Electronic States of Germanium-Oxide Clusters and Their Visible Emission

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Electronic properties of germanium-oxide (Ge_nO_m) and tin-oxide (Sn_nO_m) clusters were studied using photoelectron spectroscopy (PES) with a magnetic bottle-type electron spectrometer. In the mass spectra, the abundant clusters of both Ge-O and Sn-O were produced at the composition of 1:1. Compared between the PES of $Ge_nO_n^-$ and those of $Sn_nO_n^-$, it was found that those electronic and geometric structures are quite similar each other. Our developed method of halogen atom doping enables us to determine the HOMO-LUMO gap of the corresponding neutral Ge_nO_n/Sn_nO_n clusters experimentally, and it was found that the gap of the Ge_nO_n/Sn_nO_n clusters (n=2-6) correspond to the energy of the visible light. Correspondingly the strong visible photoluminescence peaked at 500 nm was observed under the excitation of 325 nm laser light from a deposited Ge-O sample which were made through the deposition of the Ge_nO_n clusters onto a substrate. This result implies that the Ge_nO_n clusters can be ascribed to the center of visible photoluminescence.
Key word: germanium-oxide, tin-oxide, photoelectron spectroscopy, visible photoluminescence

1. INTRODUCTION

From the viewpoint of technological application, a lot of attempts have recently been made to fabricate quantum-size structures based upon silicon or germanium,[1-3] since Canham has reported that intense visible photoluminescence (PL) could be observed form porous silicon of a quantum wire or train of quantum dots.[4] The usual PL spectrum of the quantum-size Ge nanocrystals embedded in a SiO_2 matrix with an average size of 6-8 nm is a broad band centered at 2.1-2.4 eV.[5,6] In spite of the numerous number of the reports, however, the luminescence mechanism of Ge nanocrystals is still a subject of controversy; nanocrystal itself and an oxide layer on the surface, since the emission wavelength in Ge nanocrystals does not show the size-dependence expected from simple quantum confinement models.[7] There are very few reliable reports on the relationship between the size and PL properties.

Recently, photoelectron spectroscopy has been proven to be a powerful technique to study the electronic and geometric structures of atomic clusters in gas phase as a function of cluster-size,[8,9] due to its ability to combine size selectivity with quantitative spectral sensitivity. Since photodetachment is a process of transition from the ground state of anion into the ground state or electronic excited states of the corresponding neutral, therefore, the electronic properties of the neutral clusters are readily observed from the photoelectron spectra

Very recently, we investigated the electronic properties of Ge_n clusters by the anion PES experiment combined with the doping of the halogen atom.[10] The HOMO-LUMO gap determined are 0.8-1.0 eV around n=30, indicating that the Ge_n cluster itself can never emit visible emission. In this work, we apply this methodology of the halogen-atom doping to investigate the electronic properties of Ge_nO_n and Sn_nO_n clusters and determine those HOMO-LUMO gaps. Since Sn belongs to the same group-14 as Ge in the periodic table, the electronic properties of Sn_nO_m are expected to be similar to those of Ge_nO_m. By measuring PL from germanium-oxide cluster deposited on a substrate, we will discuss the possibility of germanium-oxide and tin-oxide cluster as a center of visible emission.

2. EXPERIMENTS

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 have been described in detail previously.[11] Germanium-oxide and tin-oxide clusters were generated by a laser vaporization of germanium-oxide/tin-oxide rod which was prepared by pressing GeO_2/SnO_2 powder. The generated cluster ions were mass-analyzed in the TOF mass spectrometer accelerated with a pulsed electric field to 3 keV for mass analysis or to 900 eV for photoelectron detachment. After mass-separation, only the target anion selected by a mass gate was allowed to enter the deceleration region. The fourth (266 nm, 4.66 eV) harmonics of a pulsed Nd^{3+}-YAG laser was mainly employed for photodetachment.

After monitoring the mass distribution by TOF mass spectrometer, the substrate was put behind the skimmer, and the germanium-oxide produced were deposited onto the substrate under 10^{-5} Torr. The PL spectra from the deposited sample taken out under the atmosphere were measured with the excitation of a He-Cd laser (325 nm; 3.82 eV). The spectra were observed in the region from 350 nm to 850 nm.

3. RESULTS AND DISCUSSION

The abundant clusters were generated at the composition of Ge:O/Sn:O =1:1 in the mass spectra for both cation and anion, respectively. The distributions, not depending on the charge, show that the abundance of those clusters can be attributed to the stability of the corresponding neutral cluster. Indeed, those clusters are known to be geometrically stable in the neutral state due to a high symmetry.[12-15] Namely, it seems that the prominent neutral cluster produced by a laser vaporization should be Ge_nO_n/Sn_nO_n cluster.

Figure 1 shows the PES spectra of $Ge_nO_n^-$ and $Sn_nO_n^-$ (n=2-6) clusters at the 266 nm excitation. In the spectra, the horizontal axis corresponds to the electron binding energy, E_b, defined as $E_b = hv - E_k$ where E_k is the kinetic energy of the photoelectron. Arrows indicate threshold energies (E_T), and the E_T value corresponds to the upper limit of the adiabatic electron affinity (EA). Only for $Sn_4O_4^-$, the PES spectrum was taken with the 355 nm (3.49 eV) photon due to its low abundance.

On comparison between the PES spectra of $Ge_nO_n^-$ and those of $Sn_nO_n^-$ (n=2-6), it was found that the spectra are alike in the peak positions and the peak shapes except n=4. Together with the fact that Sn belongs to the same
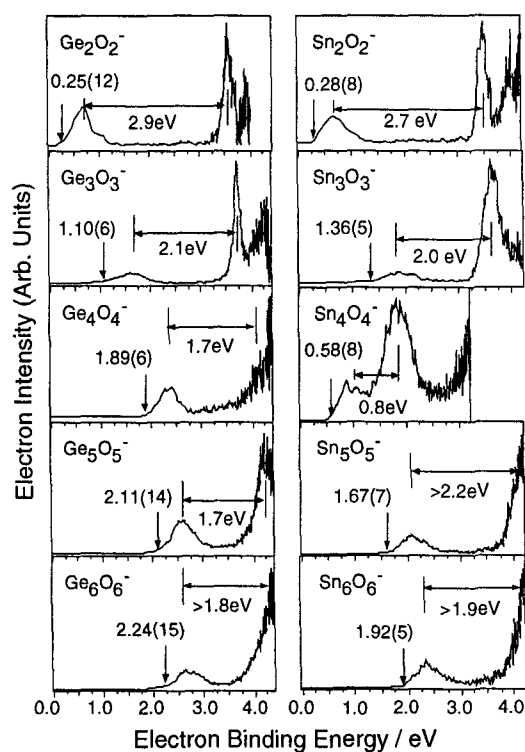
Figure 1. Photoelectron spectra of $Ge_nO_n^-$ and $Sn_nO_n^-$ (n=2-6) at 266 nm. Arrows indicate thresholds energies (E_T). The intervals of a sidewise arrow show the corresponding neutral HOMO-LUMO gap of Ge_nO_n and Sn_nO_n. The values of E_T are shown and numbers in parentheses indicate uncertainties in derived quantities;0.25(12) represent. 0.25±12.

group as Ge in the periodic table, this result convincingly implies that Ge_nO_n and Sn_nO_n clusters take a similar electronic and geometrical structure. This conclusion is consistent with the other reports on Ge_2O_2/Sn_2O_2 and Ge_3O_3/Sn_3O_3; the structures of Ge_2O_2/Sn_2O_2 and Ge_3O_3/Sn_3O_3 are a D_{2h} planar ring and a D_{3h} ring, respectively, which were determined by IR spectra,[12-14] Raman spectra,[13] PES spectra,[12,15] and ab initio calculations.[14,15]

Compared among the PES of $Ge_nO_n^-$ (n=2-6), it is found that those spectral features are essentially the same except that EA is shifted to higher binding energy with the increase of n; a sizable gap between the first and second electronic band is commonly observed. As mentioned above, Ge_2O_2 and Ge_3O_3 take ring structures and the structure of Ge_4O_4 determined by IR spectrum is also a C_{4v} ring.[12] Although there have been no previous work for n=5-6, based on this spectral similarity, we propose Ge_nO_n (n=5-6) to have a ring structure in common. The comparison among the PES of $Sn_nO_n^-$

gives the insight that the Sn_nO_n clusters also take ring structures except n=4. For Sn_4O_4, the heterocubanelike structure was derived from IR and Raman spectroscopic investigations of matrix-isolation species.[14] This result strongly suggests that Ge_nO_n/Sn_nO_n having a ring structure have a large energy gap between the first two peaks.

As mentioned in the previous work,[10] for a closed-shell semiconductor cluster, the least bound electron in the cluster anions resides alone in what corresponds to the LUMO of the neutral cluster and the next most weakly bound electrons resides in the HOMO of the neutral clusters because the extra charge produces no large-scale changes both in geometry and in electronic state. Without degeneracy in the electronic state, the energy gap should correspond to a HOMO-LUMO gap and this gap originates from the closed-shell electronic structures of the neutral species. Unless the HOMO has any vacancy due to degeneracy, the first peak in the spectra could be assigned to the singly occupied MO (SOMO) with the excess electron. Therefore, it is indispensable to distinguish the degeneracy of the HOMO in the neutral.

Figure 2 shows the PES spectra of $Ge_5O_5^-$ and $Ge_5O_5F^-$ at 266 nm. When the PES spectra are compared between them, it was found that the first small peak disappears with the F atom doping and the other features in the succeeding peaks seem almost the same. From this similarity of the photoelectron spectra, we are convinced that (1) the first small bump in the PES of $Ge_5O_5^-$ cluster anions is attributed to the LUMO in the corresponding neutral cluster (the SOMO in the cluster anion) and (2) the F atom can be added on the surface of their frameworks without any major geometric deformation. Namely, the electron in the SOMO can be removed from $Ge_5O_5^-$ cluster anion with the F-atom doping and the Ge_5O_5 framework is neutralized as well
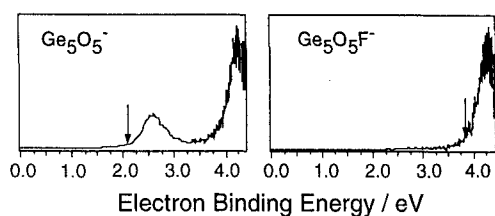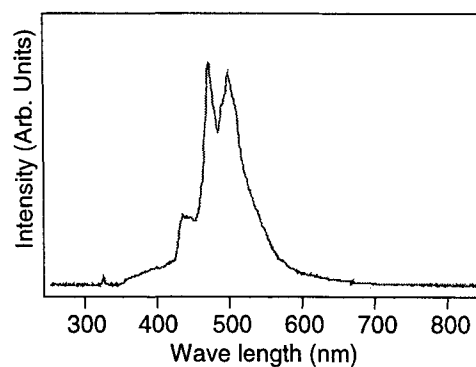
Figure 3. Photoluminescence spectra of Ge_nO_m clusters deposited on the silicon substrate.

as the case of Si_nF^- and Ge_nF^-.[16] Thus, the F atom doping method provides us with useful implement to determine the HOMO-LUMO gap of the neutral cluster. For the other Ge_nO_n (n=2-4,6) clusters, the HOMO-LUMO gap was determined with this methodology of the halogen-atom doping, although no PES spectra for the corresponding $Ge_nO_nF^-$ were shown in figure 1. The HOMO-LUMO gap of Sn_nO_n (n=2-6) was estimated by the similarity between the PES of $Ge_nO_n^-$ and those of $Sn_nO_n^-$. The HOMO-LUMO gap was indicated by a sidewise arrow in figure 1. However, the HOMO-LUMO gap obtained corresponds to the energy gap between the ground state and the lowest excited triplet state. Since the triplet state is located below the lowest singlet excited state because of coulomb repulsion, the energy of the fluorescence should be derived by the addition of the singlet-triplet splitting to the HOMO-LUMO gap if $\Delta S = 0$ selection rule applies. Although, there is no report on the energy of the singlet-triplet splitting for both Ge_nO_n and Sn_nO_n clusters, the splitting can be estimated to be blow 0.5 eV from the spectral feature. Namely, the estimated emission energies of Ge_nO_n and Sn_nO_n clusters correspond to the energy of visible light, implying that those ring species are likely to act as the center of visible emission.

In order to examine whether these Ge_nO_n clusters can really emit visible PL, PL spectra were measured. Figure 3 shows the PL spectra of Ge_nO_n clusters deposited on the silicon substrate. There was no detectable PL observed from only the substrate itself in the visible range. In the spectrum, the sharp and the strong visible PL peaked at 450 nm (2.9 eV), 480 nm (2.6 eV), and 500 nm (2.5 eV) were observed. These peak energies roughly consist with the emission energies

Figure 2. Photoelectron spectra of $Ge_5O_5^-$ and $Ge_5O_5F^-$ at 266 nm. Arrows indicate thresholds energies (E_T).

of Ge_nO_n clusters estimated by PES experiment and are independent of a variety of the substrate. As well as the fact that the abundant neutral clusters in the plasma produced by a laser vaporization are the Ge_nO_n clusters, these results imply that the origin of the visible PL is attributed to the ring Ge_nO_n species deposited on the substrate. Based on the spectral similarity, the ring Sn_nO_n species can be regarded as a luminous cluster, although no PL spectrum for clusters has been measured yet. When the method can be developed for the deposition of these clusters with the size selection, these Ge_nO_n/Sn_nO_n clusters are promising clusters for the fabrication of a new luminous device.

Acknowledgements

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