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Multilayer structural determination of the GaAs($\bar{1}\bar{1}\bar{1}$) 2×2 reconstruction by automated tensor LEED

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The multilayer atomic coordinates for the GaAs($\bar{1}\bar{1}\bar{1}$)(2×2) surface have been determined using automated tensor low-energy electron diffraction. The results confirm the As adatom trimer model found by total-energy calculations and scanning tunneling microscopy studies although details of the displacements are different. The low-energy electron diffraction analysis, being sensitive to multilayer spacings in the surface region, shows that substantial subsurface relaxations are present. [S0163-1829(99)15115-4]

We have determined the multilayer reconstruction structure of GaAs($\bar{1}\bar{1}\bar{1}$)(2×2) using automated tensor low-energy electron diffraction (ATLEED).¹ The (2×2) reconstruction structure of GaAs($\bar{1}\bar{1}\bar{1}$) has been studied by total-energy calculations^{2,3} and scanning tunneling microscopy (STM).³ The total energy calculations have found that a reconstruction structure consisting of As adatom trimers, ordered in a (2×2) periodicity above an underlying As-Ga bilayer, has a very low energy compared to the ideal surface.^{2,3} Images from STM of this surface are consistent with the presence of As trimers.³ Because the As-As bonds both within the trimer and between the trimer and the substrate are very much nonbulk sp^3 like, one would expect substantial multilayer relaxations to be present in the near surface region. Since STM is not sensitive to subsurface information, there has been no multilayer structural information obtained from experiment to date and the only such information obtained so far is from total-energy calculations.^{2,3}

In this study, we use quantitative LEED IV spectra analysis to determine the multilayer reconstruction structure. LEED IV spectra between 20 and 200 eV are measured for 10 beams (five integral order and five fractional order) at normal incidence with the sample held at 100 K. The beam intensities are measured using a spot photometer, and are corrected for variations in the incident beam current. After insertion into the UHV system the sample is cleaned by several cycles of Ar bombardment (400 eV Ar ions) and annealing (750 K), until Auger measurements show no surface contamination. The sample is then heated to 750 K in the presence of 10^{-6} Torr of As vapor produced by heating an As-filled crucible. The sample is cooled to 100 K in the As vapor and a thick As layer is deposited on the surface. Excess As is removed by heating the sample to approximately 600 K in UHV. When cooled, a sharp (2×2) LEED pattern

is observed. The LEED pattern and IV curves do not change after subsequent anneals up to 700 K, indicating that the surface is stable.

The quantitative analysis of LEED spectra is carried out by the ATLEED method.¹ In the automated structural search, we vary the atomic positions in the first seven layers: i.e., the As trimer layer and three bilayers below. Deeper atomic layers are included in the multiple scattering calculation, but the atomic positions are fixed at bulk sites. For atoms in the bilayers, the As and Ga potentials are generated using the self-consistent full linearized augmented-plane-wave (LAPW) method.⁴ We then calculate phase shifts from the spherical approximation of each potential (i.e., the muffin-tin potential). Because the As trimer sites are not bulklike, we generate the As adatom potential by the superposition and spherical averaging method of Mattheiss,⁵ using self-consistent atomic charge densities. The multiple scattering includes nine phase shifts. The average potential, i.e., the muffin-tin average, within the adatom layer is 7.43 eV, while in the deeper layers, it is 11.22 eV. To account for this difference, we have modified the ATLEED code to accept different energies used for the phase shifts, the layer scattering matrices and the propagators. The structural determination searches through many models, including a number of vacancy^{6,7} and adsorption models previously proposed for this and other semiconductor (111) surfaces. The search confirms that the As trimer model produces the best fit for the IV spectra. The minimum Van Hove-Tong R factor [R_{VHT} (Refs. 8, 9)] is 0.1962, which is among the best obtained for overlayer systems on semiconductors. In particular, the Ga-vacancy model,^{7,10-14} previously identified to give the best LEED agreement for the GaAs(111) (2×2) surface, is found to produce very poor agreement here. In contrast, the As-trimer model has been found to compare poorly in LEED IV spectra analysis for the GaAs(111) (2×2) surface.¹⁵ The

TABLE I. Atomic coordinates for the As trimer and the top three bilayers, both the bulk and best-fit structures are listed.

Atom			Bulk terminated surface			Best-fit structure		
			X	Y	Z	X	Y	Z
As trimer						3.9976	-0.9017	2.3504
						2.7797	-3.0113	2.3504
						5.2155	-3.0113	2.3504
First bilayer	1	As	0.0000	0.0000	0.0000	0.0000	0.0000	0.6557
	2	As	1.9988	-3.4620	0.0000	2.0742	-3.4183	0.0000
	3	As	1.9988	3.4620	0.0000	1.9234	3.5057	0.0000
	4	As	3.9976	0.0000	0.0000	3.9976	-0.0872	0.0000
	5	Ga	3.9976	4.6160	-0.8160	3.9976	4.7226	-0.5094
	6	Ga	1.9988	1.1540	-0.8160	1.9065	1.1007	-0.5094
	7	Ga	5.9964	1.1540	-0.8160	6.0887	1.1007	-0.5094
Second bilayer	8	Ga	3.9976	-2.3080	-0.8160	3.9976	-2.3080	-1.0242
	9	As	3.9976	4.6160	-3.2640	3.9976	4.5921	-3.0032
	10	As	1.9988	1.1540	-3.2640	2.0195	1.1661	-3.0032
	11	As	5.9964	1.1540	-3.2640	5.9757	1.1661	-3.0032
	12	As	3.9976	-2.3080	-3.2640	3.9976	-2.3080	-3.3198
	13	Ga	3.9976	2.3080	-4.0800	3.9976	2.3080	-3.8239
	14	Ga	1.9988	-1.1540	-4.0800	1.9450	-1.1230	-3.9020
Third bilayer	15	Ga	5.9964	-1.1540	-4.0800	6.0502	-1.1230	-3.9020
	16	Ga	3.9976	-4.6160	-4.0800	3.9976	-4.6780	-3.9020
	17	As	3.9976	2.3080	-6.5280	3.9976	2.3080	-6.2711
	18	As	1.9988	-1.1540	-6.5280	2.0177	-1.1649	-6.3462
	19	As	5.9964	-1.1540	-6.5280	5.9775	-1.1649	-6.3462
	20	As	3.9976	-4.6160	-6.5280	3.9976	-4.5941	-6.3462
	21	Ga	5.9964	3.4620	-7.3440	6.0140	3.4721	-7.1474
Third bilayer	22	Ga	1.9988	3.4620	-7.3440	1.9811	3.4721	-7.1474
	23	Ga	3.9976	0.0000	-7.3440	3.9976	-0.0203	-7.1474
	24	Ga	0.0000	0.0000	-7.3440	0.0000	0.0000	-7.2207

difference between these two surfaces has been discussed before.¹⁴ The position coordinates for atoms in the first seven layers of the best fit structure are listed in Table I. The Z axis is normal to the surface. The IV spectra comparisons between theory and experiment for the best fit structure are shown in Figs. 1 and 2, respectively, for the integral and fractional order beams. In the following, we shall discuss the significance of the multilayer relaxation structure and compare our numbers to those obtained by total-energy calculation, wherever the latter are available. We shall show the numbers from total energy calculations³ in square brackets.

Referring to the schematic top and side views of the As trimer model shown in Figs. 3 and 4 respectively, our determination of the As-As bond length in the trimer is 2.44 Å, which is in exact agreement with the total energy result. The bond length between the As atom in the trimer and As atom in the first bilayer is 2.49 Å, compared to [2.42 Å]. The trimer layer is $d_1 = 2.35$ Å above the bilayer below compared to [2.28 Å]. A major difference is that we find the As atoms below the trimer, i.e., atoms 2, 3, and 4 in Fig. 3, are sub-

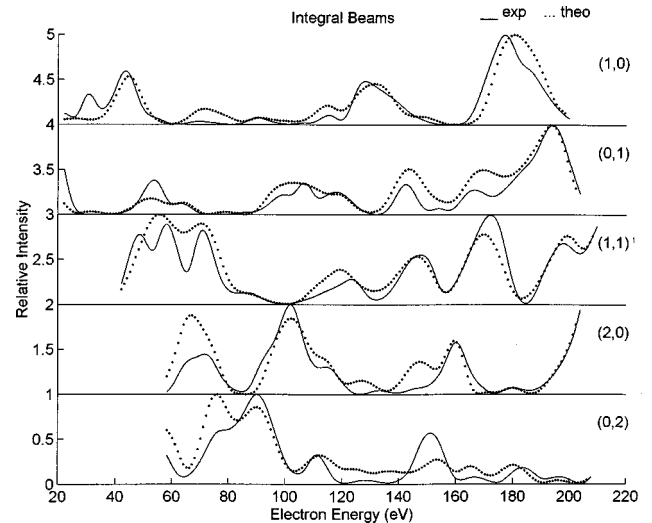


FIG. 1. IV spectra for the integral order beams, experiment and theory for the best-fit structure.

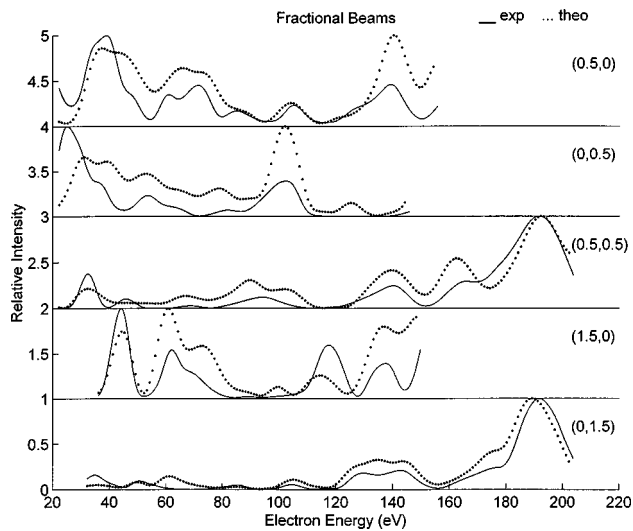


FIG. 2. Same as in Fig. 1, for the fractional order beams.

stantially pushed downward. The bilayer distance d_3 in Fig. 4 is reduced to 0.51 Å, compared to the bulk value of 0.82 Å. Unfortunately, the total energy calculation³ did not provide information on this compression. Due to the downward shift of atoms 2, 3, and 4, the rest atom, i.e., atom 1, is pushed upwards to relieve the stress. Our study finds that atom 1 is 0.66 Å above the plane formed by atoms 2, 3, and 4. This number is substantially bigger than the total energy result [0.39 Å]. In our structure, the rest atom is $d_2 = 1.17$ Å above the three Ga atoms below and the bond angle is 99.9°, which is much smaller than the sp^3 bond angle of 109.47°. The rest atom forms a prismatic unit of $AsGa_3$, with p_x , p_y , p_z , and s^2 -like bonds. This configuration has been found to be preferred and stable in a number of group-V atom terminated structures.^{15,16} The fourth Ga atom, i.e., atom 8, is $d_4 = 1.02$ Å below the plane formed by atoms 2, 3, and 4. The As-Ga bond length is 2.45 Å, same as the bulk value. It is interesting to compare the adsorption of group-V metal tri-

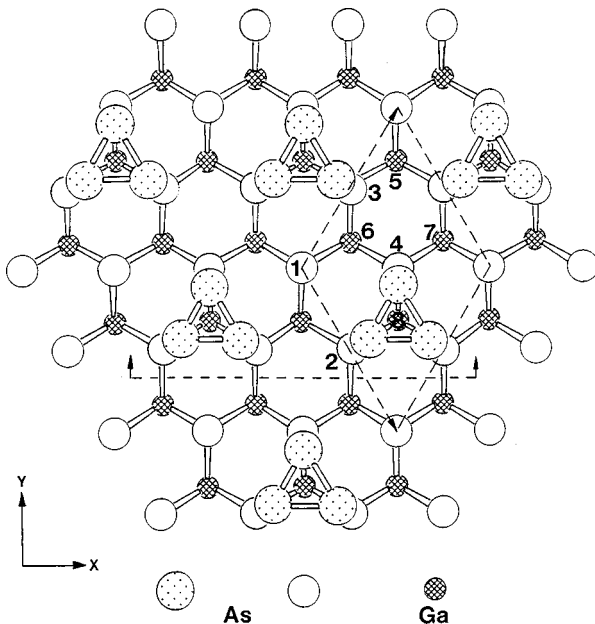


FIG. 3. Schematic top view of the As-trimer model.

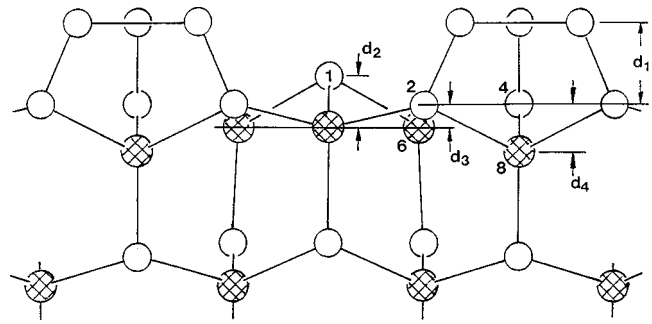


FIG. 4. Schematic side view of the As-trimer model.

mers on this surface and on Si(111) or Ge(111). In all cases, each trimer contributes three dangling bonds which are paired with those on the preadsorbed surface. For $GaAs(\bar{1}\bar{1}\bar{1})$, the unit cell is (2×2) because while three As atoms in the unit cell on the preadsorbed surface provide dangling bonds to pair with those in the trimer, a fourth As atom in the unit cell forms the prismatic unit described above. In contrast, on either Si(111) or Ge(111), a Si or Ge atom has no tendency to form the prismatic unit, hence the energetically favored periodicity is $\sqrt{3} \times \sqrt{3} R 30^\circ$, wherein three surface Si or Ge atoms in the unit cell on the preadsorbed surface contribute dangling bonds to pair with those in the trimer.¹⁷⁻¹⁹

In summary, we have used quantitative LEED *IV* spectra analysis to determine the multilayer relaxation structure of $GaAs(\bar{1}\bar{1}\bar{1})(2 \times 2)$. Our results confirm the As adatom trimer model found by total energy calculations^{2,3} and STM.³ We find substantial compression of the first bilayer spacing. It may be that the compression is energetically favorable because it reduces the surface dipole energy. We also find that the rest atom is substantially pushed upwards to form a preferred prismatic configuration. The structural relaxations determined in this study are in good qualitative agreement with results of total energy calculations,³ although the magnitudes of some of the displacements are different. The analysis confirms that substantial subsurface relaxations are present in this system.

Note added on proof. After this paper was submitted, we became aware of a new quantitative LEED intensity analysis of $GaAs(\bar{1}\bar{1}\bar{1})(2 \times 2)$.²⁰ While details of the LEED analysis have yet to be published, the authors of the new work have provided a summary of the structural results,²⁰ which are in very good agreement with the present work. Comparing the major structural numbers, the As-As bond length in the trimer is 2.44 Å (this work), compared to 2.37 Å.²⁰ The trimer layer is $d_1 = 2.35$ Å above the bilayer below (this work), compared to 2.29 Å.²⁰ Most important, both works find that the three As atoms below the trimer are pushed substantially downward, resulting in a much compressed bilayer distance of 0.51 Å (this work), compared to 0.56 Å.²⁰ Both works find that the fourth As atom (atom 1) is raised by 0.66 Å (this work), compared to 0.56 Å.²⁰

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