

# Supersonic cluster beams of III-V semiconductors: Ga<sub>x</sub>As<sub>y</sub>

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Supersonic beams of semiconductor clusters with the formula Ga<sub>x</sub>As<sub>y</sub> were generated by laser vaporization of a disc of pure GaAs mounted on the side of a pulsed supersonic nozzle. These cluster beams were characterized by laser photoionization with various fixed-frequency lasers followed by time-of-flight mass spectrometry. Mass analysis of the clusters with  $x + y > 10$  showed all clusters in the composition range from Ga<sub>x+y</sub> through Ga<sub>x</sub>As<sub>y</sub> to As<sub>x+y</sub> to be present in roughly the amount expected from a binomial distribution. In the smaller clusters strong variations were observed from this expected binomial distribution as a result of kinetic effects in the cluster formation process. Photoionization with an ArF excimer laser at very low pulse energy revealed a pronounced even/odd alternation in the photoionization cross section of the Ga<sub>x</sub>As<sub>y</sub> clusters, depending only on the total number of atoms in the cluster. Clusters in the 5–21 atom range with an odd number of atoms were one-photon ionized by the 6.4 eV ArF excimer laser photons. This even/odd alternation in ionization properties of the clusters supports the view that the even clusters have fully paired singlet ground states with no dangling bonds. At higher ArF excimer laser fluences, the observed mass spectrum became increasingly affected by fragmentation. As is true with bulk GaAs surfaces, these Ga<sub>x</sub>As<sub>y</sub> clusters evaporate largely by the loss of arsenic (probably As<sub>2</sub>) when heated by the laser, leaving behind clusters which are richer in gallium.

## I. INTRODUCTION

Driven by the extreme technological importance of new breeds of semiconducting materials, there has been quite an active interest in theoretical models of III–V semiconductors. This activity has been particularly high in the case of GaAs, much of the recent work focusing on the properties of the GaAs surface and its interface with other materials and dopants.<sup>1–7</sup>

A review of the by now quite extensive theoretical literature in this field shows that there is a real need for experimental data which probes the physical and chemical nature of the semiconductor surface at the most microscopic, molecular scale possible. Virtually all theoretical approaches to semiconductor surfaces and interfaces start with a relatively small cluster of atoms and are then faced with the highly difficult task of casting these cluster calculations in such a way that they can realistically compare to bulk surface measurements. However sensitive and reliable these bulk surface measurements may be, there is still a potentially severe mismatch between the essentially microscopic theory and essentially macroscopic experiments.

One appealing way out of this problem is to bring the experiment to the theorist by developing techniques for generating and probing the very clusters the theory is best able to handle. Certainly this will not be a universal solution. Particularly for semiconductors (where the major device-driven interest often focuses on such intrinsically macro-

scopic phenomena as depletion layers, etc.) not all properties of bulk interfaces will be accessible through the study of microscopic clusters. But the crucial short-range phenomena such as the way in which surface atoms hybridize to form an interface with the vacuum, or react with other semiconductors, insulators, or metals occur in the small clusters as well. Even though they are obviously not bulk semiconductors, the small clusters serve as superb models for some fundamental studies.

Although this approach seems reasonable enough, it constitutes quite a challenge to the experimental community. Difficult as it is, at least a few small steps along this direction are already possible. After it proved possible to routinely generate intense supersonic beams of refractory metal clusters using a new laser-vaporization technique,<sup>8,9</sup> we have recently turned to the application of these new techniques to the simple group IV semiconductor clusters, Si<sub>x</sub> and Ge<sub>x</sub>.<sup>10</sup> In the following sections, this paper describes a first application of laser-vaporization, supersonic beam techniques to the study of III–V semiconductors, particularly GaAs.

## II. EXPERIMENTAL

GaAs is much more readily available in the form of wafers than in the form of rods as required for cluster source developed by this group several years ago.<sup>8</sup> Therefore, a rotating disc laser-vaporization cluster beam source was developed for this research. Schematic front and side views of this new rotating disc source are shown in Fig. 1.

The disc in these experiments was a 2.5 cm diam circle cut from a standard wafer of GaAs. This disc was mounted in a circular aluminum housing and attached to a rod which

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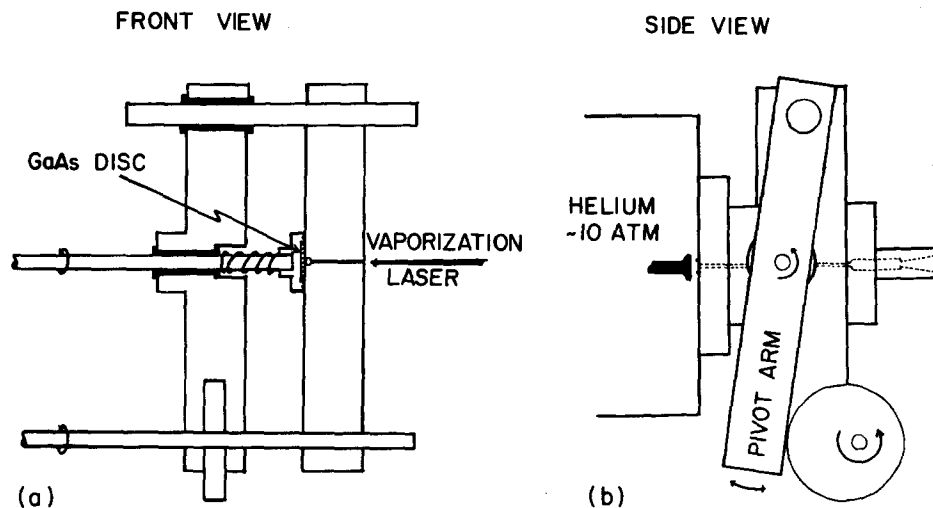


FIG. 1. Rotating disc supersonic cluster source utilizing laser vaporization. The front view (a) shows a cross section such that the 0.1 cm diam vaporization-laser access tube is clearly visible. The target semiconductor disc (crosshatched) is mounted in an aluminum holder, and rotated at 0.18 rpm while pressed against the side of the nozzle block. The cam rotates once every 2.5 h, causing the disc to swing through a short arc, and producing a vaporization path which spirals across the surface of the disc. The side view (b) shows the rotation/pivoting mechanism more clearly, and shows in dashed outline the inner flow channel arrangement which produces the supersonic cluster beam in a helium carrier gas.

rotated at 0.18 rpm. As shown in Fig. 1, this disc housing was pressed flush to the side of the supersonic nozzle and held in place during its motion by a compression spring. By careful seating of the GaAs disc in this aluminum mount, the clearance gap between the disc and the side of the nozzle was adjusted to within 0.003 cm. As shown in the figure, gas leakage around this gap was prevented by an O-ring seal.

Much as in the previous rotating rod designs, this semiconductor cluster source used the second harmonic output of a Nd:YAG laser (30 mJ per pulse, 5 ns pulse width) to vaporize the target material, the super-heated plasma being entrained in a near-sonic flow of helium carrier gas from a pulsed double-solenoid valve.<sup>8,9</sup> As seen in the front view of Fig. 1, this vaporization laser was focused onto the GaAs disc through a 0.1 cm diam tube drilled through the 304 stainless steel nozzle body. The pulsed helium carrier gas was directed down a 0.2 cm diam tube drilled in the nozzle body perpendicular to the laser access tube and just 0.01 cm beneath the rotating surface of the GaAs disc.

In addition to the slow rotation of the semiconductor target disc, the axis of this rotation was swept gradually over a 0.7 cm long arc, thereby causing a spiral erosion pattern to be traced out on the disc by the vaporization laser. As seen in Fig. 1, this sweeping motion was generated by the action of a cam running against a pivot arm which in turn carried the rotating disc assembly.

Rough measurements of the amount of material removed from the disc indicated that typically 300 to 1000 monolayers are vaporized per shot over the 0.1 cm diam focal spot of the vaporization laser. The slow spiral motion of the disc effectively prevented successive shots from drilling too deeply in any one region of the disc. With a 2.5 h period for the sweeping motion, the vaporization laser was found to quite smoothly remove material from the disc over extended periods of operation.

Clustering and thermalization of the laser-vaporized material was promoted by passing the flowing helium through a 0.4 cm diam, 2 cm long tube with a 0.28 cm diam sonic exit orifice. The side view of Fig. 1 shows this clustering/thermalization region in dashed outline. In the previous work on silicon and germanium cluster beams,<sup>10</sup> this en-

larged region in the flow pattern within the nozzle was found to greatly enhance both the intensity and pulse-to-pulse stability of cluster beams produced by laser vaporization. Primarily, such a region acts as a surge vessel with a residence time of roughly 150  $\mu$ s. During this time the short section of helium carrier gas flow initially carrying the laser-evaporated material mixes effectively with cool helium from earlier and later portions of the nozzle flow, thus producing a much cooler clustering environment than would otherwise be possible. In addition, this nozzle design quite effectively evens out time-of-flight jitter for the cluster beam due to fluctuations in the effective source temperature of the supersonic expansion (arising from shot-to-shot energy fluctuations of the vaporization laser).

Also visible in dashed outline within the side view of Fig. 1 is a 10 deg total internal angle supersonic expansion cone (1.5 cm length, with a 0.28 cm diam sonic throat). The earlier work of Hagena *et al.*<sup>11</sup> demonstrated that such cones substantially increase the on-axis concentration of clusters. In this case of clusters from fairly high boiling elements, we suspect the enhancement is primarily due to the more directional nature of the flow from these conical nozzles, rather than any additional clustering above that already achieved in the expanded flow region prior to the sonic orifice.

The intense supersonic jet produced by this nozzle was allowed to expand freely into a 100 cm diam, 100 cm high main vacuum chamber evacuated between pulses to  $10^{-5}$  Torr by a 20 000  $\ell$ s<sup>-1</sup> diffusion pump. The supersonic cluster beam was collimated from this free jet by a 55° conical skimmer situated 45 cm downstream from the exit of the supersonic nozzle. The remainder of the apparatus was identical to that described previously.<sup>8-10</sup> In brief, the beam entered a region of differential pumping at  $10^{-7}$  Torr and was skimmed again before passing through the ionization region of a time-of-flight mass spectrometer (TOFMS). For the experiments described below, an excimer laser beam crossed the cluster beam as it passed through the TOFMS ion source, the resultant ions being mass analyzed and detected with an electron multiplier (Johnston Labs. MM-1). The apparatus was pulsed at a repetition rate of 9.1 Hz, all timing and data acquisition being under the control of an IBM-AT micro-

computer with CAMAC interface.

Initial characterization of the new rotating disc cluster source was performed with a silicon disc so that the cluster beam intensity could be directly compared to that achieved with the conventional rod source in an earlier silicon cluster study.<sup>10</sup> The new disc source actually generated more intense  $\text{Si}_x$  cluster beams than were ever generated with the older rod source—a difference that was particularly evident with the larger clusters (12–60 atoms). We suspect the added efficiency in cluster generation is a consequence of the better sealing around the target material and smaller trapped volume achievable with the rotating disc design.

### III. RESULTS AND DISCUSSION

Several mass spectra of supersonic gallium arsenide clusters produced by the new disc source are shown in Fig. 2. The top spectrum was obtained by photoionization with an ArF excimer laser (6.4 eV) at a fluence of roughly 1

$\text{mJ cm}^{-2}$  in a 12 ns pulse. Since the atomic mass of gallium (69.7 amu) is near that of arsenic (74.9 amu), it is difficult at the mass resolution of Fig. 2 to cleanly resolve peaks due to clusters having the same total number of atoms but having different compositions. For this reason the peaks are labeled only by the total atom count. As has always been true for TOFMS data obtained by this cluster beam apparatus,<sup>8–10</sup> the observed cluster distribution is distorted by the fact that the collection ion optics is not mass independent. For the mass spectra shown in Fig. 2(a), the apparatus was optimized for detection of cluster ions in the size range of 10 to 15 atoms, while for Figs. 2(b) and 2(c) the optimum detection was in the 6–10 atom range.

#### A. Even/odd alternation in ionization potential

In Fig. 2(a) there is a pronounced even/odd alternation in the measured peak intensities—particularly in the clusters with less than 20 atoms. Figure 2(b) displays the same mass spectrum taken with the ArF laser fluence reduced by a factor of about 300, clearly revealing that only the clusters in this size range with an *odd* total atom count are one-photon ionized with 6.4 eV photons. The bottom mass spectrum [Fig. 2(c)] was taken with an  $\text{F}_2$  excimer laser at low fluence, showing that all clusters can be readily one-photon ionized at 7.9 eV, and that the nascent cluster distribution in the beam has roughly equal amounts of odd and even clusters.

This even/odd intensity alternation is reminiscent of the ArF photoionization mass spectrum reported previously from this lab in the case of copper clusters,<sup>12</sup> and has been seen in other group IA (Li, Na, K) and IB (Ag, Au) metal clusters as well.<sup>13,14</sup> In these pure metal cluster systems the effect is currently understood as a consequence of the even/odd alternation in the occupancy and energy of the highest occupied molecular orbital (HOMO). The even group IA and IB clusters are expected to have singlet ground states, whereas the odd clusters have doublet ground states with the unpaired electron in a fairly weakly bound HOMO. In the case of the copper trimer, this HOMO has been calculated to have a  $3p$  Rydberg-like character.<sup>15</sup>

In the case of semiconductor clusters, however, this even/odd alternation in the electronic structure is unprecedented. Earlier research both in this group<sup>10</sup> and in that of Freeman and co-workers<sup>16</sup> has shown that neither silicon, nor germanium clusters show an even/odd alternation in their ionization behavior. Since  $\text{Si}_x$  and  $\text{Ge}_x$  clusters must be even-electron systems for all  $x$ , this absence of even/odd alternation is not particularly surprising—assuming either that all such clusters have fully paired singlet ground states, or that all have an equal tendency to have unpaired electrons in “dangling bonds” on the surface of the cluster. But the observation here of a clear even/odd alternation in properties of  $\text{Ga}_x\text{As}_y$  clusters is rather interesting. It suggests that all even clusters have fully paired singlet ground states with no dangling bonds. Even more interesting is the fact that (as discussed below) these clusters are nonstoichiometric mixtures of gallium and arsenic atoms, and the even/odd alternation in ionization potential for  $\text{Ga}_x\text{As}_y$  appears to be true regardless of the  $x/y$  composition ratio.

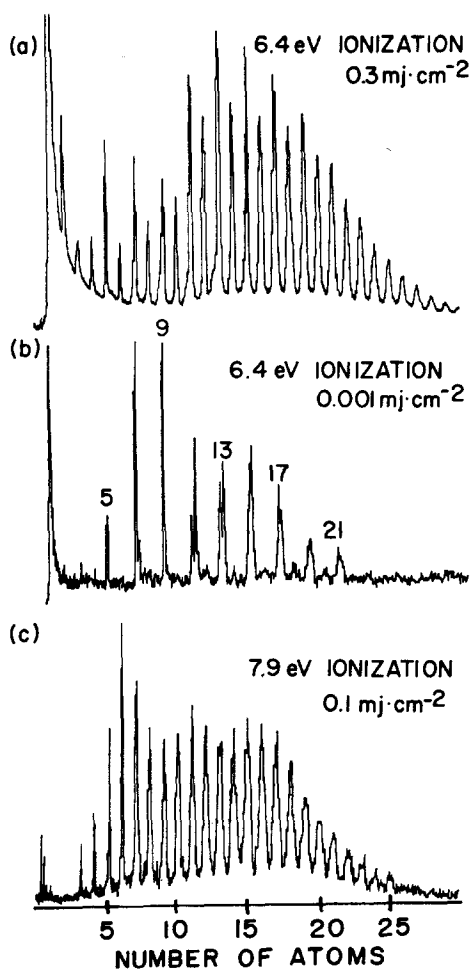


FIG. 2. Time-of-flight mass spectrum of  $\text{Ga}_x\text{As}_y$  clusters ionized with excimer lasers. The total number of atoms in the cluster (regardless of Ga/As composition) is shown on the horizontal axis. The top mass spectrum (a) was obtained with ArF excimer laser excitation at  $0.3 \text{ mJ cm}^{-2}$  fluence, the middle (b) at a much lower fluence ( $0.001 \text{ mJ cm}^{-2}$ ) so as to eliminate multiphoton ionization effects. The bottom mass spectrum (c) was obtained with  $\text{F}_2$  excimer excitation (7.9 eV) at  $0.1 \text{ mJ cm}^{-2}$  fluence. Note that only odd-numbered clusters are one-photon ionized with the ArF laser.

## B. Ga/As composition of clusters

From the outset of this work a key issue has been the question of what the composition would be for clusters generated by laser vaporization of a III-V semiconductor. In the case of GaAs single crystals cut along the (111) direction (such as the GaAs discs used in this study) the surface alternates between planes of pure arsenic and planes of pure gallium. Extensive studies have been published concerning the vaporization properties of these surfaces under long time scale, conductive heating.<sup>17,18</sup> To a remarkable degree the only vapor one obtains from heating GaAs crystals is arsenic ( $\text{As}_2$  and  $\text{As}_4$ ), the gallium simply forming a molten metallic phase on the surface—hardly what one would want for the generation of  $\text{Ga}_x\text{As}_y$  clusters!

However, vaporization by a 30–40 mJ, 6 ns pulse of green light over a 0.1 cm diam spot is quite a different process from simple conductive heating of the entire lattice over a time period of minutes. From work with tungsten and molybdenum targets in this same cluster beam source,<sup>9</sup> we know that these laser-vaporization conditions are quite adequate to atomize several hundred monolayers of materials with boiling points in the 5000–6000 K range. Even if a small liquid phase of gallium metal did begin to form, it would have a boiling point of less than 2300 K and would certainly be readily vaporized by the laser. Since each laser shot vaporizes material to a depth of 300–1000 monolayers on a nanosecond time scale, it is reasonable to expect the hot plasma formed will initially have an overall composition close to that of the bulk.

Careful examination of the photoionization mass spectrum of the cluster beam prepared by laser vaporization of GaAs shows that, as expected, both gallium and arsenic atoms are present with roughly equal concentrations in the cluster formation portion of the nozzle. Figure 3, e.g., displays the observed mass spectrum in the 400–450 amu region appropriate to  $\text{Ga}_x\text{As}_y$ , with  $x + y = 6$ . This spectrum was obtained using the  $\text{F}_2$  excimer laser at low fluence—ionization conditions which should give a fairly reliable indication of the true composition. In the case of these six-atom clusters, the dominant species is found to be  $\text{Ga}_3\text{As}_3$ . Repeated measures of the mass spectrum in this six-atom cluster region with slightly higher mass resolution than that seen in Fig. 3 revealed that 70% of the six-atom clusters were  $\text{Ga}_3\text{As}_3$ , 20% were  $\text{Ga}_4\text{As}_2$ , and most of the remaining 10% were  $\text{Ga}_2\text{As}_4$  (assuming that the peak heights in the mass spectrum with  $\text{F}_2$  laser ionization faithfully reflect the concentrations in the beam).

This is considerably more concentrated in the  $\text{Ga}_3\text{As}_3$  cluster than would be expected on statistical grounds. If the clusters formed in an entirely random manner from a vapor having equal concentrations of gallium and arsenic atoms, the concentrations of the six-atom clusters would follow a binomial distribution:

$$F(n,x) = p^x q^{n-x} n! / [x!(n-x)!], \quad (1)$$

where  $F(n,x)$  = the fraction of  $n$ -atom clusters of type  $\text{Ga}_x\text{As}_{n-x}$ ,  $n$  = the total number of atoms in the cluster,  $x$  = the number of these atoms which are gallium,  $p$  = the

probability an atom is gallium ( $= 0.5$ ), and  $q = 1 - p$  (the probability an atom is arsenic).

Figure 3 plots the predictions of this binomial distribution for the case of the six-atom clusters. Clearly, the observed distribution is peaked too heavily at the 1:1 composition to fit the binomial curve.

In the cluster formation/thermalization zone of the supersonic nozzle we estimate the effective helium buffer gas pressure to be roughly 1 atm, with a temperature in the range of 300–400 K (based on the measured beam velocity, as well as a heat balance assuming 50% of the vaporization laser pulse energy is ultimately taken up in the heat capacity of the helium buffer gas). During the 100–150  $\mu\text{s}$  mean residence time in this clustering zone, ions in the gallium and arsenic plasma produced by the laser have ample time to recombine to neutral atoms, atoms (both present originally and formed by ion recombination) experience sufficient three-body collisions to generate small clusters, and these clusters grow to produce the final distribution present in the beam.

For the very small clusters, these clustering conditions need not produce a binomial distribution of cluster compositions. A collision between gallium atom and an arsenic dimer, e.g., need not always result in a stable  $\text{GaAs}_2$  molecule. The collision complex may fall apart before it can be stabilized in thermalizing collisions with the helium buffer gas (at 1 atm helium for small molecules in this size range, as a very rough guess it probably requires about a microsecond to thermalize a cluster by many collisions with He). If the encounter complex does fall apart, it might well do so to produce  $\text{GaAs} + \text{As}$  if the relative binding energies favor this set of products.

At the other extreme, consider a fairly large cluster such as  $\text{Ga}_9\text{As}_{10}$ . This cluster has 51 vibrational modes amongst which to dissipate the heat of adsorption of an additional gallium atom. Even in the absence of thermalizing collisions with the helium buffer gas, the  $\text{Ga} + \text{Ga}_9\text{As}_{10}$  encounter complex would have a lifetime of milliseconds.<sup>19</sup> Given that the buffer gas temperature is hundreds of degrees below the

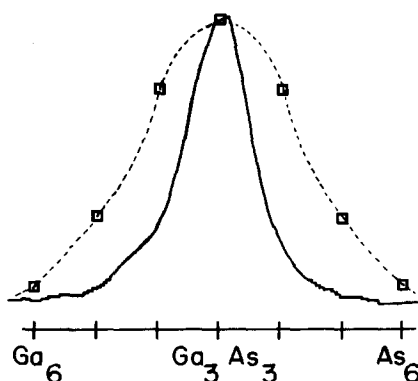


FIG. 3. Time-of-flight mass spectrum in the region of six atom  $\text{Ga}_x\text{As}_y$  clusters ionized with the  $\text{F}_2$  excimer laser at 7.9 eV. The horizontal axis is marked at the correct mass positions for the various possible Ga/As compositions for  $x + y = 6$ . The calculated intensities expected from a binomial composition distribution are shown on the mass spectrum as open boxes. The  $\text{Ga}_x\text{As}_y$  distribution in the beam appears to be far more concentrated in  $\text{Ga}_3\text{As}_3$  than expected statistically.

vaporization temperature of bulk GaAs crystals (1000–1200 K),<sup>17,18</sup> the effect of collisions with the buffer gas will be to stabilize the Ga...Ga<sub>9</sub>As<sub>10</sub> encounter complex—the subsequent breakup of the Ga<sub>10</sub>As<sub>10</sub> product at 300–400 K being highly unlikely. In other words, for the larger clusters, whatever hits, sticks.

Therefore, it is reasonable to expect a composition distribution for the larger clusters that quite closely follows a binomial curve. For the smaller clusters, on the other hand, rather large deviations from this statistical distribution might be expected as a result of details in the binding energies and reaction dynamics.

As discussed above for the case of the six-atom clusters, such deviations from a binomial distribution are, in fact, observed for small clusters. Clusters with less than six atoms were found to display even larger deviations (although some of the deviations may be ascribable to variations in ionization potentials and cross sections). The diatomics, e.g., are found to be mostly GaAs and As<sub>2</sub>, with very little Ga<sub>2</sub> detectable—a result quite consistent with the estimate dissociation energies of these species. The three-atom cluster composition distribution was found to be heavily skewed to the GaAs<sub>2</sub> (30%) and As<sub>3</sub> (50%) species, whereas the four-atom species appeared under F<sub>2</sub> ionization conditions to fall fairly close to a binomial distribution, but slightly over represented in Ga<sub>2</sub>As<sub>2</sub> and GaAs<sub>3</sub>. The five-atom clusters were found to be dominated by GaAs<sub>4</sub>, although significant concentrations of clusters down through Ga<sub>4</sub>As were seen as well.

Under F<sub>2</sub> laser ionization, the Ga<sub>x</sub>As<sub>y</sub> clusters with more than six atoms show composition distributions increasingly well described by a binomial curve. By the time there are nine or ten atoms in the clusters, the observed distributions are binomial within experimental error—although the best fit indicates there is slightly more arsenic than gallium in the cluster formation region [i.e.,  $p$  in Eq. (1) is better chosen near 0.48].

### C. Evaporative loss of arsenic from Ga<sub>x</sub>As<sub>y</sub> clusters

Figure 4 shows one final interesting aspect of these III-V semiconductor clusters revealed in these initial laser-ionization survey experiments. The displayed mass spectra are in the region of the 19-atom clusters, and both were obtained using the ArF excimer laser line at 6.4 eV to accomplish the cluster ionization. The difference between the two mass spectra is laser fluence. The mass spectrum drawn with a solid line was obtained with an ArF laser fluence of only 0.01 mJ cm<sup>-2</sup>. As can be seen by comparison with the black squares which plot the expected binomial distribution (with  $P = 0.48$ ), this low laser fluence mass spectrum shows the expected statistical distribution of clusters in the beam.

On the other hand, the mass spectrum shown as a dashed line in Fig. 4 was obtained with 30 times higher ArF excimer laser fluence. Clearly, this higher laser intensity has resulted in the absorption of further photons, and caused considerable fragmentation to produce clusters which are more concentrated in gallium. This same shift to more gallium-rich clusters was observed in all size ranges of the cluster distribution, and suggests that loss of As (or, more likely,

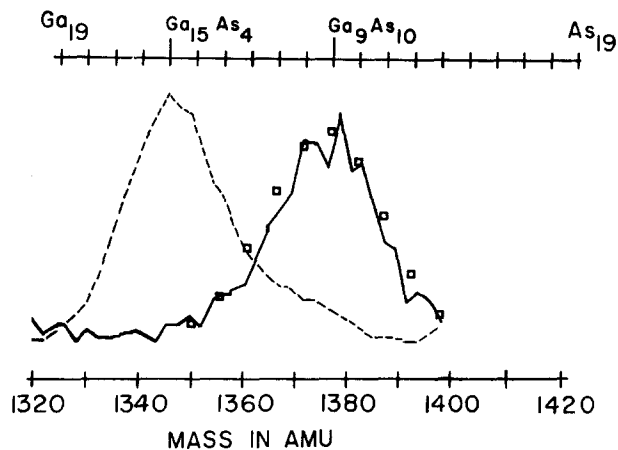


FIG. 4. Time-of-flight mass spectrum in the region of the various possible 19 atom clusters of Ga<sub>x</sub>As<sub>y</sub>, under weak (solid line) and strong (dashed line) ArF excimer laser irradiation. The cluster distribution observed under weak (0.01 mJ cm<sup>-2</sup>) ArF excitation is indistinguishable from the binomial distribution expected statistically (boxes). At higher ArF excimer laser powers (0.3 mJ cm<sup>-2</sup> for the dashed spectrum) the mass spectrum is seen shifted by fragmentation of the parent ions to clusters richer in gallium.

As<sub>2</sub>) is the dominant evaporative process in these small Ga<sub>x</sub>As<sub>y</sub> particles.

This evaporation by loss of arsenic is in agreement with the vaporization dynamics of the bulk GaAs crystal surface<sup>18</sup> previously mentioned.

### IV. SUMMARY AND CONCLUSIONS

Laser vaporization of semiconductor discs in the new supersonic nozzle source has been shown to provide quite an acceptable source of cold clusters at the III-V semiconductors. In the case of GaAs, these clusters have compositions which closely follow a binomial distribution once the size of the cluster exceeds seven to ten atoms. In view of the low temperature and high helium buffer gas density in the cluster formation region, this observation of a binomial distribution is not particularly surprising. Similar results have been observed in hot oven clustering experiments by Martin.<sup>20</sup> In our case, the laser-vaporization process quite efficiently atomizes the top several hundred atomic layers of the semiconductor, producing a vapor which has roughly the 1:1 composition ratio of the bulk. Once the cluster size is more than a few atoms, the temperature and helium collision rate are such that virtually all potential cluster growth collisions are successful—whatever hits, sticks—regardless of whether an arsenic or gallium atom is involved. The resultant binomial distribution is peaked at the 1:1 composition of the bulk. This is desirable since 1:1 clusters are needed to model the chemical bonding, electronic, and vibrational structure of the bulk surface.

Although detailed spectral characterization of these clusters is yet to be done, the ionization behavior described here for fixed frequency lasers is already quite informative. The even/odd alternation in the photoionization cross section seen with the ArF laser at 6.4 eV is very striking—particularly when one considers the large variety of compositions represented in the beam at any one cluster size. The

data indicates that *all* even clusters in the 2–20 atom size range have ionization thresholds above 6.4 eV, whereas clusters with an odd total number of atoms in this same size range have thresholds below 6.4 eV. The only reasonable explanation we can advance for this behavior is that the binding pattern in the even clusters is such that they have fully paired singlet ground states, with all valence electrons involved in fairly substantial bonds. The addition of one more atom then produces an odd-electron system where the extra electron is more weakly bound, and therefore more readily photoionized.

This sort of electronic structure would only be possible in  $\text{Ga}_x\text{As}_y$  clusters if they had extensively reconstructed from the tetrahedral,  $sp^3$  hybridization of the bulk. In fact, the reconstructed structure currently believed to apply to the (110) surface of bulk gallium arsenide,<sup>1–7,21</sup> would result in just such a full-paired ground state singlet electronic structure for the even clusters. The even/odd alternation in ionization properties may therefore indicate that such clusters have no dangling bonds—they are, in the language of surface science, completely reconstructed.

It will be interesting in further, more detailed experiments to see if these simple conclusions bear up to scrutiny, and even more fascinating if new experiments can provide data which can be compared with theoretical calculations on microscopic clusters.

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