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9. This condition is fully equivalent to the disappearance of the dihedral angle θ between contacting phases in the classical Young-Dupre equation $\gamma_{c\beta} = \gamma_{c\alpha} + \gamma_{\alpha\beta} \cos\theta$. A clear discussion of this is given by Schick [in (*4*)].
10. This is so because $(\gamma_{c\beta} - \gamma_{c\alpha})$ is proportional to the difference between the densities of the α and β phases (or, in the case of binary mixtures, to the difference between their compositions), and this difference is known from experiment (*4*) to decrease to zero more slowly with $(T_c - T)$ than does $\gamma_{\alpha\beta}$.
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13. It is essential, when floating spin-cast films of these rubbery polymers on water to create the bilayers, that contact with the water be minimized. Details of the procedure are to be published (*15*).
14. In this technique a beam of ^{3}He particles is incident on the thin, partially deuterated polymer sample, and energetic α-particles [^{4}He] from the reaction

$$^3\text{He} + {}^2\text{H} \rightarrow {}^4\text{He} + {}^1\text{H} + 18.352\ \text{MeV}$$

are detected at a forward angle. From the energy spectrum of the α-particles, known energy losses within the sample, and the reaction cross section, composition-depth profiles of the deuterium-labeled chains are directly obtained. Details are given in the following: U. K. Chaturvedi, U. Steiner, G. Krausch, G. Schatz, J. Klein, *Phys. Rev. Lett.* **63**, 616 (1989); *Appl. Phys. Lett.* **56**, 1228 (1990); J. Klein, *Science* **250**, 640 (1990); (*15*).

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16. In contrast to the polymer-air interface which is wetted by the dC-rich phase, we saw no wetting by either phase at the polymer-silicon interface. After very long annealing times, we observed nucleation and the growth of holes in the polymer layer.
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22. We are currently extending our experiments to probe the question of where the partial-to-complete wetting transition occurs, and its order in polymer mixtures, as well as to characterize explicitly the surface interaction parameters that are involved. Partial wetting in the configuration of our experiments would result in wetting layers of finite thickness (comparable with bulk correlation lengths) in equilibrium, as in the studies (*8*) showing surface enrichment from a one-phase polymer mixture.
23. We thank K. Binder, P. Pincus, and S. Safran for fruitful discussions and critical reading of the manuscript. This work was supported by the German-Israel Foundation, the U.S.–Israel Binational Science Foundation, and the Minerva Foundation. J.K. is the incumbent of the Herman Mark Chair in Polymer Physics at the Weizmann Institute.

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Electron Photodetachment Cross Sections of Small Carbon Clusters: Evidence for Nonlinear Isomers

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Absolute cross sections for photodetachment of negative carbon clusters are reported for C_n^- ($n = 3, \ldots, 8$). The results indicate that various neutral isomers exist, some with electron affinities as low as 1 electron volt. The method of production plays an important role in the characteristics of carbon clusters.

Pure carbon molecules are currently under intense experimental and theoretical scrutiny. These molecules are believed to play an important role in the formation of soot in flames and have been detected in interstellar space, being produced in giant carbon stars.

A review of the large amount of research that has been devoted to these molecules has been given by Weltner and van Zee (*1*). Until recently, the question of the molecular structure of such species was mainly addressed theoretically. The first theoretical calculation (*2*) suggested that carbon clusters of n atoms were either linear ($n \leq 10$) or rings ($n > 10$). Several recent high-level calculations (*3*) predict that planar monocyclic isomers exist for small even-numbered clusters (n = 4, 6, and 8). Experiments were not able to confirm this prediction, and only linear species were reported to have been detected (*4–6*). A sharp even-odd alternation in the electronic structure and stability was found: the even-numbered clusters are open-shell species with $^3\Sigma_g^-$ ground states and high electron affinities, whereas the odd clusters are closed-shell species with $^1\Sigma_g^+$ ground states and lower electron affinities. However, in recent photoelectron detachment studies there were indications that nonlinear isomers may exist (*6*). Also, indications for the existence of both linear and nonlinear isomers of C_7^+ to C_{10}^+ were reported recently (*7*).

In a previous experiment, we reported the observation of a cyclic C_4 (*8, 9*) using the Coulomb explosion imaging (CEI) technique (*10*) combined with laser photodetachment. We have extended these measurements to other clusters ($3 \leq n \leq 8$). We have measured the absolute photodetachment cross section of these clusters as a function of photon wavelength.

Figure 1 illustrates schematically the experimental arrangement. Negative ions were produced in either the standard Hiconex 834 cesium-beam sputter source or by a laser vaporization–pulsed molecular beam source. In the latter, a carrier gas could be introduced from a pulsed nozzle operating at a backing pressure of several atmospheres, which allowed relaxation of molecular degrees of freedom by collisions with the gas atoms as well as creation of larger clusters. After acceleration to an energy of ~100 keV, the negative ions were collimated by an aperture (2-mm diameter). A laser beam was directed colinearly with the ion beam and in the opposite direction. Either a Nd:Yag (fundamental, second, and third harmonic) or an excimer pumped dye laser was used in this experiment. The lasers operated at 25 Hz and were synchronized with an electrostatic chopper placed at the exit of the ion source, pulsing the negative ion beam into 20-μs-long pulses. The negative ions surviving the laser interaction were mass analyzed by a 90° magnet and detected by a microchannel plate (MCP). The laser intensity was measured by introducing a prism that deflected the light through a window to a power meter (Fig. 1).

The depletion of the negative ions due to the interaction with the laser photons was monitored by digital recording of the ion current (amplified by the MCP electron multiplier) as a function of time. A typical depletion curve as a function of time is shown in Fig. 2. The time resolution was chosen to be 0.25 μs, which is equivalent to a typical ion flight path of 10 cm. For a

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reliable absolute cross-section measurement, the overlap of the ion beam with the laser beam has to be uniform within the 2-mm-diameter aperture and along a path that is longer than 10 cm. This requirement was achieved, and the depletion curve shown in Fig. 2 represents faithfully the ratio of the cross section to the area of the 2-mm diameter aperture per photon.

We used the setup shown in Fig. 1 to measure the absolute cross section for photodetachment as a function of photon energy for all clusters up to C_8. The results obtained for C_4 and C_7 prepared by the Cs sputtering source are shown in Fig. 3. For C_4, a threshold at ~2.1 eV is observed. This value agrees with the theoretically predicted electron affinity of the rhombus isomer and also with our previous results (8, 9). For C_7, a threshold at 2 eV is also clearly visible. This value is less than the observed threshold in other experiments (4, 6) by more than 1 eV. The threshold for photodetachment of C_3^- was found at 2 eV, in full agreement with previous observations (6). An interesting feature of these data is that the cross section for photodetachment is significantly different from zero, even at photon energies slightly greater than 1 eV. This result indicates the existence of isomers with electron affinity lower than 1 eV. For C_2^-, no depletion was seen at energies below the known electron affinity (3.2 eV). The cross section at 1.16 eV for C_4^-, C_6^-, and C_8^- was systematically greater than the cross section for the odd-numbered clusters. Because the quantity measured is photodepletion, it could be that part of the depletion observed is related to photodissociation and not photodetachment. In separate experiments applying the CEI technique (*10*), the number of atoms in each neutralized molecule was counted and it was confirmed that photodissociation does not contribute significantly to the photodepletion cross section.

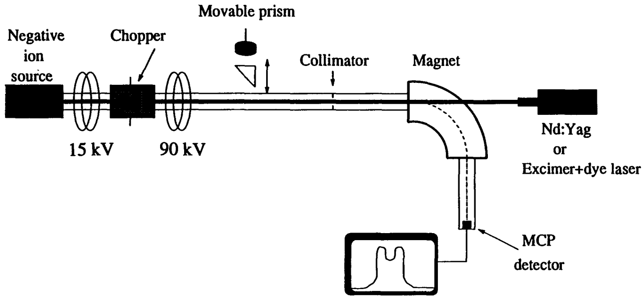

Fig. 1. The experimental setup for the photodepletion measurements.

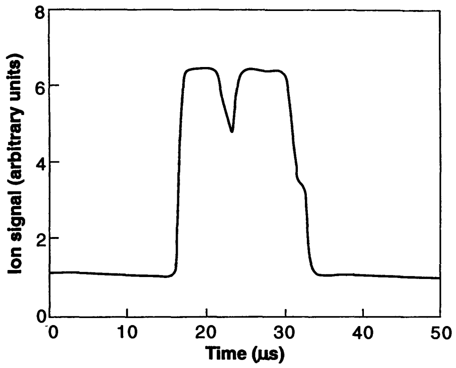

Fig. 2. Typical depletion curve. The laser power through the 2-mm collimator was 90 mW and the wavelength λ was 5320 Å.

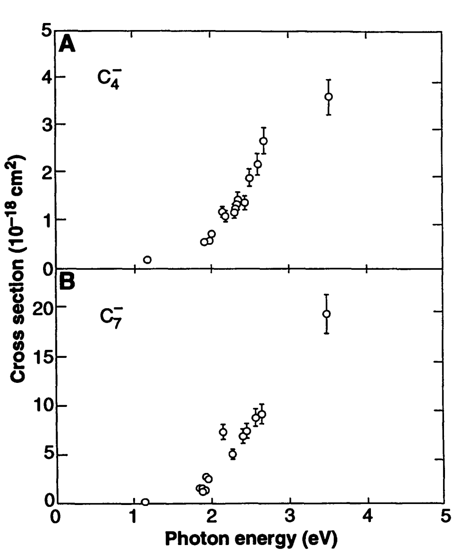

Fig. 3. Neutral production cross section for (**A**) C_4 and (**B**) C_7 as a function of photon energy.

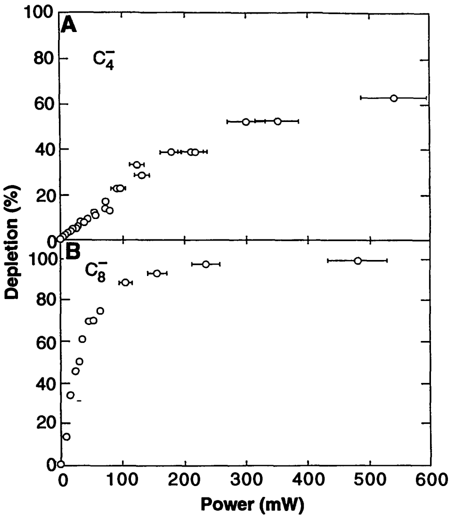

Fig. 4. Laser intensity dependence of the depletion of (**A**) C_4^- and (**B**) C_8^-. The photon energy was 1.16 eV.

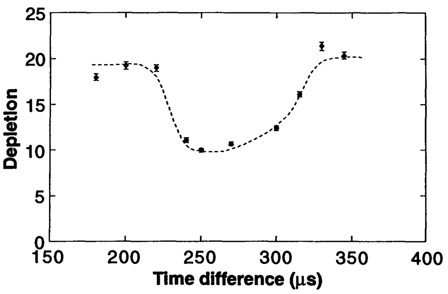

Fig. 5. Dependence of the depletion of C_4^- at a photon energy of 2.33 eV on the time difference between the pulsed valve opening and the impact of the vaporization laser. The carrier gas was Ar at a pressure of 5 atm. The line is drawn to guide the eye.

In Fig. 4, the laser-intensity dependence of the depletion of C_4^- and C_8^- is presented for photon energy of 1.16 eV. Both depletion curves show the characteristic exponential behavior of saturation for a single-photon excitation. Accordingly, they were fitted to the following curve: $D = D_0[1 - \exp(-I/I_0]$, where D_0 is the saturation level, I is the laser intensity, and I_0 is a fit parameter used later to compute the cross section. For the C_4^- clusters, the saturation level is at ~70% of the total C_4^- produced by this source, whereas it is at 100% for the C_8^- clusters. If the negative ion source is producing a single isomeric structure, then we expect that at each photon energy above the ground-state electron affinity, the photodetachment process would reach full (100%) saturation at a high enough photon intensity. This latter case is the situation for the C_8^- isomer, whereas for C_4^-, these results indicate the existence of more than one isomer. These very high depletion yield indicates that high vibrational state population is not responsible for the low thresholds observed.

The production of neutral carbon clusters by photodetachment with such low photon energy is in apparent contradiction with previous results. For example, a recent photodetachment experiment (6) of C_4^- with 4.7 eV photons shows an electron affinity of 3.882 eV. That experiment shows no indication of the 2.1 eV threshold shown in Fig. 3A. In an attempt to clarify this dilemma, we have repeated the experiments described above for the C_4^- cluster with one modification: the replacement of the ion source by a supersonic expansion source arrangement.

Measurements of the photodetachment with this source were made at three different photon energies: 1.16 eV, 2.33 eV, and 3.50 eV. At the energy of 2.33 eV (just above a threshold), the depleted fraction was very sensitive to source conditions, such as the time difference between the opening of the pulsed valve and the impact of the laser on the graphite rod (see Fig. 5), the duration of the gas pulse, or the location of the laser impact on the rod. Under some conditions, the depleted fraction was reduced to ~10%. Very little depletion variation was observed at the two other photon energies. In comparison with the Cs sputter source results, some reduction of the depleted fraction was observed. These results are consistent with cooling of the C_4^- clusters in the pulsed nozzle source because the region just above the measured threshold is very sensitive to the thermal vibrational state population of the negative cluster. The variation between the Cs sputter and the laser vaporization source indicates that the method of production of the clusters changes the ratio between the different isomers present in the beam.

Why were the lower thresholds found in the present experiment not detected in the previous experiments? Two possibilities can be advanced. First, as described above, the method of formation influences the population ratio between the different isomers. Thus, it is possible that some types of ion sources would preferentially "quench" the low-affinity population. In previous experiments, slightly different ion sources were used [supersonic expansion with "waiting room" (6) and high-energy vaporization laser]. Another possibility is the difference in the photodetachment sensitivity of the experimental methods. Previous experiments measured the threshold with electron spectroscopy with a higher laser energy (4.66 or 3.5 eV). The main electron signal comes from the transition having the largest cross section, thus overlooking the lower transition. An example of this phenomenon can be seen in the recent study by Arnold *et al.* (6), where for C_3, the transition to the $^3\Pi_u$ excited state is much stronger than the transition to the $^1\Sigma_g^+$ ground state. In the same paper, high electron kinetic energy tails are found for some of the clusters at the lowest photon energy used (3.5 eV).

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A Liquid-Solution-Phase Synthesis of Crystalline Silicon

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A liquid-solution-phase technique for preparing submicrometer-sized silicon single crystals is presented. The synthesis is based on the reduction of $SiCl_4$ and $RSiCl_3$ (R = H, octyl) by sodium metal in a nonpolar organic solvent at high temperatures (385°C) and high pressures (>100 atmospheres). For R = H, the synthesis produces hexagonal-shaped silicon single crystals ranging from 5 to 3000 nanometers in size. For R = octyl, the synthesis also produces hexagonal-shaped silicon single crystals; however, the size range is controlled to 5.5 ± 2.5 nanometers.

Crystalline Si is one of the most useful and exploited materials in modern technology. Indeed, single-crystal Si wafers form the foundation of the electronics industry. Polycrystalline Si finds applications in the fabrication of microcircuitry and photocells. Because of its many applications, much research and development have been aimed at producing high-quality crystalline and polycrystalline Si (*1*). Well-established methods for the production of single-crystal thin films include molecular beam epitaxy of evaporated Si and chemical vapor deposition of silanes, polysilanes, and halosilanes. Methods for the production of large single crystals include the Czochralski (*2*) and floating zone methods (*3*). Polycrystalline Si and nanophase Si crystallites are produced by well-known techniques such as gas-phase pyrolysis, photolysis, and discharge cracking of silanes and polysilanes (*4*, *5*).

To date, very little attention has been paid to the production of crystalline Si (or any other group IVA element) by wet-chemical synthesis. Such a synthesis, although unlikely to produce wafer quality Si, could have many advantages. Namely, with this technique it should be possible to control both crystal size and surface functionality, enabling production of well-characterized crystals in the size range below or near the characteristic electronic wavelengths of Si. Such control has been exhibited in a number of syntheses developed over the past few years for the production of the II-VIA (*6*, *7*) and III-VA (*8*) families of semiconductor crystals.

I report here a liquid-solution–based technique for the production of micrometer and submicrometer-sized Si single crystals. The synthesis is based on the reduction of $SiCl_4$ and $RSiCl_3$ (R = H, octyl) in a nonpolar organic solvent (pentane or hexane). The reaction is:

$$SiCl_4 + RSiCl_3 + Na \rightarrow$$
$$\text{Si (diamond lattice)} + NaCl \qquad (1)$$

and the function of the R group is discussed later in the text.

This synthesis was carried out in a high-temperature, high-pressure, 300-ml bomb (Parr Instruments) manufactured from the alloy Inconel and equipped with a magnetically coupled stir drive. The bomb was adapted with a syringe inlet port for introduction of reagents and a vacuum port for attachment to a diffusion-pumped vacuum line. Before loading, the bomb was connected to the vacuum line and evacuated to 1×10^{-4} torr for several hours. Hexane (or pentane) was dried over a mixture of Na and benzophenone, and the reactants $SiCl_4$ (99%; Johnson Matthey), $RSiCl_3$ (99%; Johnson Matthey), and 28 to 32% Na dispersion in toluene (Johnson Matthey) were used without further purification. All components (150 ml of hexane, 1 ml of $SiCl_4$, 1 ml of $RSiCl_3$, and 10 ml of Na-toluene dispersion) were transferred into the bomb by either vacuum transfer or clean syringe transfer techniques. The bomb was back-filled with Ar to 1 atm and fitted with a heating mantle. The bomb was

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