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Probing structural transitions of nanosize silicon clusters via anion photoelectron spectroscopy at 7.9 eV

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Abstract

Photoelectron spectra of silicon cluster anions as large as Si_{35}^- have been obtained with vacuum ultraviolet radiation at 157 nm (7.9 eV). The data show spectroscopic trends consistent with the structural transformation from prolate to more spherical clusters previously observed in ion mobility experiments. In addition, we observe signal at high electron binding energy that may be analogous to the second band seen in the photoemission spectrum of bulk silicon.

Determination of the spectroscopy and structure of semiconductor clusters remains a central problem in cluster science. Silicon clusters are of particular interest, in part because of the key role that silicon plays in semiconductor fabrication, and considerable experimental and theoretical effort has been expended in understanding the evolution of their properties as a function of size. Several relatively small neutral and charged Si_n clusters ($n \leqslant 10$) have been investigated in detail through a combination of vibrationally resolved anion photoelectron spectroscopy in the gas phase [1–3], infrared, Raman and electronic spectra of matrix-isolated neutral and anionic clusters [4–6], and electronic structure calculations [7–9], yielding information on the geometries and vibrational frequencies of the ground and low lying electronic states. Studies of larger silicon clusters are greatly complicated by the increasing occurrence of low-lying local minima [10–14]. Ion mobility studies of silicon cation and anion clusters have proved very valuable in this regard [15–18]; these experiments have indicated that the clusters evolve from prolate to more compact spherical structures in the size range of $n = 20$–30, with the size at which this transition occurs dependent on the charge state of the cluster. The presence of such a structural transition in this size regime is supported by electronic structure calculations and, less directly, by measurements of the ionization potential of neutral silicon clusters [19].

In this Letter, we present vacuum ultraviolet photoelectron spectra of size-selected Si cluster anions as large as Si_{35}^- obtained at a photodetachment wavelength of 157 nm (7.9 eV), a higher photon energy than was previously used in anion PE spectroscopy studies in this cluster size range [20–23]. These spectra map out transitions between electronic states of the anionic and neutral clusters. This work was motivated by two considerations. First, we wanted to see if there was a spectroscopic signature associated with the prolate → spherical structural transition in these clusters. In addition, following on our recent investigation of the PE spectroscopy of $In_xP_x^-$ clusters at 157 nm [24], we wished to explore connections between the bulk photoemission spectrum of silicon and the cluster PE spectra in this nanosize regime.

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The anion photoelectron spectrometer used in these studies has been described elsewhere in detail [24,25]. Key features are as follows: Si_n^- clusters were produced in a pulsed laser ablation molecular beam source using Ar as carrier gas. The negative ions were mass-analyzed in a linear reflection time-of-flight mass spectrometer for which $m/\Delta m \approx 2000$ at an average beam energy of 3.75 keV, and photodetached with a pulsed fixed frequency, F_2 excimer laser (GAM EX50F), operating at 157 nm, 20 Hz repetition rate, and 2 mJ/pulse, with unstable resonator optics. The electron kinetic energy (eKE) of the photodetached electrons were determined by time-of-flight measurements using a magnetic bottle analyzer. To reduce the background photoelectron intensity all the spectra shown here were background-subtracted.

The PE spectra of Si_n^- ($n = 4$–35) taken at 157 nm are displayed in Fig. 1. The spectra are plotted as a function of electron binding energy (eBE), defined as eBE = hv − eKE, where hv is the laser detachment energy (7.9 eV). The spectra for $n \leqslant 22$ comprise an intense feature about 2 eV wide located between 2 and 6 eV, and generally shifting toward higher eBE with increasing cluster size. In addition, there is a distinct dip around 6–7 eV, and sharply rising signal for eBE > 7 eV. Starting at $n = 19$, the gap in signal in the 6–7 eV range begins to fill, and by $n = 27$ the low eBE feature has broadened and dropped in intensity relatively to the signal at higher eBE to the point where it is barely distinguishable.

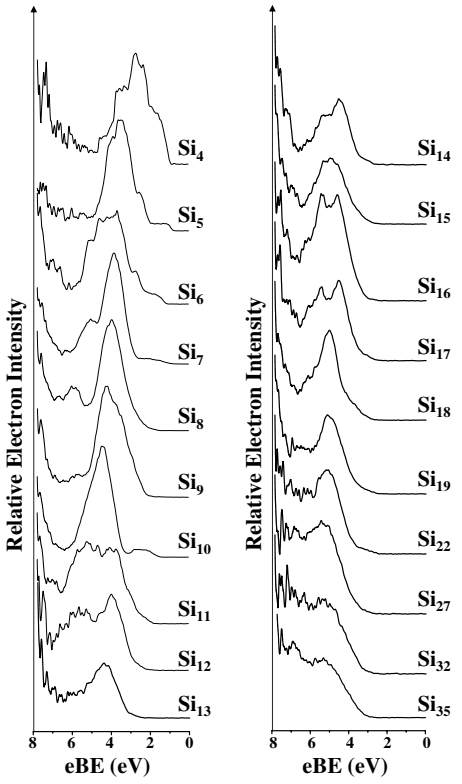

Fig. 1. Anion photoelectron spectra of Si_n^- ($n = 4$–35) clusters at 7.9 eV photon detachment energy.

Neither the dip from 6–7 eV nor the rise in signal above 7 eV were seen in previously reported PE spectra of silicon cluster anions in this size range because of the lower photon energy (6.4 eV) used in those experiments [22,23]. The signal between 2 and 6 eV appears as a single peak in some spectra ($n = 8$, 10, 15, 18–22) and a series of partially resolved features in the other spectra. However, our spectra are somewhat lower resolution than those previously reported at 6.4 eV, in part because photoelectrons corresponding to features with the same eBE are faster in our experiment owing to the higher photon energy; comparison with the earlier spectra shows in all cases that the signal in this energy range is composed of overlapping transitions to various electronic states of the neutral clusters.

The main new result seen in our PE spectra is the evolution of the signal at eBE = 6 eV from $n = 19$ to 35. The gradual disappearance of spectral structure in this size range might at first be attributed to greater spectral congestion as the cluster size increases. While this explanation cannot be ruled out, we point out that in our recent PE spectra of $In_xP_x^-$ clusters at 7.9 eV, the spectra from $x = 9$–13 all showed two distinct peaks with little evidence for increased broadening from spectral congestion [24].

A more intriguing interpretation of the Si_n^- PE spectra is that the observed trends result from structural evolution of the clusters. The ion mobility experiments of Jarrold and co-workers [17] showed that silicon cluster cations undergo a transition from extended prolate to compact, more spherical structures between $n = 24$ and 28, and that a similar structural transformation for anions occurs between $n = 26$ and 30. While these are the cluster sizes over which the most change occurs in the mobility experiments, Jarrold observes traces of the spherical structure for clusters as small as Si_{22}^-, and still sees signal from the prolate structure for Si_{35}^-.

Our spectra can be explained within this conceptual framework if we attribute the filling in of the gap from 6 to 7 eV and the decrease in intensity of the low eBE peak to an increasing population of the more spherical anion structure at the expense of the prolate structure. Hence, the low eBE feature for $n \leqslant 22$ is from transitions between prolate structures of the anion and neutral clusters, and the signal that is first apparent between 6 and 7 eV is from transitions between more spherical anion and neutral clusters. Since photodetachment is vertical, photodetachment transitions between anion and neutral states with very different geometries (prolate → spherical, for example) will be very weak in the PE spectra.

This interpretation of the PE spectrum implies that photodetachment transitions between more spherical

structures cover a wider energy range than those between prolate structures. This range is determined by the energy spectrum of the electronic states of the neutral cluster, since transitions to individual electronic states are not resolved in the $n = 19$–35 size range. We can use Koopman's theorem to obtain vertical detachment energies and electronic bandwidths from the spectrum of molecular orbital binding energies ε_i in neutral Si_n clusters. These energies have been calculated and reported by Sieck et al. [26] for a series of Si cluster sizes and geometries. In the case of Si_{25}, it was found that the energies for the highest occupied MOs formed a band about 1.5 eV wide for the prolate structures, while for the lowest energy spherical structure this band was over 2 eV wide. The broader band for spherical geometries is consistent with our interpretation of the PE spectra.

We close by discussing what relationships may exist between our PE spectra and the photoemission spectrum of bulk silicon. The photoemission spectrum maps out the valence bands of bulk silicon. The anion cluster PE spectrum yields the binding energy of the excess electron in the cluster (the electron affinity), but most of the signal in our spectra is from more tightly bound electrons and can therefore be compared to the bulk photoemission spectrum to test the effects of finite size, non-tetrahedral bonding motifs, etc. The valence photoemission spectrum comprises three bands with maxima at 2.2, 6.6 and 9.2 eV [27]; the electronic states contributing to the band at 2.2 eV are from linear combinations of Si 3pπ orbitals, while the 6.6 eV band is from linear combinations of Si 3p and 3s orbitals [28,29].

As mentioned above, the anion PE spectra generally show an increase in signal at binding energies above 7 eV. In comparing the bulk vs. cluster spectra, the excess electron in the anion should have little effect on the energies of the more tightly bound orbitals (Koopman's theorem, again), so it is valid to compare splittings between bulk and cluster PE spectra but not absolute values of binding energies. Such a comparison suggests that the claim that the band at low eBE (for $n \leqslant 27$) and rising signal above 7 eV in the cluster PE spectra are analogous to the two most weakly bound bands in the photoemission spectrum. Unfortunately, our photon energy of 7.9 eV is insufficient to map out the full extent of the signal at high eBE in the cluster spectra, and we cannot tell if it is the tail of a real peak. One concern, for example, is that this signal could instead result from cluster thermionic emission, as has been seen in the photoelectron spectra of negatively charged and neutral clusters [30]. Planned experiments at higher photon energy and using velocity-map imaging detection of the photoelectrons [31] should resolve this issue.

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