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Modeled microscopic structures of monatomic and diatomic Al on stepped and unstepped GaP(110) surfaces

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We have modeled the behavior of monatomic and diatomic Al on unstepped and stepped GaP(110) surfaces. For monatomic Al, the preferred chemisorption site for both types of surfaces is the bridging site, involving a surface Ga atom on a surface atomic zigzag chain and a surface P atom on a neighboring zigzag chain. Hence, Al does not exhibit any preference to bind at step edges or step sites. Al is also found to display an anisotropic diffusion profile, parallel to the surface zigzag chains, with an activation energy of 0.35 eV. For diatomic Al, the two Al atoms prefer to pair up, irrespective of the surface, forming a dimer, possibly a precursor to cluster formation as observed from scanning tunneling microscope experiments. Patrin *et al.* also found no evidence that clustering occurred preferentially on stepped GaAs(110) surfaces, consistent with our findings for Al on stepped GaP(110). In addition, one Al atom appears to gain some charge at the expense of the other Al atom. Investigating further the mechanism underlying the pairing of these two Al atoms, total energy calculations of Al^+ and Al^- on GaP(110) show that diatomic Al exhibits a small negative-U behavior, favoring Al^+ and Al^- rather than two neutral Al atoms. Thus, a slight charge transfer between the two Al atoms subsequently leads to ionic attraction, and hence dimer formation.

I. INTRODUCTION

The advent of the scanning tunneling microscope (STM) has increased our knowledge of the nature of defects on semiconductor surfaces. However, recent development of a cluster deposition growth technique on semiconductor surfaces[1] has also yielded phenomena such as abrupt and defect-free interfaces whose formations are still not well understood. Experimental work on GaAs(110) surfaces[2,3] shows that metal atoms on the surface bond with surface Ga atoms in the low coverage regime [less than 0.1 monolayer (ML) coverage]. However, the situation is not so clear with the case of the Al-GaAs(110) interface, where it has not been possible to determine a favored chemisorption site because cluster formation occurs even for the lowest coverage (0.015 ML) studied under the STM.[4] Such an observation tends to support the notion that individual Al atoms interact weakly with the surface, unlike the case for some metallic elements,[2,3] preferring instead to cluster together. In addition, Patrin, Li, and Weaver[4] found no evidence that clustering occurred preferentially on stepped GaAs(110) surfaces, providing further support to the weak interaction between Al adsorbates and the surface. Photoemission spectroscopy experiments[5] on GaP(110) surfaces with Ag, Cu, and Au overlayers also exhibit this differential interaction between the metal adsorbates and the surface, with Cu and Au reacting strongly with GaP(110) while Ag is found to be relatively unreactive with the surface

On the theoretical side, most work has been performed on GaAs(110). For the case of individual Al atoms on GaAs(110), self-consistent calculations of Ihm and Joannopoulos[6] suggest that the Ga-As bridge site (see Fig. 1) is the most stable chemisorption site. Their calculations also found Al clusters to have lower free energy than chemisorbed Al atoms. Recently, Menon and Allen[7] also found that for a case where the dimer broke up, the dissociated atoms are found to have a higher energy, i.e., the dissociated atoms are metastable with respect to the formation of metallic two-atom clusters. Yi and Bernholc,[8] using an *ab initio* molecular-dynamics (MD) method based on local-density theory and plane-wave basis set, have also found that Al dimer formation is favored over single-atom adsorption, although their dimer bond length is relatively large (0.687 nm). Earlier calculations by

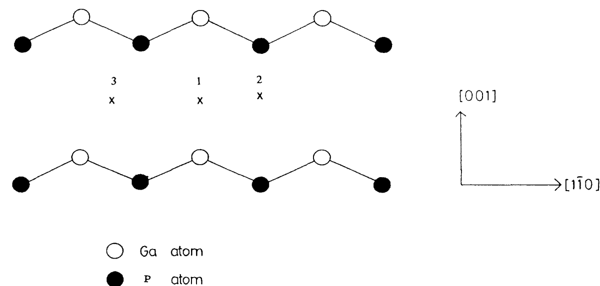

FIG. 1. Usual chemisorption sites considered in the calculation. Sites 1 and 2 refer to the dangling bond sites of the surface Ga and P atoms, respectively, on the GaP(110) surface, while site 3 refers to the bridge site between the surface Ga and P atoms on neighboring zigzag chains.

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Chelikowsky, Chadi, and Cohen[9] and Zunger[10] had already suggested strongly that even the single Al atom on the GaAs(110) surface does not interact strongly with the substrate, with the Ga-Al bond length of the order of 0.3 nm, and Zunger[10] had also proposed the predominant species to be Al clusters which interact weakly with the substrate. Thus, both experiment[4,11] and theory[6–10] indicate that individual Al atoms interact weakly with GaAs(110), exhibiting a greater tendency to clustering.

But, while most studies tend to explain the clustering phenomena in terms of the smaller binding energy of the individual Al atoms to the surface compared to that for the formation of bulk Al,[6,8] Allan and Lannoo[12] have recently advanced an alternative mechanism whereby adatom pairing is a consequence of an initial negative-U (Ref. 13) interaction between adatom-substrate bonds. Still, the question to ask here is why certain metallic elements such as Al prefer to cluster together rather than bond with the substrate, for example, like Au or Sm, with the surface Ga atoms. The motivation to relate the Al dimer pairing to the negative-U interaction model comes partly from the theoretical work of Menon and Allen,[7] whereby they found the dissociated Al atoms to be metastable with respect to the formation of metallic two-atom clusters, typical of the behavior of a negative-U center in the bulk of semiconductors where metastability eventually leads to a stable state with electron or hole pairing aided by lattice rearrangement. This provides the driving force for us to investigate the behavior of individual Al atoms and diatomic Al_2 molecules on GaP(110) to see whether (i) clustering is also favored over single-atom adsorption and (ii) a charge-transfer reaction (negative-U behavior) may provide the pathway for the initial Al_2 pairing, the precursor to the growth of larger Al metallic clusters, aside from the fact that similar data and modeling for Al on (110) surfaces of other III-V compounds like GaP are still scarce, compared to GaAs(110) surfaces. Lastly, as far as we know, no theoretical work of Al on stepped semiconductor surfaces has been reported, and thus, we also feel that it would be appropriate to consider the structural aspects of monatomic and diatomic Al on a stepped surface, in order to relate to the experimental observation[4] that there is no preferred clustering on stepped surfaces.

Our results outlined in the following sections may be seen to be consistent with those for GaAs(110).[4,6–10] The activation energy for Al diffusion on GaP(110) surface is about 0.35 eV, with diffusion being anisotropic along a channel parallel to and between neighboring surface atomic zigzag chains. For diatomic Al, the Al atoms atop a stepped and unstepped GaP(110) surfaces tend to form clusters, but with one Al atom gaining charge while the other loses charge in the equilibrium configuration for the Al_2 dimer. In addition, the Al-Al bond length for the diatomic dimer on GaP(110) in the equilibrium configuration is calculated to be 0.291 nm, compatible with the value for bulk Al (0.286 nm). Therefore, the Al_2 dimer formation initiates from a charge-transfer reaction between two neighboring Al adatoms on bridging sites, the stable chemisorption site for the individual Al atom for both the unstepped and stepped surfaces. The ionic interaction between these two atoms then leads to adatom pairing, similar to the negative-U model on the surface, first suggested by Allan and Lannoo,[12] where the charge transfer occurs between adatom-substrate bonds. Thus, Al dimer formation is favored over single-atom adsorption on GaP(110) surfaces. The bridging site favored for chemisorption by individual Al atoms rather than the surface Ga site preferred by other metals implies that the broken bonds of both the surface P and Ga atoms on adjacent zigzag chains of the (110) surface are initially saturated by the Al atoms, leaving one unpaired electron on each Al atom; the dangling bond of each surface P atom is doubly occupied and can contribute to bonding with the Al atom at the bridge site while the Al atom contributes two electrons for bonding with the empty dangling bond of the surface Ga leaving one of its valence electrons unpaired. The unpaired electron of this Al atom at the bridge site may then interact with the unpaired electron of another Al atom on a neighboring bridge site, resulting in Al pairing or cluster formation as outlined above.

II. THEORETICAL METHOD

We implement the complete neglect of differential overlap (CNDO) method[14] in which the matrix elements of the Hamiltonian are systematically approximated by introducing three semiempirical parameters: the orbital exponent, the electronegativities, and the bonding parameter. The parameters for GaP reproduce its bulk properties like the valence bandwidth, lattice constant, and cohesive energy, consistent with experimental data[15] and have been used to study H (Ref. 15) in GaP as well as desorption induced by electronic transitions (DIET) processes on the GaP(110) surface.[16–20] The parameters of Al are from Pople and Beveridge[14] which have also been used to investigate H-induced passivation of Al-doped Si.[21] We use the MOSES code[22] to perform our calculations on an 84-atom GaP(110) surface cluster used previously for DIET studies,[16–20] details of which have already been given.

III. CALCULATIONS

Calculations are made at over 50 different points on five traverses, P, Q, R, S, and T, within the rectangular grid $ABCD$ on the reconstructed GaP(110) surface (see Fig. 2). The reconstruction leads to the surface P atoms relaxing outwards while the surface Ga atoms relax inwards with the bond angle tilt calculated to be 24.4°, slightly smaller than the experimental value of 27.5°.[23] Sites 1 and 2 refer to the Ga site and the P site, respectively, with the Al atom attached to the dangling bond of the surface Ga or P atom in each case (see Fig. 1). Klepeis and Harrison[24] considered only these two sites in their tight-binding calculations of isolated metal adatoms on GaAs(110) and found that the Al atom prefers to bond with the surface Ga atom, indicating the stable site is site 1. Site 3 is the bridge site between the surface Ga and P atoms and all these three sites have been considered by other theoretical works on the GaAs(110) surface men-

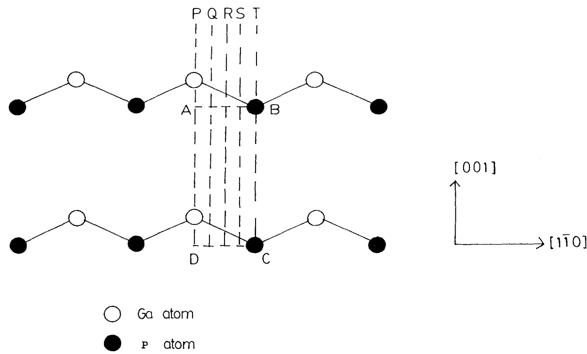

FIG. 2. Total-energy calculations are performed for the Al atom at various positions along the five traverses, $P-T$, within the rectangular grid $ABCD$. By repeating the values of the minimum energy at each point within $ABCD$ along the whole surface, the total-energy surface for Al on the perfect or unstepped GaP(110) surface can be obtained as shown in Fig. 4.

tioned earlier,[6–8] with site 3 (the bridge site) being the most stable from the simulations of Menon and Allen[7] and Ihm and Joannopoulos,[6] while Yi and Bernholc[8] found site 1 to be the most stable. In addition, we also calculate the total energies for the equilibrium configurations of Al^+ and Al^- adatoms on the GaP(110) surface to investigate whether a charge-transfer reaction is plausible.

In our investigation of Al dimer formation, the Al atoms are placed on (i) adatom sites of neighboring Ga atoms along the same zigzag row of substrate (sites a and a' in Fig. 3), (ii) bridge sites of surface P and Ga atoms lying on neighboring zigzag rows (sites b and c in Fig. 3), (iii) adatom sites of surface P and Ga atoms on neighboring zigzag chains (sites a' and d in Fig. 3), and (iv) adatom sites of surface Ga atoms on neighboring zigzag rows (sites a and e in Fig. 3). The total energies for these four configurations of typical chemisorption sites are first calculated without relaxation of the two Al atoms to obtain the local minimum configuration. Once the local minimum configuration is obtained, the two Al atoms are then relaxed to achieve the global minimum configuration of the Al_2 dimer.

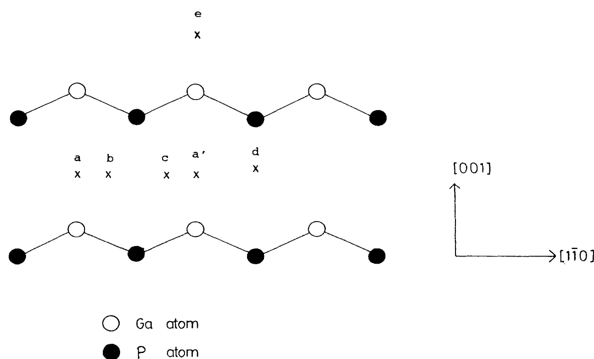

FIG. 3. Diagrammatic representation of the different configurations of two Al atoms on perfect GaP(110) surface. Details of geometries (i)–(iv) are given in the text.

IV. RESULTS AND DISCUSSION

A. Perfect or unstepped GaP(110) surface

1. Monatomic Al

We first consider our total-energy results for sites 1 and 2 in Fig. 1. For each case, the Al atom is relaxed from the perfect adatom site and our results reveal that the neutral Al atom prefers the Ga site rather than the P site, with the energy at the Ga site lower by 0.38 eV, consistent with the results of Klepeis and Harrison[24] for the GaAs(110) surface. The Al-Ga bond for chemisorption at the Ga site has a bond length of 0.255 nm, compatible with the sum of their radii (0.252 nm) when in tetrahedral covalent bonds.[25] However, calculations performed on site 3 yield the lowest-energy configuration after relaxation of the Al atom at this site. In this relaxed configuration of the Al atom at the bridge site of the surface P and Ga atoms on neighboring zigzag rows, the Al-Ga and Al-P bond lengths are, respectively, 0.271 and 0.265 nm, and the energy is lower than that at the Ga site by 0.35 eV. These extended bond lengths (compared to the sum of their atomic radii) are compatible with those of Chelikowsky, Chadi, and Cohen[9] and Zunger,[10] suggesting that monatomic Al interacts weakly with the GaP(110) surface, consistent with the findings for GaAs(110).[4–10] Moreover, our calculations for Al along the five traverses in Fig. 2 yield the total-energy surface as illustrated in Fig. 4, also verifying that site 3 is the lowest-energy configuration for the isolated Al atom on GaP(110). Our findings based on Fig. 4 are similar to that obtained by Ihm and Joannopoulos[6] for the total-energy surface of an Al atom adsorbed on GaAs(110).

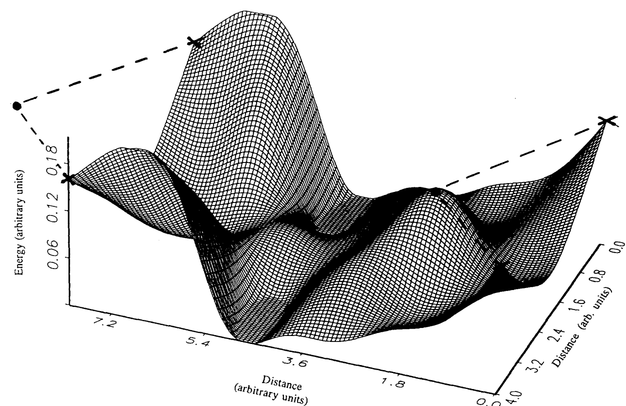

FIG. 4. Total-energy surface for the Al/GaP(110) system. The crosses (×) mark the locations of the surface Ga atoms while the dark circles represent the surface P atoms. Notice the highly anisotropic nature of Al diffusion, with a low-energy channel between the surface atomic zigzag chains, together with a shallower path on the plateau.

There appears to be two favorable paths of diffusion for the surface Al on GaP(110). A deep channel in the "valley" between two surface atomic zigzag chains, is the lower-energy path, with the barrier for Al diffusion along the ⟨011⟩ direction between the zigzag rows as it moves from a bridge site to another via a Ga site being 0.35 eV, compatible with the value of 0.5 eV (Ref. 6) for GaAs(110) but smaller than 0.75 eV.[8] A shallower diffusion channel (higher-energy path) exists on the "plateau" of the surface atomic zigzag chains, whereby the Al atom can easily slide down into the deeper channel. Both diffusion channels favor migration of the Al atom parallel to the zigzag chains, reflecting the anisotropy of Al diffusion on the GaP(110) surface. The Al atom at the bridge site saturates the broken bonds of both the surface P and Ga atoms on adjacent zigzag chains. Diffusion via the Bourgoin-Corbett mechanism[26] where the equilibrium geometry of the Al atom on GaP(110) surface is charge state dependent may also be another possibility leading to a smaller barrier (as suggested by Klepeis and Harrison[24] where their calculations show that neutral Al prefers the Ga site while positively charged Al favors the As site).

Further calculations are then performed to determine the lowest-energy configuration of Al^+ and Al^- on GaP(110). To verify the charge-transfer model discussed earlier, we need to show that two neutral Al atoms are metastable with respect to the Al atoms with different charge states, i.e.,

$$2\,Al^0 \rightarrow Al^+ + Al^- \; . \tag{1}$$

For Al^+, its minimum configuration occurs when it is sited at the centered site between a Ga atom and two P atoms between adjacent zigzag chains. For Al^-, the equilibrium configuration is maintained at the bridge site. Thus, Al can diffuse via the Bourgoin-Corbett mechanism on GaP(110) in the positive and neutral charge states. When the respective total energies of Al^+ Al^0, and Al^- on GaP(110) are summed up according to Eq. (1), Al^+ and Al^- are found to be more stable than two neutral Al^0 atoms by merely 0.17 eV, giving a small effective negative U. Thus, two separate neutral Al adatoms are metastable with respect to the formation of Al^+ and Al^-, which may then pair up by virtue of their ionic interaction, forming Al_2 dimer, the precursor to the growth of larger metallic clusters. Our findings for diatomic Al on GaP(110) presented in the next section suggests that this charge-transfer mechanism leading to Al_2 dimer formation is plausible.

2. *Diatomic Al*

For the above four geometries (i), (ii), (iii), and (iv) for the two Al atoms on GaP(110), we use the energy minimization approach to investigate whether dimer or cluster formation is preferred to any other chemisorption arrangement. Without any initial relaxation of the two Al atoms, geometries (i), (ii), and (iii) are favored over geometry (iv), indicating strongly that the two Al atoms prefer sites where they are closer together, especially in between the zigzag rows, thus enhancing the probability of interacting with each other. Geometry (ii), corresponding to the two Al atoms on neighboring bridge sites, is the most stable, with its total energy 3.51 and 5.82 eV below those of geometries (iii) and (i), respectively. At this point, it should be borne in mind that geometry (ii) may also be obtained from geometries (i) and (iii) via relaxation of the Al atoms between the zigzag rows and which explains why geometry (ii) is the most stable. Since the favored site for monatomic Al is the bridge site between the Ga and P atoms on adjacent zigzag rows (site 3 in Fig. 1), it is logical to expect that interaction of Al atoms would most likely occur between the zigzag rows as illustrated by the strong bias for geometries (i), (ii), and (iii), and we will only consider the local minimum configuration, i.e., geometry (ii) in what follows.

Starting with the unrelaxed configuration of geometry (ii), we relax the two Al atoms until the global minimum energy configuration is obtained. In this minimum energy state arising from geometry (ii), the total energy has decreased by 0.38 eV with the Al-Al distance being 0.291 nm, compatible with bulk Al (0.286 nm). Therefore, our findings provide further strong theoretical evidence in favor of Al cluster formation at the expense of ordered chemisorption, with one of the Al atoms losing a charge of about 0.15 while the other gains roughly the same amount. Examination of the lowest unoccupied and highest occupied orbitals also supports this charge transfer with a hole localized on the Al atom which has lost charge, while the highest occupied orbital is localized on the other Al atom which has gained charge. Although, the calculated charge transfer between these two Al atoms is not that big, the charge-transfer reaction represented by Eq. (1) can still elucidate the stronger interaction between the Al atoms rather than with the substrate. The initial attraction between the two Al atoms can be ionic and after pairing, the Al_2 dimer equilibrates to the metallic configuration where both atoms may eventually attain the same charge, accounting for their small difference in charge in the equilibrium dimer. However, the small negative effective U obtained for this reaction does not preclude the possibility of adatom pairing via covalent bonds. But our findings illustrate clearly that when two Al atoms are initially located at usual chemisorption sites, represented by geometries (i)–(iii), the final state has both the Al atoms interacting with each other resulting in dimer formation with an Al-Al bond length of 0.291 nm, compatible with bulk Al (0.286 nm).

3. *Comparison with diatomic Al on the GaAs(110) surface*

Supplementary calculations are also performed for two Al atoms on the unstepped GaAs(110) surface for comparison with the findings for the GaP(110) surface. The parameters for GaAs also reproduce its bulk properties, such as the valence bandwidth, lattice constant, and cohesive energy, consistent with experimental data[27] and have been used to study H in GaAs as well as H-induced passivation of Be acceptors on the GaAs(110) surface.[27] Repeating the procedure as for GaP(110) above, we find that the two Al atoms prefer to pair up as a dimer rather than remain separate on adjacent bridging sites between

the surface Ga and As atoms. The equilibrium Al-Al bond length is about 0.295 nm, close to the value calculated for the GaP(110) surface, but much smaller than that calculated by Yi and Bernholc.[8] Hence, clustering of Al on both GaP(110) and GaAs(110) appears to be similar, and our findings for Al on GaP(110) surfaces here may equally apply to the GaAs(110) surface.

B. Stepped GaP(110) surface

A step is simulated along the ⟨100⟩ direction where the surface atomic zigzag chains are abruptly terminated [see Fig. 5(a)]. This results in an upper terrace which represents the ideal surface before termination of the zigzag chains, and a lower terrace after removal of the first layer of the surface atoms, from the step onwards [see the cross-sectional view of the surface in Fig. 5(b)]. Repeating the calculations as for the perfect surface with an isolated Al atom at various points along several traverses ($P-X$) in the rectangular grid $ABCD$, both on the upper and lower terraces around the vicinity of the step edge, as shown in Fig. 6, the equilibrium geometry for an Al atom on a stepped GaP(110) surface is still determined to be the bridge site (3) labeled in Fig. 6. Hence, a step edge does not appear to bind an Al atom more strongly than the bridge site, and is not likely to act as a nucleation site for Al cluster formation.

Introducing another Al atom leads to an equilibrium configuration for an Al_2 dimer on the stepped GaP(110) surface where both Al atoms are located on the upper terrace (see Fig. 6). The Al-Al bond length is determined to be 0.288 nm, once again compatible with bulk Al (0.286 nm) and with that calculated for the Al_2 dimer on the unstepped GaP(110) surface. Hence, our findings here strongly support the notion that step sites need not necessarily act as active sites where Al nucleation is favored. Perhaps the presence of foreign impurities at steps, which is not considered here, may have a stronger enhancing effect on clustering of metal atoms at steps. Thus, our results are also consistent with experimental observations[4] that there is no evidence of preferential clustering of Al atoms at step sites.

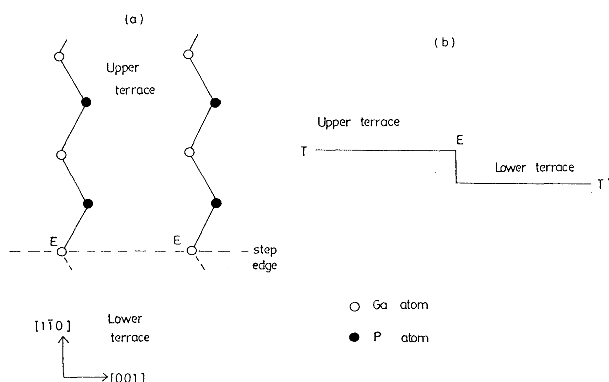

FIG. 5. (a) Top view of stepped GaP(110) surface with the step edge perpendicular to the surface atomic zigzag chain in the [110] direction. The surface Ga atoms at the edge are represented by E. (b) Side view of the stepped GaP(110) surface to illustrate the lower and upper terraces. The lower terrace is obtained by removing all the surface atoms of the perfect surface from the step edge onwards, exposing the atoms in the second layer of the original surface.

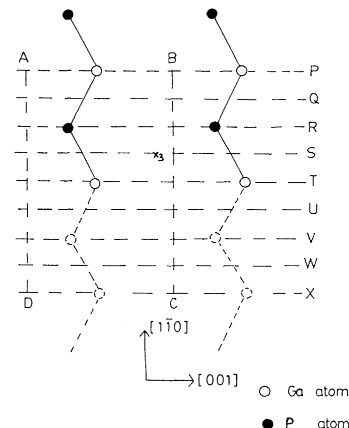

FIG. 6. Schematic illustration of total energy calculations to determine the equilibrium geometry of Al in the vicinity of a step edge on the stepped GaP(110) surface.

V. CONCLUSION

Our findings suggest that Al does not interact strongly with the GaP(110) substrate, which is consistent with the findings for GaAs(110).[4–10] For monatomic Al, the most favored site is the Ga-P bridge site located between two zigzag rows with the Al-Ga and Al-P bonds being comparatively long, suggesting a weak interaction with the substrate. This finding applies equally for both the unstepped and stepped surfaces. In the diatomic case, ordered chemisorption of the Al atoms on the surface Ga or P sites is unstable with respect to Al cluster formation, consistent with the recent findings via molecular-dynamics simulations of Menon and Allen[7] for diatomic Al on GaAs(110) specifically, and in good agreement with experiment[4,11] and other theoretical work.[6–10] The diatomic Al-Al bond length is also in good agreement with that of bulk Al, providing further support to the notion that Al prefers cluster formation as observed under the STM.[4] Our calculations for two Al atoms in the vicinity of a step edge on the stepped GaP(110) surface also do not yield evidence of preferential clustering of Al atoms at step sites. This is consistent with the experimental results of Patrin, Li, and Weaver.[4] Therefore, the interaction between the Al adsorbates at low coverage with the compound semiconductor substrate appears to be independent of the nature of the surface (whether stepped or unstepped), being weak throughout due to a stronger interaction between the Al adsorbates themselves, leading to dimer formation and subsequently, growth of larger metallic clusters. Thus, clustering of Al is favored with

the general behavior for Al on both GaP(110) and GaAs(110) surfaces very similar.[4–10] This finding can explain why it has not been possible to determine a favored chemisorption site for Al on GaAs(110) or GaP(110) surface because cluster formation occurs even for the lowest coverage (0.015 ML) studied under the STM.[4] It would be useful if our findings for Al on GaP(110) were to be complemented or verified by experimental data so that a more consolidated model could be established for Al-compound semiconductor surface interactions.

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