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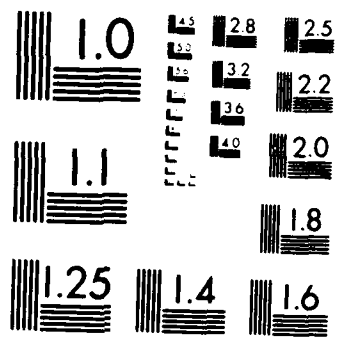

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The principal thrust of the research carried out during this grant has been concerned with the study of cluster beam spectroscopy of semiconducting elements such as silicon and germanium, as well as III-V semiconductors, such as Ga_xAs_y based on rapid advances in the art of generating and probing supersonic cluster beams developed by one of the principal investigators (R.E.S.) at Rice University. This approach allows the study of small, bare clusters in the high vacuum of a

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20. ABSTRACT CONTINUED

molecular beam apparatus in much the same way that the more conventional type of surface science uses perfect single crystals in an ultra high vacuum surface machine. In both cases the object of study is a highly idealized model of the real polycrystalline surfaces of practical importance, but in the case of the clusters beam approach, this model has the advantage of a far more immediate connection to high level *ab initio* theory. It can be argued that cluster beam techniques are a means of getting away from the macroscopic, low symmetry aspects of surfaces and bringing surface science experiments into the microscopic, molecular realm ideal for theory. Although there have been substantial studies of metal and rare gas clusters, only recently attention has begun to focus on clusters of semiconductor elements. During the past two-year period, we have successfully developed an effective source, utilizing a laser-vaporization based supersonic molecular beam technique to produce both neutral and ionic semiconductor clusters. Laser spectroscopic methods such as resonant two photon ionization (R2PI), photodetachment, photofragmentation, and photoelectron spectroscopy have been employed to study bare Si and Ge clusters as well as GaAS clusters.

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SUPERSONIC BEAM OBSERVATIONS OF SEMICONDUCTOR CLUSTERS

FINAL REPORT

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AUGUST 31, 1987

U. S. ARMY RESEARCH OFFICE

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A. *Report on Research Activities and Accomplishments*

January 1, 1985 – August 31, 1987

The principal thrust of the research carried out during this grant has been concerned with the study of cluster beam spectroscopy of semiconducting elements such as silicon and germanium, as well as III-V semiconductors, such as Ga_xAs_y based on rapid advances in the art of generating and probing supersonic cluster beams developed by one of the principal investigators (R.E.S.) at Rice University and elsewhere [1-4]. This approach allows the study of small, bare clusters in the high vacuum of a molecular beam apparatus in much the same way that the more conventional type of surface science uses perfect single crystals in an ultra high vacuum surface machine. In both cases the object of study is a highly idealized model of the real polycrystalline surfaces of practical importance, but in the case of the clusters beam approach, this model has the advantage of a far more immediate connection to high level *ab initio* theory [5]. It can be argued that cluster beam techniques are a means of getting away from the macroscopic, low symmetry aspects of surfaces and bringing surface science experiments into the microscopic, molecular realm ideal for theory.

Although there have been substantial studies of metal and rare gas clusters, only recently attention has begun to focus on clusters of semiconductor elements. During the past two-year period, we have successfully developed an effective source, utilizing a laser-vaporization based supersonic molecular beam technique to produce both neutral and ionic semiconductor clusters. Laser spectroscopic methods such as resonant two photon ionization (R2PI), photodetachment, photofragmentation, and photoelectron spectroscopy have been employed to study bare Si and Ge clusters as well as GaAs clusters. Our work is summarized in the following sections.

1. Development of a Semiconductor Cluster Apparatus

Our semiconductor cluster apparatus was initially an extension of a metal cluster source [1-4] where a rod of the material to be studied was used. Supersonic cluster beams of Si and Ge were generated using this rod source [6]. However, since semiconductor materials are more readily available in forms of wafers, a novel and highly effective rotating disc source was developed. A detailed description of this rotating disc design can be found in Ref. 7. In fact, the disc source proved to be much more efficient in cluster generation than a rod source, owing to its better sealing and smaller trapped volume around the target material. Intense supersonic semiconductor beams containing clusters of up to 50 atoms can be routinely generated with this source.

Another significant development during the grant period was achieving the capability of producing and studying ionic semiconductor clusters in our apparatus (8). Neutral semiconductor clusters were found to fragment easily upon laser irradiation, which made it difficult to explore the structures of individual clusters. Ions have the advantage that they can be guided and mass selected at will by electromagnetic fields. The study of semiconductor cluster ions, therefore, opens an exciting area which is able to provide a wealth of detailed information, from electronic structure to electron affinity, for each cluster. We have obtained both positive and negative semiconductor cluster ions by direct laser vaporization. In particular, small Si, Ge, and GaAs negative ions have been studied by photodetachment and photofragmentation techniques.

With the ability to produce ionic clusters, we have recently begun to apply photoelectron spectroscopy to the study of semiconductor cluster anions in our laboratory. Electrons are photo-detached from mass-selected negative clusters and studied by time-of-flight (TOF) analysis. A pulsed magnetic TOF photoelectron spectrometer was developed, which can increase the electron collecting efficiency by up to 50% with a reasonable energy resolution (9). Photoelectron spectroscopy (PES) has been one of the most informative methods in studies of bulk and surface energy band structures. Therefore, by applying PES to semiconductor clusters, it should be possible to obtain information directly about their electronic "band" structure and to study the evolution of this structure with increasing cluster size.

2. Ioniz... studies of Si, Ge, and GaAs Clusters

Properties of Si, Ge, and GaAs neutral clusters were explored by one- and two-color laser ionization followed by TOF mass analysis. Two striking properties were observed in Si and Ge clusters.

First, Si and Ge clusters have about the same fragmentation patterns upon laser ionization. Their TOF mass spectra, ionized with moderate ArF excimer laser fluence (about 0.5 mJ/cm^2), were remarkably similar. Cluster ion signals in the size range of 6-11 atoms were particularly intense and showed predominant contributions from fragments of larger clusters (see Fig. 2 in Ref. 6. More careful studies indicated that both Si and Ge clusters mainly fragmented by fission into small clusters of 6-11 atoms. This similarity, which was also observed when we studied the fragmentation patterns of their negative cluster ions, suggests that Si and Ge clusters have similar structures. On the other hand, the fragmentation patterns of Si and Ge clusters are quite different from that of metal clusters which were found to fragment only by losing a single atom.

Second, excited electronic states with approximately 100 ns lifetime were observed for Si and Ge clusters of 6-11 atoms via two-color R2PI studies, where the initial excitation was promoted with the 2nd or 3rd harmonic output of a Nd:YAG laser and the final ionization was obtained with an ArF excimer laser. Compared to metals, the existence of such long-lived excited states is quite unique. There is no excited electronic state known for any trimer or larger metal clusters, except Cu_3, which lives longes than 1 ns. This long lifetime may be associated with certain semiconductor properties, such as the band gap of Si and Ge clusters.

GaAs clusters were found to exhibit a very interesting ionization behavior [6]. An even/odd alternation in the ionization potential (IP) was observed, which only depended upon the total number of atoms in clusters. Clusters with an odd total number of atoms had lower IP than their neighboring even ones. Since both Ga and As are odd electron elements, this may suggest that all even clusters have fully paired singlet ground states with no dangling bonds on the surfaces, while the odd ones have the unpaired electron in a nonbonding frontier orbital. Such an electronic structure may only be possible if the bonding in GaAs clusters are completely reconstructed from the sp^3 hybridization bonds of the bulk, which is commonly found on surfaces.

3. Photodetachment of Si, Ge, and GaAs Anions

Electron affinities (EA) of Si, Ge, and GaAs clusters were determined as a function of cluster size by measuring the dependence upon the probing laser fluence of the detached electron intensity from the negative ions. With several discrete laser wavelengths, it was possible to roughly bracket the EA's of these clusters for up to 30 atoms in size. Although extensive fragmentations that occur during the Si and Ge negative cluster ion laser irradiation have made it difficult to determine the EA's of such clusters, more detailed measurements of EA's for GaAs clusters have been obtained. The evolution of EA as a function of GaAs cluster size is presented in Fig. 5 in Ref. 8 (attached in Appendix III). The most interesting observation is that an even/odd alternation in the EA's of GaAs clusters is evident, similar to that observed in their ionization potentials. GaAs clusters with odd total number of atoms have higher EA than their neighboring even ones. This result supports the suggestion that even GaAs clusters have singlet ground states with no dangling bonds. In these measurements, the GaAs clusters studied were those with approximately equal numbers of Ga and As atoms. Each GaAs cluster mass peak observed actually consisted of clusters with the same total number of atoms but different compositions which, however, could not be resolved in our present apparatus. The EA's of Ga rich or As rich clusters have also been studied. The conclusion is that for Ga_xAs_y with $x+y$ constant, the EA increases with an increasing ratio of y to x. This result is not surprising, since As is more electronegative than Ga.

4. Photofragmentation of Si, Ge, and GaAs Anions

Photodissociation processes were found to be quite competitive with photodetachment for the negative cluster ions. Both electrons and fragmentation products could be observed for GaAs anions with electron signals always much more intense. For Si and Ge anions the relative importance of detachment and fragmentation depended strongly upon the laser wavelengths. One-photon detachment and one-photon fragmentation existed simultaneously with the fragmentation signal dominant when the photon energy was just above the detachment threshold of the clusters. However, as the photon energy was increased, detachment processes became rapidly dominant.

The difference between the fragmentation patterns of Si or Ge and GaAs proved quite interesting. Like metals, GaAs negative cluster ions fragmented by a nonfission process: one, two, or more atoms may be eliminated. There was, however, the same even/odd alternation in the fragmentation ion products with odd daughters more abundant than the even ones. On the other hand, Si and Ge anions fragmented, like their neutral clusters, into only a few channels, mainly in the 5-10 atom size range. No dependence of the fragmentation patterns upon the photon energy was observed in the range of our present studies. Although the relative intensities of their daughters were not equal, Si and Ge negative cluster ions exhibited nearly the same fragmentation patterns, implying that they may have almost the same structures. Table II in Ref. 8 (attached in Appendix III) lists the observed fragmentation channels for Si and Ge negative cluster ions.

Si_{10}^- and Ge_{10}^- clusters had unique position in the fragmentation patterns. Some clusters such as 16, 17, and 20, appear to fragment only into the 10 atom negative ion daughters for a wide range of probing laser wavelengths (more than 1 eV photon energy change). It seems that the 10 atom cluster has a much more stable structure than other clusters. Furthermore, the fragmentation patterns between different Si and Ge clusters vary, which appears to indicate large changes in structure with cluster size

5. Ultraviolet Photoelectron Spectroscopy of Semiconductor Clusters

A new type of time-of-flight photoelectron spectrometer particularly suited to the study of cold metal and semiconductor anions prepared in a supersonic molecular beam has been developed. The desired cluster is extracted from the molecular beam, mass-selected after an initial time-of-flight, and decelerated as it enters the photoelectron spectrometer. Photoelectrons ejected from the cluster by an ArF excimer laser are collected with >98% efficiency in an intense pulsed magnetic field of carefully controlled divergence. This divergent field parallelizes the photoelectron trajectories and maps smoothly onto a low, uniform magnetic field which guides the electrons along a 234 cm flight tube leading to a microchannel plate detector. The strong magnetic fields and simple, open design provide excellent rejection of stray photoelectrons in a clean, ultra high vacuum environment. Using this spectrometer, ultraviolet photoelectron spectra (UPS), were obtained for mass-selected negative cluster ions of silicon and germanium in the 3-12 atom size range. An ArF excimer laser (6.4 eV) was used for photodetachment, enabling the first 3-4 eV of the valence band structure of the clusters to be probed. With few exceptions, the UPS data for corresponding clusters of the two semiconductors were remarkably similar. The spectra suggest clusters 4, 6, 7, and 10 of silicon and 4, 6, and 7 of germanium are closed shall species with band gaps in the range of 1 to 1.5 eV.

6. Silicon Cluster Chemistry by FT-ICR Probes

More recently, we have developed a Fourier transform ion cyclotron resonance (FT-ICR) apparatus which is capable of probing very large silicon clusters prepared in a supersonic beam machine external to the FT-ICR cell. This apparatus was used to probe the surface chemistry of isolated silicon cluster ions in the 7-65 atom size range. Dissociative chemisorption reactions with NH_3 were observed to proceed with rates which varied widely with cluster size. One particular cluster, Si_{39}^+, was found to be remarkably inert. Clusters with 20, 25, 33, and 45 atoms were found to be unreactive as well, while those with 18, 23, 30, 36, 43, or 46 atoms were quite reactive. Similarly oscillating reaction patterns were observed with CH_3OH, whereas highly reactive free radical scavengers such as O_2 and NO showed little selectivity. These results suggest the silicon clusters in this size range have well-defined structures which vary in ability to catalyze dissociative chemisorption at the surface.

7. Photodissociation of Semiconductor Positive Cluster Ions

In addition, laser photofragmentation of Si, Ge, and GaAs positive cluster ions prepared by laser vaporization and supersonic beam expansion has been investigated using tandem time-of-flight mass spectrometry. Si clusters up to size 80, Ge clusters to size 40, and GaAs clusters up to a total of 31 atoms were studied. Si_n+ and Ge_n+ for n up to about 30 exhibit rather similar fragmentation patterns. For n in the range 12-26 the fragmentation appears to be a fissioning into roughly equal size fragments often, but not always, in a very similar way to the previously reported fragmentaiton patterns of the negative ions. This fissioning of the positive ions appears to be over for both Si and Ge to loss of neutral clusters of seven and ten atoms, but for Si_n+ the range of n values of this type is rather small. At low fluences, the larger Ge_n+ clusters up to the maximum size, $n = 50$, observable exhibit the striking behavior of Sequentially losing Ge_{10} (and in some cases with lower intensity Ge_7). Larger Si_n+ clusters ($n > 30$) always fragment primarily to produce positive ion clusters in the 6-11 size range with a subsidiary channel corresponding to the loss of a single Si atom. At low laser fluences, Si_{10}+ and Si_{11}+ are dominant. At high laser fluences, Ge_n+ also fragments to produce primarily positive ion clusters in the 6-11 size range in an intensity pattern which is essentially identical to the fragmentation pattern of Si_n+ at similar fluences. $Ga_x As_y$+ clusters lose one or more atoms in what is probably a sequential process with positive ion clusters in which the total number of atoms, $x + y$, is odd being more prominent.

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C. *List of Manuscripts Submitted or Published Under ARO Sponsorship During Grant Period*

1. J.R. Heath, Y. Liu, S.C. O'Brien, Q.L. Zhang, R.F. Curl, F.K. Tittel, and R.E. Smalley, "Semiconductor cluster beams: One and two color ionization studies of Si_x and Ge_x," *J. Chem. Phys.* 83, 5520-5526 (1985).
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8. O. Cheshnovsky, S.H. Yang, C.L. Pettiette, M.J. Craycraft, Y. Liu, and R.E. Smalley, "Ultraviolet Photoelectron Spectroscopy of Semiconductor Clusters: Silicon and Germanium," submitted May 1987 to *Chem. Phys. Lett.*

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11. Q.L. Zhang, Y. Liu, R.F. Curl, F.K. Tittel, and R.E. Smalley, "Photodissociation of Semiconductor Positive Cluster Ions," submitted July 1987 to *J. Chem. Phys.*

D. Scientific Personnel Supported by this Project and Degrees Awarded During Grant Period:
Y. Liu (Ph.D., May 1987; M.S., May 1985), Q.L. Zhang.

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