longer high temperature field avoiding unfavorable recirculation vortex in the torch. This longer high-temperature region can evaporate refractory feedstock more. Another important advantage is that the tandem-MITP can offer a tempo-spatial varying temperature field by modulating two induction coils independently [3,6,7]. For instance, setting different phase differences between the two amplitude-modulated currents can make different complicated temperature behaviors in thermal plasmas. Such a modulation of two coil current can be expected to control various reactions in thermal plasma. Here, we attempt to apply this tandem-MITP to nanoparticle synthesis.

This contribution describes adoption of the developed tandem-MITP for silicon (Si) nanoparticle synthesis. Silicon nanoparticle is anticipated as anode for of next generation lithium ion battery [8]. In our experiment, a tandem-MITP was used with modulation of both the upper-coil current and the lower-coil current simultaneously. The lower coil current is largely modulated to produce largely modulated temperature field, whereas the upper coil current is modulated just in a small degree to keep its robustness. Results showed that amplitude-modulation of the upper- and the lower-coil current can reduce the diameter of synthesized particles compared to that under non-modulation condition. The collected particles were analyzed by FE-SEM for morphologies and their size distributions, by XRD for their crystalline structures. As a result of these analysis, we can obtain Si nanoparticles which has nearly smaller than 100 nm.

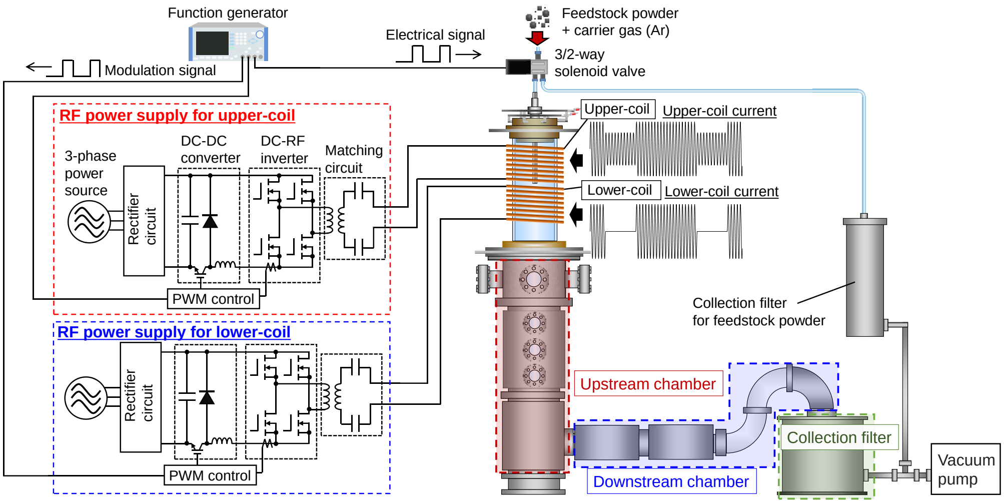


Fig. 1. A schematic diagram of tandem-modulated induction thermal plasmas system for nanoparticle synthesis.

2. Experimental setup

Fig. 1 depicts the developed tandem-MITP system for nanoparticle synthesis. The tandem-MITP system contains one plasma torch with two eight-turn coils (upper coil and lower coil), and two radio-frequency (RF) power sources. The RF power sources can supply RF current to each respective coil. The operating frequencies of the upper and lower coil currents were set to different ones each other to avoid resonant electromagnetic coupling between them. The different operating frequencies for MOSFETs in the two RF sources were used with different matching capacitances for two independent RF circuits. The coil currents were both amplitude-modulated by switching insulated-gate bipolar transistors (IGBTs) in two power circuit followed by modulation signals from a function generator.

The plasma torch is composed of two coaxial quartz tubes. Between these tubes, cooling water flows to keep the wall temperature around 300 K. The torch has a height of 440 mm, and an inner diameter of 70 mm. From the head center of the torch, a water-cooled tube is inserted for feedstock powder injection. Downstream of the torch, an upstream chamber, a downstream chamber and a collection filter are connected in series. These chambers are made of stainless steel, and these walls are all water-cooled.

Feedstock injection was controlled to be supplied intermittently and synchronously to the tandem-MITP using a solenoid valve installed between the plasma torch and a powder feeder. We call this feeding method the time-controlled feeding of feedstock (TCFF) [2]. Such intermittent and synchronous feeding of feedstock enables complete and efficient evaporation of the feedstock. In addition, it also provides a rapid cooling of evaporated material to promote nucleation.

3. Experimental conditions

Experimental conditions were set as follows: Time-averaged input power was fixed at 10 kW for the upper-coil, and 10 kW for the lower-coil, respectively. The frequency of the upper-coil current was set at 460 kHz, while that of the lower-coil current was set at 320 kHz simultaneously. Pressure inside the chamber was fixed at 300 torr. Argon sheath gas was supplied with a flow rate of 90 L/min. Quenching gas was not supplied in the present work. Feedstock was Si powder with 97% purity. The volume mean diameter of the feedstock powder is 26 μm. The feedstock powder is provided into the thermal plasma with Ar carrier gas flow of 4 L/min. This feedstock was intermittently fed into the plasma torch through the solenoid valve. **Fig. 2** indicates a schematic of pulse-modulated current. Shimmer current level (SCL) of the modulated current was defined as a ratio of lower current level (LCL) to higher current level (HCL). **Table 1** shows SCLs for each condition. The combinations of SCLs for upper- and lower-coil currents were set to (i)90%SCL-0%SCL, (ii)100%SCL-0%SCL, and (iii)100%SCL-100%SCL. Here, 100%SCL is equivalent to non-modulational state, while 0%SCL offers 0 A for coil current during 'off-time'. The 'on-time' means the time duration during HCL, and 'off-time' also means the time duration during LCL. The on-time and off-time were fixed at 10 ms, and 5 ms even for upper- and lower-coil modulation. Feed rate of feedstock were set as 3.0, 1.5, and 2.8 g/min, respectively, for (i), (ii) and (iii) in **Table 1**.

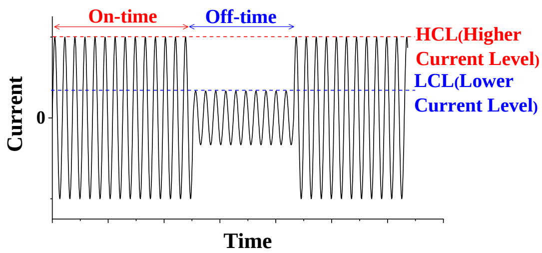


Fig. 2. Amplitude modulated coil current.

Table 1. Condition for silicon nanoparticle synthesis

Designation	(i)	(ii)	(iii)
SCL for upper-coil [%]	90	100	100
SCL for lower-coil [%]	0	0	100
Feedstock feeding rate [g/min]	3.0	1.5	2.8

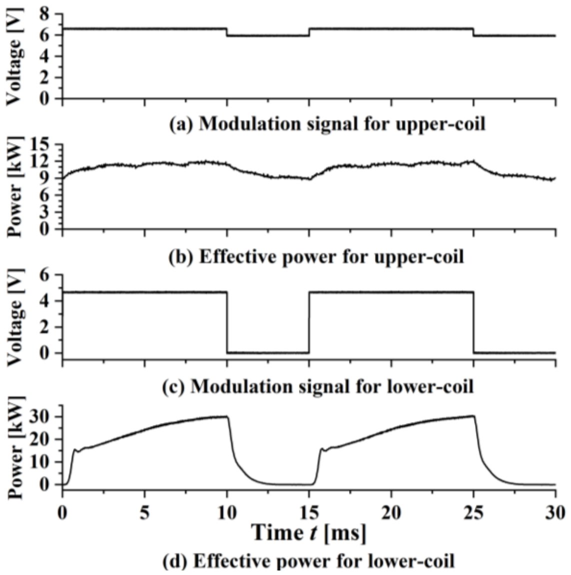


Fig. 3. Modulation signals and effective powers for upper- and lower-coil under condition (i) 90%SCL-0%SCL for upper and lower coil currents.

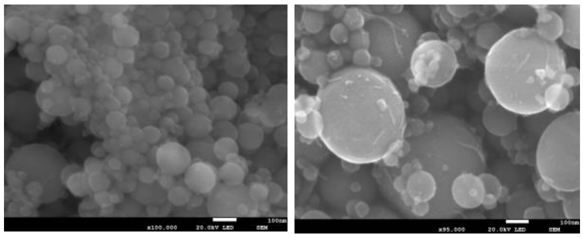
4. Results and discussions

4.1. Modulation signals and output powers

Fig. 3 shows modulation signals and effective output power from the inverter circuit to the upper- and lower-coil under the condition of (i) upper: 90%SCL, lower: 0%SCL. This condition is designated by 90%SCL-0%SCL. The effective power was computed by averaging instantaneous electric output power during 10 cycles. As seen in this figure, the output power follows the modulation signal. In upper-coil, the power changed from ~9 kW to ~12 kW following the signal. On the other hands, larger modulation could be obtained in lower-coil power. The minimum power to the lower-coil is ~0 kW, whereas the maximum power reaches to much higher power ~30 kW. This is due to larger modulation of lower-coil current. In addition, the sum of input power of two coils attains to 42 kW at on-time, and the power was decreased to 8 kW at off-time. Therefore, it can be found that this larger variation of input power makes larger change of temperature field in the plasma torch. It is noted that from this experiment results, a largely-modulated ITP was successfully maintained with higher robustness by tandem two coils than a single coil MITP.

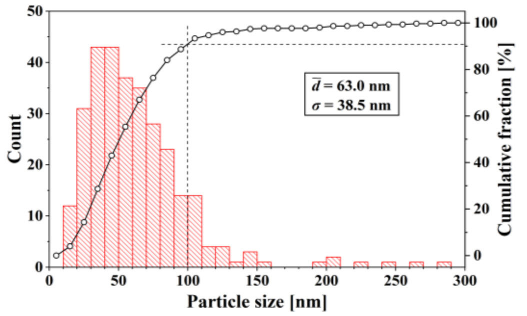
4.2. Morphology of synthesized particles and particles size distribution

Fig. 4 displays FE-SEM images of synthesized particles collected in downstream chamber for morphology under conditions of (i) upper: 90%SCL, lower: 0%SCL (90%SCL-0%SCL) for modulation case, and (iii) upper: 100%SCL, lower :100%SCL(100%SCL-100%SCL) for non-modulation case. From these images, many nano-sized particles are found, which indicates that nanoparticle was successfully fabricated. Furthermore, spherical particles are formed, showing that nanoparticles grew up in vapor

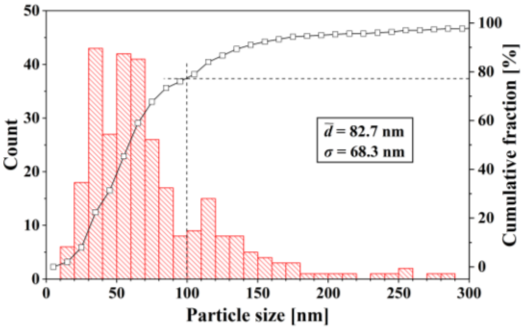


(a) 90%SCL-0%SCL (b) 100%SCL-100%SCL

Fig. 4. SEM image of synthesized particle under condition (i) 90%SCL-0%SCL and (iii) 100%SCL-100%SCL for upper and lower coil currents.



(a) 90%SCL-0%SCL



(b) 100%SCL-100%SCL

Fig. 5. Particle size distribution for synthesized particle under condition (i) 90%SCL-0%SCL and (iii) 100%SCL-100%SCL for upper and lower coil currents.

phase by minimalization of surface energy. The particles collected from other positions under different conditions also have spherical shape similarly.

Particle size distributions were evaluated from randomly selected 300 particles by measuring their diameters from several SEM images. **Fig. 5** shows the particle size distribution of synthesized particles collected in downstream chamber under conditions of (i) 90%SCL-0%SCL and (iii) 100%SCL-100%SCL. From **Fig. 5**, nanoparticles with diameter less than 100 nm were produced in both cases but the fraction of nanoparticles was ~91% for condition (i), and ~78% for condition (iii). The mean diameter $\bar{d}$ for conditions (i) and (iii) were estimated as 63.0 nm and 82.7 nm, respectively. The

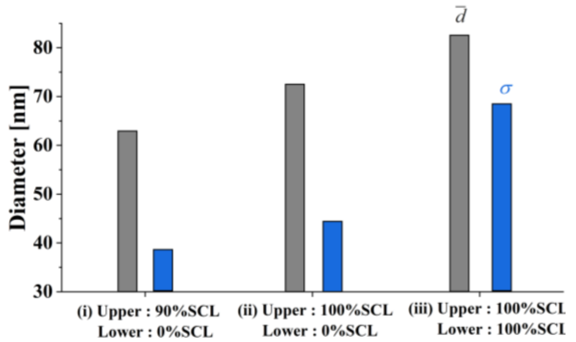


Fig. 6. Mean diameters and standard deviations of synthesized particles for each condition.

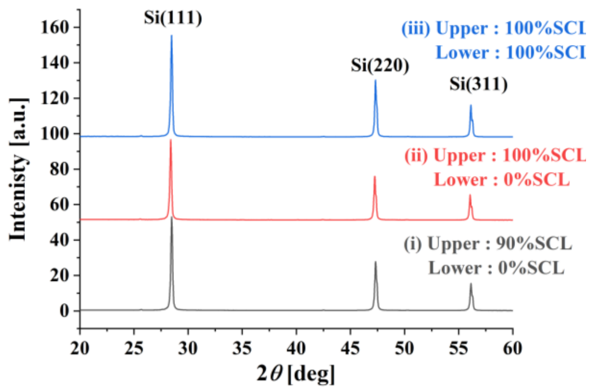


Fig. 7. XRD spectra of synthesized particles with different conditions.

standard deviations σ of particles synthesized for conditions (i) and (iii) were 38.5 nm and 68.3 nm, respectively. These shows that modulation condition can create nanoparticles more efficiently than non-modulation condition (iii). **Fig. 6** compares the mean diameter $\bar{d}$ and standard deviation σ with different three conditions (i), (ii), and (iii). From this figure, the mean diameter for condition (ii) with only lower coil current modulation is lower than that for non-modulation condition (iii). Moreover, the diameter is found to decrease by additional modulation of the upper-coil current at 90%SCL. This smaller nanoparticle may be synthesized in 90%SCL-0%SCL condition because more highly quenching rate is provided from dual simultaneous modulated thermal plasma. The modulation makes the temperature of vaporized gas decrease rapidly. Then, the growth to larger size particles was inhibited. Therefore, the larger modulation reduces diameter of synthesized particle. Further, these results suggest that particle diameter is controlled by modulation condition.

4.3. Constituents and crystallinity

To investigate constituents and crystallinity of synthesized particles, XRD analysis was conducted in the range of 20-60 degrees in 2θ. **Fig. 7** shows XRD spectra for synthesized particles collected at downstream chamber under different conditions (i), (ii) and (iii). From this figure, silicon peaks with Miller indices (111), (220), and (311) were detected under all three conditions. No strong peak was found expect Si crystalline peaks. These XRD results thus suggest that synthesized particles contain the large ratio of Si crystalline. Therefore, Si nanoparticle was synthesized under the three conditions.

5. Conclusion

A tandem type of modulated induction thermal plasmas with two independent induction coils was applied for nanoparticles synthesis. The modulated rf coil currents in upper-coil and lower-coil were measured to clarify the modulation of the power. Tamdem-MITP was successfully obtained with large modulation in power. Effect of the upper-coil and lower-coil current modulation was studied to synthesize Si nanoparticles. Synthesized nanoparticles were analyzed by FE-SEM for morphology and particle size distribution, and by XRD for crystallinity. The FE-SEM images and particle size distribution showed that smaller nanoparticles were obtained with both modulation of the upper-coil and lower-coil current. These results suggested modulating two coil currents made larger varying-temperature field with a high quenching rate. From XRD results, Si crystalline were mostly contained in synthesized nanoparticles. Therefore, modulating upper-coil and lower-coil for tandem-MITPs enhances efficiency of nanoparticle synthesis with a high production rate.

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