Spectroscopy of Neutral Silicon Clusters, Si_{18}–Si_{41}: Spectra Are Remarkably Size Independent

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Absorption spectra from 0.94–5.58 eV are obtained for gas-phase neutral silicon clusters Si_{18}–Si_{41} using resonant one- and two-color photodissociation spectroscopy. The spectra of all clusters are essentially identical. Above 3.0 eV, they exhibit six sharp absorption peaks with cross sections of 1–2 Å^2. Multiple photon absorption peaks dominate the spectrum below 3.0 eV. Comparisons of the silicon cluster spectra to those of various forms of silicon show that they have much in common with the spectrum of bulk diamond-lattice crystalline silicon.

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The first optical spectra have been recorded for neutral silicon clusters containing 18–41 atoms. These spectra reveal a surprise: Minute silicon clusters have numerous strong, sharp absorptions which do not shift in energy over this entire cluster size range. Our results are totally unexpected since theoretical calculations predict a wide variation in structure over the size range of these clusters [1]. Moreover, we expect that these tiny pieces of silicon where most of the atoms are on the surface should be greatly reconstructed from bulk silicon. Yet, the optical signature of these clusters has much in common with that of crystalline silicon.

Photodissociation spectroscopy is used to record the absorption spectra of neutral silicon clusters as detailed elsewhere [2,3]. Both one- and two-color resonant photodissociation (R1PD and R2PD) studies are performed so as to clearly separate the absorption spectra from dissociation events, particularly at energies below the dissociation threshold [2,3]. Briefly, a supersonic beam containing neutral silicon clusters is generated by laser evaporation of 99.999% pure silicon into a high-pressure He carrier gas pulse which then expands through a nozzle into vacuum. R1PD or R2PD spectroscopy is performed by intercepting the cluster beam with one or two collinear counterpropagating laser beams when the clusters have traveled a distance of 4–6 cm from the nozzle. The clusters then travel for 400 μs before they reach the ionization region of a time-of-flight mass spectrometer. Ionization is accomplished with the 7.9-eV output of a F_2 excimer laser which is kept below 0.1–0.3 mJ/cm^2 in order to prevent fragmentation during ionization. Absorption of the laser photons is observed when it results in dissociation of the excited cluster and thus a depletion of the ion-mass signal. The fraction of clusters which photodissociate at a given laser wavelength is determined by recording cluster mass spectra with and without the R1PD-R2PD incident laser photons. We emphasize that we are careful to perform spectroscopy on a well-established silicon cluster population in a collision-free molecular beam. We do not, e.g., irradiate the clusters while they are still in the source and expansion region as

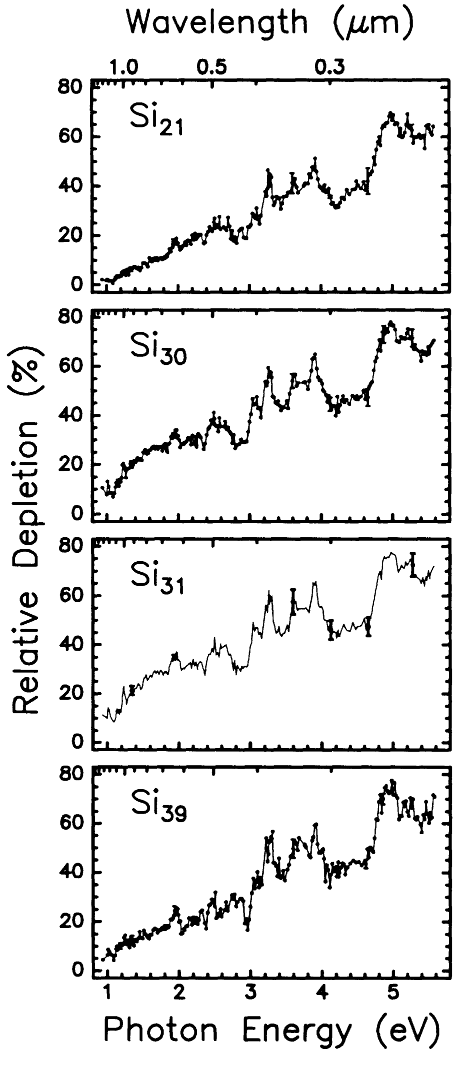

FIG. 1. Photodissociation spectra of Si_{21}, Si_{30}, Si_{31}, and Si_{39}. These spectra combine R2PD (0.94–1.51 eV) and R1PD (> 1.51 eV) data [3]. Data points (●) are connected by straight lines but are omitted for Si_{31} so that the representative error bars (at 1.16, 1.35, 1.94, 3.60, 4.13, 4.66, and 5.28 eV) can be seen.

this is known to introduce anomalous photodepletion of various clusters as a result of seriously perturbing the cluster population during its formation and cooling [2-4]. Thus we know that we are recording spectra of isolated silicon clusters whose size and photodissociation can be measured with confidence.

The spectra reported herein are for the size range of Si_{18}-Si_{41} which can be simultaneously monitored in the present configuration of our mass spectrometer. These spectra span 0.94-5.58 eV which is the tuning range of our various R1PD-R2PD lasers. Four representative cluster spectra are shown in Fig. 1. These spectra are recorded at different laser fluences depending on the excitation energy: 60 mJ/cm^2 for 0.93-2.26 eV, 15 mJ/cm^2 for 2.26-2.74 eV, and 10 mJ/cm^2 for >2.74 eV. Full spectra are obtained by scaling these data ranges with respect to each other using common data points [3]. Based on previous studies of InP clusters formed under similar conditions, we estimate that the silicon cluster internal temperatures are 700-900 K [2,3].

Silicon clusters exhibit rich spectra as exemplified in Fig. 1. Excitation laser power-dependence studies, Fig. 2, show that the spectra can be divided into two parts. The first lies at energies above 3 eV. Here the peaks result from transitions which are rate limited by one-photon absorptions. Many of these peaks exhibit saturation power dependencies even at the lowest laser fluences that we are able to use for our experiments, e.g., at 3.68 eV in Fig. 2. The second part of these spectra lies below 3 eV where various peaks in the spectra arise from multiple photon excitations. Furthermore, these peaks ride on a broad background absorption. The power dependencies of these peaks, e.g., at 1.98 and 2.58 eV in Fig. 2, have slopes which are less than the expected photon order (see below), indicating that the broad background absorption results from transitions which are rate limited by one-photon transitions.

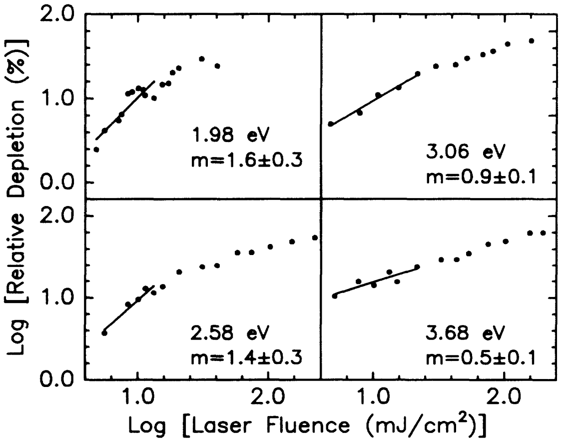

FIG. 2. Laser fluence dependence of four selected peaks in the Si_{30} spectrum. The early portion of each graph is fitted to a line whose slope m indicates the photon order of the absorption.

Six distinct spectral peaks are seen between 3.0 and 5.6 eV. Using a Lorentzian line-shape analysis, the six peak maxima are determined to be at 3.05, 3.27, 3.63, 3.90, 4.94, and 5.25 eV. *Remarkably, all of the* Si_{18}-Si_{41} *spectra exhibit all six peaks at the same six energy maxima to within* ± 0.02 *eV*. The positions of these peaks do not correspond to any known spectra of a pure silicon entity such as the atom or dimer [5]. Thus we are confident that we do not have interferences from atomic lines such as have been observed in other cluster photodissociation experiments when the clusters are irradiated during formation [4].

The intensities of these six peaks do vary with cluster size. Overall, the peak heights increase ~20% between Si_{18} and Si_{31} and then decrease slightly above Si_{31}, Fig. 1. The greatest variation can be seen by comparing spectra of Si_{21} and Si_{31}. However, only slight variations occur between spectra of neighboring clusters, e.g., Si_{30} and Si_{31}. All clusters have high photodissociation fractions at these six peaks. From these fractions, we estimate that the absorption cross sections are 1-2 Å^2. This estimate should be considered to be a lower bound for many peaks since saturation occurs, Fig. 2. Where the photodissociation fractions exceed 50% we also conclude that the relaxation time of the initially excited states for these clusters must be short compared to the 10-nsec excitation laser pulse and that the dissociation probability exceeds the radiative probability.

Numerous peaks appear in these cluster absorption spectra below 3 eV. From their peak positions and higher-order power dependencies, we can assign all of these features to multiple photon versions of the six peaks in the higher energy portion of the spectrum. For example, the sharp feature at 1.96 eV in the spectra in Fig. 1 is a two-photon absorption corresponding to the 3.90-eV peak. The position and splitting of the 2.55-eV feature matches very well to a two-photon version of the 4.94- and 5.25-eV peaks. A concentration of two- and three-photon absorptions contributes to the broad shoulder between 1.5 and 1.8 eV. Three- and four-photon absorptions also appear as peaks at 1.02 and 1.23 eV in many of the spectra. The amassing of multiple photon absorptions below 3.0 eV makes it experimentally difficult to map out the underlying broad background which contains single-photon transitions, according to the power dependencies.

Our most startling finding is that the absorption spectra for all of these clusters are essentially identical. Furthermore, we have obtained partial spectra of silicon clusters smaller than Si_{18} and larger than Si_{41}. These preliminary survey data indicate that the spectral signature common to Si_{18}-Si_{41} grows in at about Si_{15} and persists for sizes up to at least 70 atoms. This spectral similarity is completely unexpected from both a molecular and a bulk perspective. In both cases, silicon clusters in this size range are expected to undergo rapid structural changes because of the large surface/interior atom ratio.

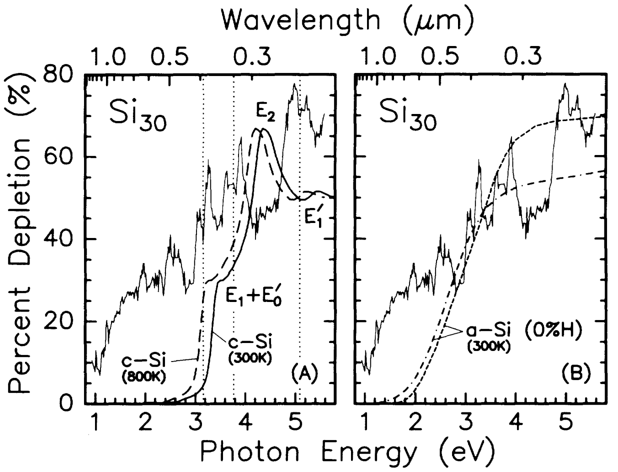

FIG. 3. Comparison of a representative silicon cluster spectrum, Si_{30}, with the absorption spectra of (a) bulk silicon at 300 [8] and 800 K as determined from the temperature coefficients of the critical points [9], and (b) 0% H amorphous silicon (300 K) produced by sputtering (---) and electron-beam evaporation (-·-·) [8]. "E_i" denote the various bulk absorption peaks according to conventional nomenclature; see Ref. [12]. Vertical dotted lines indicate the energetic centroids of the three pairs of peaks in the silicon cluster spectrum. Intensity axes are arbitrarily scaled for comparison.

From a molecular point of view, these clusters span a sufficiently large size range to have structural differences which should show up in their optical spectra. A number of theoretical studies have explored the geometries of small silicon clusters [1]. Despite their differing methodologies, all of these studies find that these silicon clusters should be strongly reconstructed from bulk silicon. The nature of this reconstruction remains open to intense debate. Some calculations predict that silicon clusters in our size range have tetrahedrally bonded network structures whereas others predict more compact structures. Nonetheless, all of these calculations find that major changes occur in the geometric structures of silicon clusters as a function of size below 50 atoms. Such changes are mirrored in the photoelectron spectra measured for silicon cluster anions containing 3–12 atoms [6]. Structural differences in our cluster size range for positively charged silicon clusters have also been inferred from mobility and chemical reactivity data [7]. Thus, we are quite surprised to find that the electronic spectra of neutral silicon clusters larger than $\sim Si_{15}$ show no evidence for any such structural changes. This leads us to conclude that all of these small silicon clusters share one or more common structural entities which are strong chromophores. One possibility is that small silicon clusters share a common bonding network which persists and extends as the cluster grows in size. As described below, this network may be related to that of bulk silicon. Another possibility is that all of these clusters contain at least one loosely bound smaller cluster such as the abundant Si_{10} which is responsible for the sharp spectral structure. This explanation is less appealing since the smaller cluster would have to have an appreciable binding interaction in order to remain bound to the quite warm silicon clusters for a long time. This interaction would have to be similar for all of the clusters in order to produce the observed spectral similarity. However, we cannot rule this out since the excitation spectra of these small clusters are unknown at this time in the energy range of interest.

Thinking of these clusters as minute pieces of bulk silicon is difficult since they consist almost entirely of surface atoms. Yet, the absorption spectrum of crystalline silicon has much in common with the silicon cluster spectra. Figure 3(a) shows one of the cluster spectra superimposed on the crystalline silicon absorption spectrum at 300 and 800 K (the estimated cluster internal temperature) [8,9]. Both cluster and bulk spectra are dominated by strong absorption features at energies above 3 eV. Grouping the six cluster features into three pairs of features allows for a comparison of the resulting centroids of each pair with the three direct gap absorptions of crystalline silicon. The centroids of the first and third pairs of absorptions in the cluster spectra match quite well with the lowest energy, E_1+E_0', and highest energy, E_1', peaks in the 800-K bulk spectrum. Note that the 800-K bulk spectrum, which is redshifted by the thermal expansion of the lattice, more closely corresponds to the cluster spectrum. The silicon cluster spectrum also rides on a background absorption tailing to the red. This is qualitatively similar to the indirect transitions tailing to the red in bulk silicon. Nonetheless, a number of discrepancies between the bulk and cluster spectrum must still be explained. The cluster spectrum has six peaks between 3.0 and 5.6 eV whereas the bulk spectrum contains only three features. We cannot say whether the cluster spectra include absorptions above 5.6 eV, although we do not find any evidence for such absorptions in the form of multiple photon peaks within our experimental range. If these should occur in the cluster spectra they would clash with the bulk silicon spectrum. Furthermore, a simple comparison to the 800-K bulk spectrum neglects effects of lattice contraction and quantum confinement which are known for nanometer-size II-VI semiconductor particles [10]. We would expect these effects to change as a function of size over the cluster size range of our experiments. Pseudopotential calculations have been recently performed to study the size dependence of the absorptions of diamond-lattice-like silicon clusters with 10–100 Å diameters [11]. These calculations predict that direct gap transitions in small silicon crystallites should redshift with decreasing size and that new features should appear greatly shifted to the blue as a result of lifting of the degeneracies of the critical points.

Given that silicon clusters containing only few tens of atoms are too small to have either band structures or bulk excitations, the similarity of their optical signature to crystalline silicon is unexpected. Moreover, these cluster spectra are far more similar to the spectrum of the most stable crystalline form of silicon than to the spectra of other silicon forms. For example, the structural disorder and numerous defects present in amorphous silicon suggest that it would be a better match to silicon clusters. Furthermore, optical spectra of small InP clusters exhibit continuumlike absorptions analogous to amorphous InP [2,3]. Figure 3(b), however, shows the contrast between the single broad feature of the amorphous silicon spectrum and the sharp spectral features of silicon cluster spectra, although the amorphous silicon spectral envelope does span the cluster spectral features [8]. Other forms of more compact silicon such as the β-tin and primitive hexagonal metallic phases, and the BC-8 and ST-12 metastable phases are also candidates for comparison in light of the theoretical calculations which predict high coordination numbers in small silicon clusters. None of these alternative structures have optical properties which are as closely related to our cluster spectra as diamond crystalline silicon [12]. Finally, our silicon cluster spectra cannot easily be compared to silicon surface spectra. Various silicon surfaces exhibit strong sharp resonances at energies below our spectral range and weaker broad absorptions below the direct band gap, a region obstructed by multiple photon excitations in our spectra [13].

In summary, our data showing the spectral regularity of small silicon clusters challenge all existing theories about their structures. This leads to the intriguing conclusion that silicon clusters containing tens of atoms are derived from a common structural entity. We do not know the nature of this entity but its spectral similarities to the bulk crystalline spectrum provide a proving ground for further investigation.

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