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Ammonia chemisorption on gallium arsenide clusters

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Gallium arsenide clusters in the 6–16-atom size range were generated by laser vaporization in a supersonic nozzle and trapped as positive ions in Fourier transform ion-cyclotron resonance mass spectrometer. Measurements of the rate of attachment of ammonia revealed that all clusters larger than seven atoms were most reactive near the 1/1 composition ratio of gallium/arsenic. The results suggest that even at this small size the clusters begin to adopt the alternating gallium–arsenic bonding arrangement characteristic of bulk GaAs crystal surfaces where gallium–arsenic bonding activates gallium atoms for ammonia chemisorption.

1. Introduction

As the active elements of semiconductor devices become increasingly smaller, the effects of surfaces upon bulk properties become more important. Surfaces can be modified by wanted or unwanted reactions affecting the bulk properties. By starting with small clusters of atoms, surface effects can be emphasized. Over the past decade supersonic cluster beam techniques have been developed which now permit a wide range of such semiconductor clusters to be studied [1]. From a chemical viewpoint these methods are intriguing because they can deal with completely bare, coordinatively unsaturated species. They serve as an approach to much of the chemistry of bulk surfaces while retaining the advantages of an explicit molecular scale.

One of the most promising developments along these lines has used Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR) to follow the surface chemistry of separately prepared, mass-selected cluster ions exposed to various reagent gases in an otherwise ultrahigh vacuum [1]. Early examples have included studies of dissociative chemisorption of H_2 on transition metals such as niobium [2], and NH_3 absorption on silicon clusters in the 5–70-atom size range [1,3].

For silicon positive cluster ions [1], the reaction rates with NH_3 depend strikingly upon cluster size varying from about 10^{-13} cm^3 s^{-1} for Si_{45}^+ to about 10^{-10} cm^3 s^{-1} for Si_{43}^+. These results strongly suggest that in many cases only a single structural isomer is formed and that the observed variations in reactivity are the result of the valence structure of this isomer. Models for the bonding in these clusters capable of explaining the colorful experimental observations are beginning to be developed [4].

Clearly, valuable insights into the bonding and structure of the III–V semiconductors may result from studies employing these cluster methods. The first study of GaAs cluster reactions using FT-ICR techniques was carried out by Reents [5], who reported an ICR study of the reactions of HCl with smaller GaAs negative clusters containing up to six atoms. Reents found that the principal reaction was an etching process in which GaCl was lost converting $Ga_xAs_y^-$ into $Ga_{x-1}As_y^-$. Remarkably several of these small anionic clusters exhibited dual populations which could be differentiated kinetically.

Reents was limited by his cluster source technology to the negatively charged clusters of less than seven atoms. It is possible in our apparatus to produce larger clusters, and this work on positively charged gallium arsenide clusters was begun in the hope that these larger clusters would be large enough to begin to model the chemistry of the real GaAs bulk surface.

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2. Experimental

The apparatus used in this work has been described in more detail previously [1,2]. In brief, the positive cluster ions studied are generated by laser vaporizing (20 mJ, 532 nm) GaAs from the surface of a rotating disk into a helium carrier gas pulse. The gas stream travels about 1 cm down a 1 mm diameter channel (where clustering takes place) and then expands supersonically into a vacuum. The resulting supersonic jet is collimated into a molecular beam. About 30 cm downstream, the residual positive cluster ions remaining from the vaporization plasma are pulse extracted and directed towards the ICR cell. The ions are decelerated by a pulsed decelerator and then injected into the ICR cell by dropping its reflecting electrostatic field at the cell entrance as the ion pulse approaches. In the cell, the ions spiral along the field lines of the axial magnetic field of 6 Tesla supplied by a superconducting solenoid magnet and reflect from electrostatic fields at each end of the trap. Cluster ions can be trapped in the cell for several minutes. In order to obtain sufficient cluster ion concentrations for study, the 10 to 100 injection pulses are accumulated. After the cell is filled, the ions are thermalized by collisions with argon (2×10^{-5} Torr) added for a few seconds.

The ICR cell is cylindrical about 15 cm long, 4.8 cm inner diameter. In the uniform magnetic field of its central portion, four electrodes are placed around the axis of the cell. These permit the coherent excitation of the cyclotron motion of the ion by rf pulses and allow the observation through induced rf voltages on the electrodes of the transient decay of this coherent motion. Fourier analysis of this transient provides a high resolution mass spectrum of the ions trapped in the cell. Of particular interest for surface reaction studies is the ability to remove all ions except those in a narrow mass range from the cell by strong excitation of their cyclotron motion using an rf pulse tailored by "SWIFT" technology [6]. Thus we have the capability of producing in the ICR cell $Ga_xAs_y^+$ ions of only one $x+y$ value.

These ions are then allowed to react with a suitable reagent (in this work, NH_3) for a definite period of time by shuttering off the pump and injecting the reagent with a pulsed valve (R. M. Jordan, Inc.). Typical reagent pressures used here are 10^{-5} to 10^{-6} Torr with typical reaction times of 2 to 60 s. The reagent gas is then pumped away and the mass spectrum of the product ions is obtained by FT-ICR. Reaction studies are limited to 10^4–5×10^4 collisions because after more collisions the ions are lost from the trapping region.

The fact that gallium has two naturally occurring isotopes ^{71}Ga (40%) and ^{69}Ga (60%) complicates the analysis of the mass spectrum. The top panel of fig. 1 shows the observed FT-ICR mass spectrum of the Ga_xAs_y cluster ion distribution injected from our cluster source [2,3] such that $x+y=10$ atoms. Although the major mass peaks here are spaced by 2.00 amu and extremely well resolved, each has contributions from several different Ga_xAs_y compositions.

As was noted by Reents [5], the difference in mass between ^{71}Ga (40%) and ^{69}Ga (60%) is almost exactly 1/2 of the mass difference between ^{71}Ga and the only isotope of As (^{75}As). This means that the mass peaks of $^{71}Ga_a{}^{69}Ga_bAs_y^+$ are completely unresolved from those of $^{71}Ga_{a-3}{}^{69}Ga_{b+2}As_{y+1}^+$ even with the very high mass resolution of FT-ICR. In order to determine the distribution of x and y values, it is necessary to least-squares fit the peak intensities with the total signal intensities, I_x (counting all ^{71}Ga and ^{69}Ga possibilities) for all x at given $x+y$. This pro-

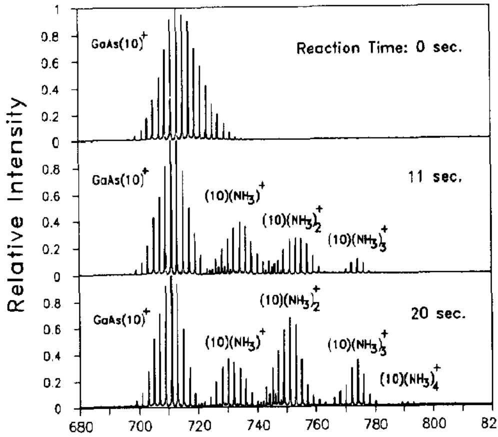

Fig. 1. FT-ICR mass spectrum of 10-atom $Ga_xAs_y^+$ clusters before (top) and after (middle and bottom) exposures to a mixture of 10% ammonia, 90% Ar at P(NH_3) of 2×10^{-6} Torr at 300 K. In the middle panel the exposure time is 11 s and in the bottom 20 s.

cedure proved to be straightforward except that occasionally the least-squares result gave $I_x < 0$ for some of the less abundant species. When such a non-physical answer resulted from the least-squares process, the distribution was refitted with this I_x fixed to zero. Least-squares analysis of the peak intensities of the 10-atom GaAs cluster of fig. 1 shows this sample to be composed of roughly 3% Ga_9As_1, 20% Ga_8As_2, 47% Ga_7As_3, 14% Ga_6As_4, 12% Ga_5As_5, 3% Ga_4As_6, 0.4% Ga_3As_7, with traces of the other compositions.

Because the excitation of the cyclotron frequency accelerates the ions to large orbits, a particular mass region can only be observed once in a single run. Only the intensities after a known exposure to the reagent, NH_3, are available for a given run. The intensities before exposure are not observable. Fortunately the total ion content of the cell has become quite reproducible from run-to-run as a result of a recent modification of the source in which the solenoid valve was replaced by a magnetic leaf valve (R. M. Jordan, Inc.). In the reaction studies, the desired data are ion intensities as a function of exposure time. If it can be assumed that all reaction product ions are observed and none of these observed products result from Ga or As loss, the intensity of any $Ga_xAs_y(NH_3)_z$ combination can be normalized by dividing by the sum over z for a given x, y. These conditions appear to be well-satisfied, and such normalization is satisfactory.

3. Observations and results

The laser vaporization technique produces cluster positive ions ($Ga_xAs_y^+$) ranging in $x+y$ values from two to more than thirty atoms. When the chemical compositions of the $x+y$ groups are analyzed by the least-squares procedure described above, the resulting distributions are generally found to be peaked on the gallium-rich side of the stoichiometric 1:1 Ga to As ratio as in the illustration previously given with the 10-atom cluster of fig. 1.

A particular $x+y$ value may be selected by SWIFTing out all the other ions, and then subjected to chemical reaction with an added reagent gas. In the middle panel of fig. 1, the FT-ICR mass spectrum has been taken after the 10-atom $Ga_xAs_y^+$ clusters were exposed to NH_3 gas at a pressure of 2×10^{-6} Torr for 11 s. Note that the successive NH_3 attachment products do not appear to have the same mass spectral distribution as the parent bare cluster. In fact, if one looks closely at the middle panel of fig. 1, a distinct dip can be recognized in the bare cluster ion distribution near the 1:1 stoichiometry. This is made much clearer in fig. 2, where the spectrum has been expanded and the peaks due to product ions with one NH_3 have been deleted.

Detailed least-squares analysis of the mass patterns reveals that reactivity depends strongly upon composition. Fig. 3 shows signal intensities of the unreacted clusters with $x+y=10$ as a function of exposure time to NH_3. In this figure, in order to compare the behavior of clusters which have widely different initial concentrations, all initial concentrations have been normalized to unity. The figure summarizes the average of five independent sets of data. Each data set can be fitted with a decay constant which when combined with NH_3 pressure and an estimated gas kinetic collision cross-section yields a sticking coefficient to the cluster for NH_3. Fig. 4 shows such data for the 10-atom cluster. The remarkable result is that the reaction rate for ammonia chemisorption peaks near the 1/1 composition, $Ga_5As_5^+$. Studies on both odd- and even-numbered clusters in the 8–16-atom size range show this to be

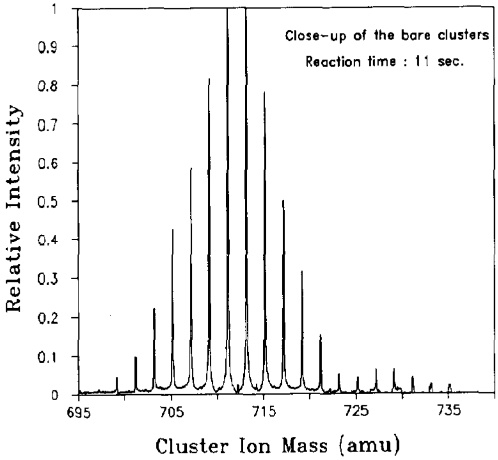

Fig. 2. Expansion of the unreacted clusters for the middle panel of fig. 1. In this figure, the peaks due to the reaction products have been deliberately erased to show the dip near 723–725 amu. This mass region corresponds to the most abundant isotopomers of $Ga_5As_5^+$ ($^{69}Ga_3{}^{71}Ga_2As_5^+ = 723.23$ amu).

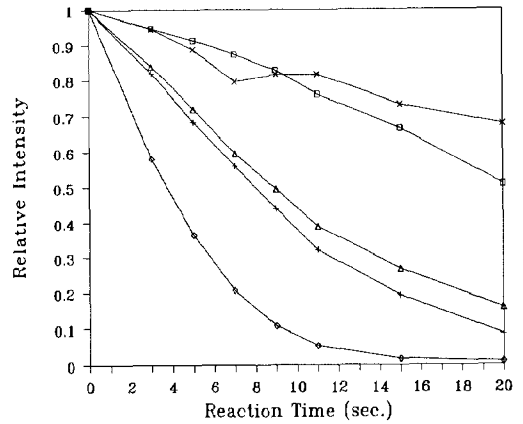

Fig. 3. Relative concentration as a function of exposure time to NH_3 for bare 10-atom cluster ions. The data for five different sets of runs are summarized in this figure. For each cluster at each time, the point is the average of the five sets. The clusters are exposed to a mixture of 10% NH_3, 90% Ar at a pressure of 2×10^{-6} Torr. (□) Ga_7As_3, (+) Ga_6As_4, (◇) Ga_5As_5, (△) Ga_4As_6, (×) Ga_3As_7.

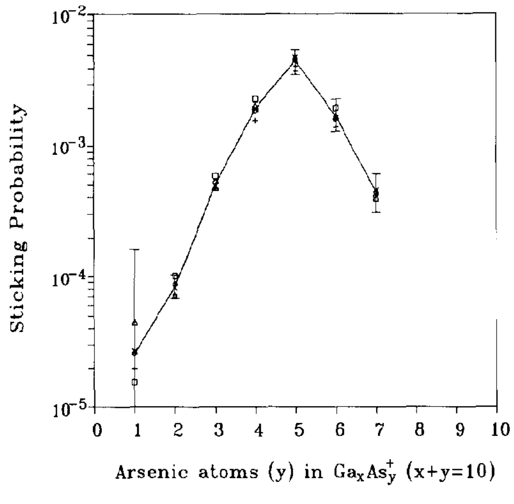

Fig. 4. Approximate sticking probability (reaction rate/ion–molecule collision rate) for the chemisorption of the first NH_3 on bare 10-atom $Ga_xAs_y^+$ clusters as a number of As atoms in the cluster. The result from each of the five data sets is shown as point. □, +, △, ◇, × correspond to the different sets. The line connects the average.

a general result: clusters near the stoichiometric 1/1 composition of bulk gallium arsenide are the most reactive toward chemisorption of NH_3.

The 6- and 7-atom $Ga_xAs_y^+$ clusters behave differently: they are generally less reactive than the larger clusters, and this reactivity is highest on the gallium-rich side of the composition range. Thus it appears that in terms of kinetic behavior with ammonia chemisorption the transition to bulk behavior takes place at clusters containing 8 atoms total!

As can be seen in the lower panels of fig. 1, the reaction does not stop with the addition of one NH_3, but adds up to four NH_3's in the case of the 10-atom clusters. The time behavior of these subsequent additions for $Ga_5As_5^+$ is shown in fig. 5 as a typical case and is qualitatively as expected. The relative signals at the longest time in fig. 5 are not very different from those for much longer exposure times. The results of such ammonia titrations are the subject of a later paper [7]. Here we merely note that they suggest the existence of several isomers for many compositions as was found for the small anions by Reents [5].

4. Discussion

At first glance, these gallium arsenide clusters appear to present a complex and perplexing picture as a result of the wide range of possible chemical compositions and the evidence for isomers found by Reents [5]. However, in spite of this apparent complexity, there appear to be some simplifying generalizations which can be made concerning GaAs clusters. One key simplifying factor was noted in earlier work from this group where photoionization studies of the neutral GaAs cluster beam revealed a strong even/odd alternation in the ionization potentials [8] and photodetachment studies of the negative clusters showed corresponding odd/even alternation in the electron affinities [9] of the clusters. This is evidence that, over a broad range of chemical compositions, clusters containing an even number of electrons are electronically closed shell, with singlet ground states and a substantial HOMO–LUMO gap. This behavior is reminiscent of the bulk GaAs (110) surface where relaxation adjusts the dangling bonds sufficiently to open a large gap in the surface band structure [10].

In the kinetic studies reported here, it is found that clusters near the stoichiometric 1/1 composition of bulk gallium arsenide are the most reactive toward chemisorption of NH_3. The active site for NH_3 at-

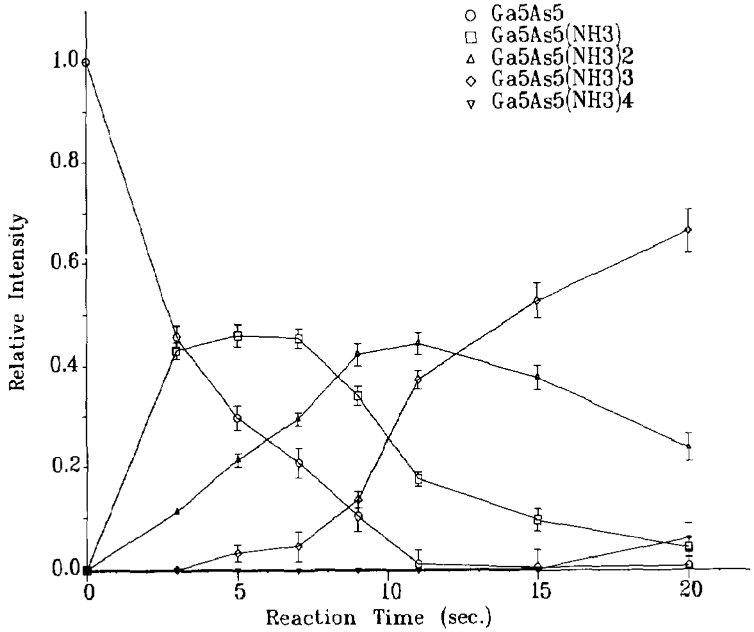

Fig. 5. Relative intensity of the bare and various NH_3 addition products for $Ga_5A_5^+(NH_3)_z$ as a function of time. The NH_3 pressure is still 2×10^{-6} Torr.

tack must therefore involve both gallium and arsenic. The simplest and most plausible model is one where each surface Ga atom is surrounded as much as possible by As atoms (and vice versa), much like the bulk GaAs crystal surface. Tripathi et al. [11] have studied the chemisorption of NH_3 on single-crystal GaAs, and found facile NH_3 adsorption on the (111)A dipolar surface (which consists solely of Ga atoms bonded to three underlying As atoms), but no reactivity on the corresponding (111)B arsenic surface. It seems likely that a similar chemistry is occurring on the surface of these nanometer scale clusters where the As–Ga bonding activates the gallium as a Lewis acid site for adsorption of NH_3 (perhaps followed by dissociation to produce $-NH_2$ or $=NH$, and surface hydrides).

Indeed, As–Ga bonding appears to perform such an activation role on bulk GaAs surfaces. Surface reconstruction on the (111) and (110) planes of bulk gallium arsenide is thought to result in one "dangling hybrid" orbital per surface atom, with a lone pair on the (slightly negative) arsenic, and an empty orbital on the surface gallium atoms which end up with a slight positive charge [12]. In addition to opening up a broad surface band gap (i.e. a large HOMO–LUMO gap) this reconstruction promotes the surface Ga atoms into excellent Lewis acid binding sites for the chemisorption of ammonia.

Gallium arsenide clusters of as few as eight atoms therefore appear to be behave much like pieces of the bulk GaAs surface. Further experiments and extensive electronic structure calculations will be necessary to test the validity of this chemically appealing model. If correct, it will provide a major simplification in the study of GaAs clusters, and will greatly increase their utility as molecular models of the real bulk surface.

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