Plume analysis during pulsed laser ablation of silicon in hydrogen gas

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Abstract. Recently, surface passivated Si nanocrystallites are prepared by pulsed laser ablation (PLA) of Si target in hydrogen gas. Plume analysis during PLA is one of the available methods to clarify a mechanism of surface hydrogenation. We observed plume emission by time- and space-resolved spectroscopy. The dominant species were exited neutral Si atoms and SiH species when the delay time is longer than 100 ns. The Si atoms and SiH species existed throughout the plume. This indicates that nanocrystallites grow in the mixture of Si and SiH vapor. The surfaces of Si nanocrystallites are considered to be hydrogenated by SiH species during the growth. It seems that surface hydrogenation is not due to the spatial separation of Si and H species but due to surface reaction with SiH and/or Si species.

1. Introduction
The pulsed laser ablation (PLA) technique in inert background gas is a promising technique to prepare nanoparticles. There are many reports on the preparation of silicon nanoparticles by this method and photoluminescence properties are discussed [1-3]. Inert background gas is used in these papers to prevent reaction with silicon. Although reactive PLA is widely used to prepare thin films, this technique is not popular for preparation of nanocrystallites. Recently, we prepared Si nanocrystallites by PLA of Si target in hydrogen gas instead of inert gas. The photoluminescence efficiency of this specimen was much larger than that prepared in inert background gas due to the passivation of surface dangling bonds [4]. We found that this material was not alloy of silicon and hydrogen but was silicon nanocrystallites covered by Si-H bonds [5]. This means that the PLA is a promising method to prepare surface controlled Si nanocrystallites. It is necessary to reveal mechanism of surface hydrogenation to control surface property. Since hydrogen is a reactive gas, we can also obtain information on collisions and reactions between ejected Si species and background hydrogen gas. In the plume, optical emission spectroscopy can be employed as simple technique for diagnostics of the PLA plume. Emission spectroscopy is principally utilized to identify the species in the plume and spatially and temporally resolved measurements are necessary to observe species’ TOF and local populations [6-9]. Although there are some reports on the nanocrystallization of the Si by plume analysis [3, 10], growth of the surface layer of nanocrystal is not discussed. In the present work, we measured plasma emission line of the plume to discuss the process of hydrogenation of the surface of Si nanocrystallites.
2. Experiment
A fourth harmonic of pulsed Nd:YAG laser beam (wavelength: 266 nm, pulse width: 10 ns, repetition rate: 10 Hz) was focused onto the surface of the single-crystalline Si target. The energy density on the target was 1.5 J/cm². The target was mounted on a rotating holder and placed in a vacuum chamber. The base pressure of the chamber was on the order of 10⁻⁶ Pa and H₂ gas was introduced into the chamber at a flow rate of 10 sccm and the chamber was maintained at 260 and 1100 Pa during the deposition. The background gas pressure is important to determine the morphology of deposits [11].

The schematic of the optical measurement is shown in Fig. 1. A gatable image-intensified charge coupled device (ICCD) camera was mounted on the monochromator. The slit of the monochromator was set perpendicular to the target surface. This configuration enables us to observe emission spectra, decay time and plume expansion simultaneously.

![Schematic of the experimental setup](image)

Fig. 1. The schematic of the experimental setup. (L and M refer to lens and mirror). Time- and space-resolved spectra can be detected by this setup.

![Graph](image)

Fig. 2. The dotted line shows experimental data of the leading edges of the plume emission as a function of time after the laser pulse at (a) 260 Pa and (b) 1100 Pa. The dashed and solid lines are calculated curves according to the point blast and drag-force models.

3. Results and discussion
The leading edges of the plume emission are plotted in Fig. 2 as a function of time after the laser pulse. Point blast and drag-force models are proposed for plume expansion in the earlier and later stages, respectively [12]. The point blast model is given by

\[ R = \xi_0 (E_0 / \rho_0)^{1/5} t^{2/5}, \]

where \( \xi_0 \) is a constant which depends on the specific heat capacity. This model describes the propagation of a shock wave, caused by an explosive release of energy \( E_0 \), through a background gas of density \( \rho_0 \). The drag-force model is given by

\[ R = R_{\text{max}} [1 - \exp(-\beta t)], \]

where \( R_{\text{max}} \) is the stopping distance of the plume and \( \beta \) is the slowing coefficient. This model is based on the assumption that the deceleration of the plume is related to a drag force (viscosity) from ambient gas. The experimental data were fitted by these models and fitting curves for shock and drag models are shown in Fig. 2 as solid and dashed lines, respectively. The point blast model agree well
with experimental data up to several hundreds ns, and drag model describes in the longer stage of plume expansion. These results are consistent with previous report of PLA in non-reactive gas at moderate gas pressure. [8, 9]

![Figure 3. Optical emission spectra of Si plume at four different delay times $t$: (a) 10 ns, (b) 100 ns, (c) 1000 ns, and (d) 3000 ns.](image)

![Figure 4. Spatial distribution of emissions from Si I (dashed line) and SiH species (solid line) as a function of distance from target in (a) 260 Pa and (b) 1100 Pa hydrogen gas pressure.](image)

Figure 3 shows the emission spectra measured at delay times, $t$, are 10, 100, 1000, and 3000 ns. The CCD signal was binned along the slit of monochromator. The binned area on the CCD chip corresponds to area of $20 \times 0.5$ mm in the chamber. Since the distance between target and plume edge is less than 20 mm, the binned area covers the area in the chamber along the normal to the target. At delay time of 10 ns, we observed a continuum emission due to Bremsstrahlung emission from the hot plasma [13, 14]. In this stage, it is difficult to retrieve detailed information about atoms and ions, however, we can confirm the existence of the emission lines attributed to the singly ionized Si (Si II: 386, 413, 506, 635 nm). When delay time is larger than 100 ns, isolated lines of the excited neutral Si atoms (Si I: 391 nm) and SiH species (410-420 nm) are clearly observed. Since intensity of Si II lines decrease rapidly, we cannot observe Si II in this stage. If we assume that concentration of an excited state is proportional to the intensity of the spectral lines, this result shows that major species in the plume are Si II at about 10 ns and Si I and SiH are dominant in later stage. The relative intensity of SiH is small up to several hundred ns.

Figure 4 depicts the emission intensity of Si I (391 nm) and SiH (414 nm) as a function of distance from target along normal direction at delay times of 100, 500, and 1300 ns. The background gas pressures are 260 and 1100 Pa for Figs. 4 (a) and (b) respectively. Each curve has been normalized to the maximum intensity. Although the intensity of SiH emission line is slightly distributed inside of the plume compared to that of Si I at delay time of 500 ns, the emission curves for Si I and SiH are
basically similar for all delay times at 260 Pa. The peak position of the SiH emission is nearer to the target compared to that of Si I emission at 1100 Pa. The distribution of the species changed by background gas pressure. It is noteworthy that SiH species did exist not only around the plume edge but also inside of the plume. This result indicates the surface hydrogenation is not due to the spatial separation of Si and H species.

According to the calculations of Luk’yanchuk et al. [15, 16], nucleation starts at tens of ns. Rough estimates of integrated relative intensities of SiH to Si I from Fig.3 are 0.0, 0.03, 0.7 and 1.5 for 10, 100, 1000 and 3000 ns, respectively. At the earlier stage of plume expansion, relatively few number of SiH species exists in the plume as shown in Fig. 3. Therefore there is a possibility that time scale of nucleation and hydrogenation is different and this is an origin of surface hydrogenation. In the case of PLA of Si in inert gas, nanocrystallites are formed inside of the plume after a few hundred µs after the laser pulse [10, 17, 18]. This means that nanocrystallites dominantly grow in later stage of our measurements. Since both Si and SiH species exists in this time scale, the origin of surface hydrogenation is not due to spatial nor temporal separation. It is considered that the surface of nanocrystal react with SiH and/or Si species in the plume and the surface grows presumably by breaking Si-H bond on the surface such as CVD growth of Si from silane gas.

4. Conclusion
We measured time- and space-resolved plasma emission in the plume to study the process of surface hydrogenation. The results show that dominant elements are singly ionized Si atoms in the early stage of the plume evolution. When the delay time was longer than 100 ns, dominant elements changed to exited neutral Si atoms and SiH species. The spatial separation of Si and SiH species were not observed in the space and time region of the growth. These results indicate that nanocrystallites grows in the mixture of Si and SiH vapor with creating Si-H bond on the surface.

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