Photoelectron spectroscopy of chromium-doped silicon cluster anions

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The photoelectron spectra of chromium-doped silicon cluster anions, $CrSi_n^-$, were measured over the size range, $n=8-12$. Their vertical detachment energies were measured to be 2.71, 2.88, 2.87, 2.95, and 3.18 eV, respectively. Our results support theoretical calculations by Khanna, Rao, and Jena [Phys. Rev. Lett. **89**, 016803 (2002)] which found $CrSi_{12}$ to be an enhanced stability (magic) cluster with its chromium atom encapsulated inside a silicon cage and with its magnetic moment completely quenched by the effects of the surrounding cage. © *2005 American Institute of Physics.*
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Silicon and carbon possess many similarities due to periodicity. In contrast to carbon, however, elemental silicon favors sp^3 hybridization and thus prefers to be tetrahedrally coordinated. At the microscopic size level, where many experimental and theoretical studies of homogeneous silicon clusters have been conducted,[1–12] silicon fails to show carbon's propensity for forming clusters with hollow cage structures. Endohedral cage structures, on the other hand, are another matter. These are well known in the fullerenes, and their viability has stimulated numerous theoretical and experimental studies of silicon-encapsulated, metal atom, cage-like clusters, MSi_n, which are also sometimes denoted by $M@Si_n$. The earliest experimental study of metal-doped silicon clusters was conducted by Beck.[13,14] He reported a mass spectrometric study of MSi_n^+ cluster cations (M=Cr, Mo, W, and Cu), finding MSi_{15}^+ and MSi_{16}^+ to be the most intense species when M=Cr, Mo, or W. The earliest reported theoretical calculations on such cluster systems were performed by Jackson *et al.*[15] who found $Zr@Si_{20}$ to be a very stable cluster. Subsequent theoretical calculations by Han and Shi[16] on MSi_{15} (M=Cr, Mo, and W) and by Kumar and Kawazoe[17] on MSi_{16} (M=Hf, Zr, and Ti) were carried out to study their stability and electronic structure. Then came a particularly important experiment by Hiura, Kanayama, and co-workers[18] on complexes involving metal atoms and Si_n clusters. It substantiated the above ideas by demonstrating that clusters such as WSi_{12} are both endohedral and very stable. Assuming that each silicon atom contributes one electron and the tungsten atom contributes 6 electrons, the authors suggested that the enhanced stability of WSi_{12} could be a consequence of the 18-electron rule, well known in chemistry. The discovery of stable, endohedral WSi_{12} ignited a flurry of theoretical activity. Hiura and co-workers themselves explored the topology and energetics of metal-encapsulating silicon cage clusters.[19] Khanna *et al.* performed calculations on silicon-encapsulated, chromium and iron atom clusters.[20,21] Hagelberg *et al.*[22–27] conducted extensive calculations on the geometric and electronic structures of MSi_n (M=Cu, Sc, Mo, and W). Sun and co-workers[28] did

calculations investigating dodecahedral cages of silicon encapsulating Ba, Sr, Ca, Zr, and Pb atoms, and Lu *et al.*[29] conducted calculations exploring the metal-doped silicon clusters, MSi_n (M=W, Zr, Os, Pt, and Co). On the experimental front, Kaya, Nakajima, and co-workers[30,31] measured the photoelectron spectra of MSi_n^- (M=Tb, Ti, Hf, Mo, and W). Kumar and Kawazoe conducted calculations[32,33] that showed metal-doped silicon clusters are capable of forming fullerene-like, cubic, or Frank–Kasper polyhedron structures, and they also investigated the possibility of forming metal-doped silicon nanotubes. Additionally, Mitas *et al.*[34] carried out computational studies of the electronic structures of numerous transition metal atoms in Si_{12} hexagonal prism cages, finding the 18 electron rule to have only limited applicability in these systems.

Along with fundamental interest in the stabilities of metal-doped silicon clusters, there are also technological reasons for being excited about them. The properties of this class of clusters may be valuable to several related industries. If specific sizes are stable enough to form cluster assembled materials, silicon-encapsulated metal atom nanoclusters could be used to tailor band gaps with heretofore unattainable specificity. This could lead to applications in both the microelectronics and optoelectronic industries. One can also imagine impregnating silicon clusters with metal atoms that carry sizable magnetic moments, since these may be important in the emerging field of spintronics. Cluster-assembled materials of this type could provide a transitional stepping-stone between the traditional world of silicon-based electronics and the futuristic world of spintronics.

In this paper, we report the photoelectron spectroscopic study of silicon-chromium cluster anions, $n=8-12$, focusing on $n=12$. Calculations by Khanna, Rao, and Jena[20] have explored the structure, stability, electronic, and magnetic properties of $CrSi_{12}$. They found the chromium atom to be encapsulated in a silicon cage, which it stabilizes. Interestingly, they also found the magnetic moment of chromium, the largest among the first row transition metals, to be completely quenched by its interaction with its silicon cage. Here, we compare results derived from our measured photoelectron spectrum of $CrSi_{12}^-$ with the vertical detachment energy predicted by their calculations as a way of testing the validity of

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their findings. The excellent agreement between these measured and calculated electronic properties suggests that the calculated structural and magnetic results are also correct.

Negative ion photoelectron (photodetachment) spectroscopy is conducted by crossing a mass-selected beam of anions with a fixed-frequency photon beam and energy analyzing the resultant photodetached electrons. This technique is a direct approach to measuring electron binding energies, and it is governed by the energy-conserving relationship, $h\nu$ =EKE+EBE, where $h\nu$ is the photon energy, EBE is the electron binding energy (the photodetachment transition energy) and EKE is the measured electron kinetic energy. The details of our apparatus have been given elsewhere.[35] Briefly, both mass spectra and photoelectron spectra were collected on an apparatus consisting of a laser vaporization source employing a Nd:YAG laser, a linear time-of-flight mass spectrometer for mass analysis and selection, a second Nd:YAG laser for photodetachment, and a magnetic bottle for electron energy analysis. Cr/Si cluster anions were generated by laser vaporization (2.331 eV/photon) of a rotating and translating chromium-coated silicon rod. The carrier gas used for the laser vaporization source was highly purified helium which issued from a pulsed valve having a ~4 atm backing pressure. Size-selected $CrSi_n^-$ cluster anions were photodetached with 3.493 eV photons. The resolution of our magnetic bottle electron energy analyzer is ~35 meV at an EKE of ~1 eV.

Chromium-coated silicon rods were prepared in a separate, dedicated vacuum vaporization apparatus. Inside, several small pieces of chromium chip were placed in a tungsten boat, which itself was heated to ~1500 °K by running ~220 amperes of direct current through it to sublime the chromium metal. A pure silicon rod (99.999%, 5 mm diameter, from Goodfellow) was positioned ~4 cm above the tungsten boat, and it was rotated by a motor at the speed of one turn per minute for an exposure time of about an hour. During vaporization, the pressure in the chamber was kept below 2×10^{-4} Pa. Also, the electric bus bar connections and the wall of the chamber were continuously cooled with flowing water. Once the heating current was turned off, and the boat and rod had cooled, the chamber was bled with argon. The chromium coated silicon rod was then moved rapidly into the laser ablation source chamber where it was placed under vacuum in order to minimize oxidation.

Our mass spectrum showing Si_n^-, $CrSi_n^-$, and OSi_n^- cluster anions is shown in Fig. 1. Unit mass resolution was achieved throughout the mass range shown. The dominant peaks in the mass spectrum are those of homogeneous silicon cluster anions. At cluster sizes below $n=8$, $CrSi_n^-$ ion intensities are significantly weaker than they are at $n=8$ and larger. No $Cr_2Si_n^-$ was observed, probably because of the thinness of chromium deposited on the silicon rod. Mass peaks belonging to OSi_n^- were due to the oxidation of the silicon rod.

The photoelectron spectra of $CrSi_n^-$ ($n=8-12$) cluster anions are presented in Fig. 2. Each of these spectra are dominated by a relatively narrow peak on the low EBE side of the observed spectrum. A second feature at higher EBE is also partially visible. These features are primarily electronic transitions from the ground states of the $CrSi_n^-$ cluster anions to the ground and first excited states of their corresponding neu-
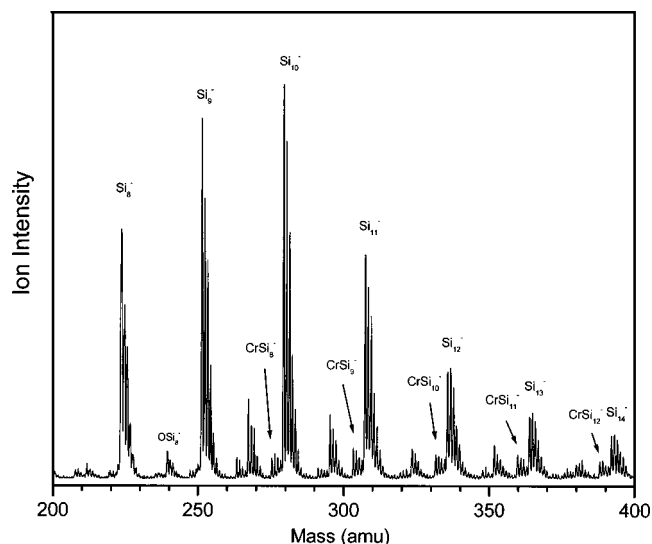

FIG. 1. A typical anion mass spectrum observed during these experiments. It was produced by laser vaporizing a translating, rotating chromium-coated silicon rod during the open cycle of a pulsed valve of helium gas.

tral clusters, $CrSi_n$, respectively. The narrow width of the lower EBE peaks (the ground state-to-ground state transitions) implies that the structures of the cluster anions and their corresponding neutral clusters are somewhat similar. The EBE of the maximum in this peak is interpreted as the vertical detachment energy, VDE, of a given cluster anion. The VDE values of $CrSi_n^-$ are 2.71, 2.88, 2.87, 2.95, and 3.18 eV for $n=8-12$, respectively. The uncertainty in these values is typically ±0.05 eV. Since adiabatic electron affinities are difficult to extract with confidence from these spectra, and since VDE values are well-defined, we focus here on comparisons between theoretical and our experimental VDE values.

In a theoretical study of the equilibrium geometries and total energies of a chromium atom encapsulated in silicon cages, Khanna, Rao, and Jena[20] found $CrSi_{12}$ to show special stability, i.e., to exhibit magic behavior. Their calculations showed $CrSi_{12}$ to have a hexagonal bi-prism structure with D_{6h} symmetry. In this structure, the chromium atom is sandwiched by two Si_6 hexagonal rings. The enhanced stability of $CrSi_{12}$ is consistent with the 18-electron rule of organometallic chemistry. Since the electronic configuration of Cr is $3d^54s^1$, chromium has 6 valence electrons, and assuming that each silicon atom can contribute one electron, the total number of available valence electrons is 18. Especially interesting was the predicted effect of caging on the magnetic moment of the chromium atom. Chromium has the highest magnetic moment (6 μB) of the first row, transition metal atoms, and yet, when it is trapped in the above-mentioned cage of 12 silicon atoms, its magnetic moment is *completely quenched*.

In addition to geometrical structures and magnetic moments, Khanna and co-workers also calculated the vertical detachment energies of $CrSi_{11}^-$ and $CrSi_{12}^-$ cluster anions. Correctly calculating these electronic properties is a stringent test of the theoretical methods utilized in their study. A comparison of measured versus predicted VDE values thus provides a criterion for evaluating the broader validity of their
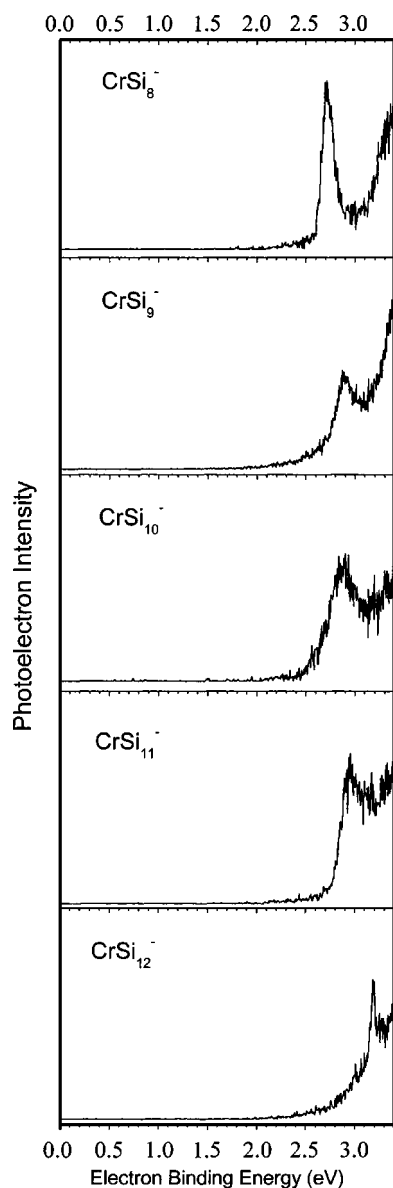
FIG. 2. The photoelectron spectra of $CrSi_n^-$ cluster anions, $n=8-12$. These spectra were recorded using the 355 nm (3.49 eV) output of a Nd:YAG laser.

tally. Experimentally, the main tool has been negative ion photoelectron spectroscopy, where Kaya *et al.*[30,31] measured the spectra of $MoSi_n^-$ and WSi_n^-, and where we measured the spectra of $CrSi_n^-$. The spectra of $MoSi_n^-$ and WSi_n^-, which are similar to one another, are relatively dissimilar to the spectra of $CrSi_n^-$. The lowest EBE peaks in the spectra of $CrSi_n^-$ tend to be sharper and more distinct than the lowest EBE peaks in the spectra $MoSi_n^-$ and WSi_n^-. In fact, by $n=10-12$, those peaks in the spectra of $MoSi_n^-$ and WSi_n^- have diminished in intensity to the point that they are becoming difficult to discern. These observations indicate that there are significant differences between $CrSi_n$ clusters versus $MoSi_n$ and WSi_n clusters. For $MoSi_n$ and WSi_n clusters, Nakajima and co-workers[30,31] have interpreted their data as indicating that Mo and W atom encapsulation in a silicon cage occurs at $n \geqslant 15$. The smallest size considered in the $CrSi_n$ study conducted by Jena and co-workers[20,21] was $n=11$, but even by that size, the chromium atom had become encapsulated. Theoretical studies by Han and Hagelberg[22] did not find Cr encapsulation up to size, $n=6$ for $CrSi_n$ neutral clusters, while at $n=15$, computations by Han and Shi[16] found encapsulation for $CrSi_{15}^+$ cations but not for $CrSi_{15}$ neutral. We note that the atomic radius of chromium is smaller than that of molybdenum and tungsten, which are about equal to one another, and that the intensities of $CrSi_n^-$ cluster anions below $n=8$ were significantly lower than those at $n \geqslant 8$ in our mass spectra. We speculate that the onset of metal encapsulation in $CrSi_n^-$ cluster anions occurs at $n=8$, and we urge theorists to look into this possibility.

findings. Their calculations found a VDE of 3.11 eV for $CrSi_{12}^-$. We measured the VDE of $CrSi_{12}^-$ to be 3.18 eV. The sharp, narrow peak representing the ground state anion-to-ground state neutral transition in our spectrum is consistent with the theoretical prediction that $CrSi_{12}^-$ and $CrSi_{12}$ must have similar structures. For $CrSi_{11}^-$, Khanna and coworkers predicted a VDE of 2.86 eV. We measured the VDE of $CrSi_{11}^-$ to be 2.95 eV. The pertinent spectral peak in the spectrum of $CrSi_{11}^-$ is not as narrow as it was in the case of $CrSi_{12}^-$, suggesting that the difference between anion and neutral structures is greater for $n=11$ than it was for $n=12$. That too is consistent with the theoretically predicted results. The agreement between these measured and calculated electronic properties suggests that the calculated structural and magnetic results are also on the right track.

MSi_n clusters for all three of the transition metal atoms in the Group VIB column of the periodic table (M=Cr, Mo, and W) have been studied both theoretically and experimen-

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