

## Compensating Surface Defects Induced by Si Doping of GaAs

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We have made direct experimental observation of a new mechanism for Fermi-level pinning in Si-doped (001) GaAs. Scanning-tunneling-microscope images show that high levels of Si doping cause the GaAs(001)-(2×4) unit cells to reorder by the formation of kinks in the dimer vacancy rows. We are able to show that these kinks are surface acceptors, which form in the required numbers to exactly compensate the GaAs surface region. We find that in the depleted surface layer all the incorporated Si atoms are donors up to Si concentrations of at least  $1 \times 10^{19} \text{ cm}^{-3}$ .

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There has been considerable interest over many years in Schottky-barrier formation and the mechanisms involved in Fermi-level pinning due to its importance in device technology. While many different models for Fermi-level pinning have been proposed, the experimental verification of these models is limited. In this Letter, we report a new mechanism which involves the formation of surface acceptors induced by Si doping of (001) GaAs, which we are able to directly observe experimentally. We have used the scanning tunneling microscope (STM) to study the effects of Si doping on the structure of the (2×4) reconstructed surface of molecular-beam-epitaxy (MBE) grown on (001) GaAs. We find that the ordering of the (2×4) unit cells changes with Si doping so as to create kinks in the dimer vacancy rows. These kinks act as surface acceptors and result in depletion of the GaAs surface region.

Experiments were carried out in a combined STM-MBE system, which has been described elsewhere [1]. The samples used for STM studies were grown on approximately  $10 \times 10 \text{ mm}$  pieces cut from a GaAs(001)  $n^+$  substrate mounted on a molybdenum specimen holder with indium. Prior to growth the substrates were degassed in UHV at  $350^\circ\text{C}$ . Growth was done in a small MBE chamber equipped with Ga and  $\text{As}_4$  effusion cells and a Si effusion cell for  $n$ -type doping. Growth was carried out at a substrate temperature of  $560^\circ\text{C}$  as measured with an optical pyrometer, at a growth rate of  $0.2 \mu\text{m}$  per hour determined from reflection high-energy-diffraction (RHEED) oscillations. A buffer layer of at least  $0.2 \mu\text{m}$  was grown on the substrate. All growth was under arsenic-rich growth conditions with a (2×4) surface reconstruction. When growth was complete the surface was allowed to recover at the growth temperature for 2 min in an arsenic flux. The sample was then rapidly removed from the growth chamber, resulting in quenching to room temperature, and transferred under UHV to the analytical chamber. Low-energy electron diffraction (LEED) showed that the (2×4) reconstruction was preserved. All STM images were taken at room temperature with a tunnel voltage of between  $-2$  and  $-2.5 \text{ V}$  and a tunnel current of  $0.1 \text{ nA}$ . The images are of filled states on the surface.

The Si doping level was calibrated by measuring the electrical resistivity of doped layers approximately  $0.5 \mu\text{m}$  thick grown on semi-insulating GaAs(001) substrates. The donor concentration was then determined from the donor concentration versus resistivity data given by Sze (p. 33 of Ref. [2]). The donor concentration is plotted as a function of the Si-effusion-cell temperature in Fig. 1. The solid line is a least-squares fit to the calibration points below a doping level of  $3 \times 10^{18} \text{ cm}^{-3}$ .

The STM image in Fig. 2(a) shows the (2×4) surface of a  $0.2\text{-}\mu\text{m}$ -thick GaAs(001) film doped with Si at  $7 \times 10^{17} \text{ cm}^{-3}$ . The (2×4) periodicity arises from a regular array of dimer vacancies [3,4]. The dimer vacancy rows, seen as dark lines along the  $[\bar{1}10]$  direction in Fig. 2(a), run straight across the entire image. The  $2 \times$  periodicity in the  $[\bar{1}10]$  direction can be clearly seen, but the individual dimers are not resolved in this image. Each bright feature corresponds to the group of arsenic dimers that make up one (2×4) unit cell. The (2×4)

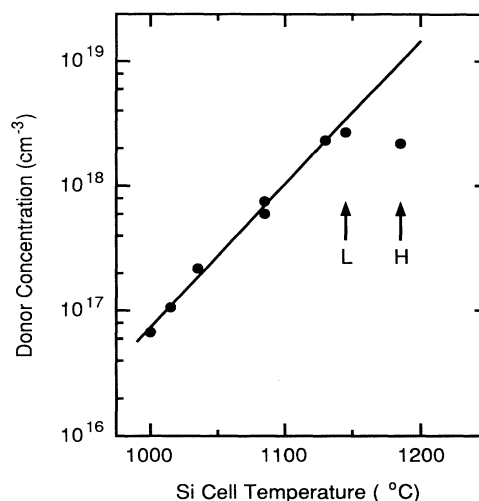


FIG. 1. Donor concentration determined from resistivity measurements as a function of Si cell temperatures (circles). The solid line is a fit to the points corresponding to a donor concentration below  $3 \times 10^{18} \text{ cm}^{-3}$ , and represents the total Si concentration in the GaAs layer.

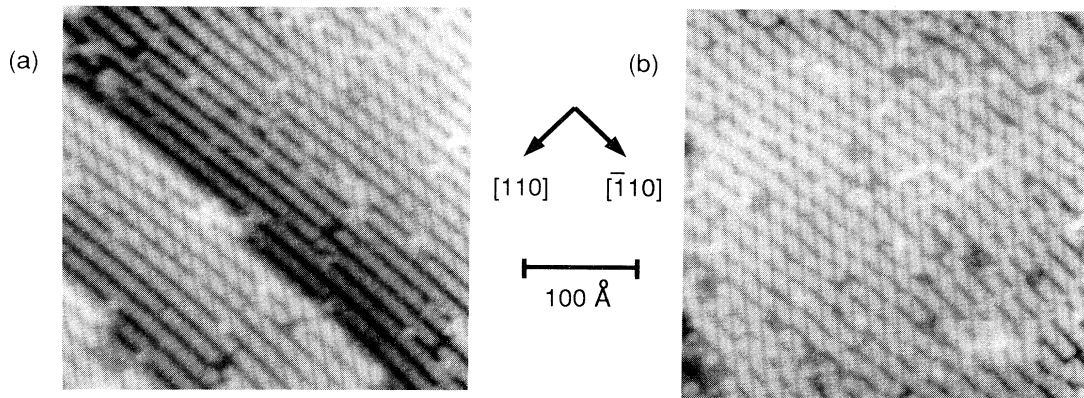


FIG. 2. (a) An STM image of the GaAs(001)-(2×4)/c(2×8) reconstructed surface showing the straight dimer vacancy rows obtained at a Si doping level of  $7 \times 10^{17} \text{ cm}^{-3}$ . (b) An STM image of the GaAs(001)-c(2×8) reconstructed surface of a thick film with a measured donor concentration of  $2.2 \times 10^{18} \text{ cm}^{-3}$ . A high density of kinks has formed in the dimer vacancy rows.

unit cells are ordered to give a mixture of (2×4) and c(2×8) periodicities. This surface is typical of the surface of all layers grown at this doping level or lower.

At higher doping levels we observe significant effects on the ordering of the (2×4) unit cells. The STM image shown in Fig. 2(b) is of the surface of a thick (0.2- $\mu\text{m}$ ) GaAs(001) layer with net donor concentration measured to be  $2.2 \times 10^{18} \text{ cm}^{-3}$  (Si-cell temperature of 1185 °C, labeled *H* in Fig. 1). The calibration in Fig. 1 shows the total Si concentration of this layer to be  $9.8 \times 10^{18} \text{ cm}^{-3}$ , indicating that some of the Si atoms are in acceptor sites. It is apparent from Fig. 2(b) that the dimer vacancy rows are no longer straight. Every few unit cells along the  $[\bar{1}10]$  direction the dimer vacancy rows kink one spacing in the [110] direction. There is a density of approximately  $1.6 \times 10^{13} \text{ cm}^{-2}$  of these kinks on the surface. The (2×4) units cells are ordered to give a predominantly c(2×8) periodicity.

The (2×4) reconstruction is known to exist with either two arsenic dimers and two dimer vacancies or three arsenic dimers and one dimer vacancy per unit cell [5,6]. On our *in situ* grown samples, we find mostly two arsenic dimers per unit cell [7]. There are two models for the two-arsenic-dimer (2×4) structure, the difference between them being in the second and third layers [3,6]. The three-arsenic-dimer structure [3,4] and two proposed models for the two-arsenic-dimer structure [3,6] have the correct number of electrons per unit cell for all arsenic dangling bonds to be filled and all gallium dangling bonds to be empty [6,8]. Structures obeying this electron counting model are expected to be stable and to have no states in the band gap [8]. When kinks are introduced in the dimer vacancy rows on a c(2×8) surface, the electron counting model is no longer satisfied. It is not possible to fill all arsenic dangling bonds while leaving all gallium dangling bonds empty. The kink sites will therefore introduce new electronic states on the surface. A schematic of the structure of the kinks with two arsenic dimers per

unit cell, showing only the arsenic dimers, can be seen in Fig. 3. Since we do not yet precisely know the atomic structure of the kink sites, we are not able to predict the electronic structure of the kinks.

Further investigation showed that the density of these kinks is a function of the thickness of the doped layer. In order to study this, samples were grown with a buffer layer in excess of 0.15  $\mu\text{m}$  of undoped material followed by a film of a given thickness of doped material. The thickness of the doped layer was varied between 30 and 80 monolayers (ML) of GaAs (1 ML=2.8 Å), and two different doping levels were studied. The surface of each sample was imaged by STM. At each thickness, the surface density of kinks was determined from at least six different STM images of approximately  $400 \times 400 \text{ Å}$  covering two macroscopically separate areas of the sample. For each image, the area was determined from the dimensions of the (2×4) unit cell (thus correcting for thermal drift), and the number of kinks was counted. The results are plotted in Fig. 4. The circles show the average kink density for the sample and the error bars show the standard deviation of the kink densities determined from the individual images. We can make four important observations from the results. First, the kink

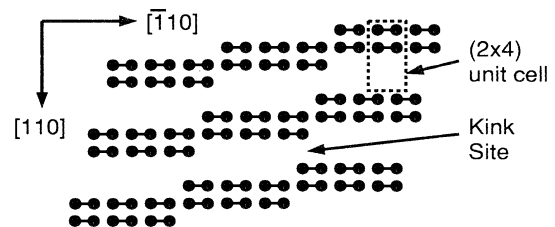


FIG. 3. Schematic of the (2×4) unit-cell structure with two arsenic dimers per unit cell, showing the structure of kinks in the dimer vacancy rows. Only the surface-layer arsenic atoms are shown.

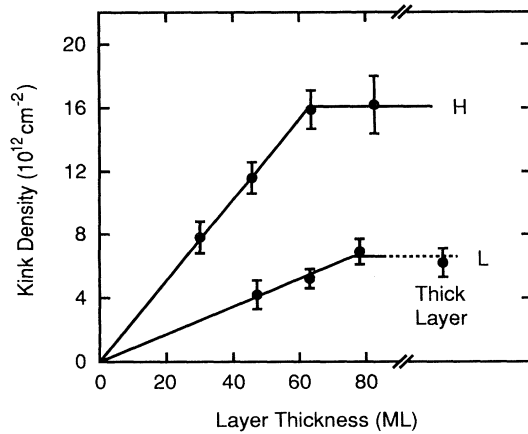


FIG. 4. The density of kinks in the dimer vacancy rows, as determined from STM images, as a function of the thickness (in monolayers) of a Si-doped GaAs(001) layer grown on top of an undoped buffer layer. Results are plotted for two doping levels,  $L$  and  $H$  (see Fig. 1). The solid lines show the fit to the data that was used in the model. The thickest layer for the  $L$  doping level is a few depletion widths thick.

density rises linearly with the thickness of the doped layer. Second, zero kink density corresponds to zero layer thickness. Third, for each doping level there is a layer thickness at which the kink density saturates. Finally, the saturation kink density depends upon the doping level.

We have been able to develop a simple model to explain this behavior. In undoped material, the lowest-energy surface is the ordered  $(2 \times 4)/c(2 \times 8)$  reconstruction, which will have no states in the gap since, as discussed above, all dangling bond states are either completely filled or completely empty. When the material is highly doped, it would be energetically favorable for electrons at the Fermi level (which is close to the conduction-band minimum) to drop into lower-energy states. Such states do not exist on the perfect  $(2 \times 4)/c(2 \times 8)$  surface, but by forming the kinks these states are created. We therefore associate the kinks with surface acceptor sites. While the layer is thin, exactly the required number of kinks is created to accommodate all the electrons from the donor atoms, and so the number of kinks is directly proportional to the thickness of the layer. However, as electrons move to the surface, in order to occupy these surface acceptor sites, band bending must occur due to the electric dipole that is set up by the charge transfer. Eventually, as the layer thickness is increased, the bands will bend sufficiently to make it energetically unfavorable to form any more kinks. The kink density then saturates. The layer thickness at which this saturation occurs corresponds to the depletion width resulting from the Fermi level being pinned by the surface acceptor state. This mechanism relies on the formation energy of the kink structure being small. The energy difference between the  $(2 \times 4)$  and  $c(2 \times 8)$  structure is very small—about 0.1 eV per  $c(2 \times 8)$  unit cell [3]. It is reasonable to assume that

the energy required to form the kink will also be of this order.

The kink density at saturation ( $\rho_k$ ) should be related to the donor concentration ( $N_D$ ) by

$$\rho_k = N_D w / n_e, \quad (1)$$

where  $w$  is the depletion width and  $n_e$  is the number of electrons per kink site. Thus  $N_D$  should be proportional to  $\rho_k / w$ . The two different doping levels ( $L$  and  $H$ ) in Fig. 4 correspond to Si-cell temperatures labeled  $L$  and  $H$  in Fig. 1. The measured saturation kink densities are  $6.6 \times 10^{12}$  and  $1.6 \times 10^{13} \text{ cm}^{-2}$ , respectively, with depletion widths of 76 ML (213 Å) and 63 ML (176 Å), respectively. From Eq. (1) we expect the ratio of these two donor concentrations,  $(N_D)_H / (N_D)_L$ , to be 2.9. It is clear from Fig. 1 that the ratio of the bulk donor concentrations for these doping levels (indicated by circles) is much smaller than a factor of 2.9. However, the ratio of the total silicon concentrations ( $3.4 \times 10^{18}$  and  $9.8 \times 10^{18} \text{ cm}^{-3}$ , respectively) is 2.9, in agreement with the expected donor concentration ratio. We therefore conclude that within the depletion layer all the incorporated Si atoms are donors.

The thermodynamics of the incorporation of an amphoteric dopant such as Si in GaAs shows that the fraction of dopant atoms that are incorporated as donors is proportional to  $p/n$ , where  $p$  and  $n$  are the hole and electron concentrations, respectively [9,10]. At high doping levels, where  $n$  becomes large, some of the Si atoms incorporate as acceptors. However, since the surface region is depleted of electrons due to the presence of the kinks,  $p/n$  will be close to unity as it is in undoped material. All the Si atoms incident on the surface during growth will initially incorporate as donors. However, once these Si donors are more than a depletion width below the surface they will no longer be in equilibrium. In order to reach equilibrium, up to half the incorporated Si atoms must change from a gallium site to an arsenic site. This will require gallium atoms to move into the crystal from the surface and arsenic atoms to move out of the crystal. Since this process occurs in a region close to the surface, it should occur quite readily at the growth temperature. This mechanism was proposed by Kirchner *et al.* [10]. They obtained low-resistance Ohmic contacts on highly doped GaAs(001) indicating that the surface donor concentration could be as high as  $1 \times 10^{20} \text{ cm}^{-3}$ , equal to the total Si concentration. In addition to providing strong support for this mechanism, our results also explain *why* the required band bending at the surface occurs, allowing the silicon to initially incorporate only as donors.

The number of electrons per kink site can be calculated from Eq. (1) using the values for  $\rho_k$  and  $w$  from Fig. 4 and the total Si concentrations for the layers from Fig. 1. This gives a value of  $1.1 \pm 0.2$  electrons per kink site for both doping levels. We can therefore unambiguously associate kink sites with single acceptor states.

The position of the Fermi level at the surface can be es-

timated from the depletion width and donor concentration. Since the samples were rapidly quenched from the growth temperature to room temperature, the effective equilibrium temperature could lie anywhere in between. This alone gives a few tenths of an eV spread in the calculated Fermi-level position. Furthermore, the band bending depends on the square of the depletion width, and so errors in the measurement of the depletion width (Fig. 4) will introduce significant errors in the calculation of the Fermi-level position. Therefore, a simple calculation taking the change in band-edge positions and bulk Fermi-level position as a function of temperature into account [2] will only give a rough estimate of the surface Fermi-level position. We calculate the surface Fermi level for the lighter doped layer ( $L$ ) to be a few tenths of an eV above the valence band and the surface Fermi level for the more heavily doped layer ( $H$ ) to be several tenths of an eV below the valence-band maximum. Since our calculation is not valid for a surface Fermi level in the valence band, we conclude that it lies in the lower half of the band gap and may be close to the valence-band maximum.

The perfect  $(2\times 4)/c(2\times 8)$  surface of GaAs(001) should be a flat band since there are no states in the gap. However, we have found that as the GaAs is doped with Si, surface acceptor states form and compensate the surface region, resulting in band bending. This mechanism will prevent flat-band conditions from being obtained on highly Si-doped GaAs. It may also be responsible for Fermi-level pinning in Schottky barriers on GaAs(001), particularly when no reaction occurs between the metal and the GaAs surface. It has been shown that the density of step-edge states on low-doped vicinal GaAs(001) surfaces plays a major role in Schottky-barrier formation [11]. It is likely that the electronic states at the step edges act as acceptors, just as the kink structures do. We would therefore not expect to see any significant effects of step-edge state density on Schottky-barrier formation if the GaAs is heavily doped, since the kink sites will already provide a high density of surface acceptors.

In conclusion, we have observed a new dopant-induced surface compensating mechanism in Si-doped (001) GaAs. The surface acceptors have been imaged by STM and found to be kinks in the dimer vacancy rows of the  $c(2\times 8)$  reconstruction. Each kink site accommodates one electron, so that the surface kink density is equal to the density of Si donors in the depleted layer. This results in exact compensation of the surface region of the GaAs film. We speculate that similar dopant-induced compensating surface states could occur in other compound semiconductors provided that the energy of formation of the surface state is sufficiently small.

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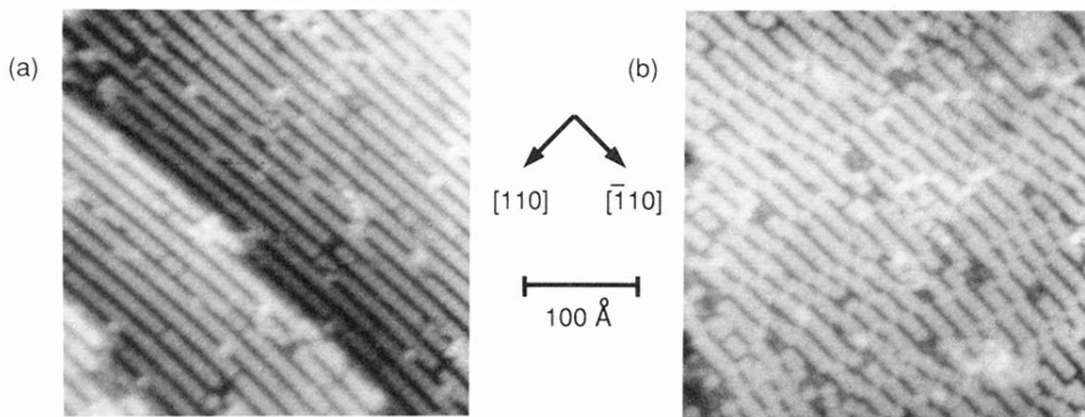


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