Site-Selective Reaction of Br_2 with Second Layer Ga Atoms on the As-rich GaAs(001)-2 × 4 Surface

Yong Liu, Andrew J. Komrowski, and Andrew C. Kummel*
Department of Chemistry, 0358, University of California at San Diego, 9500 Gilman Drive, La Jolla, California 92093

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The top layer of the GaAs(001)-(2 × 4) surface consists of rows of As-As dimers. However, our scanning tunneling microscopy study shows that, in the initial adsorption stage, monoenergetic Br_2 molecules (0.89 eV) react exclusively with the second layer Ga atoms exposed in trenches or at defects on the surface. A simple molecular orbital argument was used to explain the dynamics of forming gallium bromide species at various surface Ga sites. [S0031-9007(98)06601-0]

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This Letter presents the first evidence showing that energetic Br_2 molecules react exclusively with the second layer Ga atoms exposed in trenches or at defects on the As-rich GaAs(001)-(2 × 4) surface in the initial adsorption stage. Such a complete Ga-site selectivity is unexpected since the first layer of the surface entirely consists of dimerized As atoms directly exposed to incident Br_2 molecules. This site selectivity indicates that, although the reactions of Br_2 with both Ga and As atoms on the surface are exothermic [1], the less filled surface Ga dangling bonds are more reactive to the highest occupied molecular orbitals (HOMO) of halogens than the more filled surface As dangling bonds.

Surface site selectivity associated with halogen adsorption on the GaAs surfaces has recently been a subject of controversy because of the coexistence of Ga and As atoms on the surfaces. It was reported that the initial adsorption of Cl_2 on the As-stabilized, Ga-stabilized, and sputtered GaAs(001) surfaces occurs preferentially at the Ga sites [2]. This partial surface site selectivity was also observed for the adsorption of hydrogen atoms on the GaAs(001)-c(2 × 8) surface at 303 K [3]. Additionally, partial preference for Ga sites at low coverages during Cl_2 (or Br_2) adsorption onto the GaAs(110) surfaces was also established [4–6]. However, these observations are contrary to earlier experimental works [7,8] showing that As-Cl bonding is favored on GaAs(110) surfaces.

In our experiments, 0.89 eV Br_2 molecular beams were produced by expanding Br_2 and He mixtures at 298 K and 3.7 atmosphere through a pulsed valve. The GaAs(001) wafers (Motorola) containing two Si-doped GaAs layers grown on a $n+$ GaAs(001) substrate and were protected by a thick As layer. After thermal removal of this As layer, the sample was annealed at 450 °C for 15 min and cooled quickly to room temperature to obtain a clean and well-ordered As-rich GaAs(001)-(2 × 4) surface. A scanning tunneling microscope (STM) (Park Scientific) was used to scan the filled-state topographic images of the clean or Br_2-dosed GaAs surface.

Figure 1(a) is a filled-state STM image of the clean As-stabilized GaAs(001)-(2 × 4) surface. The image is characterized by alternating protruding columns (bright) and trenches (dark) running in the $(\bar{1}10)$ direction [9–11]. The first layer of an ideal 2 × 4 unit cell [rectangle in Figs. 1(a) and 2] contains two As-As dimers and two As-As dimer vacancies [12]. Each sp^3 hybridized top-layer As atom forms two As-Ga back bonds and a strained As-As dimer bond (bond energy $\approx$2 eV), leaving a filled dangling bond that tilts upwards. At a STM sample bias of -3 V, both the filled As dangling bonds and the As-As dimer bonds contribute to the tunneling of electrons out of the surface. In the second layer of a 2 × 4 unit cell, four of the six Ga atoms are located at the trench edges. Each edge Ga atom has an empty sp^3 dangling bond that is perpendicular to the As-As dimer rows and buckles upwards. These Ga empty dangling bonds cannot be imaged at a negative sample bias. In the third layer of a 2 × 4 unit cell, two As atoms located at the trench bottom dimerize to form an As-As dimer. Several types of surface defects have been identified in our STM images, including dark As-As dimer vacancy (V_d near a single As-As dimer *D*), dark As atomic vacancy (V_a), kinks (*K*), bright excessive arsenic (*A*), and steps (*H*) with the vacancies being most abundant. A few 2 × 4 unit cells containing three As-As dimers and one missing As-As dimer (*B*) were occasionally observed in our STM images [13,14].

A 100 Å × 100 Å STM image of an As-stabilized GaAs(001)-(2 × 4) surface dosed at 300 K with 0.89 eV Br_2 ($\sim$0.7 langmuirs) is presented in Fig. 1(b). This is a different surface region from that shown in Fig. 1(a). Surprisingly, the first-layer As-As dimers (bright) remain intact despite the exposure to Br_2. The adsorption of 0.89 eV Br_2 onto the surface produces new dim features at As atomic vacancies, at As-As dimer vacancies, and inside surface trenches. These dim features are lower than the unreacted first-layer As-As dimers and have perfect position registry in the $(\bar{1}10)$ direction with respect to the second layer Ga atoms. Thus, these new features are identified as surface gallium monobromide species ($GaBr_{(s)}$) formed at different surface sites. By manually counting the total number of these surface GaBr species

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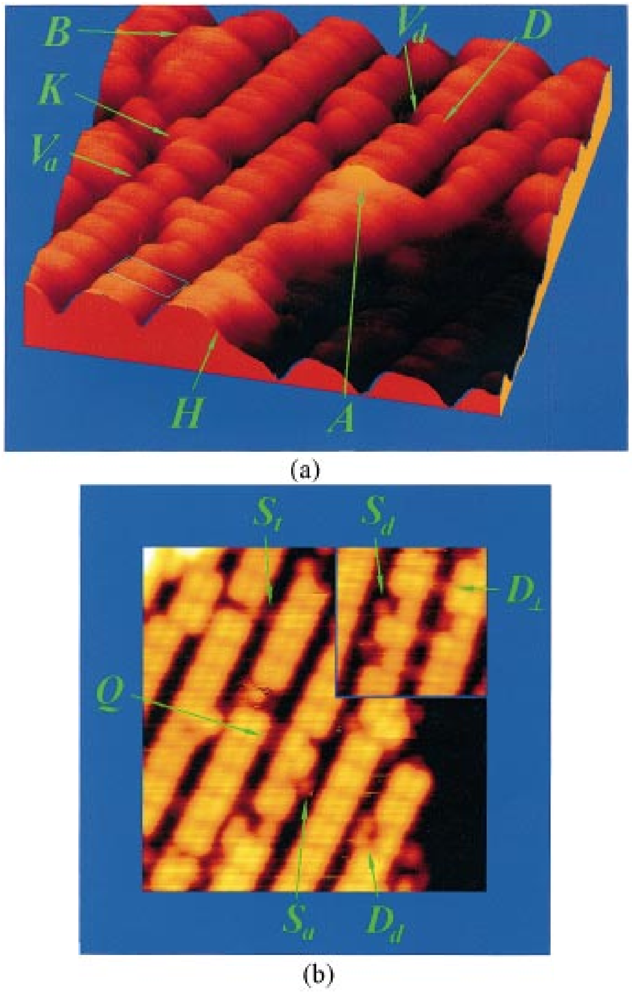

(a)

(b)

FIG. 1(color). Filled-state STM images of (a) the clean As-rich GaAs(001)-(2 × 4) surface and (b) the As-rich GaAs(001)-(2 × 4) surface dosed with 0.89 eV Br_2 to 0.39 ML coverage at a sample bias of −3 V and a tunneling current of −0.3 nA (see text for details).

over a surface area containing 789 2 × 4 unit cells, the total bromine coverage is determined to be approximately 0.039 monolayer (ML) (where 1 ML is defined as eight chemisorbed Br atoms per unit 2 × 4 cell).

A dim ball inserted into an As atomic vacancy (V_a sites) has been identified as a Br atom in an isolated S_a-$GaBr_{(s)}$ species [see Fig. 1(b)]. Height profiles along a chain of As-As dimers show that the V_a site and the S_a-GaBr site appear as 1.5 ± 0.1 and 1.1 ± 0.1 Å deep valleys relative to the maximum of an As-As dimer, respectively. By manually counting the GaBr sites, it was found that about 22% of the 0.039 ML chemisorbed Br atoms exist as S_a-GaBr on the As-rich GaAs(001)-(2 × 4) surface. About 79% of the As atomic vacancies have reacted with Br_2 at a total Br coverage of 0.039 ML, indicating that Ga atoms at V_a sites are very reactive to bromine. The relative errors of the given percentages are within ±20%. We propose that a S_a-GaBr species is formed via the abstractive adsorption mechanism [15]: one Br atom from a Br_2 forms a Ga-Br bond with a Ga atom at an As atomic vacancy, and the other is ejected back into the gas phase.

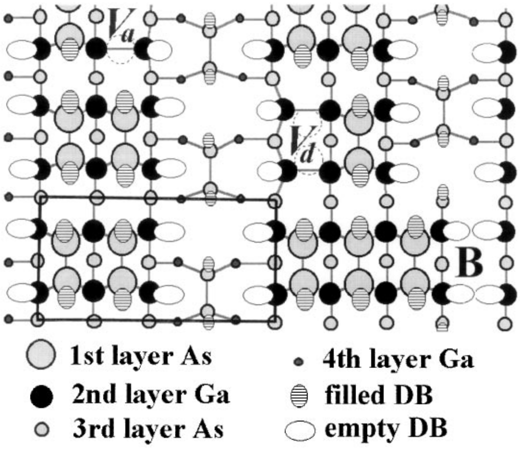

FIG. 2. The bonding structure of As and Ga atoms and the dangling bonds (DB) on the clean As-rich GaAs(001)-(2 × 4) surface, where V_a and V_d are an As atomic vacancy and an As-As dimer vacancy, respectively. A 2 × 4 unit cell has been outlined in the lower-left corner of the diagram.

A dim, oblong, and wormlike feature (D_d) in Fig. 1(b) is identified as two adjacent Br atoms in two $GaBr_{(a)}$ species at an As-As dimer vacancy. This feature is identical in size to an As-As dimer and is 1.0 ± 0.1 Å lower than a first-layer As-As dimer. Approximately 11% of the 0.039 ML chemisorbed Br atoms exists as D_d-$(Ga\text{-}Br)_2$. A D_d-$(Ga\text{-}Br)_2$ species is formed by the dissociative adsorption of a Br_2 molecule onto the two adjacent edge Ga atoms at an As-As dimer vacancy. In dissociative adsorption, the chemical bond of a Br_2 molecule breaks so that both Br atoms separately form chemical bonds with the surface [15]. Alternately, abstractive adsorption of a Br_2 molecule at an As-As dimer vacancy site forms a Br singly occupied As-As dimer vacancy and ejects a Br atom into the vacuum. This reaction pathway results in dim ball-like features (S_d) at one half of As-As dimer vacancies [see Fig. 1(b)]. Approximately 9% of the 0.039 ML chemisorbed Br atoms exist as S_d-GaBr species. Thus, the abstraction and dissociation probabilities for 0.89 eV Br_2 at an As-As dimer vacancy are 64% and 36%, respectively.

In Fig. 1(b), new dim features ($D_\perp$) inside surface trenches perpendicularly bridge two neighboring dimer columns. The height profile over a $D_\perp$ site in the (110) direction shows a narrow valley about 1.1 ± 0.1 Å lower than the first layer As-As dimers. Moreover, the height profile over the $D_\perp$ site along the central line of the trench yields a single peak that is approximately 1.7 ± 0.1 Å above the trench bottom and about one-half of an As-As dimer length in width. This $D_\perp$ feature is identified as two neighboring GaBr units at the opposite sides of a trench. A $D_\perp$-$(GaBr)_2$ species is formed from the dissociative adsorption of a Br_2 molecule onto two empty Ga dangling bonds at the opposite sides of a trench. Almost no pairs of adjacent GaBr units on the same side of a trench ($D_{\parallel}$) are found in our STM images. Therefore, the dissociative adsorption of a Br_2 molecule into a trench is orientation specific. Adjacent pairs of $D_{\perp}$-$(GaBr)_2$ units in trenches are also present in the STM images (Q). The height profile of a Q species along the central line of its trench shows two overlapping peaks with identical heights as a $D_{\perp}$-$(GaBr)_2$ and is twice as wide as a $D_{\perp}$-$(GaBr)_2$. Hence, a Q-$(GaBr)_4$ unit results from the spatial coincidence of two dissociative adsorption events involving two Br_2 molecules. Statistically, 41% of the chemisorbed Br atoms form $D_{\perp}$-$(GaBr)_2$ species while 10% form Q species.

Isolated dim bumps (S_t) protruding into trenches from As-As dimer rows are also present in the STM images. They have been attributed to isolated Br atoms bonded to the second layer edge Ga atoms. A S_t-GaBr species is formed by the abstractive adsorption of a Br_2 molecule on a Ga atom in the second layer which ejects a Br atom back to the gas phase. Only 6% of the chemisorbed Br atoms form S_t-GaBr species, indicating an abstraction probability of only 19% and a dissociation probability of 81% for a 0.89 eV Br_2 molecule in a trench. At the low coverage of 0.039 ML, neither excess GaBr formation near steps nor formation of GaBr islands were observed, indicating that precursor mediated chemisorption is not an important mechanism for Br_2 with high incident energy (0.89 eV) in the initial adsorption stage onto the As-rich GaAs(001)-(2 × 4) surface.

Figure 3 illustrates the bonding structures of the six $GaBr_{(s)}$ species present on the As-rich GaAs(001)-(2 × 4) surface at a very low coverage of Br atoms. Clearly, 0.89 eV Br_2 molecules exclusively react with the second layer edge Ga atoms. As a Br_2 molecule approaches the As-rich GaAs(001)-(2 × 4) surface, the interaction between the highest occupied molecular orbitals (i.e., $\pi^*_{x,y}$ antibonding orbitals) of the Br_2 molecule with an empty Ga dangling bond generates net attraction that steers the incident Br_2 molecule toward a Ga atom [Fig. 4(a)]. This forms a common $(Ga\cdots Br\cdots Br)$ transition state consisting of a central Br atom partially bonded to the Ga atom and the terminal Br atom. In contrast, the interaction of the HOMO of a Br_2 molecule with the filled dangling bond of a top-layer As-As dimer is repulsive [Fig. 4(b)]. This repulsive interaction acts as a shield for the strained As-As dimer bonds and As-Ga backbonds in the first layer of the surface. A similar theoretical argument has been used to interpret that the less filled center Si dangling bonds are more reactive to F_2, Cl_2, and Br_2 than the more filled corner Si dangling bonds on Si(111) [15]. The same argument was also used to explain the surface preorientation of ICl molecules into the I-end-first geometry before reacting abstractively with the partially filled Si adatom dangling bonds [16].

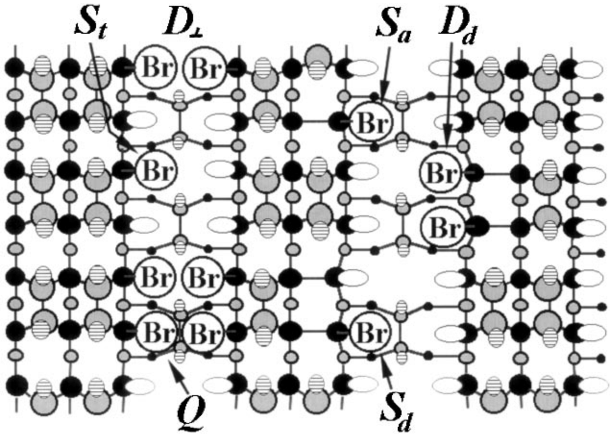

FIG. 3. The bonding structures of the adsorbed Br atoms at various Ga sties, where "S_a" represents a Br atom at an As atomic vacancy (22%), "S_d" a Br atom at an As-As dimer vacancy (9%), "S_t" a Br atom in a surface trench (6%), "D_d" two Br atoms at an As-As dimer vacancy (11%), "$D_{\perp}$" two Br atoms on opposite sides of a trench (41%), and "Q" two adjacent pairs of "$D_{\perp}$" Br atoms (10%).

The chemical surroundings of an in-trench $Ga\cdots Br\cdots Br$ transition state is responsible for the orientation specificity ($D_{\perp}$ versus $D_{\parallel}$) of the dissociative adsorption of Br_2 molecules in trenches. Since the $Ga\cdots Br$ partial bond and its opposite-side Ga empty dangling bond point at each other over the trench, the terminal Br atom in the transition state is significantly closer to the empty dangling bond of the opposite-side Ga atom than the empty dangling bonds of its two nearest Ga atoms along the trench [Fig. 5(a)]. As the weak $Br\cdots Br$ bond breaks, the ejected terminal Br will be captured readily (81%) by the opposite-side Ga atom, forming a $D_{\perp}$-$(GaBr)_2$ species. Only 19% of the terminal Br atoms escape into the gas phase to yield S_t-GaBr species. The preferred capture of the ejected Br atom by an opposite Ga atom prevents the formation of a $D_{\parallel}$-$(GaBr)_2$ species.

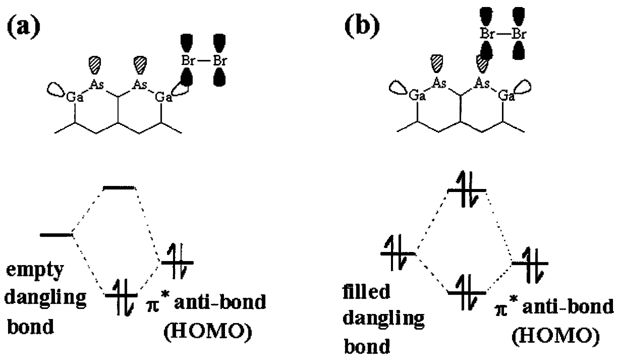

FIG. 4. Schematics of the attractive interaction of the Br_2 π^* antibond with the empty dangling bond of a trench Ga atom (a), and the repulsive interaction of a Br_2 π^* antibond with the filled dangling bond of a top-layer As atom (b).

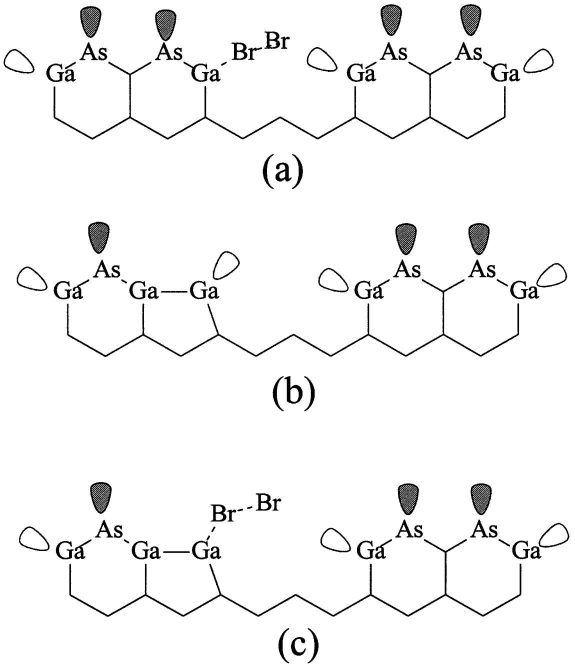

FIG. 5. Schematics (cross-section view) of (a) a transition state in a trench, (b) a buckled empty Ga dangling bond at a missing As site, and (c) a Ga ⋯ Br ⋯ Br transition state formed by the buckled Ga dangling bond.

The Ga dangling bonds at As atomic and As-As dimer vacancies buckle more upwards than those in trenches due to the formation of Ga-Ga bonds in the (110) direction at these defect sites [Fig. 5(b)]. Accordingly, the Ga ⋯ Br transition state bonding at the defect sites [compare Figs. 5(a) and 5(c)] buckles more than those in a trench. Consequently, the terminal Br atoms of Ga ⋯ Br ⋯ Br transition states at As-As dimer vacancies are far away from the empty Ga dangling bonds on the opposite sides of trenches so that most (64%) of the ejected Br atoms escape into the gas phase. Only 36% of the ejected Br atoms are captured by the buckled empty dangling bond of the adjacent Ga atom at the dimer vacancy.

The complete Ga-site selectivity of Br_2 adsorption on the As-rich GaAs(001)-(2 × 4) surface at low coverages is consistent with a theoretical study. This study shows that Cl_2 dissociation over an As-As dimer is an activated process while Cl_2 dissociation over an As-As dimer vacancy is a barrierless and exothermic reaction [17]. We have used a simple molecular orbital argument to explain the complete Ga-site selectivity and the branching between abstractive and dissociative adsorption of Br_2 on different Ga sites of the As-rich GaAs(001)-(2 × 4) surface. This argument may also be used to interpret the Ga-site selectivity of Cl_2 (or Br_2) on the GaAs(001) and GaAs(110) surfaces [2,4–6], and of H atoms on the GaAs(001)-c(2 × 8) surface [3].

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*Corresponding author.
Electronic address: akummel@ucsd.edu

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