Spectroscopic study on reaction mechanism of laser-ablated silicon ions and neutrals with benzene molecules

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Abstract. Reaction of benzene molecules with ablated silicon ions and neutrals were investigated by space- and time-resolved optical emission spectroscopy. The time-resolved emission spectrum showed production of excited C₂ and CH radicals after 180-ns delay from laser irradiation. Comparing the temporal evolution of C₂* with that of Si*, we concluded that the neutral Si atoms contribute to the production of the C₂ radicals. The emission in a mixture of benzene vapor and neon gas suggested that the neutral Si atoms could excite the buffer atoms and molecules to high-energy levels. Based on the result, the production process of the C₂ radicals is discussed.

1. Introduction
Pulsed laser deposition (PLD) in a reactive buffer gas enables us to synthesize various compound films in a single procedure by a reaction of the ablated species with the buffer gas. For example, the ablation of silicon in NH₃ or N₂ gas leads to the production of a thin Si₃N₄ film [1–3]. D’Anna et al. showed that yield of Si₃N₄ in NH₃ is about two orders of magnitude higher than that obtained in N₂ [1]. This means that it is important to select a buffer gas suitable for effective production of the objective compound. To select the buffer gas, the reaction mechanism in the PLD process should be elucidated.

From a microscopic viewpoint, the reaction in PLD should be decomposed into a combination of elementary reactions: collision, excitation, ionization, recombination, fragmentation and rearrangement. Previously we have performed the laser ablation of silicon in 1 torr of neon gas using a Nd:YAG laser (λ=1064 nm) and investigated the elementary reactions of the neon atoms with the ablated silicon ions, neutrals and electrons [4]. In the study, it was found that the neutral neon atoms are excited to 2pₙ states lying in 18–19 eV, and that they were excited by electronic-to-electronic and translational-to-electronic energy transfer from the silicon ions.

The reaction of the ablated silicon species with the neon atoms does not contain chemical reactions such as fragmentation and rearrangement, which are important in the PLD process in a reactive buffer gas. To examine the chemical reactions, we performed the laser ablation of silicon in benzene vapor. In this paper we pay attention to the fragmentation of benzene by the collision with the ablated silicon ions and neutrals. The fragments originated from benzene were investigated using space- and time-resolved optical emission spectroscopy. The fragmentation processes are discussed on the basis of the studies on the photodissociation of benzene [5, 6].
2. Experimental

Experimental set-up is similar to our previous study [4]. A single-crystal silicon wafer (0.25 mm in thickness, semiconductor grade) was put in the chamber filled with benzene vapor (Wako Chemical, purity 99.7 %) at a pressure of 0.2 torr. The fundamental beam output of a Nd:YAG laser was focused with a 250 mm focal length lens onto the target with an incident angle of 45°. The diameter of the spot size was <400 μm. The fluence of the ablation laser was estimated to be ~0.54 J/cm² at the sample surface. A weak fluence was employed in this experiment because the reaction products cover the target surface and rapidly change the ablation condition at higher fluence.

3. Results and discussion

Figure 1 shows typical emission spectra in the region of 230–530 nm after 60-ns and 180-ns delay from the laser irradiation. The observed position is 0.5 mm from the target surface. The emission spectrum at t=60 ns shows a broad band above 250 nm, which is attributed to continuous emission by electron-ion recombination [7]. The sharp lines are assigned to emission from the excited silicon ions, Siⁿ⁺* (n=1–3) [8]. In the emission spectrum at t=180 ns, the continuous emission and the sharp lines from Siⁿ⁺* disappear, while the emission from the excited silicon neutrals Si* are enhanced. In addition, we observed the emission from excited C₂ radicals in the region from 430 to 530 nm and that from excited CH radicals around 431 nm [9]. The emission from C₂* is assigned to the ρ²Π₉→ρ¹Π₈ transition (Swan bands). The radicals are fragments originated from the benzene molecules induced by the collisions with the ablated species. There was no emission from the first excited singlet state (A¹B₂; 4.71 eV) of benzene, which can be observed in the region of 260–290 nm [10, 11]. The absence of the emission is attributed to an effective excitation of benzene to the higher electronic states, followed by fragmentation. In present condition we can expect the formation of SiC or SiC₂, which is produced by the reaction of C₂ with Si. The SiC radical has an electronic transition of C³Π→X³Σ around 441 nm [12], while the SiC₂ molecule has that of A¹B₂→X¹A₁ around 497 nm [13]. We assume that SiC or SiC₂ are observable by laser-induced fluorescence excitation, although they were absent in the emission spectrum.

For the elucidation of the production process of the C₂ radicals, the temporal evolution of the emission from C₂* was measured and compared with that from Si* and Siⁿ⁺*. Figure 2 shows the temporal evolutions for C₂*, Si* and Siⁿ⁺* (n=1–3) at d=0.5 mm. The continuous emission has been subtracted in every evolution. The emissions from C₂* and Si* are most enhanced at t=130 ns and gradually decrease until t=600 ns, while those from Siⁿ⁺* peak at t=60–70 ns and completely disappear at t=200 ns. The similarity of
the temporal evolution between C$_2^*$ and Si* suggests that the neutral Si atoms contribute to the production of the C$_2$ radicals.

Here, we suppose that the C$_2$ radicals are produced by the collisions of Si with benzene. The studies of photodissociation suggest that the excited benzene molecules decompose into H, H$_2$, CH$_3$, C$_2$H$_2$, C$_3$H$_3$, C$_4$H$_n$ ($n=2,3$), C$_5$H$_3$ and C$_6$H$_n$ ($n=2–5$) [5, 6]. Therefore, it is plausible that the C$_2$ radicals are not directly originated from the benzene molecules but produced by the collisions of these fragments with Si. Most plausible precursor is C$_2$H$_2$, which produces the C$_2$ radical by photodissociation [14, 15]. The following three possible mechanism (1)–(3) are considered for the production of C$_2$H$_2$ from the benzene molecule:

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\begin{align*}
\text{C}_6\text{H}_6 & \rightarrow \text{C}_6\text{H}_5 + \text{H} \quad \Delta H=4.80 \text{ eV} \quad (1a) \\
\text{C}_6\text{H}_5 & \rightarrow \text{C}_6\text{H}_4 + \text{H} \quad \Delta H=3.97 \text{ eV} \quad (1b) \\
\text{C}_6\text{H}_4 & \rightarrow \text{C}_6\text{H}_3 + \text{C}_2\text{H}_2 \quad \Delta H=1.66 \text{ eV}; \quad (1c) \\
\text{C}_6\text{H}_6 & \rightarrow \text{C}_6\text{H}_5 + \text{H} \quad \Delta H=4.80 \text{ eV} \quad (2a) \\
\text{C}_6\text{H}_5 & \rightarrow \text{C}_6\text{H}_3 + \text{C}_2\text{H}_2 \quad \Delta H=4.41 \text{ eV}; \quad (2b) \\
\text{C}_6\text{H}_6 & \rightarrow \text{C}_6\text{H}_4 + \text{H}_2 \quad \Delta H=4.26 \text{ eV} \quad (3a) \\
\text{C}_6\text{H}_4 & \rightarrow \text{C}_6\text{H}_3 + \text{C}_2\text{H}_2 \quad \Delta H=1.66 \text{ eV}. \quad (3b)
\end{align*}
\]

The $\Delta H$ values are heats of reaction at 298 K. The sum of $\Delta H$ is 10.43 eV for the process (1), 9.21 eV for the process (2), and 5.92 eV for the process (3). The process (3) is the minimum energy path to produce C$_2$H$_2$ from benzene. On the other hand, the excited C$_2$ radicals are produced by

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\begin{align*}
\text{C}_2\text{H}_2 & \rightarrow \text{C}_2(\lambda^3\Pi_g) + 2\text{H} \quad \Delta H=13.18 \text{ eV}, \quad (4) \\
\text{C}_2\text{H}_2 & \rightarrow \text{C}_2(\lambda^3\Pi_g) + \text{H}_2 \quad \Delta H=8.72 \text{ eV}. \quad (5)
\end{align*}
\]

The process (5) is the minimum energy path to produce the excited C$_2$ radicals.

The excitation of the buffer atoms and molecules is induced by the translational-to-electronic (T–E) or the electronic-to-electronic (E–E) energy transfer from the ablated species [4]. The ionization energy of Si is 8.15 eV [8], which is below the reaction energy of the process (4) and (5). Therefore, the production of the excited C$_2$ radicals is impossible by the E–E transfer from Si*. To examine the possibility that the process (1)–(5) can be induced by the T–E transfer, we estimated the velocity of Si based on the relationship between the peak time of the emission from Si* and the distance of the observed position from the target [4]. The velocity of Si* was estimated to be $5.2\pm0.9\times10^4$ m/s, which is 0.39 keV of the translational energy in $^{28}$Si. The excited Si atoms have the translational energy enough to promote the process (1)–(5).

In the T–E transfer between atoms and molecules, only a part of the translational energy is converted into electronic one. For the further discussion of the process (1)–(5) induced by the T–E transfer from Si*, we added 0.5-torr neon gas to 0.2-torr benzene vapor and observed the emission from neon. The temporal evolution of the emission from C$_2$* did not change by the presence of neon. Figure 3(a) shows emission spectra in the region of 500–680 nm after 180-ns delay. In addition to the
emission from C₂*, Si* and Si⁺*, sharp lines of the emission from Ne* was observed in the region of 580–680 nm. The appearance of these lines indicates the neutral neon atoms are excited above 18 eV [4]. Figure 3(b) shows the temporal evolutions of the emission from Ne*, Si* and Si⁺*. The temporal evolution of the emission from Si* is overlapped with that of Ne*, while only the onset of the emission from Si⁺* agree with that of Ne* [16]. Although both of Si* and Si⁺* contribute to the excitation of neon in the present experimental conditions, the overlap of the emission between Si*, C₂* and Ne* suggests that the excited neutral Si atoms contribute to the excitation of benzene and C₂H₂ above 18 eV. If the C₂ radical is produced via processes (2)→(5) or (3)→(5), whose total heats of reaction are below 18 eV, the reactions may proceed by single collision with Si*. Even in the processes other than (2)→(5) and (3)→(5), two collisions are enough for the promotion of the reaction. For further discussion, the intermediate products in the process (1)→(5) should be investigated.

4. Conclusion
The reaction of the benzene molecules with the ablated silicon ions and neutrals were investigated by space- and time-resolved emission spectroscopy. The time-resolved emission spectrum showed the appearance of Si⁺* immediately after the laser ablation, followed by the production of C₂*, CH* and Si*. The comparison between the temporal evolutions of the emissions from C₂* and Si* suggested that the neutral Si atoms contribute to the production of C₂. Based on the studies on photodissociation of benzene, several reaction processes to produce C₂* were supposed. The estimated translational energy of Si* was sufficient to induce the reactions. For further discussion, the emission from the excited neon atoms was observed in the mixture of benzene vapor and neon gas. The results suggest that the neutral Si atoms can excite the buffer species above 18 eV, and that the C₂ radicals can be produced by single or double collisions of the benzene molecules with the neutral Si atoms.

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