Resolving the Ga Ad-Dimer Location and Orientation on the Si(100) Surface

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Quantitative x-ray standing wave measurements of the Ga ad-dimer bond length, orientation, and location for the Si(100)-(2 × 2):Ga surface combined with first-principles molecular cluster calculations on four different ad-dimer models lead to the conclusion that Ga atoms form ad-dimers which are aligned parallel to the underlying Si dimers and lie in between Si dimer rows at the valley bridge site.

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In order to develop a detailed physical description for the heteroepitaxial growth of GaAs on Si(100), the underlying initial growth mechanism of Ga and As must first be understood. Similar to other group III and V adsorbates, Ga and As form symmetric dimers on the Si(100) surface [1–6]. While several surface phases (2 × 3, 2 × 2, 2 × 5, and 1 × 8) have been observed for the Ga/Si(100) system, As adsorbed on Si(100) is much more stable and induces a dominant 2 × 1 reconstruction. This leads to an As-terminated Si surface when GaAs is grown on Si(100) [7] which in turn leads to the formation of antiphase domain defects at a real surface with monatomic steps [8]. Rigorous structural information which provides a stringent test of first-principles theoretical calculations is required to gain a detailed understanding of the origin of these qualitative observations.

In this Letter, we report the first *quantitative* high-resolution measurement of the Ga/Si(100) surface structure [or any other group III adlayer/Si(100), to our knowledge]. Using the x-ray standing wave (XSW) technique, we have measured the Ga dimer bond length, orientation, and location relative to the underlying bulk Si lattice for the Si(100)-(2 × 2):Ga surface structure at a coverage of $\Theta = 0.5$ ML, where 1 ML = 6.78×10^{14} atoms/cm^2. We have also studied several possible dimer structures using the first principles local density molecular cluster approach (DMOL) [9]. By a comparison between the XSW experimental measurement and the theoretical calculations, we conclude that the Ga ad-dimers are aligned parallel to the Si dimers and centered over the valley bridge site. The Si(100)-(2 × 1):As system, which is addressed in a separate XSW study [10], agrees with previous experimental and theoretical studies and provides added confidence to the results presented here.

The clean Si surface is known to have a 2 × 1 reconstruction with the top layer of Si atoms forming rows of dimers to reduce the number of dangling bonds. The Ga/Si(100) system has previously been studied by reflection high-energy electron diffraction (RHEED) [1], low-energy electron diffraction (LEED) [2], Auger electron spectroscopy (AES) [2], and scanning-tunneling microscopy (STM) [3,4] with several ordered phases reported for Ga coverages ranging up to 1 monolayer (ML). Below 0.5 ML of Ga, RHEED and LEED studies have reported the following ordered phases: 2 × 3 for 0.15–0.35 ML, 2 × 5 for 0.4 ML, and 2 × 2 for 0.4–0.55 ML. For the above phases, Bourguignon, Carleton, and Leone [2] have proposed a structural model, which is labeled OV in Fig. 1. This orthogonal ad-dimer model assumes that the underlying Si dimers are not broken when the Ga coverage is below $\frac{1}{2}$ ML and that the Ga ad-dimers line up between the Si dimer rows with the orientation of the Ga dimer bond perpendicular to the Si dimer bond. The spacing of the Ga ad-dimer rows can be arranged to form 2 × 3, 2 × 5, and 2 × 2 phases at coverages of $\frac{1}{3}$, $\frac{2}{5}$, and $\frac{1}{2}$ ML Ga, respectively. In recent STM [3,4] studies, Nogami and co-workers have found both 2 × 3 and 2 × 2 Ga/Si(100) surface structures, when Ga coverages are below 0.5 ML. These STM images show that the Ga ad-dimers are located between the Si dimer rows and that the Ga ad-dimers grow in rows which are perpendicular to the underlying Si dimer rows.

The resolution of these particular STM measurements [3,4] was not sufficient to distinguish single Ga atoms within a Ga ad-dimer or the orientation of an ad-dimer. Therefore, besides the OV orthogonal ad-dimer model, the parallel ad-dimer model labeled PV in Fig. 1 can also be considered consistent with the STM images and the LEED patterns. This was recently posed as an alternative solution of the Si(100)-(2 × 2):Al surface [11]. Although the two models (OV and PV) differ in the relative orientations of the Ga and Si dimers, both models are 2 × 2 at $\frac{1}{2}$ ML and have the Ga dimer located between Si dimer rows at the valley bridge site.

The orthogonal (OV) and parallel (PV) ad-dimer models were recently tested by Northrup and co-workers [5] with first-principles total-energy calculations for Al, Ga, and In on Si(100). For coverages below 0.5 ML, their

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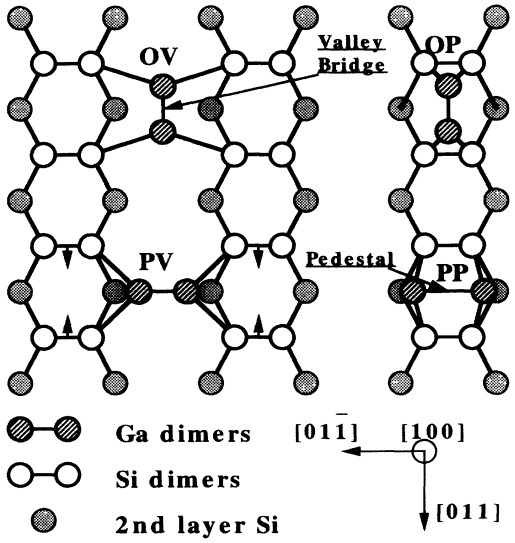

FIG. 1. Schematic drawing of four Ga ad-dimer structures on the Si(100)-(2 × 1) surface: OV, orthogonal dimer centered at valley bridge site; PV, parallel dimer at valley bridge; OP, orthogonal dimer at pedestal site; and PP, parallel dimer at pedestal.

results strongly favor the PV model over the OV model. A recent impact-collision ion-scattering spectrometry experiment found that at low coverages In adsorbed on a vicinal Si(100) surface to form parallel ad-dimers [12]. The most recent STM study of Si(100)-(2 × 2):Al also confirms the PV model [13].

Our Ga/Si(100) experiments were performed at the X15A beam line of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The UHV system at X15A (described elsewhere [14]) allows for sample preparation, LEED and AES surface characterization, and x-ray measurements to be done *in situ*. Before introduction into the UHV chamber, the Si samples were carefully oriented and cut along (100) crystal planes. The samples were then Syton polished and Shiraki etched. The base pressure in the UHV system was 9×10^{-11} torr. The samples were first outgassed at 600 °C for 5–8 h then flashed to 900 °C for 10 min, after cooling to room temperature (RT) a sharp 2-domain 2 × 1 LEED pattern for the clean Si surface was observed. Ga was deposited onto the Si from an MBE effusion cell while the Si substrate was held at RT. For $\Theta < 1$ ML, the Ga coverage was calibrated to be directly proportional to the exposure time, with a relative error of 10%. This calibration was made by using the ratio of the Ga to Si Auger peaks and by the Rutherford backscattering. Several Ga coverages between 0.35 and 0.55 ML deposited on the Si(100) clean surface at RT will be reported here. A 2 × 2 LEED pattern was observed for these coverages. As with the earlier STM study at RT [4], we did not observe 2 × 3 or 2 × 5 LEED patterns. XSW measurements were then performed for these coverages using the (400) and (220) Bragg reflections.

For surface structure determination of an adatom layer on a perfect single crystal surface, an XSW measurement [14–17] consists of monitoring the adatoms' fluorescence yield while scanning in angle through a particular *hkl* strong Bragg reflection of the crystal. This scan causes the standing wave to phase shift by one-half of a *d*-spacing relative to the *hkl* diffraction planes, which in turn induces a characteristic modulation in the adatoms' fluorescence yield. The phase of the fluorescence modulation, which is referred to as the coherent position P_{hkl} (or P_H), measures the $\Delta d/d$ weighted average position of the adatom distribution along the **H** direction. The amplitude of the modulation, which is referred to as the coherent fraction $f_{c,H}$, measures the width of the adatom distribution along the **H** direction.

For Ga/Si(100) the (400) XSW scan directly measures the height (h') of the Ga dimer and the (220) scan measures the Ga dimer bond length (L). Figure 2 shows the x-ray reflectivity and Ga $K\alpha$ fluorescence yield for both the (400) and (220) reflections for a 0.55 ML Ga coverage at RT. The incident energy was 13.0 keV for the (400) scan and 12.0 keV for the (220) scan. The XSW determined coherent position and coherent fraction from the (400) scan are $P_{400} = 0.76 \pm 0.01$ and $f_{c,400} = 0.54 \pm 0.01$. The values from the (220) scan are $P_{220} = 0.88 \pm 0.01$ and $f_{c,220} = 0.27 \pm 0.01$.

The XSW measured Ga ad-dimer height above the Si(400) bulklike atom plane is $h' = P_{400}d_{400} = 1.03 \pm 0.02$ Å. This was also found to be true at the lower coverages. The P_{220} measured values were found to be consistent with the P_{400} values; namely that $P_{220} = (1 + P_{400})/2$. This relationship is based on the Ga ad-dimers being centered above one of the twofold symmetry sites illustrated in Fig. 1.

To determine the Ga ad-dimer (L), we separate the measured coherent fraction into three factors $f_{C,H} = Ca_HD_H$ [16], where C is the Ga ordered fraction, a_H is the Ga geometrical factor, and D_H is the Ga Debye-Waller factor. For the symmetric dimer cases illustrated in Fig. 1, $a_{220} = |\cos(\pi L/2d_{220})|$. By making the simplified assumption that the Ga thermal vibration amplitude is isotropic and equal to the value found for the Si(100) surface [18] ($\langle u^2\rangle^{1/2} = 0.12$ Å), we can estimate that $D_{400} = 0.86$ and $D_{220} = 0.93$ for the Ga atoms. This D_{400} value along with the measured value of $f_{c,400}$ gives the measured value of the ordered fraction $C = f_{c,400}/D_{400} = 0.63 \pm 0.06$, since $a_{400} = 1$ for symmetric ad-dimers. With the above measured values, we can then determine a_{220} which leads us to a measured value for the Ga dimer length of $L = 2.50 \pm 0.06$ Å; the error quoted in our result for L is reasonable and includes the uncertainties for the estimates of the Debye-Waller factors. To reduce this error in the Ga dimer bond length measurement, we will directly measure the Debye-Waller factors D_{400} and D_{220} for the Ga atoms on the Si(100) surface in future studies by using higher-order harmonic XSW measurements [16].

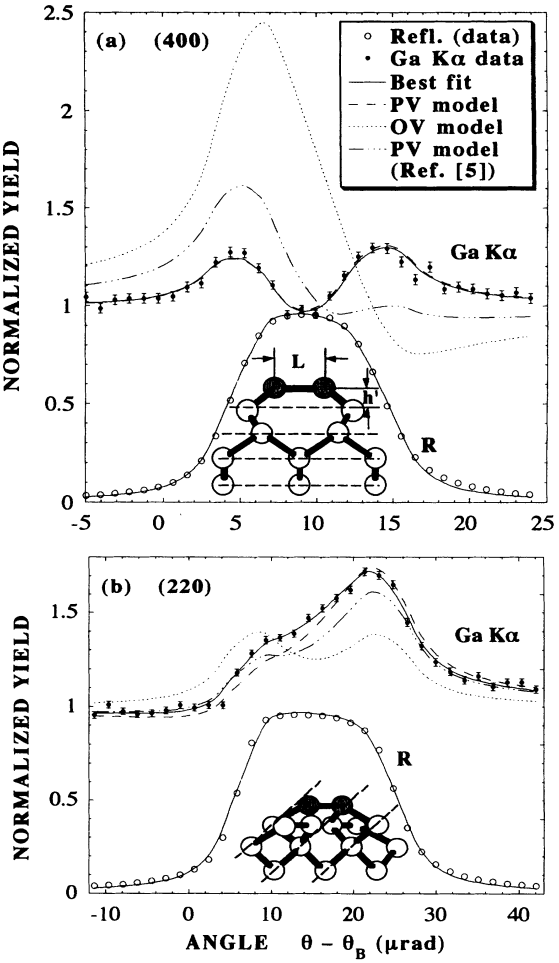

FIG. 2. Experimental data and theoretical curves for the normalized Ga $K\alpha$ fluorescence yield and Si reflectivity (R) versus Bragg reflection angle θ for (a) the Si(400) and (b) Si(220) reflections. Note that our PV model predicted yield curve is indistinguishable from the best fit in (a). The insets for (a) and (b) show the [011] and [001] projected side views of the Ga/Si(100) parallel ad-dimer surface model, respectively. The model shows the Si atoms as open circles and Ga atoms as filled circles. The dashed lines represent the (400) Miller planes in inset (a) and (220) Miller planes in inset (b). Note in (a) that the Ga $K\alpha$ dip in the middle of the (400) rocking curve corresponds to the XSW node passing over the Ga layer at this angle.

It is interesting to note that as the Ga coverage was increased from 0.35 to 0.55 ML, the Ga ordered fraction C reduced from 0.85 to 0.63. Thus the resulting ordered coverage $C\Theta$ remained constant at $\approx$0.33 ML. This feature, along with the constancy of the Ga ad-dimer bond length and height over this range of coverages, indicates that under the given growth conditions only one ordered structure is formed and that Ga in excess of $\approx$0.33 ML is disordered and presumably forms Ga clusters. The fact that our highest ordered coverage is below the ideal value of $\frac{1}{2}$ ML is consistent with STM images [3,4] which show vacancies, missing ad-dimers, and antiphase domains.

The present total-energy and force calculations were performed using the DMOL [9] molecular cluster approach within the local-density approximation to density functional theory and the Hedin-Lundqvist exchange correlation potential [19]. An extended double basis set is chosen for Si and Ga which contains a double set of valence functions plus a single d polarization function. The initial geometry of the Si(100)-(2 × 1) bare surface was taken from Ref. [20]. As usual, hydrogen atoms are used to saturate the bulk Si dangling bonds and the Si-H bond length is 1.48 Å. Cluster models ranging from 33 to 77 atoms are employed to simulate the adsorption sites in question.

Using cluster models of 33 and 37 atoms, the calculations show that two Ga atoms can form a dimer at the valley bridge and pedestal sites as shown in Fig. 1 with the Ga dimer parallel or orthogonal to the Si dimers. These include the valley bridge site orthogonal dimer (OV) and the parallel dimer (PV) models proposed in the literature [2–5] and two other models (OP and PP) at the pedestal site which have not previously been studied for Ga/Si(100). The calculated adsorption energies per atom for the four dimers are OV: −3.14 eV, OP: −3.29 eV, PV: −4.15 eV, and PP: −3.43 eV, respectively. The results clearly show that the PV model in between the Si dimer rows has a much lower energy than the other dimer configurations and thus is predicted to be the most stable structure. This is consistent with pseudopotential results [5]. It is interesting to note that the OV model in Fig. 1, which was originally proposed, is actually the least likely structure in terms of the energy. This is not surprising since in this configuration, the Ga-Si bond length is quite large; in order for Ga to bond more strongly with Si, the Ga atom has to move close to the Si surface, which will result in a π-like bonding between p_z electrons of Ga and Si [21]. [As a comparison, the calculated adsorption energy for As on the dimerized Si(100)-(2 × 1) surface is −4.82 eV.]

When two Ga atoms form a parallel dimer in between the Si dimer rows (PV), each Ga atom bonds with two top layer Si atoms and one Ga atom. This results in a maximum use of its valence electrons to form hybridized states with other atoms. In this configuration, Ga atoms can form an ordered 2 × 2 structure without disrupting the underlying Si(100)-(2 × 1) structure. To obtain the structural data for the PV model, we used a cluster with 75 atoms, which consisted of 5 layers of Si atoms and 4 Ga atoms at the surface. (For comparison with other calculations, the OV model is also calculated using the same cluster, but replacing 4 Ga atoms with 3 pairs of orthogonal Ga dimers.) The first three layers of Si atoms are allowed to relax while the fourth and fifth layers are fixed in their bulk position. The final optimized results are listed in Table I along with the pseudopotential results [5] and our x-ray standing wave measurement. While there is overall agreement between our DMOL results and the pseudopotential calculation, there is a significant difference for h'. While

TABLE I. Optimized structural parameters for the parallel (PV) and orthogonal (OV) Ga ad-dimer on Si(100)-(2 × 1): d_{Si-Si}, d_{Ga-Si} and L are the bond lengths of the Si dimer, Ga-Si and Ga ad-dimer, respectively. h, vertical height of the Ga dimer above the Si dimer; Δz, inward relaxation of the top Si layer relative to the bulklike position. h, height of the Ga dimer above the bulklike Si(400) surface atom plane.

	Parallel Model		Orthog. Model		
(Å)	DMOL	Ref. [5]	DMOL	Ref. [5]	XSW
d_{Si-Si}	2.49	2.46	2.80	2.84	
d_{Ga-Si}	2.54	2.47	2.63	2.61	
L	2.65	2.63	2.64	2.50	2.50 ± 0.06
h	1.18	1.09	0.77	0.73	
Δz	0.13	0.17	0.08	0.13	
h'	1.05	0.92	0.69	0.60	1.03 ± 0.02

both theoretical calculations for the h' values serve to rule out the OV model when compared with the XSW experiment, the DMOL results for the PV model are in better agreement with experimental values. The difference between the theoretical and experimental value for the Ga-Ga bond length for the PV model is not understood. For the parallel dimer (PV), the underlying Si dimer bond is stretched from 2.23 Å [20] to 2.49 Å as a consequence of Ga adsorption. Furthermore, it is found that two neighboring Si dimers in the same row move 0.07 Å towards each other resulting in a contracted dimer row configuration; this is indicated in the PV model in Fig. 1 by arrows. This newly proposed arrangement of Si dimers is compatible with the observed 2 × 2 LEED pattern.

To illustrate the sensitivity of our XSW measurement, Fig. 2 shows the experimental Ga $K\alpha$ fluorescence yields and our best fit by dynamical diffraction theory [14,16] in comparison to the yield curves based on h' and L values predicted by our PV and OV model as well as the PV model of Ref. [5]. For this comparison the ordered fraction was set at the value that was determined from the best fit ($C = 0.63$). Since the XSW method measures the coherent position of the adatoms with such a high precision (typically ±0.01), it is an ideal test for such theoretical models. As evident in Fig. 2(a), our measurements clearly agree with the prediction of our PV model and disagree with the OV model. Furthermore, although the predictions of the PV model of Ref. [5] are in rough agreement, the sensitivity of the XSW technique can easily discriminate between our DMOL prediction and the pseudopotential predictions. For the pedestal centered Ga ad-dimer models OP and PP, the DMOL calculated values for h' using a 33 atom cluster are 1.27 and 1.64 Å, respectively, which clearly disagree with the XSW measured result of $h' = 1.03$ Å. These models can also be ruled out by the earlier STM images [4], which show Ga dimers located between Si dimer rows.

As noted above, Ga in excess of about 0.33 ML was disordered. This lack of stability in forming the 2 × 1 dimerized 1 ML Ga/Si(100) surface structure, in contrast to As, can be explained by the following reasons. When the coverage of Ga is below the ideal $\frac{1}{2}$ ML, the Si 2 × 1 reconstruction remains unbroken on the surface and the Ga dimers are oriented parallel to the underlying Si dimers. The formation of the 2 × 1 dimerized 1 ML Ga/Si(100) surface would presumably require the removal of the Si 2 × 1 reconstruction and a 90° rotation of the Ga ad-dimers orientation (switching from parallel to orthogonal). For the case of As on Si(100), theoretical calculations [6,21] predict that the Si dimer is broken by As and the As ad-dimers are orthogonal to the Si dimers. As a result, As forms the first layer when GaAs is grown on the Si(100) surface [7].

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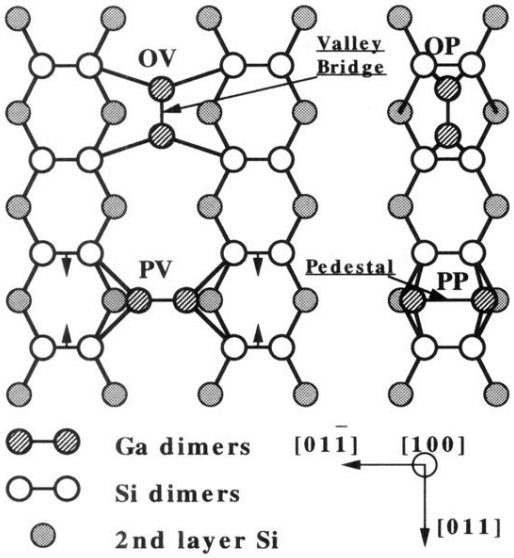

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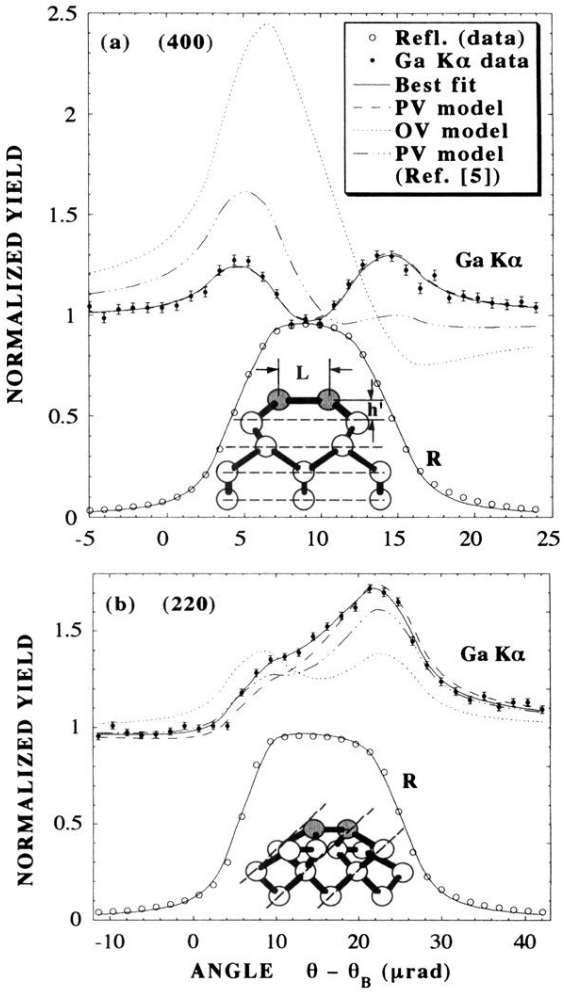

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