

The reaction of carbon tetrachloride with gallium arsenide (001)

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Carbon tetrachloride dissociatively adsorbs on the Ga-rich (4×2) reconstruction of GaAs (001) at 200 °C. Upon heating to 440 °C, the chlorine desorbs as GaCl, which etches the surface. Scanning tunneling micrographs reveal that this reaction transforms the (4×2) into a Ga-rich (3×2) structure that is interlaced with As-rich (2×4) phases. The (3×2) is well ordered, while the (2×4) phases exhibit a high degree of disorder. This work establishes the surface reaction pathway for carbon doping of GaAs with CCl₄. © 1998 American Institute of Physics. [S0003-6951(98)03808-X]

The incorporation of dopants into semiconductor lattice sites is an essential process in the manufacture of solid-state electronic devices. Dopants also have a profound effect upon the semiconductor surface physics and chemistry. These species introduce both charge and strain into the semiconductor film. The surface must accommodate the charge and the strain by adopting structures which minimize the surface free energy. For example, Pashley and Haberern¹ have shown that silicon-doped GaAs (001) films produce highly disordered (2×4) surfaces with a large number of kinks in the As dimer rows. These kinks are presumed to be acceptors which neutralize the Si donor atoms in the surface depletion layer. Wang *et al.*² found that adsorbed boron on Si (100) migrates to subsurface lattice sites to relieve the strain induced by its smaller atomic size. The doped silicon exhibits different surface reconstructions than the undoped material. In addition, several researchers have observed that dopants can disrupt the normal flow of steps during the vapor-phase epitaxial growth of III–V compound semiconductors.^{3,4}

Carbon tetrachloride is an efficient source for carbon doping of GaAs and InGaAs during metalorganic vapor-phase epitaxy (MOVPE) and metalorganic molecular beam epitaxy.^{5–8} However, it has been found that it is difficult to control the composition and film uniformity during growth with CCl₄ due to the etching of the group III elements.^{9,10} In this letter, we report on our study of the decomposition of CCl₄ on gallium-rich GaAs (001). It has been found that the chlorine etches Ga as GaCl, and that this has a profound effect on the semiconductor surface structure.

The surfaces were prepared by MOVPE growth of GaAs films, 0.5 μm thick, onto GaAs (001) substrates oriented 0.5° off-axis towards the [110] (AXT Inc., doped with 1×10¹⁸ Si atoms/cm³). The growth procedure is described in detail elsewhere.¹¹ The reaction conditions were 600 °C, 0.65 mTorr triethylgallium (TEGa), 32.5 mTorr tertiarybutylarsine (TBAs), 20 Torr H₂, and 2.5 l/min total flow rate. After deposition, the crystals were cooled to 25 °C over 10 min in 0.5 Torr TBAs and 99 Torr H₂, then quickly transferred to the ultrahigh vacuum system.

The freshly grown films were heated to 620 °C at 2.0–5.0×10⁻¹⁰ Torr to desorb the excess arsenic and other

impurities from the surface. A 30 min anneal at 620 °C was sufficient to produce a (4×2)/c(8×2) reconstruction, as confirmed by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Next, the GaAs crystals were dosed with 300 L of CCl₄ at temperatures between 25 and 200 °C. Adsorption was confirmed by the appearance of a (1×1) LEED pattern, and by the presence of a Cl 1s band in the x-ray photoemission spectrum (XPS). The uptake of CCl₄ was about three times higher at 200 °C compared to 25 °C.

Following dosing of CCl₄, the crystals were heated to decompose the adsorbed species. Temperature-programmed desorption (TPD) spectra were collected by heating samples at 4 °C/s directly in front of a nozzle to a mass spectrometer. In addition, LEED patterns, XPS spectra, and STM images were acquired after heating the GaAs (001) samples covered with CCl₄ to 440 °C for 30 min and then cooling to 25 °C. The STM images were taken while tunneling out of filled states at a sample bias between -2 and -4 V, and at a current of 0.1 to 0.5 nA.

Shown in Fig. 1 are TPD spectra obtained after CCl₄ adsorption on the (4×2) surface at 25 °C. Mass numbers were monitored for Cl, Cl₂, CCl_x (x=0–4), GaCl_x, and AsCl_x (x=0–3), but only Cl, Ga, GaCl, and a very small amount of GaCl₂ were detected. The gradual rise in the Cl signal with temperature is due to background desorption from the manipulator and chamber, as confirmed in control experiments without a GaAs sample. At 425 °C, TPD peaks are observed for Cl, Ga, and GaCl (masses 35⁺, 69⁺, and 104⁺). The relative area of the bands for these three species is characteristic of the cracking pattern of GaCl. This suggests that some of the CCl₄ molecules decompose on the Ga-rich (4×2) by the following overall reaction:



The very small peak for GaCl₂ at 425 °C could be due to the desorption of either GaCl₂ or GaCl₃.

In separate experiments, the (4×2) was exposed to 300 L of CCl₄ at 200 °C and then heated for 30 min at 440 °C to desorb the GaCl species. The crystal was then cooled to room temperature and the surface analyzed by XPS, LEED, and STM. The area ratio of the As to Ga 2p_{3/2} photoemission peaks was 1.25, indicative of a Ga-rich surface. In addition,

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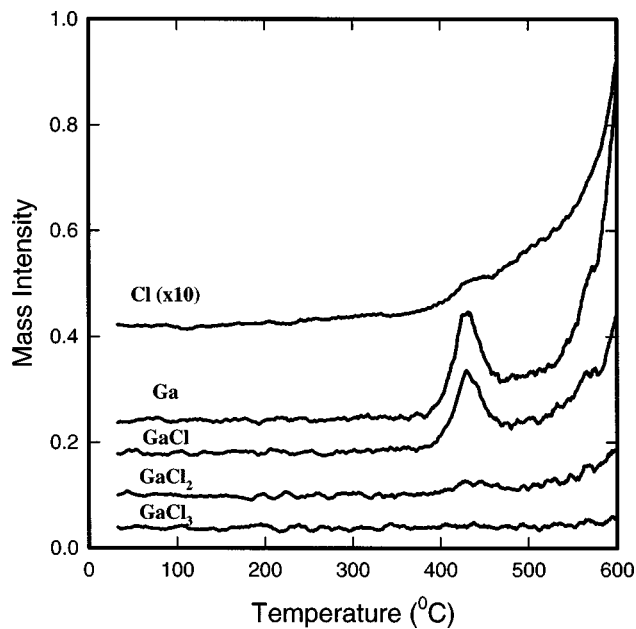


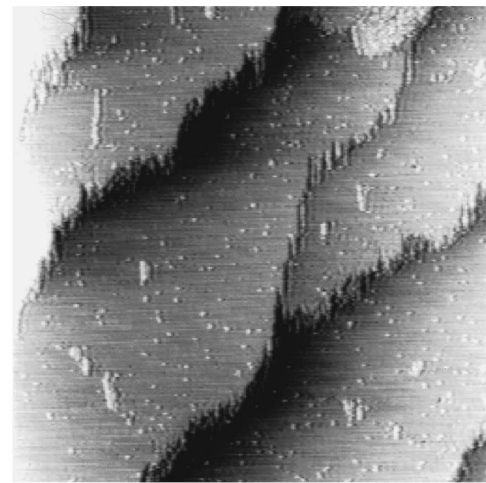
FIG. 1. Temperature-programmed desorption spectra of CCl_4 adsorbed on (4×2) GaAs (001).

no chlorine $1s$ peaks were detected, and careful scans of the carbon $1s$ region revealed that the amount of this element on the surface increased from 1.0% to 2.0% following decomposition of CCl_4 . Note that the detection limit of carbon by XPS is 0.5%. Examination of the GaAs (001) surface by LEED showed that its lattice structure had been converted from $(4 \times 2)/c(8 \times 2)$ to $(3 \times 2)/c(6 \times 4)$.

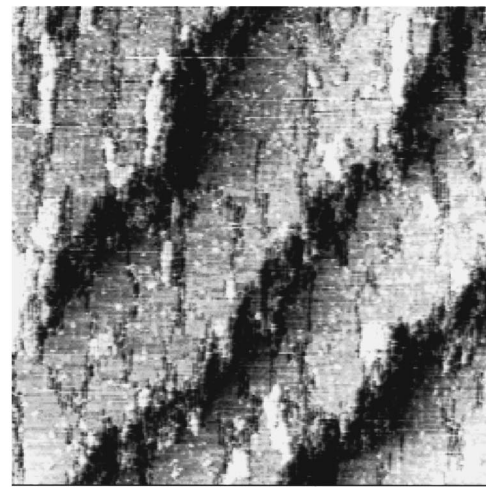
Scanning tunneling micrographs recorded of the GaAs (001) surface before and after the decomposition of CCl_4 at 440°C are shown in Fig. 2. The image in Fig. 2(a) shows a series of equally spaced terraces about 500 \AA in average width. Close up view of the terrace structure reveals the characteristic double row pattern of the (4×2) reconstruction.¹²⁻¹⁴ By contrast, the image in Fig. 2(b), obtained after CCl_4 decomposition, contains regions of high black-to-white contrast, indicative of a rougher surface morphology. These high contrast regions are created by chlorine etching of the surface gallium. The remaining three quarters of the surface are composed of flat and ordered terraces.

A higher magnification image of the GaAs (001) surface after carbon tetrachloride decomposition at 440°C is shown in Fig. 3(a). In the center of the picture is one of the etched areas. One sees that this region is terminated with rows of gray rectangles separated by thin black lines. These rows run parallel to the $[\bar{1}10]$ direction, and their unit cell is (2×4) . This surface structure is clearly that of the As-rich $(2 \times 4)/c(8 \times 2)$ reconstruction, which consists of two As dimers separated by two dimer vacancies.¹⁴ Further examination of the STM image reveals that the etched surface is highly disordered. The domains are only several unit cells wide, and contain a large number of missing dimers, kinks, and other defects.

Surrounding the etched region are flat terraces that exhibit an undulating pattern of light and dark gray rows. These rows extend along the $[110]$ direction. A close up of this region is presented in Fig. 3(b). The light gray rows are separated by 12 \AA and contain bumps that repeat every 4 \AA .



(a)



(b)

FIG. 2. Scanning tunneling micrographs of the filled states of the (4×2) GaAs (001) surface (a) before and (b) after CCl_4 adsorption at 200°C and heating to 440°C (image size = $1200 \text{ \AA} \times 1200 \text{ \AA}$).

This repeat pattern produces a (3×2) lattice. A ball-and-stick model for this reconstruction is presented in Fig. 3(c). It consists of single rows of Ga dimers that alternate between the first and third layers. Second-layer As atoms are exposed along the edges of the upper rows of Ga dimers. The gallium coverage on this surface is 0.67 monolayers (ML) compared to 0.75 ML on the (4×2) .

We have observed the (3×2) structure on the surfaces of InGaAs/GaAs (001) films that contain 1.0–5.0 at.% indium.¹⁵ Strain introduced by indium incorporation into the lattice is responsible for the formation of this phase. It is possible that the films grown in this study contained as much as 1.0 at.% indium, as a result of memory effects in the MOVPE reactor. When the GaAs films are strained by small amounts of indium, the phase diagram consists of the (2×4) at 0.25 ML Ga, the (3×2) at 0.67 ML Ga, and the (4×2) at 0.75 ML Ga. Consequently, chlorine etching of gallium from the (4×2) surface transforms it back into the (3×2) phase. Thus, the results shown in Fig. 2 can be explained by the removal of more than 0.08 ML of Ga as gallium chloride.

At the present time, we do not know how much carbon is

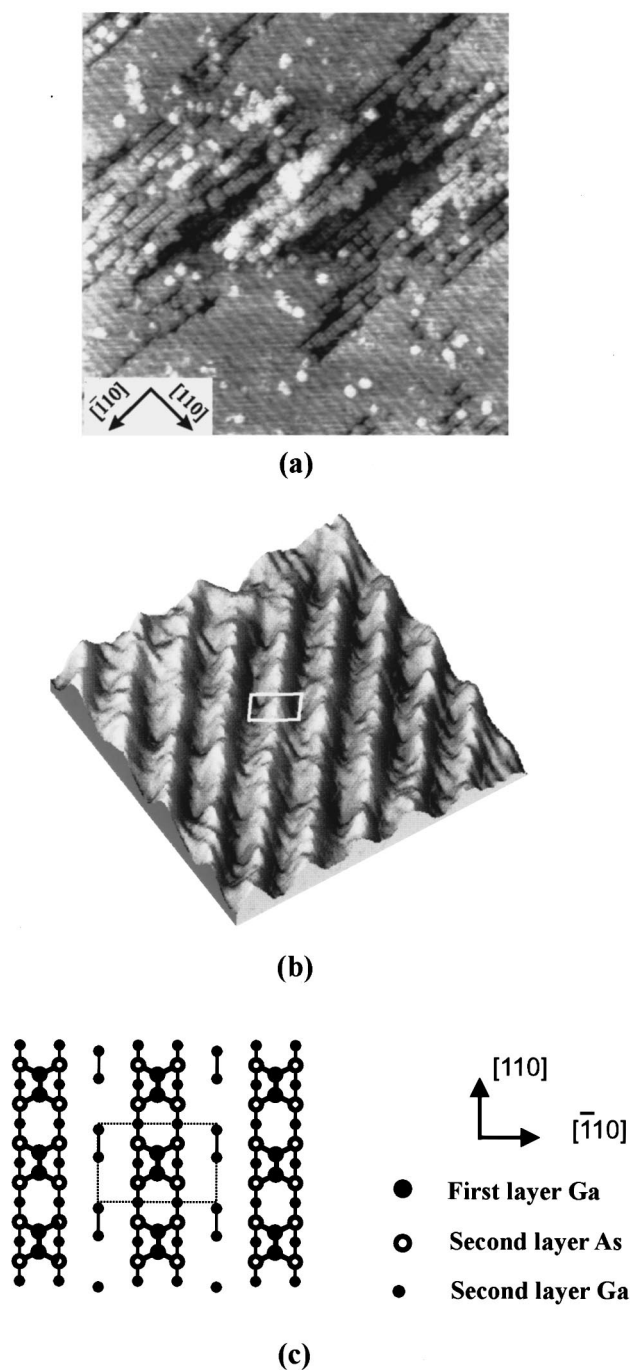


FIG. 3. Scanning tunneling micrographs of the filled states of the GaAs (001) surface following CCl_4 adsorption and decomposition: (a) image showing etched region along step edge ($350 \text{ \AA} \times 350 \text{ \AA}$); and (b) three-dimensional image of the (3×2) structure ($80 \text{ \AA} \times 80 \text{ \AA}$). The unit cell of the (3×2) is outlined. (c) Ball-and-stick model of the proposed (3×2) structure. The unit cell is outlined by the dotted line.

deposited, or which sites it occupies on the GaAs surface. Only a small increase in carbon ($\sim 1.0 \pm 0.5 \text{ at.}\%$) is observed by XPS. In an earlier study by Goulding and Pemble,¹⁶ a substantial increase in the carbon coverage was recorded by Auger electron spectroscopy. The discrepancy between their

work and ours may be partly due to different instrumental sensitivities. Nevertheless, further work is necessary to quantify the carbon deposition levels that can be attained from CCl_4 adsorption and decomposition on GaAs (001). With regard to the sites that carbon occupies, we have learned that carbon tetrachloride adsorbs only on exposed gallium atoms. The saturation coverage of CCl_4 on the (2×4) surface at $25 \text{ }^\circ\text{C}$ is one third of that on the (4×2) surface, consistent with initial Ga coverages of 0.25 and 0.75, respectively.¹⁷ If the carbon remains adsorbed on the gallium even after all the chlorine ligands have been stripped off, then it would replace the arsenic and incorporate as an acceptor in the GaAs lattice.

In summary, CCl_4 adsorbs on the Ga-rich (4×2) reconstruction and decomposes at or above $440 \text{ }^\circ\text{C}$ with the desorption of GaCl. Chlorine etching of the surface creates a rough, disordered region that is (2×4) terminated, and a smooth, ordered region that is (3×2) terminated. The relative amount of each phase depends on the extent of the reaction of CCl_4 with the surface. This work demonstrates that dopant sources dramatically affect the structure of GaAs (001), and therefore, may have far reaching effects on the surface chemistry occurring during the deposition of III/V semiconductor films by MOVPE.

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