

Infrared Study of Hydrogen Adsorbed on $c(2 \times 8)$ and (2×6) GaAs(100)

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The infrared spectra of adsorbed hydrogen and deuterium on $c(2 \times 8)$ and (2×6) GaAs(100) contain a series of bands from 2200 to 1200 (1600 to 1000) cm^{-1} that are due to arsenic hydrides, terminal gallium hydrides, and bridging gallium hydrides (and deuterides). The latter is the first known example of bridge-bonded hydrogen on a semiconductor surface. Polarized spectra reveal that the AsH and GaH bonds orient along the $[\bar{1}10]$ and $[110]$ axis, respectively. These results are consistent with a GaAs surface structure composed of As and Ga dimers with dimer bonds in the $[\bar{1}10]$ and $[110]$ directions.

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Many important electronic and photonic devices are grown on GaAs(100), and because of this, many studies have been made of the atomic structure of this surface [1-6]. In the ideal case, the (100) plane terminates the GaAs crystal with a complete layer of either Ga or As atoms. However, in reality this surface exists over a wide range of As and Ga compositions, exhibiting at least five different reconstructions. The most studied reconstruction is the (2×4) - $c(2 \times 8)$ [1-6]. A model of the As-rich form of this surface is shown in Fig. 1. It consists of three pairs of As dimers followed by a dimer vacancy. If the As dimers on both sides of the vacancy row are in phase, the lattice is (2×4) , whereas if they are out of phase, the lattice is $c(2 \times 8)$. The (2×4) can also be observed with two As dimers and two vacancies per unit cell [3]. Recently, Falta *et al.* [6] have obtained medium-energy ion scattering data which suggest that these surfaces are more Ga rich than previously assumed. To explain their results, these authors proposed that Ga atoms occupy some of the As sites in the top layer.

Also shown in Fig. 1 is a model of the (2×6) reconstruction. Biegelsen *et al.* [4] have proposed this model based on their scanning tunneling microscopy (STM) images of the surface. In low energy electron diffraction (LEED), this surface yields a (1×6) pattern which is evidently due to disorder between adjacent rows of dimers. The model shows two rows of As dimers separated by two

rows of Ga dimers. The As-dimer bond is parallel to the $[\bar{1}10]$ axis, as in the $c(2 \times 8)$, whereas the Ga-dimer bond is parallel to the $[110]$ axis. The main unresolved issue with regard to this model is the Ga dimers and their ordering, since these dimers are not evident in the STM images.

In this paper, we report on our study of hydrogen and deuterium adsorption on $c(2 \times 8)$ and (2×6) GaAs(100) by multiple internal-reflection infrared spectroscopy. Our spectra differ from those obtained previously by high resolution electron energy loss spectroscopy [2,5,7,8] in that they are of high resolution and reveal a number of different bands for the arsenic and gallium hydrides. The infrared bands arise from hydrogen adsorption on four sites: As dimers, Ga dimers, second-layer As, and second-layer Ga. These four sites are the ones molecules coordinate to on GaAs(100) during many important processes, such as deposition, etching, doping, and passivation. Since we now have a means of titrating these sites, we can begin to study the *site-specific* surface chemistry of gallium arsenide.

We have also identified the orientations of the As and Ga hydride bonds by using polarized infrared light and two GaAs crystals cut parallel to the $[\bar{1}10]$ or $[110]$ axes. The directions of the hydride bonds are characteristic of the lattice sites occupied by As and Ga, and allow us to assess whether the atoms exchange sites as proposed by Falta *et al.* [6].

The apparatus and experimental method are described in Ref. [9]. The GaAs(100) internal-reflection elements were etched in 1:1:10 $\text{H}_3\text{PO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ and 1:1 $\text{HCl}/\text{H}_2\text{O}$ solutions, dried in N_2 , transferred into the vacuum chamber, and annealed at 853 K for 1 min. After the anneal, no oxygen or carbon were detected by x-ray photoelectron spectroscopy (XPS). The $c(2 \times 8)$ was produced by exposing the crystal to 1.5×10^{-7} Torr of AsH_3 at 573 K for 15 min, and heating it at 673 K to 10 min. The (2×6) was obtained by exposing the crystal to an effusive beam of trimethylgallium at 2.3×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$ at 573 K for 15 min, followed by annealing it at 853 K for 1 min. After each treatment, the sample was cooled to 313 K and a LEED pattern and an XPS spectrum taken. The LEED indicated that both reconstruc-

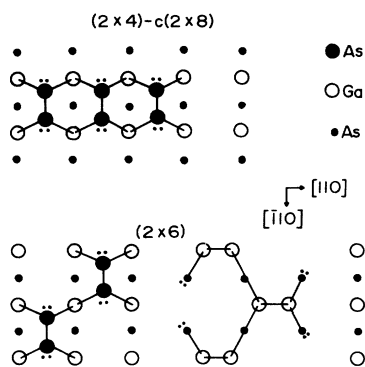


FIG. 1. Models of the $c(2 \times 8)$ and (2×6) surfaces as proposed in Refs. [1-4].

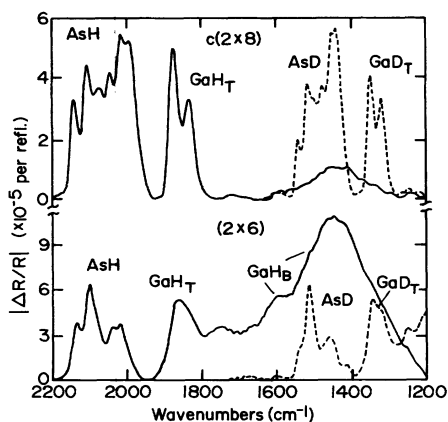


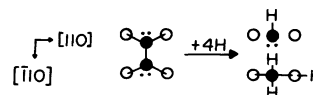
FIG. 2. Absolute change in reflectance of unpolarized infrared light due to the adsorption of hydrogen (solid line) and deuterium (dashed line) on $c(2 \times 8)$ and (2×6) GaAs(100).

tions were single domain with the $2 \times$ direction of the $c(2 \times 8)$ and the $1 \times$ direction of the (1×6) parallel to the $[\bar{1}10]$ crystal axis. The ratios of the As/Ga $2p_{3/2}$ peak areas were 1.6 for the $c(2 \times 8)$ and 1.3 for the (2×6) .

Hydrogen atoms were adsorbed onto GaAs(100) by turning on an ionizing filament 4 cm from the sample surface, and dosing 5×10^{-7} Torr H_2 into the chamber. The surface became saturated with hydrogen after 5 min ex-

posure. The intensity of the transmitted infrared light was measured by the spectrometer before and during dosing, then these spectra were ratioed to one another to give the absolute change in reflectance due to hydrogen adsorption. All spectra were obtained at 8 cm^{-1} resolution coadding 512 scans. The optics allowed spectra to be obtained at frequencies between 4000 and 1000 cm^{-1} . After hydrogen adsorption, LEED patterns were also recorded and were found to be (1×1) regardless of the starting reconstruction. These results are in agreement with prior work [7,10].

Shown in Fig. 2 are unpolarized infrared reflectance spectra for the hydrogen- and deuterium-saturated $c(2 \times 8)$ surface. The AsH and AsD vibrations appear as a series of overlapping bands from 2190 to 1950 cm^{-1} and from 1560 to 1400 cm^{-1} , respectively. The assignment of these bands to AsH and AsD stretches is consistent with prior studies of hydrogen adsorption on GaAs(110) and GaAs(100) [2,5,7-9] as well as with the stretching vibrations of gas-phase arsine compounds [11-13]. These hydride stretching frequencies are listed in Table I. The peaks seen in Fig. 2 are most likely due to arsenic monohydrides and dihydrides formed upon insertion of H atoms across the As-As and As-Ga bonds of the As dimers [9]:



This adsorption model puts the arsenic hydrides next to As atoms with lone pairs of electrons. The alternative possibility of having two hydrides next to each other between the As atoms is unlikely, since the H atoms would be so close as to bond to each other. Given an AsH bond distance of $\sim 1.51 \text{ \AA}$ [18], the H atom can be within 2.5 \AA of the lone pair on the adjacent As atom. This is close enough for hydrogen bonding. Hydrogen bonding would explain why the arsenic hydride and deuteride infrared bands are broad and overlapping. The sharp features superimposed on the broad bands may be due to isolated, non-hydrogen-bonded AsH and AsD species.

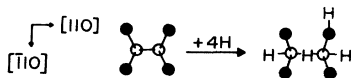
The two sharp peaks appearing at 1875 and 1835 cm^{-1} and at 1355 and 1320 cm^{-1} in the infrared spectra are due to GaH and GaD stretching vibrations. In an earlier study of hydrogen adsorption on etched and annealed GaAs(100), we proposed that these vibrations are due to H or D adsorbed on three-coordinate, sp^2 -hybridized Ga atoms [9]. However, this assignment is inconsistent with the structures of known gallane compounds. As shown in Table I, the GaH stretching vibrations of the gallane adducts are in the same frequency range, between 1900 and 1800 cm^{-1} . The Ga bonding in the adducts is approximately tetrahedral (i.e., sp^3 hybridized) with three covalent bonds to H or CH_3 and one dative bond to N or P [15,16]. Therefore, we now conclude that the two peaks at 1875 and 1835 cm^{-1} and at

TABLE I. Vibrational frequencies of As and Ga hydrides.

Compound	Frequencies (cm^{-1})	Reference
Arsines		
AsH ₃	2123,2116	[11]
Et ₂ AsH	2080	[12]
EtAsH ₂	2107-2086	[13]
tBuAsH ₂	2126-2088	[13]
GaAs(110):AsH	2150	[8]
GaAs(100):AsH	2000-2150	[2,5,7,9]
Gallane adducts		
Me ₃ NGaHMe ₂	1840,1770	[14]
Me ₃ NGaH ₃	1848-1839,1790-1782	[15,16]
[Me ₂ NGaH ₂] ₂	1911,1907,1901,1870	[16]
Me ₃ PGaH ₃	1832,1808	[15]
GaAs(110):GaH	1890	[8]
GaAs(100):GaH	1880-1840	[2,5,7,9]
H-bridged gallanes		
Ga ₂ H ₆ gas	1993,1976,1273,1202	[16]
[GaH ₃] _n solid	1978,1705,950	[16]
[Me ₂ GaH] ₂ gas	1290,1185	[16]
[Me ₂ GaH] _n solid	1705,965	[16]
[Et ₂ GaH] ₂ N ₂ matrix	1234,1162	[16]
[Et ₂ GaH] _n solid	1657-1640	[16]
α -GaAs:H	1460	[17]

1355 and 1320 cm^{-1} are due to terminal gallium hydrides and deuterides (GaH_T), in which the H or D atoms are attached to tetrahedrally coordinated Ga atoms. The likely sites for formation of these hydrides are the second-layer Ga atoms exposed along the As-dimer vacancy rows.

Also shown in Fig. 2 are infrared spectra for the hydrogen- and deuterium-saturated (2×6) surface. The most striking difference between these spectra and those of the $c(2 \times 8)$ is the presence of a broad band between 1750 and 1200 cm^{-1} for H:(2×6) and below 1250 cm^{-1} for D:(2×6). We attribute this feature to the asymmetric stretching vibration of a bridging gallium hydride (GaH_B), in which the H atom is held to two Ga atoms via a 3-center-2-electron bond. This hydride is produced by addition of H atoms to the Ga dimers:



This assignment is consistent with the vibrational properties of H-bridged gallanes [16] and of amorphous, hydrogenated GaAs ($\alpha\text{-GaAs:H}$) [17]. The stretching frequencies of these species are given in Table I. In the case of $\alpha\text{-GaAs:H}$, the bridging hydride gives rise to a broad band at exactly the same frequency as observed here for H:(2×6) GaAs(100).

A bridging hydride bound to two massive gallium atoms exhibits the following asymmetric and symmetric stretching modes [19,20]:



Valence-force theory predicts that these vibrations are related to each other as $\nu_{as}/\nu_s = \tan(\theta/2)$ [19,20]. The two modes have the same frequency for $\theta=90^\circ$, but as $\theta \rightarrow 180^\circ$, the frequency separation becomes very large. This theory also predicts that the intensity ratio, I_{as}/I_s , increases from 1 to ∞ as θ varies from 90° to 180° . These trends are borne out of the vibrational properties of the hydrogen-bridged gallanes [16]. Gallane dimers (Ga_2H_6 , $[\text{Me}_2\text{GaH}]_2$ and $[\text{Et}_2\text{GaH}]_2$) each contain two bridging hydrides which exhibit asymmetric and symmetric stretches at 1290–1234 and 1202–1162 cm^{-1} . The Ga-H-Ga bond angle in the dimers is $\sim 99^\circ$. By contrast, gallane oligomers ($[\text{GaH}_3]_n$ and $[\text{R}_2\text{GaH}]_n$ with $n \geq 4$), obtained by condensing the dimers at low temperature, contain bridging hydrides with asymmetric and symmetric stretches at 1705–1640 and 965–950 cm^{-1} . The Ga-H-Ga bond angle in the oligomers is estimated to be $\sim 120^\circ$.

The above relationship between vibrational frequency and bond angle should hold equally well for the bridging gallium hydride on GaAs(100). Close examination of the GaH spectrum in Fig. 2 reveals that the broad band is

centered at 1460 cm^{-1} and has two shoulders at 1600 and 1325 cm^{-1} . The main peak and two shoulders are probably due to the asymmetric stretching vibrations of three hydrides which differ in their Ga-H-Ga bond angles. We believe these are distinct species because the infrared bands grow in sequentially with hydrogen dosage, beginning with the shoulder at 1325 cm^{-1} , followed by the main peak at 1460 cm^{-1} and the shoulder at 1600 cm^{-1} [21]. Based on an extrapolation of the vibrational data for the gallanes, we estimate that the peaks at 1600, 1460, and 1325 cm^{-1} correspond to bond angles of 115, 105, and $100^\circ (\pm 5^\circ)$, respectively [21]. Assuming the GaH bond length is constant at 1.7 Å [16,17], these angles yield Ga-Ga distances of 2.85, 2.70, and 2.60 ± 0.1 Å. These results suggest that the Ga-dimer bond lengths vary significantly on the (2×6) GaAs(100) surface.

The main peak and two shoulders for the bridging hydrides are very broad, exhibiting full widths at half maxima of approximately 150 cm^{-1} . This band broadening can be explained by coupling of the asymmetric stretching vibration with the lower frequency phonon modes of the GaAs lattice. Band broadening due to strong coupling with low-frequency vibrations is characteristic of bridged hydrogen bonding [22].

Comparison of the As-H stretching vibrations for $c(2 \times 8)$ and (2×6) surfaces in Fig. 2 reveals that the peak at 2110 cm^{-1} is more intense for the gallium-rich reconstruction. We attribute this peak to hydrogen adsorption on second-layer arsenic atoms which are attached to the Ga dimers. These sites also may be exposed at steps and other crystal imperfections.

Shown in Fig. 3 are polarized infrared reflectance spectra of hydrogen adsorbed on $c(2 \times 8)$ and (2×6) surfaces of two GaAs(100) crystals oriented along the [110] and $[\bar{1}\bar{1}0]$ axes: *s* (dashed lines) and *p* (solid lines).

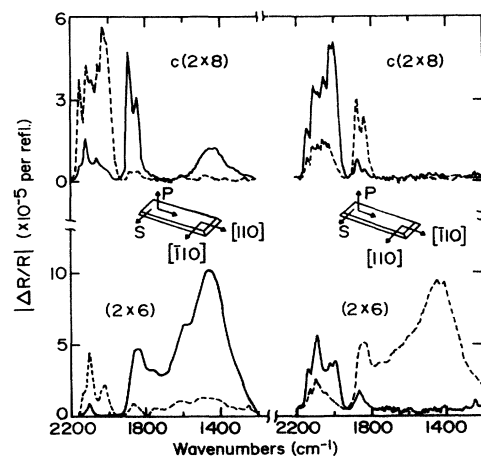


FIG. 3. Absolute change in reflectance of polarized infrared light due to hydrogen adsorption on the $c(2 \times 8)$ and (2×6) surfaces of two GaAs(100) crystals oriented along the [110] and $[\bar{1}\bar{1}0]$ axes: *s* (dashed lines) and *p* (solid lines).

used for the left- and right-hand spectra. A remarkably high degree of orientation of the hydride bonds is observed in these spectra. The arsenic hydride vibrations are predominately *s* polarized when the long crystal axis is in the [110] direction, whereas they are *p* polarized when the long crystal axis is in the $\bar{1}\bar{1}0$ direction. This polarization dependence means that the AsH bonds orient along the $\bar{1}\bar{1}0$, *parallel* to the As-dimer bonds. By contrast, the gallium hydride vibrations are mainly *p* polarized when the long crystal axis is in the [110] direction, while they are *s* polarized when the long crystal axis is in the $\bar{1}\bar{1}0$ direction. Thus, the GaH bonds orient along the [110], *perpendicular* to the As-dimer bonds. These results are exactly what one expects for H atom adsorption on the $(2\times 4)\text{-}c(2\times 8)$ surface as it is represented in Fig. 1. The bond coordination of the As and Ga atoms should be nearly tetrahedral, and since As has two bonds down to Ga along the [110], it bonds up to H in a direction parallel to the $\bar{1}\bar{1}0$. Conversely, the bonds to Ga are rotated 90° with respect to those to As so that Ga bonds up to H in a direction parallel to the [110]. The atomic structure of the $c(2\times 8)$ proposed by Falta *et al.* [6], in which Ga atoms are substituted into As sites and vice versa, is inconsistent with the results presented here. If a substantial amount of intermixing of the As and Ga atoms occurred, then the AsH and GaH stretching vibrations would not be polarized along the two crystal axis as observed.

Also shown in Fig. 3 are polarized infrared spectra of hydrogen adsorbed on (2×6) GaAs(100). The AsH and GaH_T bands between 220 and 1750 cm^{-1} exhibit the same polarization dependence as is found for these vibrations on the $c(2\times 8)$ surface. The GaH_B bands between 1750 and 1200 cm^{-1} are *p* polarized when the long crystal axis is parallel to the [110], whereas they are *s* polarized when the long crystal axis is parallel to the $\bar{1}\bar{1}0$. These results are entirely consistent with hydrogen adsorption on a (2×6) surface which contains rows of As and Ga dimers as shown in Fig. 1. In this model of the (2×6) , the Ga-dimer bond is parallel to the [110] axis. Insertion of an H atom across this bond yields a bridging hydride with an asymmetric stretch also parallel to the [110]. In summary, the polarized infrared spectra of adsorbed hydrogen on GaAs(100) agree with the structures proposed by Pashley *et al.* [3], Biegelsen *et al.* [4], and others [1,2], in which the surface consists of rows of As and/or Ga dimers with their bonds parallel to the $\bar{1}\bar{1}0$ and [110] axis, respectively.

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