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Nanometer-sized silicon particles synthesized by laser ablation of a silicon target in rare gas

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We synthesized nanometer-sized silicon particles that exhibit visible light emission. The paticles were formed by laser ablation of a silicon target in 2-Torr helium gas. An image of their atomic structure observed by an atomic force microscope shows that 2.5 nm particles are formed. In order to investigate formation process of the particles in rare gas, we measured time- and space-resolved soft X-ray absorption spectrum and time-resolved light emission in the visible wavelength range. The particles are suggested to be formed 2 μs after the laser ablation in gas phase.

1 INTRODUCTION

Nanostructured silicon-based materials can exhibit bright light emission in visible wavelength range [1–5], although silicon crystal has 1.1 eV indirect band gap. Partly because most of the materils contain undesirable chemical impurities such as hydrogen, fluorine and so on, the light emission mechanism is now under investigation. One of the novel methods to synthesize the nanostructured material is the laser ablation method. Werwa *et al.* showed that nanometer-sized silicon particles can be synthesized by ablating a silicon target by laser light in helium gas and collecting final products on a substrate [4]. They also showed that the particles exhibit the visible light emission. For controllable synthesis of the silicon particles, it is important to understand the formation process of the silicon particles.

In the present work, we have investigated the formation process. We measured time- and space-resolved soft X-ray absorption of the laser-ablated particles. This spectroscopy has the advantage that we can simultaneously observe almost all the silicon-containg materials such as highly-charged silicon ions, silicon atoms, silicon-contaning molecules, liquid silicon, bulk silicon and so on if exist enogh. We also measured time-resolved distribution of particles with light emission in the visible wavelenth range. Final product were observed by an atomic force microscope (AFM) and their optical property was measured. Finally, we will discuss the formation process of the nanometer-sized silicon particles.

2 DYNAMICS

2.1 Experimental

Figure 1 shows schematic diagram of overall experimental setup. The detail of the setup is given elsewhere [6, 7]. The laser ablation was performed by focusing a Q-switched Nd:YAG laser beam (Lumonics, HY400, $\lambda = 532\ nm$, FWHM=10 ns) on a silicon target in a vacuum chamber. Its energy density on the target is estimated to be 10 J/cm^2 per pulse. The chamber was pumped down to 2×10^{-6} Torr.

For the measurement of the time- and space-resolved soft X-ray absorption, the ablation was performed in a pulsed argon gas jet (General Valve, 9-659-900) with a pulse duration of 170 μs. As a continuum soft X-ray source for the X-ray spectroscopy, we utilized radiation from a plasma

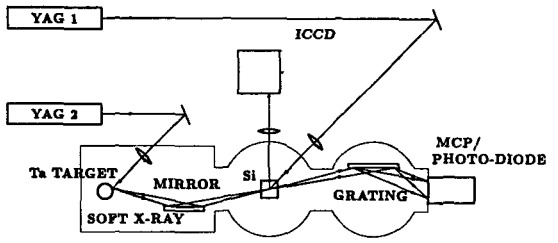

Figure 1: Experimental setup for time- and spece resolved soft X-ray absorption spectroscopy and time-resolved observation of 2-dimensional distribution of light-emitting particles.

produced by irradiation of a tantalum target with Q-switched Nd:YAG laser (Continuum, PL9010) light with a wavelength of 532 nm. The generated X-rays have a pulse duration of 10 ns. The X-ray beam was focused to a 100-μm-diameter spot at a given distance above the silicon target using a toroidal mirror (Canon, Pt/Cr/glass mirror). The X-ray beam transmitted through the laser-ablated particles was diffracted and focused using a curved grating (Hitachi, Spectrograph 001-0450) and detected using microchannel plates (Hamamatsu , F2225) and a MOS array (Hamamatsu, C4356). The absorption spectrum for the laser-ablated particles was obtained by subtracting the spectrum for the pulsed argon gas from the spectrum for both the laser-ablated particles and the argon gas.

For the measurement of the distribution of the visible light emission, the ablation was performed in a helium gas at a constant pressure. The distribution was measured using a two-dimensional CCD-array camera with an intensifier (Princeton Applied Research, LCI 1) (D_1) sensitive to wavelengths in the 400-800 nm range, with a time resolution of 10 ns.

2.2 Results

Figure 2 shows soft X-ray absorption spectrum of the silicon particles in vacuum 50 ns after the ablation, at a position 50 μm away from the silicon target. Lines and a broad band are seen in the spectrum. These lines are absorption lines due to silicon ions [8]. The positions of these lines are indicated by markers above the spectrum. The broad band is due to electron transitions from discrete levels to the continuum over the vacuum level. Figure 3 shows absorption spectrum of the laser-ablated particles in the argon gas, 2 μs after the ablation, 2 mm away from the target. An absorption line due to Si^+, which is indicated by an arrow in Fig. 3, is dominant.

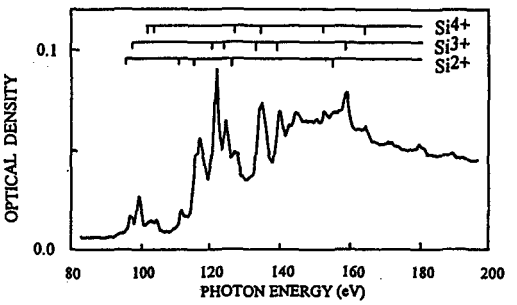

Figure 2: Soft X-ray absorption spectrum of laser-ablated silicon particles in vacuum. Probe X-ray pulse was delayed by 50 ns relative to YAG laser light pulse for the ablation of a silicon target. The X-ray beam was focused into a 100-μm diameter spot at a position 50 μm away from the silicon target.

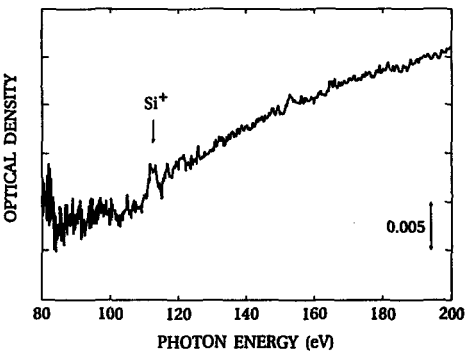

Figure 3: Time- and space-resolved soft X-ray absorption spectrum of laser-ablated silicon particles in pulsed a argon gas jet at a delay time of 2 μs at a position of 2 mm away from a silicon target.

Light emission distribution in 2-Torr helium gas at 1 μs after the ablation is shown in the inset of Figure 4. Figures 4 (a) and (b) shows the distribution at each delay (a) in vacuum and (b) in the 2-Torr helium gas in section along a center axis perpendicular to the target as is illustrated with a straight line in the inset in Fig. 4. Each distribution is normalized by its maximum. Solid lines

indicate evolutions of peak positions. At longer delay times, light-emitting particles get further away from the target. The peak position reaches a maximum position of 11 mm in the 2-Torr helium gas, while it moves at a constant velocity of 1.2×10^7 mm/s in vacuum.

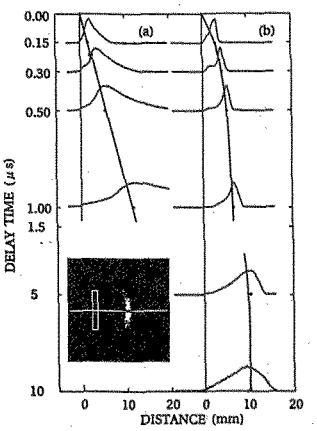

Figure 4: Inset: A time-resolved 2-dimensional distribution of light emssion form laser-ablated silicon particles in 2-Torr helium gas, at a delay time of 1 μs. A rectangle indicate a silicon target. (a),(b): distributions at given delays along a line perpendicular to the silicon target, as is illustrated by a straight line in the inset, are shown. The laser ablations were performed (a) in vacuum, (b) in the 2-Torr helium gas. Peak positions of the distributions are plotted as a function of delay time by closed circles.

3 FINAL PRODUCTS

Atomic structure of the final product was observed using the AFM (SPI3600, Seiko Denshi Kougyo). The AFM has space resolution of 0.05 nm in height, while 20 nm in the direction parallel to the sample surface. For the AFM measurement, the silicon target was ablated for 50 times and the products were deposited on a silicon substrate placed 2 cm above the target. Figure 5 (a) shows a typical AFM image of the final products. Several particles are seen in the image. To estimate each size of the particle, we obtained section along a straight line, as is illustrated in Fig. 5 (a). A typical section thus obtained is shown in Fig. 5 (b). This particle is

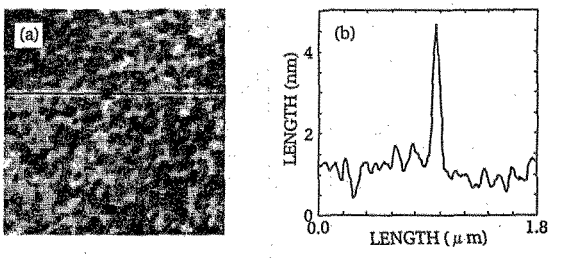

Figure 5: (a) An image of final products observed by an atomic force microscope. The image shows nanometer-sized particles, which was formed by laser ablation of a silicon target in a helium gas and then deposited on a substrate. (b) A section of the image along a straight line indicated in Fig. 5 (a).

indicated to have a size of 3 nm. A maximum of size distribution of the particles is 2.5 nm.

As a demonstration, light emission from silicon particles is shown in Fig. 6. For this measuremnet, a silicon target was irradiated with the YAG laser light in 2-Torr helium gas. The final products were deposited on a substrate placed 9 mm away from the target. The sample was excited by cw Ar^+ laser (NEC, GLS-3260J) light with a wavelength of 457.9 nm, in the air at room temperature. The deposition film exhibits light emission with a broad band peaked at 1.6 eV. It should be emphasized that silicon particles with visible light emission can be synthesized without principally containg any chemical impurities such as hydrogen, fluorine and so on.

4 DISCUSSION

The X-ray absorption spactra in Figs. 2 and 3 showed that dominant products are silicon ions in vacuum initially and Si^+ in the argon gas jet at 2 μs after the ablation. In general, either absorption lines or absorption bands due to electron transition from 2p state are seen in a range from 90 eV to 150 eV for materials that contain silicon atoms. Therefore neither silicon molecules or bulk silicon are dominant up to 2 μs in the argon gas jet. The AFM image in Fig. 5 shows that nanometer-sized particles are formed finally. These results suggests that nanometer-sized sili-

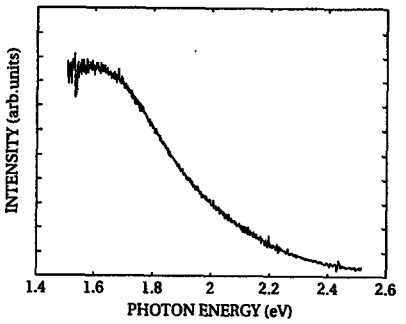

Figure 6: Light emission spectrum of deposition film of nanometer-sized silicon particles. The particles were synthesized by laser ablation of a silicon target in helum gas. The spectrum was observed under excitation by 547.9-nm cw argon ion laser light at room temperature.

con particles are formed in the argon gas in gas phase later than 2 μs after the ablation. Furthermore we found the evidences [9] that support the idea that the particles are formed in gas phase: 1) No nanometer-sized silicon particles are deposited on substrates placed nearer than the maximum position. 2) The size of the particles strongly depend on the pressure of the helium gas. These results indicate that formation process have strong correlation with dynamics of laser-ablated silicon particles in gas phase. In helium gas, particles would be formed later than those in the argon gas since the laser-ablated ions are confined more loosely [10].

The time-resolved light emission distribution in Fig. 4 (a) shows that light-emitting particles in vacuum have a kinetic energy of 20 eV on average. In the 2-Torr helium gas, the particles almost reach a maximum position in 10 μs, as shown in Fig. 4 (b). These results indicate that light-emitting silicon particles loose their kinetic energy by collision with the helium atoms. This may be an important role of the helium gas for silicon atoms to gather togher. In addition to it, helium gas may disipate cohesive energy, which is discussed by Yoshida *et al.* in terms of an inertia fluid model [5].

5 CONCLUSION

We have synthesized nanometer-sized silicon particles that exhibit visible light emission. The particles are formed by laser ablation of a silicon target in helium gas. These particles are suggested to be formed in gas phase. In our framework, helium gas plays an important role for silicon atoms to form the particles: The helium gas disipates 20-eV kinetic energy of laser-ablated silicon atoms as well as cohesive energy to form the nanometer-sized silicon particles.

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