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Nanometer-Sized Silicon Crystallites Prepared by Excimer Laser Ablation in Constant Pressure Inert Gas Ambient

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We report nanometer-sized silicon (Si) crystallites prepared by excimer laser ablation in constant pressure inert gas. Size distribution of the nanometer-sized particles depends on the pressure of inert gas. The relation between the average size and the inert gas pressure can be explained by an inertia fluid model. It is verified that size distribution of the nanometer-sized Si particles is ~3 nm and greater in diameter. Furthermore, crystallinity of the nanometer-sized particles is crystalline similar to that of bulk Si. After an oxidation process (dry O2, 800 °C), visible photoluminescence of which peak position is around 2.15 eV has been observed at room temperature.

1. Introduction

In the past several years, extensive studies have been carried out on nanoscaled silicon (Si) structures since the strong photoluminescence spectra were observed [1, 2]. The nanoscaled structures in numerous reports have meant "porous" Si formed by the liquid phase anodization [3] and subsequent surface hydrogenation or oxidation treatments, even though accurate mechanism of strong photoluminescence from the nanoscaled structures of group IV materials is currently under debate [3]. When we discuss the optical properties of nanoscaled group IV materials as one of the quantum size effect of zero dimensional materials, the ideal nanoscaled structures should be "spherical" which have well controlled size (diameter). For this purpose, physical vapor fabrication methods [4, 5] are significant, for example inert gas evaporation or laser ablation into gas ambient. However, there has been few studies where size of particles was effectively controlled in several nanoscale level, using the physical vapor methods.

In this work, we adopt the laser ablation combined with the constant pressure gas evaporation. This method has potentiality to control the nanoscale particle size as well as can be performed by a conventional apparatus. Controlling the nanoscale particle size, the pressure of inert gas ambient is varied as main process parameter. Accordingly, dependence of the average particle size on the ambient pressure can be explained by an inertia fluid model.

2. Experimental

Si nanoscaled particles were prepared using excimer laser ablation of single crystalline Si wafer in inert gas ambient at constant reduced pressure. An ArF excimer laser beam (wavelength: 193 nm, energy density: 1 J/(cm^2 • pulse), pulse duration: 12 ns, repetition rate: 10 Hz) was focused onto the surface of the single crystalline Si wafer of 2" diameter. The target Si wafer was rotated at 8 rpm. During the laser ablation of Si, He gas was introduced into a vacuum chamber and was kept at a constant pressure using a differential evacuation system, after base pressure was evacuated to 1.0X10^{-6} Pa. The pressure of He gas was varied as dominant experimental parameter. Single crystalline Si wafer (1" diam.) for deposition substrate was located at distance of 7 mm from the target Si wafer. The deposition substrate was kept at room temperature.

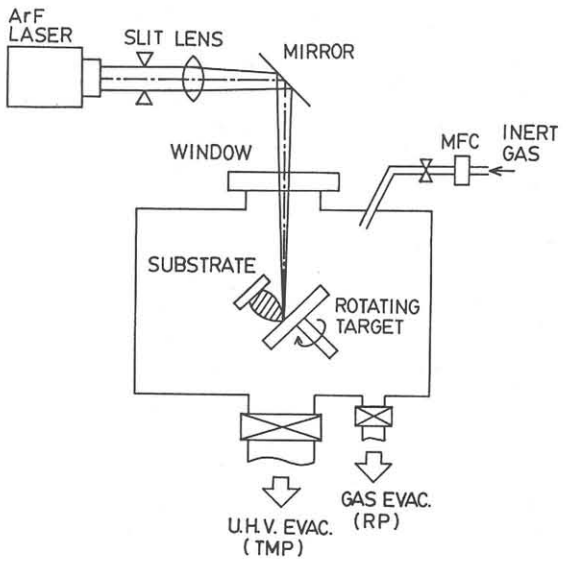

Fig.1 Schematic diagram of preparation system for nanoscaled Si particles.

Schematic diagram of present apparatus is shown in Fig. 1.

High resolution scanning electron microscope (HRSEM) observation was employed for evaluation of dependence of the Si particle size on the He ambient pressure. High resolution transmission electron microscope (HRTEM) observation was carried out, in order to evaluate not only the minimum level of the nanoscaled Si particles but also its crystallinity. The HRTEM apparatus was Akashi EM002B, 200 keV.

3. Results

The dependence of Si particle size on the He ambient pressure observed by the HRSEM is shown in Fig. 2. It was found that the average size of the Si particles increases

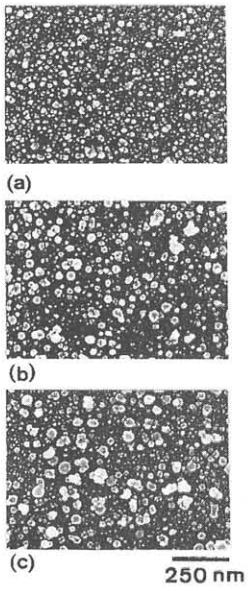

Fig.2 Size dependence of nanoscaled Si particles on He ambient pressure, observed by HRSEM. (a) Pressure of He ambient was 432 Pa; (b) 665 Pa; (c) 998 Pa.

with increasing He ambient pressure. Figure 3 shows HRTEM image of the minimum level of nanoscaled Si particles. The minimum diameter was ~3 nm. In addition, crystallinity of all nanoscaled Si particles in this experiment was evidently crystalline, because we found clear lattice plane image of which spacing was approximately 0.31 nm. This value is almost correspond to (111) plane spacing of the bulk Si (0.314 nm). In all reports which describe the photoluminescence from the nanoscaled Si structure, the crystallinity of the Si has been crystalline [3]. Therefore, it should be mentioned that preparation of the crystalline nanoscaled Si is inevitable condition for its photo-luminescence properties.

Mean diameter of the Si particles and its distribution were calculated from the HRSEM photographs in a statistical treatment. Figure 4 shows the mean diameter of nanoscaled Si particles as a function of the He ambient pressure. In Fig. 4, the experimental plots showed good

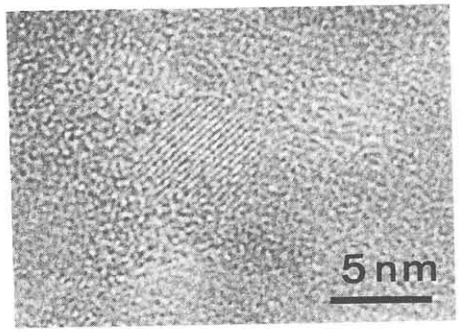

Fig.3 HRTEM image of nanoscaled Si particles. Lattice plane spacing is about 0.31 nm.

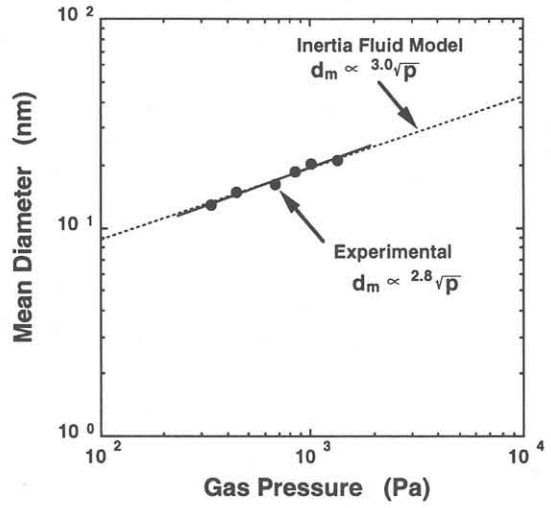

Fig.4 Mean diameter of nanoscaled Si particles as a function of He ambient pressure. Solid line is regression of experimental results. Broken line means calculated line by the inertia fluid model.

regression, and gradient of the regression (solid) line was 1/2.8.

Dry O2 (760 Torr) oxidation was performed at 800 °C for 10 min, for the nanoscaled Si particles prepared in 665 Pa He. After the oxidation, photoluminescence spectra were measured using Ar ion laser (488 nm) as excitation. Consequently, visible photoluminescence of which peak position is around 2.15 eV has been observed at room temperature. This spectrum is shown in Fig. 5.

4. Discussion

It is necessary to elucidate the relation between the size of Si crystallites and the He ambient pressure. For example of laser ablation process in gas ambient, there have been

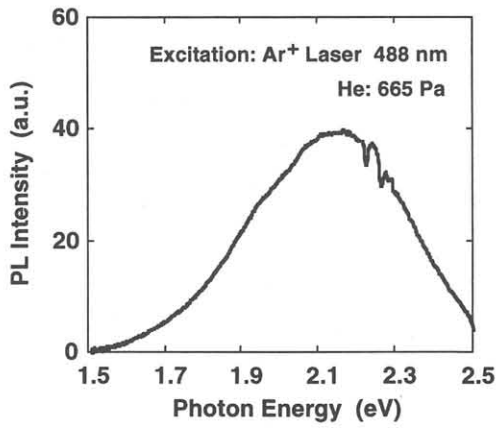

Fig. 5 A typical photoluminescence spectrum from nanoscaled Si particles which were deposited by excimer laser ablation in He gas (665 Pa), and were oxidized in dry O2 at 800 °C for 10 min.

several reports which investigate laser ablation of YBaCuO in oxygen ambient for high *Tc* superconducting thin films [6]. Geohegan [6] discussed the mechanics of the ejected materials (atoms, ions, or clusters) using classical drag force model. According to the drag model, motion of the ejected material is not dependent on the ambient pressure, is dependent on only mass of atom or molecule of ambient gas. Therefore, the experimental results of this work can not be explained by the classical drag model, because the size of Si crystallites was clearly dependent on the He ambient pressure as shown in Figs. 2 and 4. In inert gas laser ablation, the ejected materials collide with the ambient gas atoms, and dissipate their kinetic energy during mass displacement process. We regard, it is adequate assumption that dissipated kinetic energy of the ejected material throughout its flight is correspond to cohesive energy of the Si crystallites. In our experimental results, these phenomenon depended on the pressure of inert gas ambient. Moreover, the cohesive energy increased with increasing ambient pressure, because the size of the Si crystallites increased with increasing ambient pressure. An inertia fluid model can consistently explain above experimental results qualitatively. In this model, resistance force is directly composed of mass displacement, and is proportional to square of velocity (v) of the ejected material through the inert gas ambient. The equation of motion for the ejected materials is

$$m\frac{dv}{dt} = -\alpha v^2,\ v = v_0 \exp(-\alpha x/m),\ \alpha = CS\rho/2 \quad , \quad (1)$$

where m is the mass of the ejected material, v_0 is the initial velocity, S is the cross section, α is the slowing coefficient, ρ is the ambient gas density, C is proportional constant. We assume that the kinetic energy difference (ΔT) between initially ejected materials and materials at end of flight is correspond to the cohesive energy of the formed Si crystallites (ΔG),

$$\Delta G \propto \Delta T = \frac{mv_0^2}{2}\left(1-\exp(-2\alpha d/m)\right) \quad , \quad (2)$$

where d is the distance from the target to the substrate. In our experimental condition, approximation of low ambient gas density and/or short target-substrate distance ($\alpha d/m \ll 1$) can be applied. Therefore, Eq. (2) can be rewritten as follows:

$$\Delta T \approx v_0^2 \alpha d = \frac{v_0^2 CSd}{2}\rho \quad . \quad (3)$$

In this model, it can be found that the dissipated kinetic energy, namely the cohesive energy of the Si crystallites, is proportional to the inert gas ambient pressure. In isotropic materials, diameter (dm) of spherically condensed particles is proportional to cube root of ΔG, because cohesive energy for one particle (ΔG) is expressed by cohesive energy per unit volume (ΔGv); $\Delta G=(4/3)\pi r^3 \Delta Gv$. Consequently, we can derive the relation between the diameter of Si crystallites dm and the inert gas ambient pressure p as follows:

$$d_m \propto \sqrt[3]{\rho} \propto \sqrt[3]{p} \quad . \quad (4)$$

In Fig. 4, the broken line means curve calculated by the inertia fluid model (Eq. (4)). The experimental plots showed good regression, and gradient of the regression (solid) line was 1/2.8, and was almost same as that of the calculated curve (1/3.0). In other words, we can effectively control the size of nanoscaled Si particles in nanoscaled region for visible photoluminescence properties, varying the inert gas ambient pressure.

The photoluminescence properties were not observed when the oxidation process was not carried out. Roles of the oxidation process are supposed to be followings: (i) elimination of non-radiative surface states; (ii) generation of the radiative centers in the interfacial layer at SiO2/Si interface [7]; (iii) volume reduction of the nanoscaled Si crystallites. However, we have not enough experimental data to identify the relation between the nanoscaled Si structures and the photoluminescence. Further study is in progress .

5. Conclusions

In conclusion, we have suggested a preparation method for nanoscaled Si particles by excimer laser ablation in constant pressure inert gas. Average size of nanoscaled Si particles is controlled by the pressure of inert gas. Dependence of the average size on the inert gas pressure can be explained by the inertia fluid model. It is verified that the minimum size of the nanoscaled Si particles is ~3 nm in diameter. Crystallinity of the nanoscaled Si particles is crystalline which is similar to that of bulk Si. Furthermore, visible photoluminescence of which peak position is around 2.15 eV has been observed at room temperature, after the oxidation process (dry O2, 800 °C).

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