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Generation of argon-ion mixed silicon plasmas forming argon encapsulated silicon clusters

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An inductively coupled argon (Ar) plasma is superimposed on a silicon (Si) plasma generated by an electron beam gun in order to realize the formation of gas-atom encapsulated Si cage clusters. The Si clusters, which are formed and deposited on a substrate, are analyzed by laser-desorption time-of-flight mass spectrometry and are found to have the mass spectra of not only pure Si cluster (Si_n; $n=1-17$) but also Si cluster doped with Ar atom ($ArSi_n$; $n=10-20$) in the case that the large amount of Ar ions is generated in addition to the Si plasma. Together with the analysis of x-ray photoelectron spectroscopy, it is revealed that the Ar atom is included in the Si cluster, forming the structure of endohedral $Ar@Si_n$ complexes. Furthermore, the mass spectrum of $Ar@Si_n$ indicates the existence of the magic numbered cluster size $n=15$, 16 similar to the metal encapsulated Si clusters. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2404606]

Nanosized silicon (Si) clusters have been recognized to play an important role in nano- and opto-electronics and have been investigated both experimentally[1–4] and theoretically.[5,6] Especially, for three-dimensional integration in the future, the development of spherical structured Si materials and devices is desirable. Recently, *ab initio* calculation works have theoretically indicated that metal encapsulated Si cage clusters have high structural stability compared with the pure Si clusters.[7] In the experimental works, however, there are still only a few reports on the formation of the Si cage clusters, and the encapsulated materials are limited to metal atoms.[8–10] In the case of carbon fullerenes such as C_{60} and C_{70}, on the other hand, not only the metal atoms but also noble gas atoms can be doped into carbon fullerenes,[11–13] and the noble gas-atom encapsulated C_{60} has the improved property in the superconductivity compared with the pristine C_{60}.[13] Furthermore, since the gas atoms are easily ionized and a large amount of gas ions can affect the formation of the Si clusters, the high efficient formation of the atom encapsulated Si clusters is expected when suitable plasma technology is adopted for that purpose. Therefore, it is desired to develop a method for the formation of cage-shaped Si clusters including the gas atoms in their cages.

In this letter, a Si plasma is generated by irradiating an electron beam on a Si lump in solid phase for the purpose of synthesizing the nanosized Si clusters, and then an inductively coupled argon (Ar) plasma is superimposed on the electron-beam-generated Si plasma, resulting in the encapsulation of an Ar atom into the cage of Si cluster.

An experimental apparatus is shown in Fig. 1. The Si lump, which is set in the tungsten crucible located at the axial position of $z=-7$ cm, is evaporated and ionized by a high energy electron beam (~4 keV) using an electron beam gun (EB gun; ANELVA, 980-7300), as shown in the inset of Fig. 1. In the case that the Ar plasma is generated and superimposed on the electron-beam-generated Si plasma (Si–Ar plasma), Ar gas is introduced and is ionized by applying a 13.56 MHz radio frequency (rf) power with a rf antenna located at $z=0$ cm through a matching box (M.B.) and a blocking capacitor (B.C.). A grounded mesh grid which is set at $z=-5$ cm (between the rf antenna and the EB gun) is used to protect the EB gun from exposure to a large amount of Ar plasma generated by the rf discharge. Plasma parameters are measured using a Langmuir probe installed at $z=-6$ cm. The experimental conditions are as follows: background gas pressure $P \leq 1$ mPa, Ar gas pressure $P_{Ar}=0-0.2$ Pa, rf power $P_{rf}=0-500$ W, and electron emission current of the EB gun, which can decide the amount of Si evaporation, $I_{EB}=0-150$ mA. An aluminum substrate is set at $z=0$ cm (inside the rf antenna) and is electrically floated. The Si clusters are formed by the Si or Si–Ar plasmas and are deposited on the substrate.

The mass analysis of the Si clusters deposited on the substrate is performed by using a laser-desorption time-of-flight mass spectrometer (LD-TOF-MS; Shimadzu, AXIMA-CFR+). To obtain the information on the existence of gas atom inside the Si clusters, a composition analysis is per-

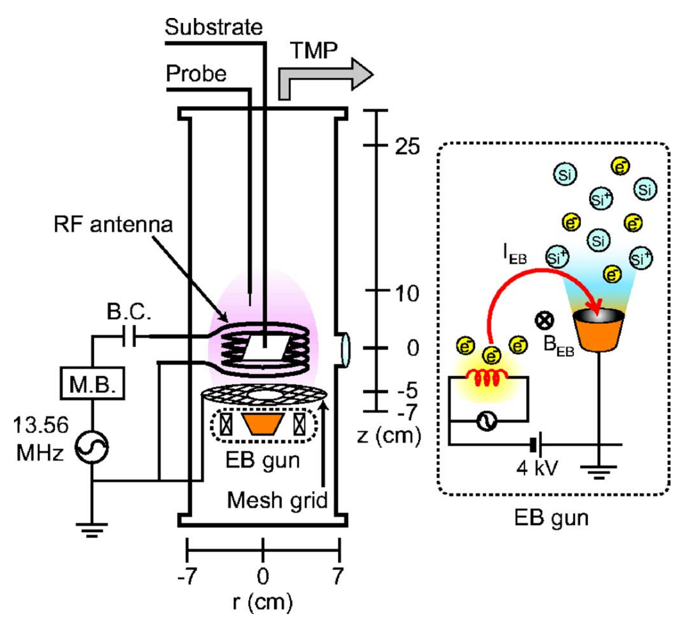

FIG. 1. (Color online) Schematic diagram of experimental setup.

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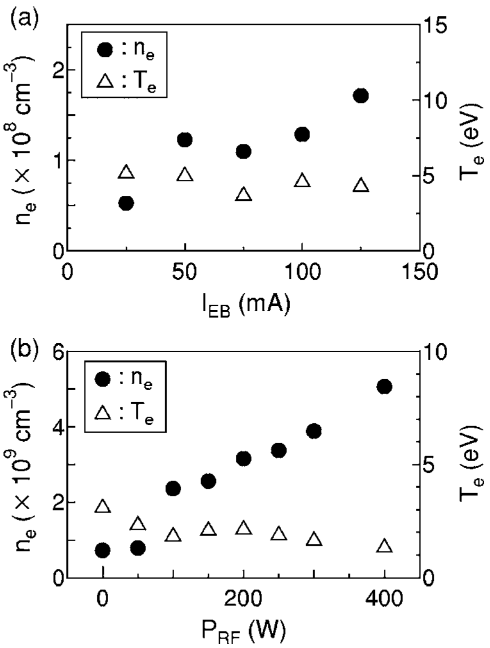

FIG. 2. Electron density n_e (closed circles) and electron temperature T_e (open triangles) as functions of (a) electron beam current I_{EB} without Ar plasma for P_{Ar}=0 Pa, P_{rf}=0 W, and (b) rf power P_{rf} for P_{Ar}=0.1 Pa, I_{EB}=100 mA.

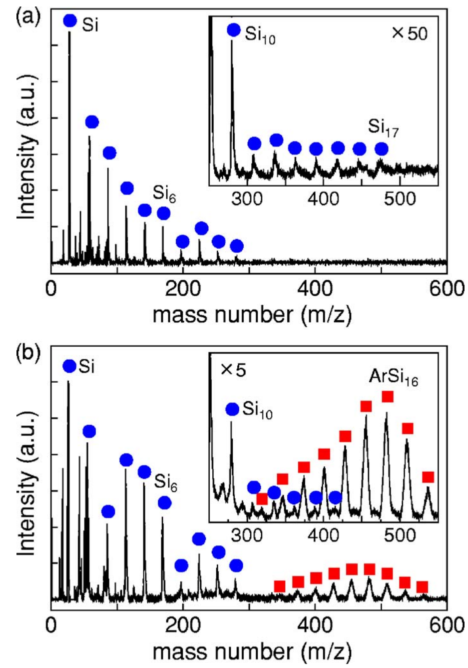

FIG. 3. (Color online) LD-TOF mass spectra of the Si clusters deposited on the substrate, which are produced by (a) the pure Si plasma for I_{EB}=100 mA, P_{Ar}=0 Pa, P_{rf}=0 W and (b) Si–Ar plasma for I_{EB}=100 mA, P_{Ar}=0.1 Pa, P_{rf}=300 W. Deposition time is t=10 min. The inset shows the magnification of the mass spectra in the range of 250–550 m/z.

formed by using an x-ray photoelectron spectrometer (XPS; JEOL, JPS-9010MC). Here, the deposited Si clusters are once taken out of the vacuum chamber and are transferred to LD-TOF-MS and XPS.

Figure 2 shows the electron density n_e (closed circles) and electron temperature T_e (open triangles) as functions of (a) electron beam current I_{EB} without Ar plasma for P_{Ar}=0 Pa, P_{rf}=0 W, and (b) rf power P_{rf} for P_{Ar}=0.1 Pa, I_{EB}=100 mA. Since the Ar plasma is absent in Fig. 2(a), the electron density denotes the Si ion density. It is found that the Si ion density gradually increases with an increase in I_{EB}, suggesting that the electron beam can evaporate and ionize Si and the Si plasma is easily generated using the electron beam gun. The electron temperature is almost kept at a constant value of 5 eV. In the case that the Ar plasma is generated, on the other hand, the electron density is one order of magnitude larger than the case in the absence of the Ar plasma and increases with an increase in P_{rf}. Since the Si ion density is determined by the electron beam current I_{EB} as mentioned above, the increment of the electron density in Fig. 2(b) is attributed to an increase in the Ar ion density. In our typical experimental condition, the density ratio of Ar to Si ions is about 40:1.

Figure 3 gives typical LD-TOF mass spectra of the Si clusters deposited on the substrate, which are produced by (a) the pure Si plasma for I_{EB}=100 mA, P_{Ar}=0 Pa, P_{rf}=0 W, and deposition time t=10 min, and (b) Si–Ar plasma for I_{EB}=100 mA, P_{Ar}=0.1 Pa, P_{rf}=300 W, and t=10 min. The Si clusters are detected as negative ions (negative ion mode) in LD-TOF-MS because the peak intensity of the LD-TOF mass spectra in the negative ion mode is larger than that in the positive ion mode. In the case of the pure Si plasma [Fig. 3(a)], the mass peaks of the Si clusters Si_n with n=1–17 are clearly observed, which are labeled by closed circles. Interestingly, it is found that the peak intensities for cluster sizes Si_n with n=7 and 11 drastically decrease compared with their neighbored clusters such as n=6 and 10, respectively. It is reported that the Si clusters structured with n=6 and 10 atoms are stable, reflecting so-called magic number.[1,5]

In the case of the Si–Ar plasma [Fig. 3(b)], on the other hand, Si clusters, the mass numbers of which are larger than the pure Si clusters by 40 m/z, are observed in the LD-TOF mass spectra in addition to the pure Si clusters Si_n (n=1–15). This mass number shift is considered to be attributed to the addition of Ar to the Si clusters, i.e., the Si clusters are doped with the Ar atom ($ArSi_n$), where the mass peaks of $ArSi_n$ are labeled by the closed squares. Furthermore, the number of Si in the formed $ArSi_n$ is found to be $n \geqslant 10$, which implies that Ar cannot interact with the small-sized Si clusters.

In order to clarify the composition of the formed Si clusters, we examine the XPS measurements. Figure 4 displays XPS peak intensities of the Si clusters deposited on the substrate, which are produced by (a) the pure Si plasma and (b) Si–Ar plasma. Both the XPS spectra in Figs. 4(a) and 4(b) show the peaks of Si 2s, Si 2$p_{3/2}$, C 1s, and O 1s, where the C and O are considered to be impurities blending in from the air in the measurement.

In the case that the Si–Ar plasma is used to form the Si cluster, on the other hand, clear peaks of Ar 2s and Ar 2$p_{3/2}$ in the XPS spectra are observed as well as Si 2s and Si 2$p_{3/2}$. These results suggest the possibilities that Ar is intercalated between the Si clusters or that Ar is encapsulated into the spherical-shaped Si cluster ($Ar@Si_n$). Based on the results of LD-TOF-MS [Fig. 3(b)] which presents the mass number shift from the pure Si cluster by 40 m/z, we can conclude that observed Ar is encapsulated into the Si cluster, because intercalated Ar might only weakly interact with the Si cluster and is believed to easily dissociate from the Si cluster when laser is irradiated in LD-TOF-MS.

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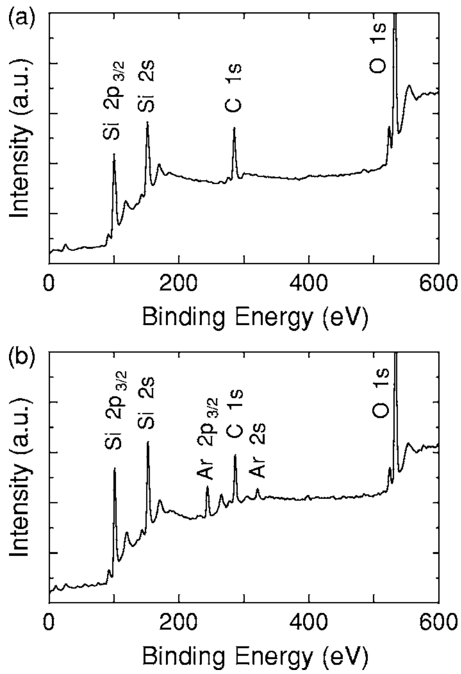

FIG. 4. XPS spectra of the Si clusters deposited on the substrate, which are produced by (a) the pure Si plasma for $I_{EB}=100$ mA, $P_{Ar}=0$ Pa, $P_{rf}=0$ W and (b) Si–Ar plasma for $I_{EB}=100$ mA, $P_{Ar}=0.1$ Pa, $P_{rf}=300$ W. Deposition time is $t=10$ min.

As mentioned above, the mass number shift by 40 m/z is considered to be caused by the encapsulation of Ar into the Si cluster. However, this mass number shift has the possibility to be attributed to a carbon (C), because the sum of C and Si mass numbers is 40 m/z which corresponds to the Ar mass number. In order to confirm whether this mass number shift is caused by Ar, we examine the formation of the Si cluster by using a krypton (Kr) plasma in place of the Ar plasma, which is superimposed on the Si plasma. In this case, the LD-TOF mass spectrum of the Si cluster is found to be similar to that in the case of the pure Si plasma, indicating no mass number shift by 40 m/z from the pure Si cluster. Based on this result, it is concluded that the mass number shift observed in the Si cluster formed by the Si–Ar plasma is caused by Ar. Meanwhile, the mass number shift by 84 m/z corresponding to Kr is also unseen. Since the atomic radius of Kr (201 pm) is larger than that of Ar (191 pm), and other metals which have been reported to be experimentally encapsulated into Si clusters, for example, hafnium (159 pm), tantalum (147 pm), tungsten (141 pm), and iridium (135 pm),[8–10] Kr is considered to be difficult to be encapsulated into the Si clusters owing to its size. This result suggests that the gas atoms smaller than Ar such as neon, halogen, and so on are expected to be encapsulated into the Si clusters.

When Ar is encapsulated into the Si cluster, the maximum peak of the LD-TOF mass spectra denotes that Ar@Si_n for $n=15-16$ is formed distinctively. These numbers of 15 and 16 are called the magic number in the case of the metal encapsulated Si clusters.[7,8,10] Thus, our results show that a notion of the magic numbered Si cluster can be applied to the case of the gas encapsulated Si cluster as well as the metal encapsulated one.

In summary, when a Si plasma is generated by an electron beam gun, the silicon clusters (Si_n; $n=1-17$) are found to be formed from a solid Si source. Furthermore, when a large amount of Ar ions is generated in addition to the Si plasma, the Si cluster doped with Ar atom ($ArSi_n$; $n=10-20$) is demonstrated to be formed. The formed $ArSi_n$ is confirmed to have a structure of Ar encapsulated Si cluster Ar@Si_n by means of LD-TOF-MS and XPS analyses and have the magic numbered cluster size $n=15$, 16 similar to the metal encapsulated Si clusters.

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