Photoelectron spectroscopy of silicon- and germanium-fluorine binary cluster anions (Si\textsubscript{n}F\textsubscript{m}\textsuperscript{−}, Ge\textsubscript{n}F\textsubscript{m}\textsuperscript{−})

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Abstract. Electronic properties of silicon-fluorine and germanium-fluorine cluster anions (Si\textsubscript{n}F\textsubscript{m}\textsuperscript{−}, Ge\textsubscript{n}F\textsubscript{m}−; \(n = 1–9, m = 1–3\), Ge\textsubscript{n}F\textsubscript{m}−; \(n = 1–9, m = 1–3\)) were investigated by photoelectron spectroscopy using a magnetic-bottle type electron spectrometer. The binary cluster anions were generated by a laser vaporization of a silicon/germanium rod in an He carrier gas mixed with a small amount of SiF\textsubscript{4} or F\textsubscript{2} gas. Comparison between photoelectron spectra of Si\textsubscript{n}F\textsubscript{m}/Ge\textsubscript{n}F\textsubscript{m} and Si\textsubscript{n}/Ge\textsubscript{n}− (\(n = 4–9\)) gives the insight that the doped F atom can remove one electron from the corresponding Si\textsubscript{n}/Ge\textsubscript{n}− cluster without any serious rearrangement of Si\textsubscript{n}/Ge\textsubscript{n} framework, because only the first peak of Si\textsubscript{n}/Ge\textsubscript{n}−, corresponding singly occupied molecular orbital (SOMO), disappears and other successive spectral features are unchanged with the F atom doping.

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I Introduction

Pure silicon and germanium clusters have been extensively studied both experimentally and theoretically, with reports on their formation and stability, physical and chemical properties, and structure [1–11]. Information on the electronic structures is especially indispensable to characterize the small silicon and germanium clusters. Furthermore, the evolution of the electronic level structure is an outstanding problem in order to determine the role that the Si\textsubscript{n} and Ge\textsubscript{n} clusters play in the deposition of amorphous silicon/germanium films.

A powerful experimental method to investigate the electronic structures of the Si\textsubscript{n}/Ge\textsubscript{n} clusters is photoelectron spectroscopy of a mass-selected cluster anion. The application of a magnetic bottle type electron spectrometer [12] to the clusters has been successfully demonstrated by Smalley and co-workers [13] and by Lutz and coworkers [14]. Recently, Eberhardt and co-workers have designed a new type of the magnetic bottle spectrometer with an improved energy resolution of less than 10 meV [15], where the Doppler broadening is reduced by an excellent deceleration technique reducing the kinetic energy of the target anions. While the resolution obtained in the photoelectron spectra of the cluster anions is typically lower than infra-red and UV/visible absorption experiments, they offer the advantage of mass separation prior to spectroscopic investigation, thereby eliminating any ambiguity concerning species identification. Electronically resolved photoelectron spectra (PES) of pure Si\textsubscript{n}− and Ge\textsubscript{n}− have been obtained by Smalley and co-workers for \(n = 3–12\) [4] and vibrationally resolved PES have been measured by Ellison and co-workers for Si\textsubscript{n}− and by Neumark and co-workers for Si\textsubscript{3}−–Si\textsubscript{15}− [5] and for Ge\textsubscript{n}− (\(n = 2–15\)) [11].

In this paper, we apply this approach to investigate electronic properties of the silicon and the germanium clusters with the doping of F atom in order to reveal their electronic states to compile a set of data for silicon fluoride. Since F atom possesses one vacant valency, the doped F atom deprives the Si\textsubscript{n}− and the Ge\textsubscript{n}− cluster anions of one valence electron. If the F atom can be added to the clusters without any changes in the geometry, then the F atom doping enables us to investigate the electronic structure of the Si\textsubscript{n} and the Ge\textsubscript{n} clusters. As reported previously [17], the Na doping into neutral Si\textsubscript{n} cluster and Si\textsubscript{n}− cluster anion results in one electron transfer from the Na atom to the corresponding cluster and provides the information on the electronic structures above the highest occupied molecular orbital (HOMO). In this work, therefore, the doping experiment of F atom is carried out to examine whether it is informative on the electronic structure of the Si\textsubscript{n} cluster as the Na atom doping was.

II Experimental section

The apparatus used in this work consists of a cluster anion source, a time-of-flight (TOF) mass spectrometer, and a magnetic-bottle type electron TOF spectrometer, and most of them was previously described elsewhere [18]. Silicon-fluorine and germanium-fluorine cluster anions were generated by a laser vaporization source. The second harmonics (532 nm) of a Nd\textsuperscript{3+}-YAG laser was focused onto a rotating and translating silicon/germanium rod and the resulting plasma was encountered in an He carrier gas (6 atm) mixed with any one of a F\textsubscript{2}/SiF\textsubscript{6}/SiF\textsubscript{4} gas from a pulsed valve. The
optimized pressures of these gases were used were 1, 10, and 20 Torr, respectively. The cluster anions grown in a channel (3 cm long, 2 mm diam.) cooled to ≈ 100 K by liquid N₂ were expanded through a skimmer. The generated anions were accelerated with a pulsed electric field to 3 keV for the TOF mass analysis or to 900 eV for photoelectron detachment. The mass resolution of the apparatus, \( M/\Delta M \), was \( \sim 100 \). After mass-separation, the only target anion selected by a mass gate was allowed to enter the deceleration region.

The improved deceleration technique [15] enabled us to achieve high resolution of 20 meV FWHM at 1 eV kinetic energy along with the enhancement of the ion density. The second (532 nm, 2.33 eV) or third (355 nm, 3.49 eV) or fourth (266 nm, 4.66 eV) harmonics of a pulsed Nd-YAG laser was used as the detachment laser light. The energy of the photoelectron was calibrated by measuring the photoelectron spectra of Au\(^{-} \) anion, at three different wavelengths of 355 nm and 266 nm, where the strong line attributed to the \( 1S_0 \rightarrow 2S_{1/2} \) transition could be observed [19, 20]. Each spectrum represents an accumulation of 10 000–30 000 shots typically. Laser powers of the detachment laser were in the range of 10–20 mJ/cm² for 355 nm and 1–3 mJ/cm² for 266 nm, and no power dependent processes for the spectrum shape were observed.

III. Results and discussion

A. Mass spectra of Si\(_{m}\)F\(_{m}^{-}\) and Ge\(_{n}\)F\(_{m}^{-}\) cluster anions

Figure 1 shows two TOF mass spectra of (a) Si\(_{n}\)F\(_{m}^{-}\) and (b) Ge\(_{n}\)F\(_{m}^{-}\) clusters produced under an He carrier gas mixed with F\(_{2}\) gas (1 Torr). In the mass spectra, relatively strong peaks are labeled with the notation \( n - m \), expressing the number of Si atoms (\( n \)) and F atoms (\( m \)), respectively. In order to generate a series of SiF\(_{m}^{-}\) and Si\(_{2}\)F\(_{m}^{-}\) \((m = 1–5)\), the SiF\(_{4}\) mixed gas was preferable for the carrier gas.

As shown in Fig.1, the F\(_{2}\) mixed gas was favorable to produce Si\(_{m}\)F\(_{m}^{-}/\text{Ge}_{m}\)F\(_{m}^{-}\) cluster anions \((n \geq 4)\) containing F atoms. In this condition the only anions containing only one F atom, Si\(_{n}\)F\(_{1}^{-}/\text{Ge}_{m}\)F\(_{1}^{-}\), were mainly produced, and the anions having more than two F atoms could not be produced efficiently. Since Si and Ge atoms have 4 valence electrons and F atoms have 7 valence electrons, the total number of valence electrons should preferably be even number.

In a series of F atom mixed clusters, the abundance of Si\(_{n}\)F\(^{-}/\text{Ge}_{m}\)F\(^{-}\) at \( n = 6, 7, \) and 10 are high compared to neighbors. This intensity distribution of Si\(_{n}\)F\(^{-}\) is strikingly similar to that obtained by photoionization of neutral Si\(_{m}\) clusters with 8.49 eV photon [7]. This similarity convincingly implies that the abundant Si\(_{n}\)F\(^{-}\) cluster is attributed to the stability of the corresponding neutral Si\(_{m}\) cluster. Namely, the F atom doped into Si\(_{m}\) cluster results in neutralization of the framework of the Si\(_{m}\) cluster. Furthermore, the doped F atom should be attached to the surface of Si\(_{m}\) cluster with no serious deformation of the geometry, otherwise the mass distribution of Si\(_{n}\)F\(^{-}\) would be different from that of the neutral Si\(_{m}\) cluster. As mentioned below in Sect. B.2., the neutralization of the Si\(_{m}\)F\(^{-}/\text{Ge}_{m}\)F\(^{-}\) framework with the F atom doping is ascertained from the viewpoint of electronic structures observed by photoelectron spectra of Si\(_{n}\)F\(^{-}/\text{Ge}_{m}\)F\(^{-}\).

III. Results and discussion

B. Photoelectron spectra of Si\(_{n}\)F\(_{m}^{-}\) and Ge\(_{n}\)F\(_{m}^{-}\) cluster anions

B.1 Si\(_{m}\)F\(_{m}^{-}\) and Si\(_{2}\)F\(_{m}^{-}\) series \((m = 1–5)\). Figure 2 shows the photoelectron spectra of Si\(_{m}\)F\(_{m}^{-}\) \((m = 1–3)\) and Si\(_{2}\)F\(_{m}^{-}\) \((m = 1–4)\) anions. In each spectrum the horizontal axis corresponds to the electron binding energy, \( E_b \), defined as \( E_b = \hbar \nu - E_k \) where \( E_k \) is the kinetic energy of the photoelectron. The detachment laser light used is 532 nm (2.33 eV) for SiF\(^{-}\) and SiF\(_{2}^{-}\), 266 nm (4.66 eV) for Si\(_{2}\)F\(_{1}^{-}\), and 355 nm (3.49 eV) for Si\(_{1}\)F\(_{m}^{-}\), respectively.

For SiF\(^{-}\), the 0-0 band is observed at the binding energy of 0.81 eV which was determined by changing the vibrational temperature of SiF\(^{-}\) with the different source conditions, e.g. different fluences of the vaporization laser. The binding energy of 0.81 eV corresponds to the EA of SiF\(^{-}\), as listed in Table I. Michels et al. [21] and Gutsev [22] have independently calculated the EA to be 0.82 and 0.76 eV by using a Pople’s G2 method and a local spin density approximation (LSDA) method, respectively, which are in good agreement with the experimental value of 0.81 eV in the present work. Furthermore, a vibrational progression can be identified with a vibrational frequency of 885 ± 70 cm\(^{-1}\) in the neutral ground state of X\(^2\)Π. This value is consistent...