Formation of nanoscale fine-structured silicon by pulsed laser ablation in hydrogen background gas

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The formation of nanoscale fine structures during pulsed laser ablation of a silicon target in a hydrogen atmosphere has been studied by analyzing the deposited silicon fine structures prepared under different conditions. Transmission electron microscopy, scanning electron microscopy (SEM), Raman scattering, and infrared absorption studies on the deposited samples indicate that silicon nanocrystallites are produced when the background gas pressure is higher than a critical value. The deposited substance is found to show hierarchical structure having surface hydrogenated silicon nanocrystallites as the primary structure and aggregates of the nanocrystallites as the secondary structure. The secondary structure depends on the hydrogen background gas pressure, while the size of the primary nanocrystallites is 4-5 nm independent of the pressure. These results suggest that the fine structure is formed in two steps; the silicon nanocrystallites having a stable surface are initially formed and they are subsequently aggregated to form the secondary structure. Analysis of surface free energy suggests that the stability is acquired by termination of the surface by creation of Si-H bonds. We carried out fractal analysis of the SEM image of the deposits and found that the secondary structure shows good self-similar structure when deposited at higher background gas pressure. The fractal dimension of aggregated secondary structure varies from 1.7 to more than 2.0 with decreasing background gas pressure. Comparison of these values with reported results for the fractal growth simulation indicates that the region at which aggregation of the nanocrystallites takes place changes from in the plume to on the substrate with decreasing background gas pressure. Effects of the hydrogen background gas on the nanocrystallization process and spatial distribution of formed nanocrystallites in the plume are discussed. The formation of surface stabilized Si nanocrystallites and their spatial confinement by background gas in the first and second steps determine the hierarchical structure of deposited substance.

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I. INTRODUCTION

Interest in studying semiconductor nanocrystallites has significantly increased in recent years. Silicon nanostructured materials have attracted a great deal of interest due to their promising optical and electrical properties as compared to bulk materials. For example, the discovery of bright visible photoluminescence (PL) from porous Si has made this material into an active research area.¹ Since the properties of these materials depend on their fine structure, great effort has been made to control the nanoscale fine structure. The topdown method such as preparation of porous Si is one of the methods to prepare Si nanocrystallite. The bottom-up process has the potential to control nanoscale fine structure since the nanostructure is build up from atoms in this process. From the viewpoint of application, the bottom-up method employing a dry process in vacuum has an advantage for the electronic devices due to the compatibility with conventional vacuum processes. A thorough understanding of the physical mechanism of the growth process in the vacuum chamber is important to control nanoscale fine structure on the substrate.

One of the conventional techniques to prepare nanocrystallites by a bottom-up dry process is the gas evaporation method,^{2–4} which has been mainly applied to the deposition of metal nanoparticles. Pulsed laser ablation (PLA) in an inert background gas is a relatively new technique to prepare semiconductor nanocrystallites.⁵⁻¹⁰ This technique has the potential to prepare novel structured materials due to a nonequilibrium process caused by the pulsed excitation, which is completely different from conventional techniques.¹¹ Application of this technique to Si leads to the preparation of high purity Si nanocrystallites since vaporization of impurities during the evaporation of the Si is small. An inert gas is usually used as a background gas to prepare Si nanocrystallites to prevent reaction between ejected Si atoms and background gas. We performed PLA of a silicon target in hydrogen gas instead of inert gas to prepare surface hydrogenated silicon nanocrystallites.^{6,28,29} The PL efficiency of silicon nanocrystallites prepared in hydrogen gas was much larger than that prepared in helium gas due to the termination of surface dangling bonds.⁶ The PLA in hydrogen gas is a promising method to prepare Si nanocrystallites having well defined surfaces.

The formation process of nanocrystallites during PLA in helium gas has been discussed by several authors. The nucleation is governed by supersaturation of the ejected Si vapor.^{12–15} There are two possible processes to accomplish this supersaturation: cooling due to (i) adiabatic expansion of the plume¹² and (ii) that due to collision with ambient gas molecules. Cooling of ejected atoms by adiabatic expansion is discussed by Luk'yanchuk *et al.* They applied Zeldovich-Raizer (ZR) theory¹³ for PLA to calculate the size distribution function of nanoclusters produced during the expansion of Si vapor into vacuum.¹² Marine *et al.* suggested that this theoretical result is consistent with experimental result of size distribution.¹⁶

The nanocrystallization of silicon in the plume can be observed by the laser-induced fluorescence (LIF) and redecomposition LIF (ReD-LIF) techniques.^{17–19} The results of these experiments suggest that the nanocrystallite is formed in the plume a few microseconds after the laser pulse. These experimental works indicate that the collision between ejected Si atoms and background gas is important to form nanocrystallite, but the adiabatic cooling process was not taken into account in their discussions. Theoretical and experimental works are suitable to discuss relatively earlier and later stages of nanocrystal formation, respectively. The full picture of the nanocrystallization process is, however, at this time insufficiently understood.

Since the fine structure of the deposit on the substrate directly correlates with the PLA process, analysis of the fine structure of deposits is one of the ways to investigate PLA processes. The Si nanocrystallites prepared by PLA in helium gas have an aggregated structure.^{20,21} The morphology of the sample is determined by the aggregation and depends on the background gas pressure. Although the nanocrystallization process has been discussed by a number of authors.^{12,17–19,22,23} the aggregation mechanism has, as yet, not been taken into account. Since the aggregation takes place after the formation of nanocrystallites, an understanding of the temporal and spatial effects on both nanocrystallization and aggregation is necessary to clarify full picture of the PLA process. The aggregation of nanocrystallites is important in practical applications such as electroluminescence device too,²⁴ since the current path also depends on the aggregated structure. Control of aggregated structure should be possible if we can reveal the full picture of the PLA process.

One of the approaches to discuss the aggregation mechanism is to evaluate aggregated structure by a fractal method. Although this does not involve direct measurement, this approach can treat the aggregated structure numerically and is an effective way to discuss the aggregation process.^{14,25} For example, it was applied for analysis of aggregated nanoscale Fe particles²⁶ and Au colloids.²⁷ These articles pointed out the existence of scale invariance in the aggregated structures, which can be well described as fractals. Since the fractal growth depends on the aggregation mechanism, fractal analysis is a good method to discuss collision kinetics of nanocrystallites during the PLA.

In the present paper, we prepared silicon nanocrystallites in hydrogen background gas. The formation of nanoscale fine structure was studied by analyzing the fine structure of deposited silicon under different hydrogen background gas pressures. The formation of stable nanocrystallites followed by aggregation of the formed nanocrystallites is discussed. Aggregated structures are analyzed by the fractal method. Finally, the effect of experimental conditions, such as background gas pressure and distance between substrate and target, on the nanoscale fine structure is discussed based on the proposed model.

II. EXPERIMENT

The hydrogenated and nonhydrogenated Si nanocrystallites were prepared by PLA in H₂ background gas. After the vacuum chamber was evacuated to less than 1.0×10^{-5} Pa, high purity (99.9999%) H₂ gas was introduced into it at a flow rate of 10 SCCM (SCCM denotes cubic centimeter per minute at STP) and maintained at a constant pressure. The fourth harmonic of a pulsed neodymium-doped yttrium aluminum garnet laser beam was focused onto the singlecrystalline Si target. The wavelength, pulse width, repetition rate, and fluence of the laser beam at the Si target were 266 nm, 10 ns, 10 Hz, and 1.5 J/cm², respectively. The twodimensional size of the plume and the time resolved plasma emission line in the plume were measured with a single spectrometer equipped with a gated intensified charge coupled device (ICCD) detector.

Ablated Si species were deposited on single-crystalline Si or synthetic quartz substrates. Size, structure, and crystallinity of the deposited nanoparticles were investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Raman scattering. The bonding configuration was estimated by Fourier transform infrared (FTIR) absorption.

III. RESULTS

A. Electron microscope image

The SEM and TEM observations give information on the nanometer and hundreds-of-nanometers scale structures, respectively. Figures 1(a)-1(c) show cross sectional SEM images of the samples prepared at 80, 400, and 1100 Pa, respectively. The morphology depended on the background hydrogen gas pressure. They can be classified into four groups: film-, columnar-, cauliflower-, and fiberlike structures. The background gas pressure regions of the four groups were about 0-20, 30-300, 300-500, and 500-1100 Pa, respectively. Boundaries of the pressure between the regions were not clear except for that between filmlike and columnarlike structures. Figures 2(a) and 2(b)show TEM images of specimens deposited on the microgrid at 390 and 1100 Pa, respectively. Hemispherical primary particles having a mean diameter of 4-5 nm were observed; they were insensitive to the background H₂ pressure.³⁰ The difference in the structure observed at the hundreds-ofnanometers scale by SEM and that observed at the nanometer scale by TEM indicates that the columnar-, cauliflower-, and fiberlike structures observed by SEM are secondary structures, which consist of the primary nanoparticles. The existence of the primary and secondary structures observed by TEM and SEM indicates that the fine structure is formed in two steps. Our discussion on these steps will



FIG. 1. Cross sectional SEM images of the deposits prepared at (a) 80 Pa, (b) 400 Pa, and (c) 1100 Pa.

therefore include information on the temporal growth of these fine structures.

B. Raman and FTIR spectra

The Raman scattering and FTIR spectra were measured to evaluate the crystallinity and local bonding structure of the deposits. The Raman scattering spectra are shown in Fig. 3



FIG. 2. TEM images of the sample prepared at (a) 390 Pa and (b) 1100 Pa.



FIG. 3. Raman scattering spectra of the sample prepared at 20, 30, 133, 390, and 530 Pa.

for various background gas pressures. Sharp and broad peaks at 520 and 480 cm⁻¹ originate from crystalline and amorphous components, respectively. The amorphous component was observed below 20 Pa and the distinctive crystalline peak above 133 Pa. This means that the nanoparticles observed in Fig. 1 are nanocrystallites. Figure 4 shows the influence of hydrogen gas pressure on the FTIR absorption spectra of the deposits. The peak intensity of each spectrum was normalized to unity. The infrared (IR) absorption peak was observed at around 2000 and 2120 cm⁻¹ for the sample prepared below 20 and above 30 Pa, respectively. The peak at 2000 cm⁻¹ is well known as the Si—H vibrational mode in bulk a-Si:H, which is denoted here as Si-H (bulk). It is also known that the IR vibrational frequency of Si-H is sensitive to the local environment surrounding the vibrating bond. For example, the IR vibrational frequencies of the



FIG. 4. The change in the FTIR spectra around 2000 cm⁻¹ with background gas pressure. The arrows shown above the figure correspond to the frequencies of Si—H and SiH₂ vibration in bulk a-Si:H and on the surface of Si.



FIG. 5. (a) The values of R_{max} and $1/R_{max}^3$ were plotted as a function of the background gas pressure. (b) The value of R_{max}^3 was plotted as a function of laser fluence.

Si—H and Si—H₂ bonds on the surface are 2090 and 2110 cm⁻¹, respectively; they are denoted as Si—H (surface) and Si—H₂ (surface) here. The configurations of the Si—H bond and the corresponding wave numbers^{22,31} are shown in Fig. 4 by arrows.

A drastic change in the morphology of the deposits from film to the assembly of nanocrystallites was observed between 20 and 30 Pa by SEM image. Following the change in morphology, Raman and IR spectra were also modified at this pressure. The Raman scattering measurement indicates that the deposits changed from amorphous film to nanocrystallites at around 30 Pa. The frequency of the Si—H vibrational mode also changed from 2000 to 2120 cm⁻¹ at around 30 Pa. The hydrogen bonding configuration changes from Si—H in bulk to Si—H or Si—H₂ on the surface. These results suggest that 30 Pa is a critical pressure to form a hydrogenated amorphous silicon film (*a*-Si:H) and surface hydrogenated silicon nanocrystallites. The effect of background gas pressure is discussed in Sec. IV.

C. Measurement of plume emission

The plume emission contains information on the behavior of the ejected Si atoms in the plume. Since the volume of the plume depends on the background gas pressure, measurement of plume volume gives information on the effects of background gas pressure on the PLA processes. To discuss the volume of the plume, we define the plume edge as the boundary between the bright and dark areas observed by ICCD camera. Although the plume expands with time, the expansion saturates after a certain period. The maximum distance between target and plume edge R_{max} was measured by ICCD camera. The maximum volume of the plume is proportional to the value of R_{max}^3 . The values of R_{max} and $1/R_{max}^3$ are plotted as a function of the background gas pressure as shown in Fig. 5(a), and the value of R_{max}^3 is plotted as a function of laser fluence in Fig. 5(b). The plasma emission spectra observed by a gated ICCD camera with monochromator are shown in Fig. 6. Figures 6(a) and 6(b) indicate the



FIG. 6. The plasma emission line observed by a gated ICCD camera with monochromator. The delay time after the laser pulse is (a) 10 ns and (b) 100 ns. The assigned peaks are shown in the figures.

spectra 10 and 100 ns after the laser irradiation. The strong sharp lines observed in Fig. 6(a) are identified to be Si II state.³² The sharp peak at 391 nm and the relatively broad peak at 414 nm in Fig. 6(b) are identified as the excited states of Si I (Ref. 32) and SiH (Refs. 33 and 34) species, respectively. The hydrogen related peak was observed only at 414 nm. These figures indicate that the hydrogen related species, SiH in this case, is not observed at 10 ns; it appears at 100 ns after the laser irradiation.

D. Surface oxidation

The morphology of the sample changed with the background gas pressure, as shown in Fig. 1. Although the porosity seems to increase with increasing background gas pressure, evaluation of porosity from the SEM image is not easy. The oxidation rate is one of the parameters used to evaluate the porosity of the sample, since the native oxidation rate is considered to correlate with the morphology of the secondary structure. FTIR spectra were measured for 250 days after the deposition to observe the oxidation process in the atmosphere at room temperature. The IR absorption intensities of the Si—O vibrational mode at 1050–1080 cm⁻¹ increased with exposure time.^{35,36} The oxidation rate was estimated from the intensities of the Si-O vibrational mode divided by the exposure time. The results are shown in Fig. 7 as a function of the hydrogen gas pressure. The observed increase in the oxidation rate with increasing background gas pressure is qualitatively consistent with the porosity of the secondary structure observed in Fig. 1. A correlation between the porosity of the sample and the aggregation mechanism is discussed in the next section.

IV. DISCUSSION

As shown in Sec. III, nanoscale and hundreds-ofnanometers scale observation by TEM and SEM show that



FIG. 7. The oxidation rate estimated by absorption intensity of Si—O vibrational mode and exposure time to the atmosphere as a function of background gas pressure.

the deposits prepared above 30 Pa have a hierarchical structure; nanoscale primary structure and aggregated secondary structure. This hierarchical structure is a result of plume kinetics and can reveal information on the mechanism of formation of nanoscale fine structure. The primary structure, consisting of nanocrystallites, is formed at first and subsequently aggregates to form the secondary structure. This means that the fine structure contains temporal information and that a stable primary structure is important to form clear secondary structures. Therefore, we discuss the creation of the primary structure first and follow that by the stability of primary structure. The aggregated secondary structure was analyzed by the fractal method and the effect of background hydrogen gas pressure is discussed based on plume volume and mean free path of primary structures. Finally, we point out that the background gas pressure determines some scales, such as the distance between target and plume edge D_{tp} and the mean free path of formed nanocrystallites L_{nc} . The PLA process is governed by these scales.

A. Creation of primary structure

1. Formation of filmlike structure

The secondary structure depends on the background gas pressure. When the PLA is performed in vacuum, the deposit is filmlike in nature. The critical pressure, which determines the boundary between the amorphous film and the assembly of nanocrystallites, was 30 Pa. The PLA mechanism drastically changes below and above this pressure. The creation of filmlike structure is discussed in this section. Since the plume edge was not observed below 30 Pa, the value of D_{tn} is larger than that of D_{ts} in this pressure range, as shown schematically in Fig. 8(a). The initial velocity of the Si species obtained by the time resolved emission measurement was $\sim 1 \times 10^6$ cm/s below 30 Pa. If we assume that the velocity is constant during the flight, the time for the ejected species to reach the substrate will be about $\sim 2 \ \mu s$. This time scale is much smaller than that of formation of nanocrystallite, 200 μ s.^{17–19} The amorphous film structure indicates that the ejected Si atoms reach the substrate before it cooled to



FIG. 8. A schematic view of the correlation between plume size and target-substrate distance. The schematic view of correlation between plume size and target-substrate distance. The distances between target and substrate and between target and plume edge are denoted as D_{ts} and D_{tp} . The difference between (a) and (b) is the D_{tp} and that between (b) and (c) is the D_{ts} .

the crystallization temperature and quenched rapidly on the substrate. Atomic scale deposition on the substrate forms amorphous film below 30 Pa, and hence a nanoscale fine structure was not observed in this pressure range.

2. Formation of nanocrystallites

The nanocrystallites were observed above 30 Pa and their diameter depended only slightly on the background gas pressure. These results are different from those of the gas evaporation technique in which the particle size increases with background gas pressure. Theoretical results of Luk'yanchuk et al.¹² indicate that the size of the nanocrystallite grown by adiabatic expansion will be constant when the input laser power is the same. This is because the size of the nanoparticle increases with initial density and decreases with increasing initial temperature.¹² The diameter of the primary structure depended little on the background gas pressure in our experimental conditions. Although this is consistent with the result of Luk'yanchuk et al.,¹² their calculation did not take into account effects of background gas pressure such as collisional cooling, which cannot be neglected under high gas pressure. Our plume analysis shows that the plume expansion follows the free expansion model up to 100 ns.³⁷ This means that the effect of background gas is small and adiabatic cooling is an appropriate model up to 100 ns. Theoretical work indicated adiabatic cooling ends at 80 ns and the number of clusters saturates.¹² The results of time scale and mean diameter theoretical calculations are not so different from our experimental results. This indicates that we can apply the adiabatic cooling model at least in the early stages of plume expansion. At later stages, after 100 ns, we have to take into account the effect of collisions with the background gas.

The experimental work gives information on the growth of nuclei to nanocrystallite under high background gas pressure. Results of work on LIF and ReD-LIF show that nanosized particles appear near the center of the plume at about 200 μ s.²³ The ejected Si atoms disappear at the time when the nanoparticles begin to grow.¹⁷ The disappearance of Si atoms suggests that almost all of the Si atoms in the plume are consumed in forming of Si nanocrystallites. Since the Si atoms are supplied by pulsed excitation in the PLA method, the density of the atomic Si in the plume decreases with the

growth of the nanocrystallite when the ejected Si density per pulse is not enough. This means that the number and size of nanocrystallites are limited by the number of Si atoms ejected during each laser pulse. In contrast to PLA, the Si atoms are continuously supplied from the source and the diameter increases with the background gas pressure in the case of the gas evaporation method.⁴ The predominant difference between PLA and gas evaporation on the formation of nanocrystallites arises from the pulsed supply of Si atoms.

Not only the number of ejected Si atoms but also the plume volume should be taken into account in discussing the growth of nanocrystallites. The number of ejected Si atoms per pulse can be changed by varying the laser fluence. Although we varied the laser fluence from 0.5 to 1.5 J/cm^2 , no change in the size of nanocrystallite was observed. The volume of the plume increased linearly with the laser fluence, as shown in Fig. 5(b). If we assume that the number of ejected Si atoms is proportional to the laser fluence, the density of Si atoms in the plume does not depend on the laser fluence. Although we can vary the number of ejected Si atoms by varying the laser fluence, it does not correspond to the change in the density of Si atoms in the plume so that the variation of the size of nanocrystallite is small. The time scale of the growth of nanocrystallite is reported to be about 200 μ s.^{17–19} The nature of primary structure is determined within this time scale. Taking into account previous theoretical and experimental results, we suggest that nuclei of nanocrystallites are formed by adiabatic cooling and their diameter continues to increase until the ejected Si atoms are consumed.

B. Stability of Si nanocrystallites

The results of the TEM, SEM, and Raman scattering suggest that the primary structure is stable. Since our sample has Si—H bonds on the surface, the effects of surface Si—H chemical bonds are important in discussing the surface stability of primary structures.

Here, we consider the stability of the surface of Si nanocrystallites by surface hydrogenation. The Gibbs free energy of a particle is described as follows:

$$G = -(4/3)\pi r^3 (kT/v) \ln(p_v/p_0) + 4\pi r^2 \gamma, \qquad (1)$$

where r, k, T, v, and γ are the radius of the particle, Boltzmann constant, absolute temperature, volume of molecule, and surface free energy, respectively. p_v/p_0 represents the super saturation ratio, i.e., the true vapor pressure divided by the equilibrium vapor pressure at the actual temperature T. The first and the second terms correspond to the formation of particle and surface, respectively. The critical diameter for crystal growth in gas phase d_c is determined by¹⁵

$$d_c = 2\gamma v [kT \ln(p_v/p_0)]^{-1}.$$
 (2)

The value of γ is estimated to be positive, 42 kcal/mol, for a dangling bond and negative, -28 kcal/mol, for the Si—H bond by using bond energies given by Pauling.³⁸ The surface Si—H bonds reduce the surface energy and the Gibbs free energy is always negative under the condition of supersaturation. This means that the surface hydrogen reduces the potential barrier to exceed critical diameter given by Eq. (2) and thereby promotes growth of the nanocrystal. Figure 6 indicates that the predominant species is Si at less than 10 ns and Si—H species appears at later stage. At the earlier stage of PLA, the temperature of these species and that of the primary structure formed are higher than the melting point of Si.

It is well known that the Si—H bonds in *a*-Si:H film are not stable at high temperature and that the number of Si—H bonds in *a*-Si:H decreases with annealing temperature. The Si—H bonds on the surface of the nanocrystallite are not stable above 700 K, too.²⁸ This means that the surface Si—H bonds are not stable and the role of the Si—H bonds during the growth of primary structure is negligible until the nanocrystallites are cooled to 700 K. After the nanocrystallite is cooled to below 700 K, surface Si—H bonds terminate further reactions. Possible reactions between SiH_n (*n* =0-3) species and surface of nanocrystallite are briefly mentioned in the Appendix.

The surface hydrogen prevents creation of the bonds between nanocrystallites. We prepared a nonhydrogenated sample by PLA in helium gas to clarify the surface stability. The porosity of the surface hydrogenated sample was larger than that of the nonhydrogenated one. The surface Si—H bonds stabilize the structure and prevent the formation of bonds between nanocrystallites as estimated in the Appendix. On the other hand, we could not observe a clear difference in the diameters of hydrogenated and nonhydrogenated nanocrystallites.²⁸ This is because the primary structure is formed under high temperature where the Si—H bonds on the surface are unstable. The effect of the surface Si—H bonds was observed for the secondary structure since it is formed after the cooling.

C. Growth of secondary structure

1. Aggregation of primary structure

The nanoscale primary structures are observed above 30 Pa. The primary structures aggregate to form secondary structure above this pressure. The temperature of the formed nanocrystallites plays an important role in forming stable primary structures. If the temperature of the primary structure is higher than the melting point, collisions of primary structures create larger structures to minimize the surface energy. The existence of nanoscale primary structures indicates that there is enough time for nanosize droplets to be cooled to form nanocrystallites in the plume before they reach the substrate. The value of D_{tp} was smaller than that of D_{ts} when the background gas pressure is above 30 Pa, as shown schematically in Fig. 8(b). The residence time of the nanocrystallites in the plume under background gas is about 200 μ s,^{17–19} which is sufficient for it to cool to form stable nanocrystallites. These stable nanostructures begin to aggregate after cooling. The mechanism of aggregation of the stable primary nanostructures is discussed here based on the crystal growth governed by atomic scale aggregation.^{14,25} There are three representative models for aggregation during crystal growth: ballistic aggregation (BA), cluster-cluster aggregation (CCA), and diffusion limited aggregation (DLA). In the BA model, the particles move along straight trajectories until they encounter the growing aggregate and stick to its surface.²⁵ Therefore, the direction of the growth is perpendicular to the substrate. This kind of kinetics is typical for experimental situations when molecules move in a lowdensity vapor. Cluster-cluster aggregation can be observed, for example, for iron smoke aggregates formed in air and for aggregated aqueous gold colloid.^{26,27} Cluster-cluster aggregation involves the random motion of many particles at the same time, sticking together to form clusters which continue to perform random walks until eventually all particles are part of one single aggregate. The main feature of the deposits formed by CCA process is their small density, that is, large porosity, which is accomplished by aggregation of random sized porous clusters.^{14,25} The DLA model is based on single particles performing Brownian motion before joining a single growing aggregate. Since this model can be applied under conditions of very low particle concentration, it is not a credible candidate to discuss the PLA process.

Figure 1(a) shows columnlike structure which indicates growth perpendicular to the substrate. This structure resembles the computer simulation of BA on the substrate.²⁵ The columnlike structure indicates that the nanocrystallite formed in the plume reaches the substrate and aggregation takes place on the substrate in this gas pressure region. At pressures above 500 Pa, the morphology of the secondary structure changed to fiberlike, as shown in Figs. 1(c) and 2(b). These figures indicate that this structure is very porous and that the growth direction shows no correlation with substrate. The cauliflowerlike structure was observed in the pressure range of 300–500 Pa, as shown in Fig. 1(b). This structure has the features of both BA and CCA; the direction of the growth has a strong correlation with substrate and the porosity of the deposits is larger than that of the columnlike structure. These features are qualitatively evaluated by measuring the fractal dimension in Sec. IV C 2.

2. Analysis of fractal dimension

The secondary structure can be quantitatively treated by fractal dimension, which gives information on the aggregation kinetics. The box counting method is one of the conventional methods to evaluate fractal dimension.²⁵ This method was applied to analyze fractal dimension of the image of Fig. 2(b). We counted the number of particles in the clusters N as a function of their linear size L in the figure. The result is shown in Fig. 9. The data are well described by power-law behavior in the range between 10 and 1000 nm, hundreds-ofnanometers scale, as expected for a self-similar structure. The fractal dimension D estimated from the slope of the figure was approximately 1.7. This value agrees well with the fractal dimension D=1.7-1.8 for CCA.^{14,25} The fractal dimension of the cauliflowerlike structure shown in Fig. 1(b) was about 1.8–1.9. The SEM image is a projection of the three-dimensional structure to a two-dimensional image. It is well known that the projection of a D-dimensional fractal structure in three-dimensional space onto a two-dimensional plane results in the same fractal dimension in threedimensional space when D is smaller than 2.0 and results in 2.0 when D is not smaller than 2.0^{25} Therefore, the obtained



FIG. 9. The result of box count measurement of fiberlike structure. The number of particles N in the clusters is plotted as a function of their linear size L.

fractal dimensions are the same as those of three-dimensional space. The evaluated fractal dimension of the columnlike structure from SEM image is 2.0. This means that the fractal dimension of the columnlike structure in three-dimensional space is estimated to be larger than 2.0. If we assume that the columnlike structure is a result of BA, as discussed in Sec. IV C 1, the fractal dimension D of this structure is estimated to be 3.0 since the known value of D for BA is the same as the embedding dimension, 3.0, in this case.^{14,25} This value is consistent with the fractal dimension of the columnlike structure, larger than 2.0. The fractal dimension of the cauliflowerlike structure, 1.8-1.9, is intermediate between that of fiberlike and columnlike structures. This is consistent with the structural feature that cauliflowerlike structure has the features of both BA and CCA, as mentioned in Sec. IV C 1. These results indicate that the fractal dimension of aggregated secondary structure increases from 1.7 to larger than 2.0 with decreasing background gas pressure from 1100 to 30 Pa. The analysis of fractal dimension ensures that the fiberlike structure is accomplished by CCA of primary structures. This indicates that collisions of nanocrystallites and those between the clusters formed by aggregation of nanocrystallites take place in the plume. Since the fractal dimension of reaction limited CCA is known to be 2.1, the CCA process in the plume is considered to be diffusion limited.

Although the fractal dimension does not directly correspond to the porosity, aggregated materials which have smaller fractal dimensions tend to have higher porosity.^{14,25} For example, the structure of the sample grown by CCA has a high porosity due to the collision of aggregated clusters. A decrease in the fractal dimension qualitatively corresponds to the increase in the porosity of the SEM image with increasing background gas pressure, as shown in Fig. 1. If we assume that the oxidation rate is a function of surface area, the oxidation rate can be used as a measure of the porosity. Here, we consider correlation between the oxidation rate and the fractal dimension. As shown in Fig. 7, the slope of oxidation rate changed at approximately 300 Pa. At around this pressure, the secondary structure changes from a column-to a cauliflowerlike structure. The fractal dimension of the sample prepared below 300 Pa is larger than 2.0 and the oxidation rate is lower due to the smaller porosity. Above 300 Pa, the oxidation rate increases due to the increase of porosity which corresponds to the decrease in the fractal dimension. Collisions between primary structures in the plume result in large porosity and small fractal dimension in this pressure range. The qualitative correlation between fractal dimension and porosity of the secondary structure was confirmed from measurement of natural oxidation. These results indicate that fractal analysis is a good method not only to discuss aggregation mechanism but also to discuss the physical properties of aggregated materials.

Here, we summarize the effect of background gas on the PLA process from the viewpoint of scale. Below 30 Pa, Si atoms reach the substrate without collision in the plume. This results in atomic scale deposition on the substrate. Above 30 Pa, atomic scale growth in the plume forms nanocrystallites. At lower gas pressure, nanometer scaled aggregation (deposition) on the substrate takes place. At higher gas pressure, nanometer scale aggregation takes place in the plume and the aggregated secondary structure deposits on the substrate. These processes form hundreds-of-nanometers scale fine structures. The existence of clear primary and secondary structures and good self-similarity indicates that the surface of the primary structure is stable, as discussed in Sec. IV B.

D. Effects of plume volume on aggregation mechanism

The correlation between the aggregation process and the background gas pressure is discussed in Sec. IV C. Since the plume volume depends on the background gas pressure, the effects of background gas pressure on plume volume and aggregation mechanism will be discussed in this section. The volume of the plume increases with time and the expansion stops at a few microseconds. The volume discussed in this section is the maximum volume since the primary structure is formed at a later stage of plume expansion.¹⁷⁻¹⁹ Figure 5(a) indicates that the volume of the plume is proportional to the inverse of the background gas pressure. Since the number of ejected Si atoms is determined by the laser fluence and the maximum volume of the plume is inversely proportional to the background gas pressure,³⁹ the mean density of Si atoms in the plume is proportional to the background gas pressure. Here, we estimate the mean free path of a particle in the plume. The elastic mean free path of the particle λ is expressed as

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2(N/V)},\tag{3}$$

where σ , *V*, and *N* are the diameter of the particle, volume, and number of particles in volume *V*, respectively. The total mass of the ejected Si per pulse in our experimental condition can be roughly estimated, from the thickness of the deposits and the deposition time, to be of the order of 10 ng. The mean free path depends only on the volume of the plume since the number of the ejected species per pulse *N* is constant. Equation (3) can be rewritten as $\lambda \sim 1 \times 10^5 \times V$ m for 4 nm Si nanocrystallite. The value of D_{tp} was less than 5 mm at above 500 Pa. The mean free path can be estimated to be 7 mm by using D_{tp} and by assuming a spherical plume shape. Since the plume size and the estimated mean free path are comparable, aggregation of Si nanocrystallites in the plume is possible above 500 Pa. The mean free path is also a function of background gas pressure due to the inversely proportional relationship between background gas pressure and the volume of the plume. At 30 Pa, the mean free path of nanocrystallites reaches 120 mm which is larger than the distance between substrate and target. These estimations are consistent with our conclusion that aggregation takes place in the plume and on the substrate depending on the background gas pressure. The self-similar CCA structure observed at higher background gas pressure indicates that not only the collisions between primary structured nanocrystallites but also those between clusters formed by aggregation take place in the plume by spatial confinement.

Since the nanocrystallites are formed in the plume as discussed in the previous reports, D_{ts} is an important parameter in the formation of secondary structures. To investigate the effect of D_{ts} , the position of the substrate was changed while keeping the gas pressure constant at 30 Pa. The columnar structure changed to the homogeneous amorphous film when the substrate was placed in the plume, as shown in Fig. 8(c). In this case, the Si atoms reach the substrate before the formation of nanocrystallite. From the viewpoint of atomic scale, the growth mechanism changed from formation of nanocrystallite in the plume to that of film on the substrate.

The essential role played by the background gas pressure is in changing the plume volume and mean free path of nanocrystallites. We show that correlation between these three lengths D_{ts} , D_{tp} , and mean free path of formed nanocrystallites λ_{nc} determines the formation process of nanoscale fine structure. When D_{tp} is larger or smaller than λ_{nc} , BA on the substrate or CCA in the plume takes place, respectively. The aggregation region moves from the surface of the substrate to inside of the plume with increasing background gas pressure.

E. Scales to characterize PLA processes

The nanoscale fine structure is governed by scales determined by experimental conditions, D_{ts} , D_{tp} , and λ_{nc} . These scales determine the scale of fine structure. The growth of nanoscale primary structure is an atomic scale phenomenon. Atomic scale growth is determined by the correlation between D_{ts} and the mean free path of ejected Si atoms. Atomic scale growth results in a film on the substrate or nanodroplets in the plume. The nanodroplets in the plume cool to become the surface hydrogenated nanocrystallites in the plume. These nanocrystallites are stable and act as nanoscale primary structures. That is, atomic scale growth changes to nanometer scale aggregation after the cooling of nanodroplets and the aggregation forms hundreds-of-nanometers scale secondary structures. Although the structure observed at hundreds-of-nanometers scale depends on the background gas pressure, the essential factor is not the pressure but the correlation between the lengths D_{ts} , D_{tp} , and λ_{nc} . These lengths determine the location of the primary structure aggregate and result in the formation of nanoscale fine structure. We clarified that primary structure is governed by spatial confinement of ejected atoms, while the secondary structure by that of formed nanocrystallites.

V. CONCLUSIONS

The formation of nanoscale fine structures during pulsed laser ablation of a silicon target in a hydrogen background

gas has been studied by analysis of the deposited silicon fine structures prepared under different conditions. TEM, SEM, Raman scattering, and infrared absorption studies on the deposited samples indicate that an amorphous silicon film is deposited on the substrate at lower background gas pressure and silicon nanocrystallites are produced when the background gas pressure is higher than the critical value. The deposited substance prepared above critical pressure has a hierarchical structure composed of surface hydrogenated silicon nanocrystallites as the primary structure and aggregates of the nanocrystallites as a secondary structure. The size of the primary nanocrystallites was 4-5 nm independent of the hydrogen pressure. These results suggest that hydrogenated silicon nanocrystallites are initially formed as a primary structure followed by aggregation of the primary structure to form the secondary structures. The temperature of the nanocrystallites during deposition and the surface hydrogenation determines the stability of primary structures, which, in turn, affect the formation of secondary structures. The nanodroplets change to nanocrystallites on decreasing their temperature during deposition. The surfaces of nanocrystallites are further stabilized by surface Si-H bonds. Aggregation starts after the primary structures are stabilized.

We carried out fractal analysis for the SEM images of the deposits and found that the secondary structure shows selfsimilarity whose fractal dimension ranges from 1.7 to 2.0. Comparison of these values with reported results for fractal growth simulation indicates that the aggregation mechanism changes from BA on the substrate to CCA in the plume with increasing background gas pressure. The aggregation of nanoscale primary structures on the substrate and in the plume results in column- and fiberlike structures, respectively.

The atomic scale growth and nanometer scale collisions depend on the mean free paths in the plume. The background gas pressure determines the plume volume and mean free paths of atoms and nanocrystallites in the plume. The lengths D_{tp} and λ_{nc} are determined by plume volume, and a correlation between these values and D_{ts} determines the nanoscale fine structure. The formation of surface stabilized Si nanocrystallites and their spatial confinement governed by background gas pressure are essential for the formation of hierarchical structure of deposited substance.

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APPENDIX: REACTION ON THE HYDROGENATED AND NONHYDROGENATED SURFACE

For the bonding reaction to take place spontaneously from the adsorbed states, the reaction has to be exothermic, i.e., the enthalpy change ΔH by the reaction has to be negative. The enthalpy change can be roughly estimated from the bond energies in the reaction; the following bond energies are given by Pauling:³⁸ Si—H bond, 70 kcal/mol; Si—Si bond, 42 kcal/mol; and H—H bond, 104 kcal/mol. Here, we assume that the surface of nanocrystallites is covered by \equiv Si—H bonds. Adsorbed SiH_n (n=0-3) species will bind to the surface by creating more than two Si—Si bonds, since singly bonded Si is not stable. Therefore, more than two adjacent Si—H bonds (\equiv Si—H+H—Si \equiv) on the surface react with the adsorbed species. The two adjacent Si—H bonds are possible at the kink or edge on the surface of a nanocrystallite. Although reaction on the surface is not clear, examples of possible reactions on the surface are as follows:

$$(\equiv Si - H + H - Si \equiv) + Si$$

$$\rightarrow \equiv Si - (SiH_2) - Si \equiv (\Delta H = -84 \text{ kcal}),$$
(A1)

$$(\equiv Si - H + H - Si \equiv) + SiH$$

$$\rightarrow \equiv Si - (SiH_2) - Si \equiv + H (\Delta H = -14 \text{ kcal}),$$
(A2)

$$(\equiv Si - H + H - Si \equiv) + SiH_2$$

$$\rightarrow \equiv Si - (SiH_2) - Si \equiv + H_2 (\Delta H = -48 \text{ kcal}),$$
(A3)

$$(\equiv Si - H + H - Si \equiv) + SiH_3$$

$$\rightarrow \equiv Si - (SiH_2) - Si \equiv +H_2 + H (\Delta H = +22 \text{ kcal}).$$
(A4)

These reactions are followed by additional SiH_n (n = 0-3) species to create three Si bonds to stabilize on the surface. If the surface of the nanocrystallite is not covered by Si—H bonds, similar reactions may be described as follows:

$$(\equiv Si - + - Si \equiv) + Si$$

$$\rightarrow \equiv Si - (Si) - Si \equiv (\Delta H = -84 \text{ kcal}), (A5)$$

$$(\equiv Si - + - Si \equiv) + SiH$$

$$\rightarrow \equiv \mathrm{Si} - (\mathrm{SiH}) - \mathrm{Si} \equiv (\Delta H = -84 \text{ kcal}), \tag{A6}$$

$$(\equiv Si - + - Si \equiv) + SiH_2$$

$$\rightarrow \equiv Si - (SiH_2) - Si \equiv (\Delta H = -84 \text{ kcal}),$$
(A7)

$$(\equiv Si - + -Si \equiv) + SiH_3$$

$$\rightarrow \equiv Si - (SiH_2) - Si \equiv + H \ (\Delta H = -14 \text{ kcal}).$$
(A8)

The surfaces formed by reactions (A5) and (A6) are not stable since both produce dangling bonds. Therefore, they

will be followed by additional exothermic reactions. The exothermic energy of the dangling-bond surface is larger than that for the Si—H surface. Furthermore, transition states to break Si—H bonds are not necessary for the surface having dangling bonds. This means that the reaction rate on the dangling-bond surface should be larger than that on the hydrogenated surface. These estimations mean that the growth of primary structure is limited by surface Si—H bond at below 700 K.

The collisions between the nanocrystallites are more important than the growth of them at a later stage as discussed previously, since the primary structures aggregate at this stage. The interface between two adjacent particles can par-

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tially create a bond if the reaction is exothermic. A possible surface reaction on the hydrogenated surface is

$$\equiv Si - H + H - Si \equiv$$

$$\rightarrow \equiv Si - Si \equiv + H_2 (\Delta H = -6 \text{ kcal}) \quad (A9)$$

and that on a dangling-bond surface is

$$\equiv Si - + - Si \equiv \rightarrow \equiv Si - Si \equiv (\Delta H = -42 \text{ kcal}).$$
(A10)

Although both reactions are possible, the dangling-bond surface is more reactive since the exothermic energy is larger and a transition state is not necessary.

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