Potential energy surfaces for the Ga$_2$As + Cl etching reaction

Dingguo Dai, K. Balasubramanian

Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, USA

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Abstract

Potential energy surfaces for the Ga$_2$As + Cl reaction are computed to model halogen-etching reactions of III–V semiconductors. The complete active space self-consistent field followed by multi-reference singles and doubles configuration interaction methods was used to compute the potential energy surfaces. Our studies reveal two low-lying bound minima with substantially different geometries for the Ga$_2$AsCl product.

1. Introduction

Halogen etching of semiconductors is one of the fundamental processes in the fabrication of microelectronic devices, since halogen-etching is more selective compared to plasma etching [1–8]. Halogen compounds such as Cl$_2$, Br$_2$, HBr, HCl, etc., are used as etchant gases. In such reactions, the halogen molecules are dissociated photochemically and the resulting halogen radicals produced in the process of photoillumination are shown to etch surfaces of III–V semiconductors such as GaAs as well as silicon. Several experimental studies have shed considerable light on the kinetics and the rate dependence of the etching reactions, although the mechanisms of the etching reactions at the molecular level have not been completely understood.

Experimental studies by Osgood and co-workers [2,4,6,7] on the dry-halogen etching of GaAs by employing an excimer laser and HBr as an etchant gas, have revealed that the Br radical produced by the laser reacts with the GaAs surface to produce primarily GaBr$_3$ and AsBr$_3$. In contrast, an experimental study by Liberman et al. [7], has shown that the etching of GaAs(110) surface produces GaCl as the only chlorine-containing species besides Cl$_2$ in thermal desorption. In this case it seems that a primary mechanism would be rearrangement of the chemisorbed surface Cl atom prior to dissociation. These authors have observed a decrease in the GaCl desorption temperature with an increase in the Cl adatom concentration. In contrast to thermal-induced desorption, laser-induced desorption produces AsCl$_3$ and AsCl$_2$ also in addition to the other species at 180 K. Toost et al. [8] have explored the GaAs + Cl$_2$ reaction, and suggested that the Cl atom is chemisorbed on the surface which induces a dipole moment thereby acting as surface electron acceptors.

Halogen etching of gallium arsenide clusters has been studied by Reents [9]. Etching of Ga$_x$As$_y$ cluster ions with HCl as an etchant gas has revealed that for smaller clusters containing less than 6 atoms, the etching reaction proceeds primarily through the loss of GaCl to form Ga$_{x-1}$As$_y$H$^-$ and Ga$_{x-2}$As$_y$H$_2$. However, clusters that do not contain Ga reacted with Cl to lose AsCl or abstract a proton and form Cl$^-$. Another notable feature of this study is that the reactivities of isomers exhibited dramatic contrast.

Smalley and co-workers [12–15] have made pio-
neering studies on mixed clusters of gallium arsenide of the general formula Ga$_x$As$_y$, generated by laser-vaporization of a GaAs crystal. These studies have revealed fascinating trends pertaining to the distribution and the reactivities of these clusters. Theoretical studies of small gallium arsenide clusters and dimers, as well as the related silicon clusters are on the increase [10,16–26]. Reviews by Mandich et al. [11], as well as the author [26] summarize the important developments pertinent to these clusters.

There is a compelling need to comprehend the nature of the surface–halogen interactions pertinent to the halogen-etching of GaAs. Small clusters of GaAs could provide viable models for detailed theoretical elucidation of the electronic structure and potential energy surfaces of such species. In this study we investigate the electronic structure and potential energy surfaces for the Ga$_2$As + Cl interaction. Our study reveals several fascinating trends in the potential energy surfaces. We find two competing potential minima in the surface, one exhibiting stronger Ga–Cl bonding while the other exhibiting stronger As–Cl bond. We use a complete active space self-consistent field (CASSCF) followed by multi-reference configuration interaction (MRSDCI) computations to study the equilibrium geometries and the potential energy surfaces of Ga$_2$As + Cl interactions.

2. Method of calculations

Relativistic effective core potentials (RECPs) with the outer 4s$^2$4p$^1$ shells of Ga, 4s$^2$4p$^3$ shells of As, and 3s$^2$3p$^3$ shells of Cl taken from Ref. [27] for the Ga, As and Cl atoms were used in the present study. Valence (3s3p) Gaussian basis sets for both Ga and As atoms were taken from Ref. [27]. We augmented them with one set of d functions ($\alpha_d = 0.2$ and 0.22 for Ga and As, respectively). For the Cl atom the (4s4p) basis set taken from Ref. [27] was contracted to (3s3p). The basis set of the Cl atom was supplemented with one set of d functions with $\alpha_d = 0.5147$. The final basis sets for Ga, As and Cl atoms were uniformly of the (3s3p1d) quality.

The complete active space multiconfiguration self-consistent field (CAS-MCSCF) method was employed as a starting point for the higher-order CI calculations of Ga$_2$AsCl. Multireference singles + doubles configuration interaction (MRSDCI) calculations were carried out following the CAS-MCSCF calculations. The calculations were made in the C$_{2v}$ point group orienting the molecule on the yz plane. The chlorine atom was placed at the origin and the arsenic atom was placed on the positive z axis. Two gallium atoms were placed symmetrically on either side of the z axis. The Ga–Cl and As–Cl bond lengths, and the Ga–Cl–Ga bond angle were fully optimized for the $^1A_1$ state of Ga$_2$AsCl.

For the Ga$_2$AsCl molecule the valence s and p orbitals of Ga, As, and Cl atoms correlate into seven $a_1$, five $b_2$, three $b_1$ and one $a_2$ orbitals. All four s orbitals were kept inactive in the sense that no excitations from these shells were allowed but these orbitals (which correlate into three $a_1$ and one $b_2$ orbitals) were allowed to relax. Thus, twelve orbitals were retained in the active space. They are four each of $a_1$ and $b_2$, three of $b_1$, and one of $a_2$ symmetries. Ten active electrons were distributed in all possible ways among these twelve active orbitals.

The MRSDCI calculations were carried out near the minima of the $^1A_1$ state to include the effects of higher-order electron correlation. All configurations in the MCSCF with coefficients $> 0.04$ were included as reference configurations in the MRSDCI. All possible single and double excitations were allowed from these reference configurations. The MCSCF calculations included 42806 configurations spin functions (CSFs) while the MRSDCI included up to 334534 CSFs. The MCSCF/MRSDCI calculations were made using one of the author's modified version [28] of ALCHEMY II codes 1 to include RECPs.

3. Results and discussion

Fig. 1a shows the bending potential energy surfaces of the $^1A_1$ state of Ga$_2$AsCl at the CAS-MCSCF level. For each Ga–Cl–Ga bond angle between 20–320° the As–Cl bond length and the two Ga–Cl equal sides were optimized, and the optimized energy was plotted in Fig. 1a. As seen from Fig. 1a,

1 The major authors of ALCHEMY II are B. Lengsfield, B. Liu and M. Yoshimine.
there are two types of potential energy curves, both of which arise from the $^1A_1$ state. One curve has somewhat shorter Ga–Cl bond length while the other with a longer Ga–Cl bond is labelled the long bond curve. We found three local minima which are labelled (a)–(c), respectively, in Fig. 1a. The geometries and energy separations of these three minima of the $^1A_1$ state of Ga$_2$AsCl at the CAS-MCSCF level are shown in Fig. 2.

If the Ga–Ga line directly crosses the As–Cl line, we define the Ga–Cl–Ga bond angle as $<180^\circ$; otherwise, we define the angle to be $>180^\circ$. Thus, the minima (a) and (b) correspond to GaClGa bond angle $<180^\circ$ while the minimum (c) represents the latter case.

As seen from Fig. 1a, the short GaCl bond curve has a lower energy near the Ga–Cl–Ga bond angle of $80^\circ$, while the longer GaCl bond curve has a lower energy in the rest of the region. As an illustration Fig. 1b shows the two potential energy surfaces for the Ga–Cl–Ga bond angle of $95^\circ$. At this bond angle, the minimum which corresponds to the long bond curve is lower than the minimum of the short bond curve. All points of the two curves in Fig. 1a at different bond angles were obtained using this way by optimizing the Ga–Cl bond lengths.
As seen from Fig. 1a, the two curves cross at 68°, 87°, and 235°. However, these are not global avoided crossings since the bond lengths of the two curves are quite different.

At the CASMCSF level, the potential minima (a) and (b) are nearly degenerate, as seen from Table 1, the actual energy difference between these minima being only 0.056 eV. The minimum labelled (a) has a Ga–Cl bond length of 2.416 Å, which is 0.56 Å shorter compared to the Ga–Cl bond length in the minimum labelled (b). The Ga–As bond lengths in these two minima are 2.443 and 2.537 Å, respectively, while the Cl–As bond lengths are 3.743 and 2.399 Å for the minima (a) and (b), respectively.

At the higher MRSDCI level the energy separation of these two minima increases to 0.18 eV while at the MRSDCI + Q (with the Davidson’s correction) level this value changes to 0.15 eV. The Ga–Cl bond lengths of both minima are longer at the MRSDCI level, while the Ga–As and Cl–As bond lengths are shortened compared to their at the CASMCSF level. The Ga–Cl–Ga and Ga–Cl–As bond angles at the MRSDCI level did not change much compared to the CASMCSF values. Although geometry (c) is a local minimum, it is of less significance as its energy is considerably higher. In Table 1 we marked the Ga–Cl–Ga bond angle of geometry (c) as 66.7°, which comes from 360°–293.3° for convenience. The (c) minimum is found to be 3.52, 3.57, and 3.56 eV higher than the 1A1 electronic state of Ga2ClAs at the CASMCSF, MRSDCI, and MRSDCI + Q levels, respectively. In geometry (c), the Ga–Cl bond lengths are 2.643 Å at the CASMCSF level, or 2.61 Å at the MRSDCI level, which is longer than the corresponding bonds in geometry (a), but shorter than the Ga–Cl bonds in geometry (b). The primary reason for the higher energy of geometry (c) is that the distance between Ga and As atoms is long. For the (a) and (b) minima, the Ga–As bond lengths are 2.43–2.53 Å, while for geometry (c) this value becomes 5.1–5.2 Å. Hence, there is very little bonding (or very weak bonding) between Ga and As atoms in geometry (c).

Table 1 shows the leading configuration(s) in the Table 2 Leading configuration(s) in the MRSDCI wavefunction of the 1A1 state of Ga2AsCl for various minima in the potential energy surface

<table>
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<tr>
<th>Label a</th>
<th>Coefficient</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a1</td>
<td>2a1</td>
<td>2b1</td>
</tr>
<tr>
<td>(a)</td>
<td>0.948</td>
<td>2</td>
</tr>
<tr>
<td>(b)</td>
<td>−0.948</td>
<td>2</td>
</tr>
<tr>
<td>(c)</td>
<td>0.721</td>
<td>2</td>
</tr>
</tbody>
</table>

* Labels (a)–(c) see Figs. 1 and 2.

We calculated the dissociation energy for the Ga2AsCl(1A1) → Ga2As(2B1) + Cl(2P)

As seen from Table 1, the dissociation energy is found to be 2.09 or 2.15 eV for the geometries (a) or (b), respectively, at the CASMCSF level. At the MRSDCI and MRSDCI + Q levels, the dissociation energy increases to 3.39 and 3.41 eV for geometry (a), respectively, and 3.57 and 3.56 eV for geometry (b), respectively.
Table 3
Mulliken population analysis for the \(^1A_1\) electronic states of Ga\(_2\)AsCl

<table>
<thead>
<tr>
<th>Label</th>
<th>((a))</th>
<th>((b))</th>
<th>((c))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>2.654</td>
<td>2.624</td>
<td>2.709</td>
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<tr>
<td>As</td>
<td>5.297</td>
<td>5.376</td>
<td>5.104</td>
</tr>
<tr>
<td>Cl</td>
<td>7.395</td>
<td>7.376</td>
<td>7.478</td>
</tr>
<tr>
<td>Ga(s)</td>
<td>1.677</td>
<td>1.894</td>
<td>1.871</td>
</tr>
<tr>
<td>Ga(p)</td>
<td>0.861</td>
<td>0.659</td>
<td>0.781</td>
</tr>
<tr>
<td>Ga(d)</td>
<td>0.116</td>
<td>0.071</td>
<td>0.057</td>
</tr>
<tr>
<td>As(s)</td>
<td>1.846</td>
<td>1.795</td>
<td>1.993</td>
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<tr>
<td>As(p)</td>
<td>3.333</td>
<td>3.409</td>
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<tr>
<td>As(d)</td>
<td>0.118</td>
<td>0.172</td>
<td>0.019</td>
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<tr>
<td>Cl(s)</td>
<td>1.962</td>
<td>1.948</td>
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<tr>
<td>Cl(p)</td>
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<td>5.442</td>
</tr>
<tr>
<td>Cl(d)</td>
<td>0.083</td>
<td>0.114</td>
<td>0.079</td>
</tr>
</tbody>
</table>

\(^a\) Labels \((a)-(c)\) see Figs. 1 and 2.
\(^b\) Represents one of the two Ga atoms.

MRSDDCI wavefunction of the \(^1A_1\) state of Ga\(_2\)AsCl for the minima in the potential energy surface considered here. The \(^1A_1\) state in geometry \((a)\) is predominantly represented by the \(1a_1^2 2a_1^2 1b_1^2 2b_1^2\) configuration with a coefficient of 0.948. This is in contrast with geometry \((b)\), which is predominantly represented by \(1a_1^2 1b_2^2 2b_1^2 2b_2^2\). The \(2a_1\) and \(2b_2\) orbitals are found to be the highest occupied molecular orbitals (HOMO) for the minima \((a)\) and \((b)\), respectively. For geometry \((a)\), the \(2a_1\) HOMO is composed of \(\text{As(s)} + \text{As(p)} + \text{Cl(p)} - \text{[Ga_2(s) + Ga_2(p)]}\), while the \(2b_2\) lowest unoccupied molecular orbital (LUMO) consists of \(\text{As(p)} + \text{As(d)} + \text{Cl(p)} - \text{[Ga_2(s) + Ga_2(p)]}\). For geometry \((b)\) the \(2a_1\) LUMO orbital is composed of \(\text{As(p)} - \text{As(s)} + \text{Cl(p)} + \text{Cl(s)} + \text{Cl(d)} - \text{[Ga_2(s) + Ga_2(p)]}\) while the \(2b_2\) HOMO orbital consists of \(\text{Cl(p)} - \text{As(p)} - \text{[Ga_2(s) + Ga_2(p)]}\).

Table 3 shows the gross Mulliken populations of the various atoms for the three potential minima considered here. As seen from Table 3, the Mulliken populations of structures \((a)\) and \((b)\) are similar, the only difference being in the As atom’s population which is enhanced in the case of the \((b)\) minimum, since the As–Cl bond is considerably stronger in the \((b)\) minimum. Consequently, the two low-lying po-
tential energy minima \((a)\) and \((b)\) can be rationalized as arising from competing bonding forces between the Ga–Cl–Ga bridge bonding and the As–Cl direct bonding, the latter one favoring the minimum \((b)\). In both minima the Cl Mulliken population is in excess of 7.0 indicating charge transfer to chlorine.

4. Conclusion

We carried out CASSCF/MRSDCI computations that included up to 334, 500 configurations on the potential energy surfaces of Ga\(_2\)As + Cl interaction. Our studies reveal the existence of two nearly degenerate minima in the potential energy surface with substantially different geometries, one with longer Ga–Cl bond lengths and shorter As–Cl bond distance, while the other with shorter Ga–Cl distances and longer As–Cl distance. This clearly suggests competition between Ga–Cl and As–Cl bonding in the Ga\(_2\)As + Cl system. This is also in contrast with a previous study \[29\] on the GaAs + Cl reaction which exhibits strong ionic Ga–Cl bonding and a very weak Ga–As bonding in the CIGa....As complex. The results of these two studies support the experimental finding by Reents \[9\] that the reactivity with Cl strongly varied with the cluster. That is, direct Ga–Cl ionic bonding is the primary factor in the GaAs + Cl reaction while both As–Cl and Ga–Cl bonds are equally favored in the Ga\(_2\)As + Cl reaction. It would be interesting to see how the reactivity varies for other clusters.

Acknowledgements

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References
