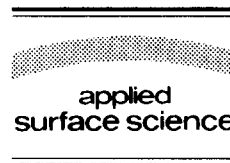




ELSEVIER

Applied Surface Science 82/83 (1994) 171–179



# Surface stoichiometry and the role of adsorbates during GaAs atomic layer epitaxy

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Received 27 June 1994; accepted for publication 11 July 1994

## Abstract

Several questions regarding the stoichiometry of atomic layer epitaxy (ALE) arise because most polar compound semiconductor surfaces reconstruct into structures terminated with less than monolayer coverage at the outermost layer. In this paper we briefly discuss how to self-consistently account for stoichiometry changes on surfaces that are not ideally terminated. The key aspect of the methodology is that surface steps are allowed to act as a reservoir where atoms may be added or removed. The methodology shows that ideal ALE of GaAs(100) cannot occur by cycling between the known adsorbate-free Ga-rich and As-rich surface reconstructions, because no such transition would yield the observed 1 monolayer (ML) per cycle growth rate. In fact, ideal ALE (1 ML/cycle) must involve at least one adsorbate induced surface reconstruction. Adsorbates may stabilize ideally terminated (i.e. vacancy free) III–V surfaces because of their ability to passivate dangling bond states. For example, methyl groups adsorbed on GaAs(100) exhibit a  $(1 \times 2)$  LEED pattern, which is not seen for the clean GaAs(100) surface reconstructions. By using the electron counting model we interpret this structure as  $\frac{1}{2}$  ML  $\text{CH}_3$  adsorbed on a complete layer (1 ML) of dimerized Ga atoms. The GaAs(100)- $(1 \times 2)\text{-CH}_3$  surface was also examined using surface infrared spectroscopy (SIRS) using a multiple internal reflection geometry. This surface exhibits relatively sharp infrared linewidths suggestive of a well ordered structure. The polarization dependence of the symmetric stretching and bending  $\text{CH}_3$  modes also supports our proposed structure of the GaAs(100)- $(1 \times 2)\text{-CH}_3$  surface. The ideal termination of the Ga-rich GaAs(100)- $(1 \times 2)\text{-CH}_3$  surface allows for a plausible ALE mechanism which yields 1 ML deposition per cycle.

## 1. Introduction

Ideally, atomic layer epitaxy (ALE) is a technique for depositing a material in a layer-by-layer fashion with precise thickness control and inherent thickness uniformity [1–3]. While much of the early work focused on deposition of II–VI material [1,2], a great deal of the recent effort has centered on ALE of III–V compound semiconductors [2–7]. Although

ALE of III–V's has held much promise, several problems have inhibited its widespread implementation. Two of the major problems for GaAs ALE have been the relatively narrow operating window and the unintentional carbon doping found when using trimethylgallium (TMGa). One reason for the narrow operating window for GaAs ALE is the loss of self-limiting gallium deposition during the TMGa cycle. A considerable effort has been made to understand the mechanism of GaAs self-limiting deposition (and its loss), but controversy still exists and a

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general consensus has not been reached. The wide disparity in the measured surface reaction kinetics and growth rates [8,9] is one factor that has inhibited our ability to reach a consensus.

Another interesting but poorly understood issue of compound semiconductor ALE is how to account for surface stoichiometry changes. The ALE stoichiometry issue and the role of adsorbates is the topic of this paper. ALE of compound semiconductors is most commonly performed on substrates oriented to expose polar surfaces. While the nonpolar surfaces, e.g. zincblende (110), generally maintain the stoichiometry of the bulk, the polar surfaces, e.g. zincblende (100), more often form complex reconstructions with incomplete layers of atoms at the surface [10–12]. GaAs(100) is the most extensively studied polar compound semiconductor surface, and a detailed review of its surface reconstructions is beyond the scope of this paper (see Refs. [11,12]). Two conclusions of the experimental and theoretical studies are that the top layer of atoms on (100) surfaces dimerize and that atom vacancies (or in some cases extra atoms) are intrinsic to most of the reconstructions. It is generally believed that on polar III–V surfaces the formation of atom vacancies creates an electronic configuration where the cation (e.g. Ga atom) dangling bond states are completely empty while the anion (e.g. As atom) dangling bond states are completely filled. By using this premise, along with a simple electron counting model [11,13–16], the stability of most compound semiconductor reconstructions can be understood. For GaAs(100) several reconstructions have been observed (see Refs. [11,12], and references therein) and their stoichiometry is summarized in the top portion of Table 1. It should be noted that the structure and stoichiometry of many of these reconstructions is still being debated.

The issue of surface stoichiometry arises for GaAs ALE because most experimental growth rates [2,3,5–7] show a plateau at 1 ML/cycle ( $G_c = 1$ ) even though none of the adsorbate-free reconstructions are ideally terminated at 1 ML (with the possible exception of the  $\gamma$ -( $2 \times 4$ ) As-rich surface). It may be possible that a cycle between two reconstructions with  $\theta \neq 1$  ( $\theta$  = coverage) could in fact yield  $G_c = 1$ , although for GaAs(100) we will show this is not the case.

Table 1

Stoichiometry of GaAs(100) reconstructions

Gallium-rich reconstructions:		Arsenic-rich reconstructions:	
( $2 \times 6$ )	$\frac{1}{2}$ ML	$\alpha$ -( $2 \times 4$ )	$\frac{1}{2}$ ML
$\beta$ -( $4 \times 2$ )	$\frac{3}{4}$ ML	$\beta$ -( $2 \times 4$ )	$\frac{3}{4}$ ML
$\beta 2$ -( $4 \times 2$ )	$\frac{3}{4}$ ML	$\beta 2$ -( $2 \times 4$ )	$\frac{3}{4}$ ML
		$\gamma$ -( $2 \times 4$ )	1 ML
		$c$ -( $4 \times 4$ )	$1\frac{1}{4}$ ML
With adsorbates:		With adsorbates:	
( $1 \times 2$ )-CH <sub>3</sub>	1 ML	( $2 \times 1$ )-H	1 ML

If a deposition cycle involves transitions between surfaces with incomplete layers of atoms ( $\theta \neq 1$ ), it is not immediately obvious how the transition may occur and how many atoms are required to effect the change. The problem is illustrated schematically in Fig. 1 for a hypothetical layered compound AB. Converting from a surface incompletely terminated with A atoms to a surface incompletely terminated with B atoms, by depositing *only* B atoms, may not look feasible because the incomplete layer of A atoms must somehow be “filled in”. In this paper we show that this apparent dilemma is resolved if surface steps are allowed to act as reservoirs where atoms may be added or removed, thus allowing for transitions between two incomplete layers. We use this procedure and demonstrate how to self-consistently account for surface stoichiometry changes on surfaces that are terminated with incomplete lay-

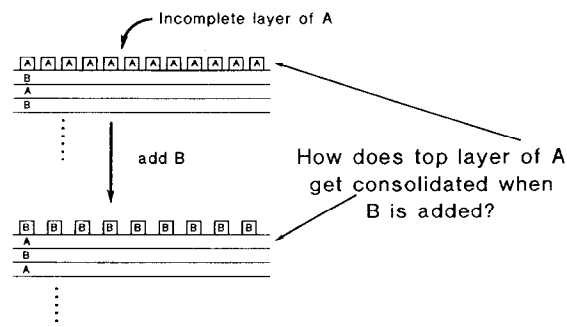


Fig. 1. Schematic of the conversion of a surface terminated with an incomplete layer of A atoms into a surface terminated with an incomplete layer of B atoms, by the addition of B. Somehow the incomplete layer of A must be converted into a complete layer.

ers. We use the methodology to explain two results from the GaAs MBE literature. We also use the methodology to examine possible GaAs(100) ALE mechanisms and conclude that the process cannot occur by cycling between the known adsorbate-free reconstructions. We instead propose that GaAs ALE involves the Ga-rich GaAs(100)-(1 × 2)-CH<sub>3</sub> reconstruction, which is stabilized at 1 ML Ga coverage by the presence of adsorbates. A detailed structure of the Ga-rich GaAs(100)-(1 × 2)-CH<sub>3</sub> surface is proposed, based on the polarization dependence of the CH<sub>3</sub> vibrational modes measured using infrared spectroscopy.

## 2. Method of accounting for stoichiometry changes

As mentioned in the Introduction most polar compound semiconductor surfaces reconstruct into structures with intrinsic vacancies (or in some cases extra adatoms). A general method for accounting for stoichiometry changes on such surfaces is needed. Rather than drawing a complete structural representation of the complex surface reconstructions, we will use simplified schematics to illustrate their stoichiometries. This approach also maintains as much generality as possible. In Fig. 2a we illustrate a one incomplete layer (1ICL) reconstruction on a vicinal surface

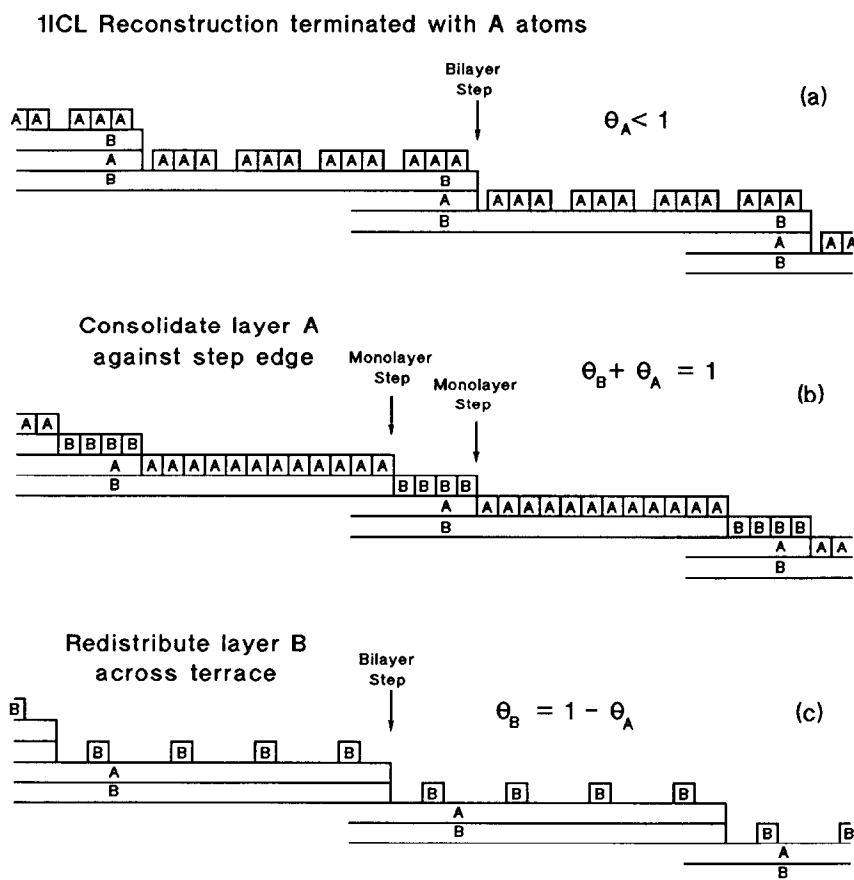


Fig. 2. Schematic demonstrating the conversion of a one incomplete layer (1ICL) reconstruction terminated with A atoms (coverage  $\theta_A$ ) into a 1ICL reconstruction terminated with B atoms (coverage  $\theta_B = 1 - \theta_A$ ). In panel (b) the partial layer of A atoms is consolidated into a complete layer aligned against the original bilayer step edges. In panel (c) the B atoms that were exposed in panel (b) are evenly distributed across the terraces. Thus, the original bilayer step served as a sink for A and a source for B.

with an incomplete layer of element A (coverage =  $\theta_A$ ) on top of a complete monolayer of element B. By simply redistributing the atoms in the top A and B layer (no deposition or desorption) we can convert this surface into a new arrangement with an incomplete layer of B atoms on top of a complete layer of A atoms. This is illustrated in Fig. 2, panels (a)–(c). In Fig. 2b, we have consolidated the incomplete layers of A atoms into complete layers aligned against the original bilayer steps. At this stage the surface appears as alternating terraces terminated with a complete layer of either A or B atoms. In this configuration it becomes obvious that fractional coverages of A and B, relative to the entire surface, must obey the simple relationship given in Eq. (1):

$$\theta_A + \theta_B = 1. \quad (1)$$

This relationship determines the amount ( $\theta_B$ ) of B “uncovered” when the A layer is consolidated at the steps. The B atoms can then be redistributed across the A terraces to form the structure given in Fig. 2c. This exercise demonstrates that any 1ICL reconstruction with a coverage of  $\theta_A$  on the outer layer can be converted to a 1ICL reconstruction with a coverage of  $\theta_B = 1 - \theta_A$  on the outer layer, without adding (depositing) or removing (desorbing) surface atoms. Even if the latter configuration is not stable, it can serve as a convenient intermediate point for cases where we will then add or subtract atoms from the surface. We also note that although we used a vicinal surface in this illustration (for simplicity), a regular array of steps is not required to achieve the above result [17].

In general, the amount of B needed ( $\Delta\theta_B$ ) to convert from a 1ICL A-rich reconstruction of coverage  $\theta_A^i$  to a 1ICL B-rich reconstruction of coverage  $\theta_B^f$  is given by Eq. (2):

$$\Delta\theta_B = \theta_B^f - \theta_B^i = \theta_B^f + \theta_A^i - 1. \quad (2)$$

In addition to examining potential ALE mechanisms (Section 3) this expression can be used to interpret two results from the MBE literature. Nearly twenty years ago Arthur [18] found that the removal of  $\sim \frac{1}{2}$  ML As by thermal desorption converted the GaAs(100) As-rich surface to the Ga-rich surface. More recently, Deparis and Massies [19] found that

deposition of  $0.53 \pm 0.04$  ML Ga converts the  $(2 \times 4)$  As-rich surface to the Ga-rich surface. These results were originally somewhat puzzling to us because the  $(2 \times 4)$  As-rich surface was normally thought to have an As coverage of  $\frac{3}{4}$  ML. However, if the Ga-rich surface created at the end of the Arthur [18] and Deparis and Massies [19] experiments corresponds to  $\theta_{Ga} = \frac{3}{4}$ , then the required amount of As removed or Ga added is in fact  $\frac{1}{2}$  ML ( $\Delta\theta = \frac{3}{4} + \frac{3}{4} - 1 = \frac{1}{2}$ , see Eq. (2)), in agreement with the two experimental results. It is not necessary to invoke the existence of the  $\alpha(2 \times 4)$  reconstruction with  $\theta_{As} = \frac{1}{2}$  in order to explain these results.

It should be recognized that the formalism used above to derive Eqs. (1) and (2) is simply a convenient method of accounting for (or bookkeeping) the surface atoms during a transformation from one surface stoichiometry to another. The intermediate stages shown in Fig. 2 are not necessarily meant to represent the mechanism by which the transformation occurs. However, by examining the initial and final structures of the reconstructions, it is obvious that substantial rearrangement of the surface atoms must occur. This rearrangement must be mediated by steps that are present (or that may be created) on the surface. In essence, the steps act as a reservoir where atoms may be removed or stored in order for the stoichiometry change to occur. The methodology can also be extended to account for changes involving more complex reconstructions involving two incomplete layers [17].

### 3. Stoichiometry of ALE

The fact that ALE of GaAs(100) yields 1 ML/cycle (using arsine and TMGa), even though no ideally terminated adsorbate-free Ga-rich (and perhaps As-rich) surface exists, has been the subject of debate and speculation [8,9]. If ALE occurred by simply alternating between the  $\beta(2 \times 4)$  As-rich and  $\beta(4 \times 2)$  Ga-rich surface [20], then Eq. (2) indicates that the growth rate would be  $\frac{1}{2}$  ML/cycle, identical to the MBE results described in Section 2. By using Eq. (2) and Table 1 we can test for possible ALE cycles that would yield  $G_c = 1$  ML/cycle. Since there is no adsorbate-free Ga-rich reconstruction with  $\theta_{Ga} = 1$ , the two Ga-rich reconstructions with  $\theta_{Ga}$

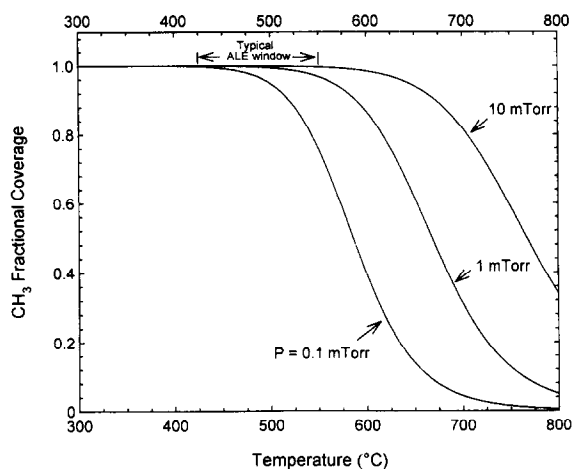


Fig. 3. Prediction of the temperature and pressure dependence of  $\text{CH}_3$  coverage on the GaAs(100) surface using a TMGa unimolecular adsorption reaction model [8,9].  $\text{CH}_3$  desorption rate constant was measured by TPD and the initial sticking coefficient was measured by molecular beam scattering. Note that for most ALE conditions the coverage of  $\text{CH}_3$  groups is near saturation.

$= \frac{1}{2}$  and  $\frac{3}{4}$  would require As-rich reconstructions with  $\theta_{\text{As}} = 1\frac{1}{2}$  and  $1\frac{1}{4}$  respectively, in order to obtain  $G_c = 1$ . There is no strong evidence supporting As-rich reconstructions with  $\theta_{\text{As}} = 1\frac{1}{2}$  and  $1\frac{1}{4}$ , so an ALE cycle with  $G_c = 1$  occurring between the known adsorbate-free Ga-rich and As-rich reconstructions does not exist. A cycle between the  $\beta(2 \times 4)$  As-rich and  $c(4 \times 4)$  As-rich reconstructions would yield 1 ML/cycle, but experimental results demonstrate that TMGa decomposes quickly on the  $(2 \times 4)$  As-rich surface [8,20,21] so this mechanism cannot be responsible for GaAs ALE.

The resolution of the ALE stoichiometry dilemma is found by realizing that there may be new stable surface reconstructions formed in the presence of adsorbates. In fact, the residence time of  $\text{CH}_3$  groups on the Ga-rich surface [8,9,20–25] indicates that the surface should be covered with adsorbed  $\text{CH}_3$  at typical ALE temperatures ( $\sim 450^\circ\text{C}$ ) and pressures at the end of the TMGa cycle. The temperature dependence for the methyl group coverage predicted using a simple unimolecular adsorption-reaction model [8,9] is shown in Fig. 3. This model uses a  $\text{CH}_3$  desorption rate constant derived from tempera-

ture programmed desorption (TPD) results [22,23] and an initial sticking coefficient derived from molecular beam scattering [8]. The TMGa adsorption-reaction model was incorporated into a more complete ALE model [9] which accurately reproduces the temperature dependence of the ALE data of DenBaars et al. [6]. The model predicts that a TMGa pressure of 1 mTorr is sufficient to maintain a  $\text{CH}_3$  coverage near saturation to temperatures well above  $500^\circ\text{C}$ . For most ALE conditions the TMGa pressure is well above 1 mTorr.

Adsorbates such as  $\text{CH}_3$  are likely to significantly change the structure of the GaAs surface because of their ability to satisfy dangling bond states. In general, adsorbates are well known for their ability to induce, or in some cases remove surface reconstructions [26]. Our previous work [22] showed that the  $\text{CH}_3$ -covered Ga-rich surface prepared by TMGa adsorption contains more gallium than the clean Ga-rich surfaces, so we know that adsorbed  $\text{CH}_3$  stabilizes the presence of additional Ga atoms. The  $\text{CH}_3$ -covered surface also exhibited a rather poor quality  $(1 \times 2)$  LEED pattern [22] which quickly disappeared due to electron beam damage. The  $(1 \times 2)$  surface could be prepared either by low temperature TMGa adsorption and annealing to  $325\text{--}350^\circ\text{C}$ , or by direct TMGa exposure around  $350^\circ\text{C}$ . Static secondary ion mass spectroscopy (SSIMS) of the TMGa dosed surface in the  $350\text{--}400^\circ\text{C}$  range demonstrates that the predominant surface species is monomethylgallium (MMGa) [27]. Improvements in the preparation of the  $\text{CH}_3$ -covered surface and data acquisition have led to a significant improvement in the recorded  $(1 \times 2)$  LEED pattern [17] so we have more confidence in this result. We also note that Chiu et al. [28] and Ohki and Hiratani [29] observed a  $(1 \times 2)$  RHEED pattern when TMGa impinged on GaAs(100) at  $420\text{--}450^\circ\text{C}$ .

We now realize that the  $(1 \times 2)$  diffraction pattern is most likely due to a  $\text{CH}_3$ -covered surface, terminated with 1 ML of Ga, which satisfies the electron counting model. In the electron counting model each Ga atom contributes  $\frac{3}{4}$  of an electron to each bond in GaAs. Each Ga atom on a Ga-terminated unreconstructed GaAs(100) surface would have two dangling bonds containing a total of  $1\frac{1}{2}$  electrons. The Ga atoms are expected to dimerize (using 1 electron each) along the (011) direction so that each atom

would then have only one dangling bond containing  $\frac{1}{2}$  of an electron. In the absence of adsorbates, this surface is apparently unstable with respect to one with  $\frac{1}{4}$  ML of Ga vacancies, as in the  $\beta(4 \times 2)$  reconstruction. However, the presence of the correct quantity and type of an adsorbate could stabilize a surface and obviate the need for creating vacancies. Since each Ga atom on an ideally terminated (i.e.  $\theta_{\text{Ga}} = 1$  ML) and dimerized surface would have one dangling bond containing  $\frac{1}{2} e^-$ , it would require  $\frac{1}{2}$  ML of an adsorbate to “tie up” the available electrons to produce a stable surface, provided that the adsorbate forms a single covalent bond (e.g.  $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$ ,  $-\text{H}$ ,  $\text{Cl}$ , etc.) to the surface. A detailed model for the  $(1 \times 2)\text{-CH}_3$  surface is proposed in Section 4 after reviewing the polarized infrared spectroscopic results.

For ALE, the most important aspect of the  $(1 \times 2)\text{-CH}_3$  Ga-rich structure is that it is terminated with 1 ML of Ga. Using this structure we can now propose some plausible ALE cycles that yield  $G_c = 1$ . One cycle would involve transitions between the  $(1 \times 2)\text{-CH}_3$  Ga-rich surface and the  $\gamma(2 \times 4)$  As-rich surface with  $\theta_{\text{As}} = 1$  (see Table 1). Recent results demonstrate that a surface with  $\theta_{\text{As}} \approx 1$ , perhaps the  $\gamma(2 \times 4)$  As-rich surface, can be created by moderate arsine exposures [30] and the surface arsenic has a residence time long enough [30,31] to survive the purge cycle between the arsine and TMGa exposure. Another possibility would involve an adsorbate covered As-rich surface, i.e.  $(2 \times 1)\text{-H}$ , (see Table 1) with  $\frac{1}{2}$  ML of H stabilizing a complete monolayer of dimerized arsenic atoms, analogous to the  $(1 \times 2)\text{-CH}_3$  Ga-rich surface. The evidence for such a surface is tenuous, but we did observe a  $(2 \times 1) + 1/2X^*$  LEED pattern after intermediate stages of arsine exposure at high temperatures [8].

The ideal results for GaAs(100) ALE (i.e.  $G_c = 1$ ) may be somewhat unique. Most of the early work on II–VI semiconductors [1] generally showed growth saturation considerable less than one monolayer. Recent ALE results for InP [32,33] exhibit a tendency to saturate at  $G_c = \frac{1}{2}$  under some conditions, and most attempts at “digital” etching of GaAs [34,35] have yielded etch rates less than 1 ML/cycle. For these systems the stoichiometry accounting methodology developed in Section 2 may be required to explain the observations.

#### 4. Infrared spectroscopy of the GaAs(100)- $(1 \times 2)\text{-CH}_3$ surface

In order to further characterize the GaAs(100)- $(1 \times 2)\text{-CH}_3$  surface we have measured its vibrational properties using surface infrared spectroscopy (SIRS) [36] with a multiple internal reflection geometry [36,37]. Most of the experimental details will be published at a latter date [38]. Briefly, modulated light from a BOMEM DA3 FTIR was imaged (with  $\sim f/4$  reflective optics) onto the edge of a GaAs(100) crystal cut into a parallelogram prism for multiple internal reflection [37,38]. The light reflected about 20 times off the front (and 20 times off the back) surface before exiting the crystal, whereupon it was collected and focused onto a narrow band MCT detector (low frequency cutoff  $\sim 800 \text{ cm}^{-1}$ ). The internal angle of incidence was  $45^\circ$ . The spectra presented in this paper were measured at  $4 \text{ cm}^{-1}$  resolution using Hamming apodization. The infrared light could be polarized using a  $\text{BaF}_2$  wire grid polarizer. The GaAs(100) crystal was oriented so the plane of incidence on the front face was perpendicular to the (011) direction. In this configuration the Ga–Ga dimers (if they exist) would lie perpendicular to the plane of incidence. Due to zincblende symmetry, the Ga–Ga dimers on the back face of the GaAs sample would be parallel to the plane of incidence. Both the front and back face of the crystal could be sputter cleaned and examined with LEED and Auger spectroscopy. Using a collimated TMGa doser we could preferentially dose either the front or back face of the crystal with a high degree of selectivity. This was useful when examining the polarization dependence of the vibrational modes because performing experiments independently on the front and back face of the crystal was equivalent to examining the crystal along two unique azimuthal directions.

The unpolarized infrared spectrum of the  $(1 \times 2)\text{-CH}_3$  surface between  $800$  and  $3200 \text{ cm}^{-1}$  is shown in Fig. 4. Both front and back faces of the crystal were exposed to TMGa at  $350^\circ\text{C}$  to create the  $(1 \times 2)\text{-CH}_3$  surface. There are eight peaks apparent in Fig. 4, corresponding to symmetric and asymmetric  $\text{CH}_3$  bending and stretching modes, as well as some overtone and combination bands. All peak positions are in good agreement with the literature values for  $\text{CH}_3$  groups bonded to Ga atoms [39].

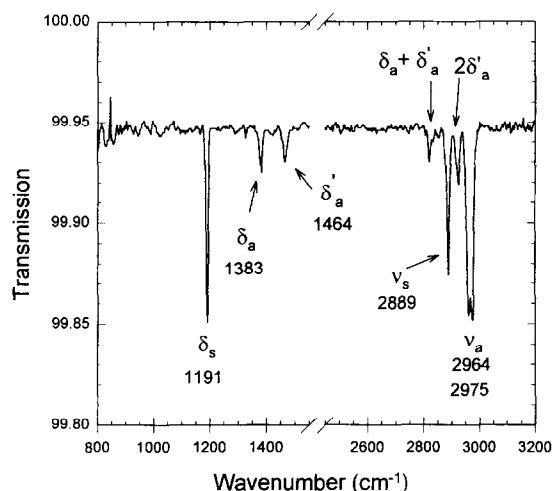


Fig. 4. Unpolarized IR spectrum of the Ga-rich GaAs(100)-(1 × 2)-CH<sub>3</sub> surface prepared by TMGa adsorption at 350°C. Both front and back face of the GaAs crystal were exposed to TMGa and the spectrum was recorded at ~ 120 K.

Note that all of the modes exhibit relatively narrow linewidths, with FWHM = 8–9 cm<sup>-1</sup> for the  $\delta_s$  mode. This is in contrast to molecular TMGa ad-

sorbed at 180 K, which exhibits linewidths of 50–150 cm<sup>-1</sup> [38]. The observation that the (1 × 2)-CH<sub>3</sub> surface exhibits such narrow linewidths strongly suggests that it is a well ordered structure containing only one type of CH<sub>3</sub> binding site.

In the remainder of this section we will only discuss the behavior of the symmetric CH<sub>3</sub> bending ( $\delta_s$ ), and stretching ( $\nu_s$ ) modes at 1191 and 2889 cm<sup>-1</sup>, respectively. For CH<sub>3</sub> groups bonded to a metal atom (M) with C<sub>3v</sub> symmetry, the symmetric vibrational modes have dynamic dipoles that are parallel to the M–C bond axis [39]. Therefore, if we can determine the dipole orientation of the  $\delta_s$  and  $\nu_s$  modes; this information will automatically tell us the orientation of the Ga–C bond. The orientation of the  $\delta_s$  and  $\nu_s$  modes can be determined by their polarization dependence for the two unique azimuthal configurations (front and back face of crystal). The polarization dependence of the (1 × 2)-CH<sub>3</sub> state with the plane of incidence parallel to the Ga–Ga dimers is shown in Fig. 5a. Note that the  $\delta_s$  and  $\nu_s$  modes absorb strongly when the light is p-polarized, but no measurable absorption occurs when the light

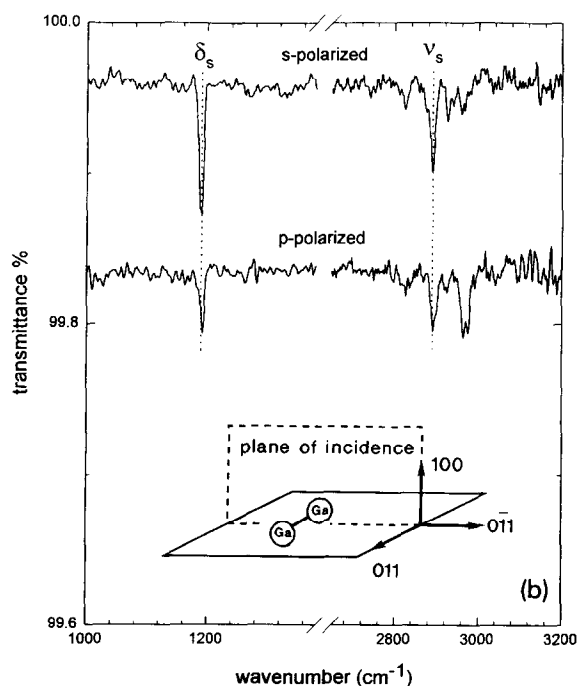
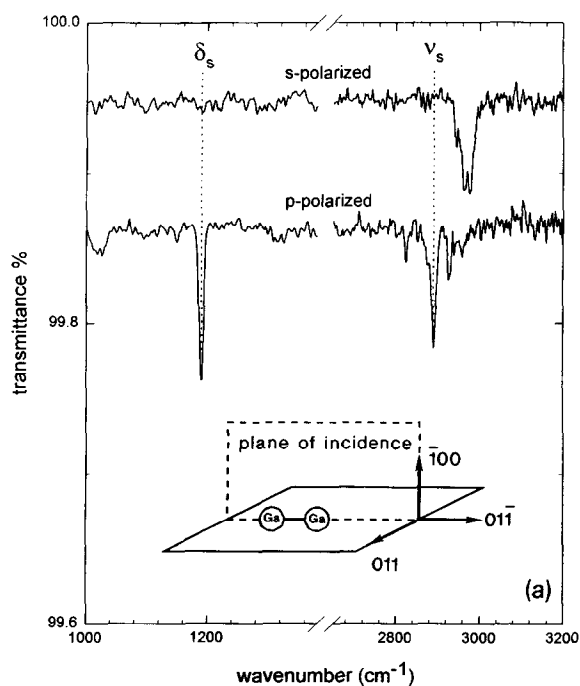


Fig. 5. (a) Polarized IR spectra of the Ga-rich GaAs(100)-(1 × 2)-CH<sub>3</sub> surface with the plane of incidence parallel to the Ga–Ga dimers (b) Polarized IR spectra of the Ga-rich GaAs(100)-(1 × 2)-CH<sub>3</sub> surface with the plane of incidence perpendicular to the Ga–Ga dimers.

is s-polarized. If there was a component of the  $\delta_s$  and  $\nu_s$  dipoles perpendicular to the plane of incidence it would exhibit s-polarized absorption. Therefore, the dipole for the  $\delta_s$  and  $\nu_s$  modes is strictly parallel to the plane of incidence [40]. This result indicates that the  $\text{CH}_3$  groups are bonded exclusively to the surface Ga atoms because the dangling bonds on the surface Ga atoms are also parallel to the plane of incidence for this azimuthal configuration.

We can learn more about the  $\text{CH}_3$  group orientation by examining the polarization dependence when the plane of incidence is perpendicular to the Ga–Ga dimers, as in Fig. 5b. In this configuration there is strong s- and p-polarized absorption by the  $\delta_s$  and  $\nu_s$  modes, which indicates that the  $\delta_s$  and  $\nu_s$  dipoles are tilted out of the plane of incidence. This automatically shows that the  $\text{CH}_3$  groups are not oriented perpendicular to the surface, so we can rule out a bonding configuration where the  $\text{CH}_3$  group is symmetrically centered between two Ga atoms via a three-center two-electron bond. We can calculate the tilt angle (see Eq. (3)) of the Ga– $\text{CH}_3$  bond using the ratio of the s- and p-polarized integrated absorption (i.e.  $A_s/A_p$ ) and accounting for the slight difference in the electric field intensities along the (011), i.e.  $I_y$ , and (100), i.e.  $I_z$ , directions [36,37]:

$$\theta = \tan^{-1} \left[ (A_s/A_p)(I_z/I_y) \right]^{1/2}. \quad (3)$$

An average of six measurements (three experiments measuring both  $\delta_s$  and  $\nu_s$ ) yields a value for the tilt angle of  $\theta = 55^\circ \pm 5^\circ$ . This value should be viewed as approximate because Eq. (3) does not account for self-screening of the z-component (perpendicular to surface) of the dipoles [36]. Self-screening, which only effects the z-component, lowers the measured absorption and is evident by the small upward shift in frequency ( $\sim 2 \text{ cm}^{-1}$ ) of the p-polarized peaks in Fig. 5b. We are in the process of performing a detailed accounting of the self-screening effect [38], but from the magnitude of the frequency shift we can tentatively estimate that it will lower the calculated tilt angle by  $5^\circ$ – $10^\circ$ . For this reason we estimate the Ga– $\text{CH}_3$  bond angle from the surface normal to be  $50^\circ \pm 10^\circ$ .

By combining the knowledge of the Ga– $\text{CH}_3$  orientation obtained from the polarized SIRS mea-

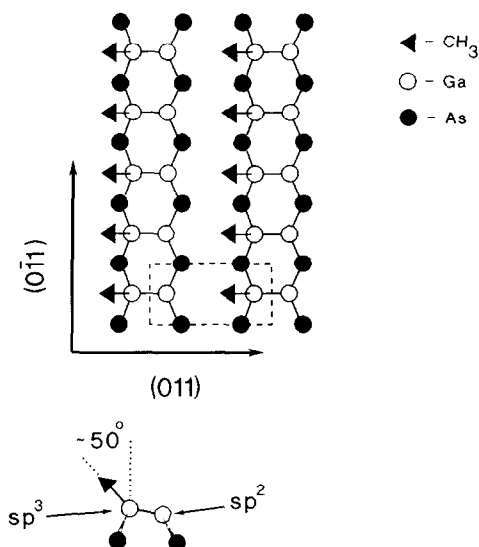


Fig. 6. Proposed structure of the Ga-rich GaAs(100)-(1×2)- $\text{CH}_3$  surface. The surface is terminated with a complete layer of dimerized Ga atoms and  $\frac{1}{2}$  ML of  $\text{CH}_3$  groups.

surements with the LEED [17,22] and SSIMS observations [27] we propose a detailed structural model for the Ga-rich GaAs(100)-(1×2)- $\text{CH}_3$  surface in Fig. 6. In the proposed configuration half of the surface Ga atoms are bonded to  $\text{CH}_3$  groups and should have  $\text{sp}^3$  hybridization while the remaining Ga atoms should be  $\text{sp}^2$  hybridized with an empty dangling bond state (p-orbital). The assessment of the Ga atom hybridization is based on the requirements of the electron counting model. For ideal ALE (as discussed in Section 3), the most important aspect of the structure in Fig. 6 is that it contains a complete monolayer of Ga atoms.

## 5. Summary

We developed a simple self-consistent method to account for stoichiometry changes on surfaces that reconstruct into complex structures containing incomplete layers of atoms, e.g. polar compound semiconductor surfaces. The key aspect of the methodology is that surface steps are allowed to act as a reservoir where atoms may be added or removed. The methodology shows that ALE of GaAs(100) does not occur by cycling between the known adsor-



bate-free Ga-rich and As-rich surface reconstructions, because no such cycle would yield the observed 1 ML growth per cycle. We propose that the ALE cycle must involve at least one reconstruction that is stabilized by adsorbates. For example, methyl groups adsorbed on GaAs(100) exhibit a  $(1 \times 2)$  LEED pattern, which is not seen for the clean GaAs(100) surface reconstructions. We interpret this structure as  $\frac{1}{2}$  ML  $\text{CH}_3$  adsorbed on a complete layer (1 ML) of dimerized Ga atoms. The proposed Ga-rich GaAs(100)- $(1 \times 2)$ - $\text{CH}_3$  structure satisfies the electron counting model because it contains the exact quantity of  $\text{CH}_3$  groups needed to bind to the dangling bond states. The structure is also supported by the polarization dependence of the symmetric bending and stretching infrared modes of the  $\text{CH}_3$  groups. The SIRS results show that the methyl groups are bonded exclusively to the surface Ga atom dangling bonds and are tilted from the surface normal by  $50^\circ \pm 10^\circ$ . The ideal termination of the Ga-rich GaAs(100)- $(1 \times 2)$ - $\text{CH}_3$  surface now allows for a plausible ALE mechanism which yields 1 ML deposition per cycle. The ALE cycle occurs by transitions between the Ga-rich  $(1 \times 2)$ - $\text{CH}_3$  surface and an As-rich surface with  $\theta_{\text{As}} = 1$  ML, e.g. the As-rich  $\gamma$ -( $4 \times 2$ ).

## Acknowledgments

This work was performed at Sandia National Laboratories supported by the US Department of Energy under contract #DE-AC04-76DP000789 for the Office of Basic Energy Sciences.

## References

- [1] C.H.L. Goodman and M.V. Pessa, *J. Appl. Phys.* 60 (1986) R65.
- [2] A. Usui and H. Watanabe, *Annu. Rev. Mater. Sci.* 21 (1991) 185.
- [3] G.B. Stringfellow, *Organometallic Vapor Phase Epitaxy: Theory and Practice* (Academic Press, Boston, MA, 1989) ch. 7.1.
- [4] J. Nishizawa, T. Kurabayashi, H. Abe and N. Sakurai, *J. Electrochem. Soc.* 134 (1987) 945.
- [5] M. Ozeki, N. Ohtsuka, Y. Sakuma and K. Kodama, *J. Cryst. Growth* 107 (1991) 102.
- [6] S.P. DenBaars, P.D. Dapkus, C.A. Beyler, A. Hariz and K.M. Dzurko, *J. Cryst. Growth* 93 (1988) 195.
- [7] K.G. Reid, H.M. Urdianvk and S.M. Bedair, *Appl. Phys. Lett.* 59 (1991) 2397.
- [8] J.R. Creighton and B.A. Banse, *MRS Symp. Proc.* 222 (1991) 15.
- [9] J.R. Creighton and B.A. Bansenauer, *Thin Solid Films* 225 (1993) 17.
- [10] A. Kahn, *Surf. Sci. Rep.* 3 (1983) 193.
- [11] W. Mönch, *Semiconductor Surfaces and Interfaces* (Springer, Berlin, 1993) chs. 7, 8.
- [12] C.B. Duke, *J. Vac. Sci. Technol. B* 11 (1993) 1336.
- [13] D.K. Biegelsen, R.D. Bringans, J.E. Northrup and L.-E. Swartz, *Phys. Rev. B* 41 (1990) 5701.
- [14] D.J. Chadi, *J. Vac. Sci. Technol. A* 5 (1987) 834.
- [15] J.A. Appelbaum, G.A. Baraff and D.R. Hamann, *Phys. Rev. B* 14 (1976) 1623.
- [16] M.D. Pashley, *Phys. Rev. B* 40 (1989) 10481.
- [17] J.R. Creighton, *J. Cryst. Growth*, submitted.
- [18] J.R. Arthur, *Surf. Sci.* 43 (1974) 449.
- [19] C. Deparis and J. Massies, *J. Cryst. Growth* 108 (1991) 157.
- [20] B.Y. Maa and P.D. Dapkus, *Thin Solid Films* 225 (1993) 12.
- [21] M. Yu, U. Memmert and T.F. Kuech, *Appl. Phys. Lett.* 55 (1989) 1011.
- [22] J.R. Creighton, *Surf. Sci.* 234 (1990) 287.
- [23] J.R. Creighton, K.R. Lykke, V.A. Shamamian and B.D. Kay, *Appl. Phys. Lett.* 57 (1990) 279.
- [24] B.Y. Maa and P.D. Dapkus, *Appl. Phys. Lett.* 58 (1991) 2261.
- [25] V.M. Donnelly, J.A. McCaulley and R.J. Shul, *MRS Symp. Proc.* 204 (1991) 15.
- [26] M.A. Van Hove and G.A. Somorjai, *Surf. Sci.* 299/300 (1994) 487.
- [27] J.R. Creighton, *J. Vac. Sci. Technol. A* 9 (1991) 2895.
- [28] T.H. Chiu, J.E. Cunningham, A. Robertson, Jr. and D.L. Malm, *J. Cryst. Growth* 105 (1990) 155.
- [29] Y. Ohki and Y. Hiratani, *J. Cryst. Growth* 105 (1990) 77.
- [30] B.A. Banse and J.R. Creighton, *Appl. Phys. Lett.* 60 (1992) 856.
- [31] C. Sasaoka, Y. Kato and A. Usui, *Surf. Sci.* 265 (1992) L239.
- [32] Y. Sakuma, K. Kodama and M. Ozeki, *Jpn. J. Appl. Phys.* 27 (1988) L2189.
- [33] D. Bertone, *J. Electron. Mater.* 21 (1992) 265.
- [34] T. Meguro, M. Ishii, K. Kodama, Y. Yamamoto, K. Gamo and Y. Aoyagi, *Thin Solid Films* 225 (1993) 136.
- [35] Y. Aoyagi, K. Shinmura, K. Kawasaki, I. Nakamoto, K. Gamo and S. Namba, *Thin Solid Films* 225 (1993) 120.
- [36] Y. Chabal, *Surf. Sci. Rep.* 8 (1988) 211.
- [37] N.J. Harrick, *Internal Reflection Spectroscopy* (Harrick Scientific Corp., Ossining, NY, 1979).
- [38] J.R. Creighton, in preparation.
- [39] E. Maslowsky, Jr., in: *Vibrational Spectra of Organometallic Compounds* (Wiley, New York, 1977) pp. 1–9.
- [40] For the signal to noise ratio of about 10:1, the deviation of the dipole out of the plane of incidence is  $\leq 6^\circ$ .