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Laser Synthesis of Uniform Silicon Single Nanodots

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ABSTRACT

Uniform silicon single nanodots were synthesized by laser ablation with a differential mobility analyzer (DMA) technique. The Si nanoparticles generated by laser irradiation of a silicon target were actively classified by a DMA and were impacted on the solid surface by a "nanoparticle beam". By measuring the current of the beam, we determined the size distribution of generated particles in situ. From transmission electron microscope (TEM) observation of deposited dots, it was found that they were well-isolated and uniform in size. High-resolution TEM images indicated that they were single crystals with a diameter of 10, 7, and 5 nm. However, the particles less than 4 nm seemed to have no crystallinity (amorphous).

Nanometer-sized dots (nanodots) that exhibit unique properties based on their quantum size effects are expected to be the building blocks of new functional materials as those used in quantum dot (QD) devices[1] and single electron transistor memory.[2] Especially, nanodots of group IV elements (Si, Ge) show the emission of visible light at room temperature.[1] It is a key to control size, impurity level, and number density of nanodots since these parameters determine the band gap, wavelength of emitted light, and dot-to-dot interactions. Recently, Raman scattering of single Ag nanodots[3] and a few particle effects on the photoluminescence of InAs nanodots in GaAs[4] have been discussed. But in order to analyze the electrical, optical, and mechanical properties of each "single dot" ultimately, it is essential to establish a way to prepare the isolated single nanodots of required size without any impurities. Several approaches have been done by using a self-organization process in liquid solution,[5] by ion sputtering,[6] by an aerosol route,[7,8] and by a time-of-flight technique[9] for the synthesis of the "close-packed" uniform structure of nanodots. However, removing impurities and controlling density and size distribution were difficult in the these processes.

The laser ablation method in a low-pressure inert gas is one of the novel approaches for producing very high purity silicon nanodots[1,10] where only silicon and inert gas species exist in the system. Laser synthesis of a one-dimensional

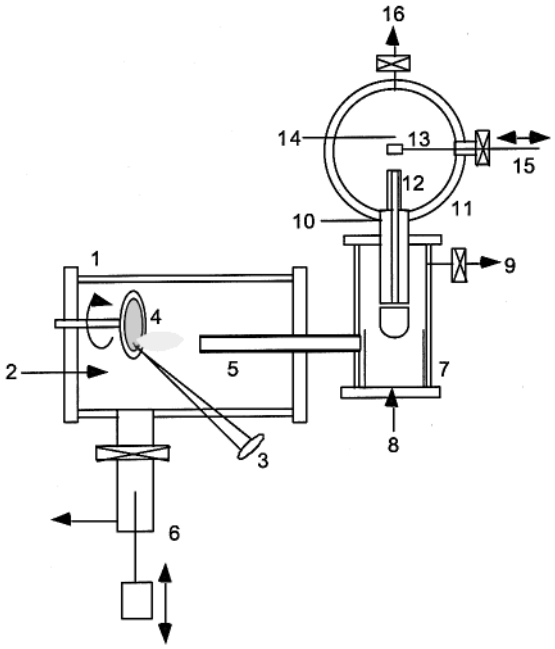

Figure 1. Schematic of the silicon single dots synthesis apparatus. In the laser ablation chamber (1), the laser beam is focused (3) on the silicon target (4) in the helium background gas (2). The target is rotated at 8 rpm. Generated nanoparticles are sampled (5) by the gas stream and introduced to the DMA (7). The size of the nanoparticles is controlled by the balance of sheath gas flow (8) and applied voltage (10). The size-selected nanoparticle beam is focused (12) on the substrate (TEM grid (13)). Current from the nanoparticles is measured by an electrometer (14). The whole system is pumped by a turbomolecular pump, a mechanical booster pump, and a rotary pump. Si targets (4) and substrates (13) are exchanged through load-lock systems (6, 15).

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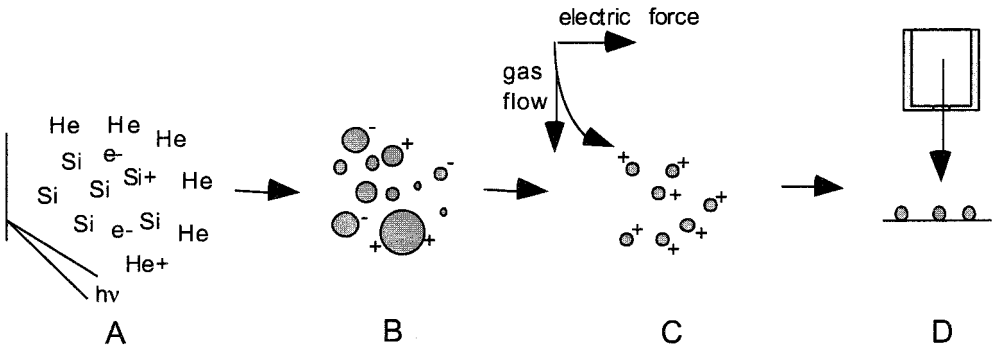

Figure 2. Schematic of generation, classification, and deposition of nanodots. (A) Si is vaporized by focused laser beam irradiation. The laser plasma is formed by excitation of Si and He. (B) Polydisperse Si nanoparticles are generated by sudden cooling. Some of the particle have charge during multiphoton excitation process in the laser plasma. (C) After the classification by DMA, the size of the nanoparticles is controlled. Most of the particles have single charge, but some particles have double charges (same mobility). (D) Isolated nanodots are formed by the supersonic nanoparticle beam deposition onto the substrate. By measuring the current from the nanoparticle beam, we can control the density on the surface.

(1D) structure (nanowires) has been reported by some groups.[11] A uniform zero dimensional (0D) structure of single silicon nanoparticles might be the next step for the quantum size effect to be utilized for real application in electrooptical materials. In this study, high-purity silicon nanoparticles were generated by laser ablation; the size of the generated nanoparticles was actively controlled by using a low-pressure operating differential mobility analyzer (DMA) technique. They were ejected as a nanoparticle beam and impacted on the substrate. With this new sequential process, pure, size-selected, and well-isolated single nanodots were successfully produced. A transmission electron microscope (TEM) was used to analyze their size distribution and crystal structures.

Figure 1 shows the experimental system used in this study. The laser ablation chamber, the DMA, deposition chamber, and all gas lines were made of polished stainless steel, and the whole system was baked and evacuated before ablation to a vacuum level of 2×10^{-6} Pa with a pumping system using a turbomolecular pump. Silicon targets and deposition samples can be exchanged by load-lock systems. A q-switched pulse Nd:YAG laser (Spectra-Physics INDI-50, wavelength 532 nm, power 210 mJ/pulse, full width at half-maximum of pulse length 5.4 ns, frequency 20 Hz) was focused on the surface of a Si wafer (o.d. 50 mm) with an incident angle of 45°. The wafer rotated with a speed of 8 rpm. The diameter of the irradiated spot was about 1.3 mm (laser fluence was 16 J/cm^2). The background helium gas was introduced by controlling its flow rate and pressure by mass flow controllers and variable conductance valves. The flow rate and pressure were varied from 0.2 to 1 SLM (standard liter per minute) and 333 to 930 Pa, respectively.

When the silicon target was irradiated by a focused laser beam, a plasma plume with radius of about 30 mm from the irradiation spot was observed. The size of generated particles, which were collected at 30 mm from the silicon target and observed by electron microscope images, was found to range widely from two to several hundred nanometers, as schematically illustrated in Figure 2B. The generated nanoparticles were exhausted from the laser ablation chamber with a He gas flow and introduced to a size classifier, a DMA. The DMA was a modified version of the Vienna type

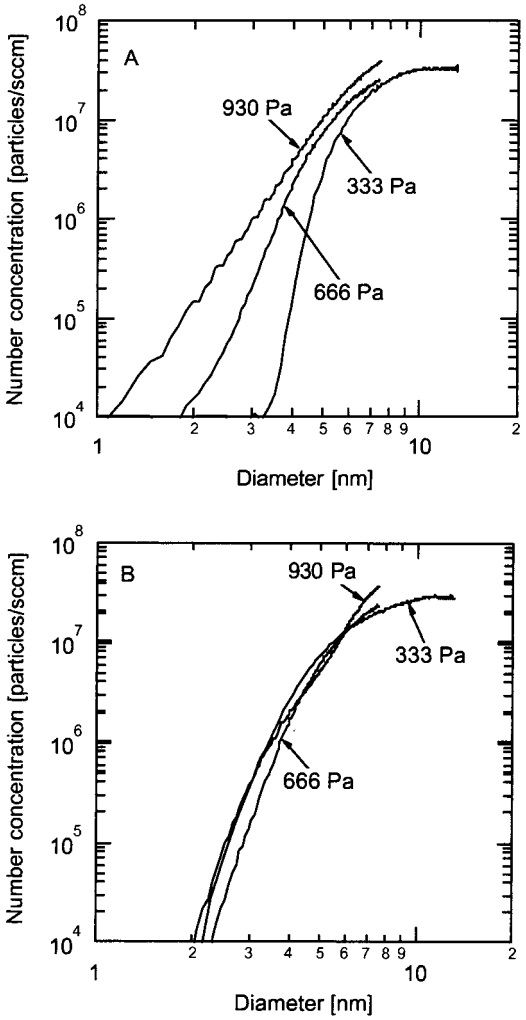

Figure 3. Size distribution of (A) positively charged and (B) negatively charged Si nanoparticles generated by laser ablation at different background He gas pressure. Number concentrations of the classified particle beam are obtained from the electric current measured by an electrometer. The flow rates of carrier gas, Qc, and DMA sheath gas, Qs, are (1) 0.2 and 1.7 SLM for 333 Pa, (2) Qc = 0.6 and Qs = 5 SLM for 666 Pa, and (3) Qc = 1.0 and Qs = 5.0 SLM for 930 Pa.

DMA.[12−14] It is capable of operating down to a pressure of a 333 Pa using a mechanical booster pump (MBP; 500 m^3/

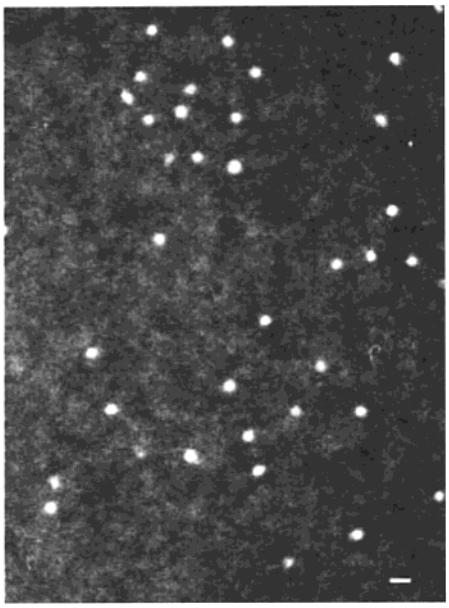

Figure 4. Dark field TEM image of the nanodots classified at 7 nm by DMA. The scale bar is 20 nm. A total of 35 dots are shown in the area of 550 × 400 nm (133 dots/μm^2).

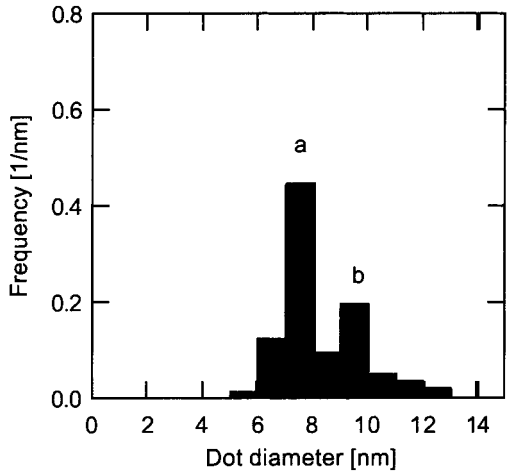

Figure 5. Distribution of surface area equivalent diameter of nanodots measured by TEM. The first peak (a) is close to the diameter of the setting value of the DMA (7 nm). The second peak at about 10 nm is considered to be that of doubly charged particles, which have the same electrical mobility as 7 nm particles.

h) and a rotary pump (RP; 1.0 m^3/min). Clean helium gas with a flow rate of 1.7 or 5 SLM was introduced to a DMA as a sheath gas, which transports nanoparticles in a vertical direction. A dc voltage was applied to the center rod of DMA to carry the charged nanoparticles in a horizontal direction by electric force. As a result, particles move toward the center rod depending on their electrical mobility. The specific electrical mobility of the particles was drawn from the slit, which was located at the center rod (Figure 2C). Since the electrical mobility of the particle is a function of particle size and charge, the size of the nanoparticles can be controlled by the voltage applied to the DMA. Finally, the size-selected particles were ejected from a nozzle of 2 mm in diameter (Figure 2D). Since the pressure in the deposition chamber is less than 10 Pa, the velocity of the ejected nanoparticles is as large as sonic velocity and a nanoparticle

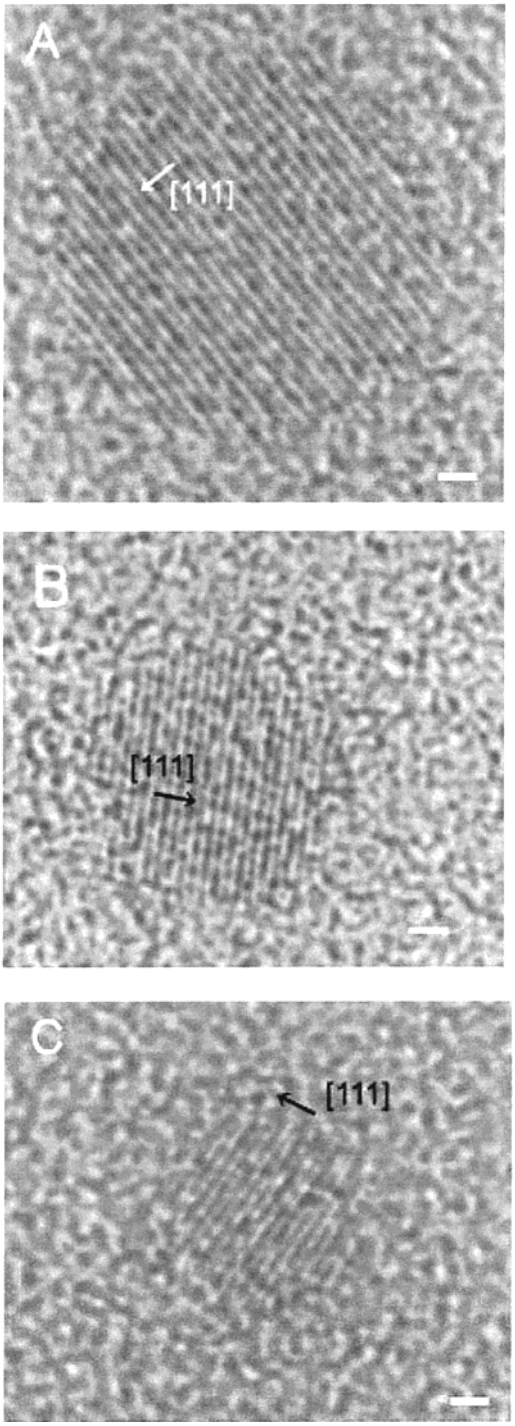

Figure 6. High-resolution TEM image of single nanodots of (A) 10 nm, (B) 7 nm, and (C) 5 nm in diameter. The lattice parameters of these dots were about 0.3 nm and close to that of the [111] face of silicon nanowire.

beam is generated. A TEM observation sample holder was directly installed in the deposition chamber. The TEM microogrid faced the nanoparticle beam to capture them by the impact of the nanoparticle beam. After the deposition, the tip of the TEM holder was sealed by an O-ring to prevent oxidation of generated silicon nanodots by room air. The nanoparticle beam also impacted an electrode that was connected to an electrometer to measure the concentration of nanoparticles from the electric current of the charged

nanoparticles. By scanning the DMA applied voltage, i.e., scanning the size, and measuring the current, we measured the size distribution of nanoparticle in the gas phase.

Figure 3 shows the measured size distribution of silicon nanoparticles by a LP-DMA and an electrometer. The upper limit of the size of classified particles was less than 13 nm because of problems with discharge of the helium gas at a DMA voltage of about 160 V under low-pressure conditions. It was found that particles were charged both positively and negatively by multiphoton excitation in the ablation process (Figure 2A,B). The results indicated a peak of the particle distribution at more than 10 nm. The concentrations of classified particles were of the order of 10^4 to 10^8 particles/scc (standard cubic centimeter). The pressure slightly affects the size distribution, especially in the case of positively charged particles less than 5 nm, probably due to the different charging mechanisms of nanoparticles in the plasma plume. The time for the deposition of nanoparticles can be easily estimated by these graphs.

The dark field TEM image of the deposited nanodots, which were classified to be 7 nm by DMA, shows almost spherical, size-selected, and well-isolated dots (Figure 4). The system pressure was 666 Pa, and the positive nanoparticles were deposited for 5 min on the TEM microgrid. The density of the nanodots in this picture is 133 dots/μm^2. The size distribution measured from TEM images indicates a bimodal distribution with peaks at 7 and 10 nm (Figure 5). The first peak at about 7 nm was close to the DMA setting value and uniform in size. The second peak at about 10 nm is considered to be that of doubly charged particles that have the same mobility as singly charged particles of smaller size.[15]

The high-resolution TEM images of the (A) 10 nm, (B) 7 nm, and (C) 5 nm nanodots show that they are single crystals (Figure 6). The lattice parameter of these three particles was about 3.1 Å and were close to the reported value of the [111] face of nanowires.[11] The other oriented dots with narrower lattice parameters were also observed. We have tried the identification of chemical component of generated particles by electron diffraction and X-ray diffraction, but we could not get enough signals from the particles because the amount of particles was very low. We also tried synthesis of nanodots with diameters of 4, 3, and 2 nm. Although some visible dots were observed, it seems that they were amorphous and no crystal structure was observed. It is considered to be difficult to form single crystals less than 4 nm since the surface energy is higher than the lattice energy.[16]

The system described in this paper showed the possibility of synthesis of single nanodots of very pure silicon single crystals with the required size less than 10 nm. With this sequential processing technique using an in situ monitoring system, the generated single dots will be used immediately for the analysis of quantum photophysical properties by combining with tunneling microscopes, near-field optics, and so on. Also, this system has a potential to supply building blocks of a new kind of quantum devices such as quantum dot light emitters or single electron transistors.

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