Different Fermi-level pinning behavior on n- and p-type GaAs(001)

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Scanning-tunneling-microscopy studies of both the n- and p-type GaAs(001)-$(2\times4)/c(2\times8)$ surfaces show important differences in the Fermi-level pinning behavior of n- and p-type material. It has been shown previously that Fermi-level pinning on the n-type GaAs(001) surface results from the formation of kinks in the dimer-vacancy rows of the $(2\times4)/c(2\times8)$ surface reconstruction. These kinks form in the required number to pin the Fermi level close to midgap at all doping levels. On p-type GaAs(001) we now show that no similar surface donor state forms. As a result, at high p-doping levels (10^{19} cm^{-3} Be), the Fermi level determined by tunneling spectroscopy is found to be within 150 meV of the valence-band maximum. At lower p-doping levels the Fermi level moves towards midgap as determined by the density of "intrinsic" surface defects such as step edges, and missing unit cells.

Recent scanning-tunneling-microscopy (STM) studies by Pashley and Haberern[1] have identified the structural defect responsible for Fermi-level pinning on the $(2\times4)/c(2\times8)$ surface of n-type GaAs(001) grown by molecular-beam epitaxy (MBE). These defects are kinks in the dimer-vacancy rows of the $(2\times4)/c(2\times8)$ surface reconstruction. Scanning tunneling spectroscopy and voltage-dependent STM imaging have shown that each kink site is a single acceptor and that the Fermi level is pinned at midgap.[2] These kinks form in exactly the required number to bring the surface Fermi level to the middle of the band gap. Consequently, as the doping level is increased, the surface density of kinks increases to keep the Fermi level pinned at midgap. The effect of this "self-compensation" mechanism is that it is not possible to saturate the surface state density by increased doping, and so flat band conditions at the surface of n-type GaAs(001) cannot be achieved by simple bulk doping.

In this paper, we show that no similar "self-compensation" mechanism occurs on p-type GaAs(001). The position of the Fermi level can therefore be changed with increased p-doping level. The origin of Fermi-level pinning on p-type GaAs(001) and the significant differences between the Fermi-level pinning on n- and p-type GaAs(001) are discussed.

The previous experiments on n-type GaAs(001) were carried out on samples grown in an MBE chamber directly connected to the STM-UHV system. In these experiments it was not possible to grow the samples *in situ* as no p-type dopant was available in the STM-MBE chamber. Instead, the samples were grown in a separate MBE chamber and As capped to allow transfer through air to the STM system. This sample preparation technique has previously been used successfully for STM study of the GaAs(001)-$(2\times4)/c(2\times8)$ surface.[3] The GaAs(001) MBE layers were typically 1 μm thick. Doping was achieved with Si as an n dopant and Be as a p dopant. After growth, the samples were capped with an amorphous As_4 layer and transferred through air to the STM-UHV system. The samples were then heated inside the MBE chamber attached to the STM-UHV system to the normal growth temperature of 580 °C in an As_4 flux to desorb the As capping layer. The decapping procedure was monitored by reflection high-energy electron diffraction (RHEED), which showed that a $(2\times4)/c(2\times8)$ surface reconstruction was obtained after removal of the As capping layer. The samples were then quenched to room temperature in exactly the same way as for samples that were grown *in situ* in previous studies.[1] Low-energy electron diffraction (LEED) was used to confirm the $(2\times4)/c(2\times8)$ reconstruction at room temperature. All STM imaging and tunneling spectroscopy was carried out at room temperature. STM images were of filled states with a tunneling current of 0.1 nA and with a voltage of -2.5 V on the sample.

It was verified that the capping procedure had no influence on the formation of kinks on the surface of n-type GaAs(001). The STM image in Fig. 1 shows the surface of a GaAs(001) MBE layer doped with approximately 10^{19} cm^{-3} Si. This sample was grown in a separate MBE chamber and transferred through air using the As capping procedure described above. It was shown previously that on the surface of low-doped GaAs(001), the dimer-vacancy rows of the $(2\times4)/c(2\times8)$ reconstruction (dark vertical lines in the $[\bar{1}10]$ direction of Fig. 1) are straight for several hundred Å.[1] In Fig. 1, the dimer-vacancy rows appear to run in slightly different directions in different parts of the image. Close examination of the image shows that this is actually due to a high density of kinks in the dimer-vacancy rows. The dimer-vacancy rows are straight along the $[\bar{1}10]$ direction for distances of only a few $2x$ spacings between kinks. At the kink sites, the dimer-vacancy rows move over 4 Å in the [110] direction. It is these kink sites that were previously

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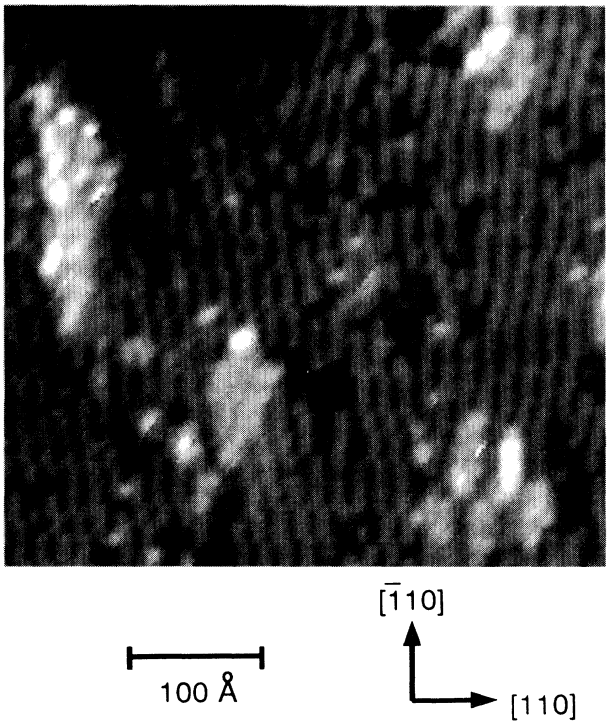

FIG. 1. A filled-state STM image of the $(2\times4)/c(2\times8)$ GaAs(001) surface of an n-type sample doped with 10^{19} cm^{-3} Si. After growth, the sample was capped with As and transferred through air to the STM system.

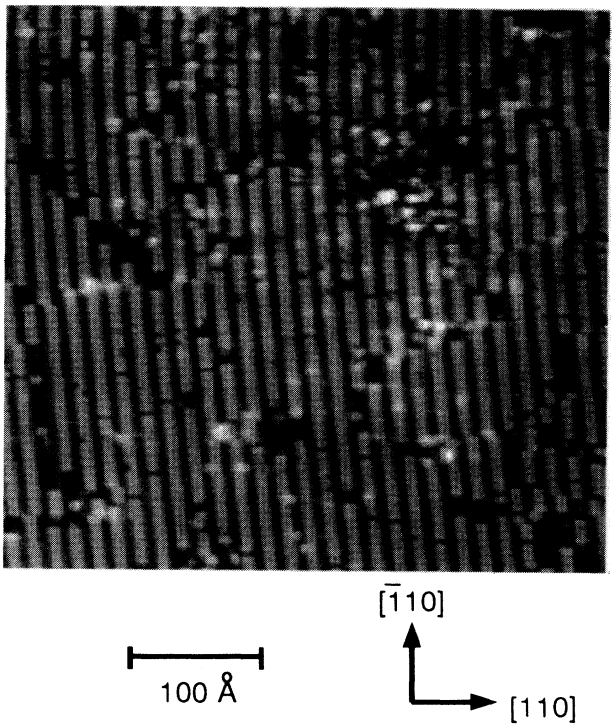

FIG. 2. A filled-state STM image of the $(2\times4)/c(2\times8)$ GaAs(001) surface of a p-type sample doped with 10^{19} cm^{-3} Be.

shown to be surface acceptors and to result in Fermi-level pinning on this surface. The STM image in Fig. 1 shows the density of kinks in the dimer-vacancy rows to be in excess of 10^{13} cm^{-2}, as seen previously for similarly doped samples grown *in situ*.[1] The LEED pattern of this surface showed a $c(2\times8)$ periodicity with some spot splitting, in agreement with the LEED patterns from *in situ* grown samples.[4] We conclude that the capping procedure does not affect the kink density on n-type GaAs(001).

In contrast, large numbers of kinks do not form on the surface of highly doped p-type GaAs(001). The STM image shown in Fig. 2 is of a p-type sample doped with approximately 10^{19} cm^{-3} Be. In this case, the dimer-vacancy rows are straight over most of the image, with very few kinks in the area of the image. Their density is very small compared with the density of kinks on the n-type material (Fig. 1). In the case of p-type material doped to the same level as the n-type sample of Fig. 1, we would expect a similar density of surface donor states if the Fermi level is also pinned close to midgap. The atomic structure of such a donor state is unclear, but it must involve some change from the ideal (2×4) surface. There is no evidence from the STM images of heavily doped p-type material for the existence of any defect structure at a sufficient density that might be such a donor state. There are several types of defect on the surface, such as step edges and incomplete unit cells, which are also seen on the n-type material. However, their density is probably insufficient to pin the Fermi level at midgap on such a highly doped surface. The role that these defects are believed to play in Fermi-level pinning will be discussed below.

A marked difference between n- and p-type GaAs(001) was also found in the surface Fermi-level position, determined by tunneling spectroscopy. As in previous studies on n-type GaAs,[2] spectra on the p-type surface were collected at specific points in the (2×4) unit cell: either on top of the As dimers or in the dimer-vacancy rows. Current-voltage (I-V) and differential conductance (dI/dV-V) curves were obtained by stopping the scan and breaking the feedback loop at the point of interest. During acquisition of the spectra the tip was moved typically 3 Å in toward the surface as the magnitude of the voltage was reduced. This technique (developed by Feenstra and Stroscio,[5] and Mårtensson and Feenstra[6]) greatly increases the sensitivity to states close to the band gap and so gives a more precise determination of the band edges. For the spectra displayed here, normalization of the spectra was done by computing the quantity $(dI/dV)/(I/V)$. This quantity is largely independent of tip-sample separation. To compare the spectra from n- and p-type GaAs(001), we show the average of a number of spectra taken from on top of the As dimers.

The tunneling spectrum from n-type material (taken from our previous studies[2]) is shown in Fig. 3(a). The observed band gap is in agreement with the bulk band gap for GaAs (1.4 eV) and is marked on the spectrum. When 0 V is applied between the tip and the sample, the Fermi levels in the tip and at the GaAs surface line up. There-

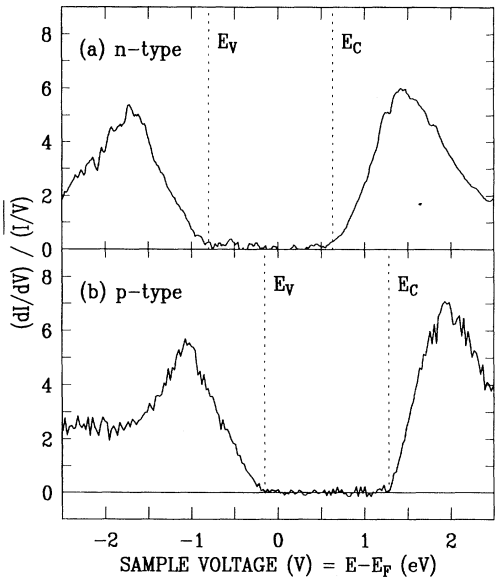

FIG. 3. Tunneling spectrum taken from on top of the As dimers on (a) an n-type GaAs(001)-(2×4)/c(2×8) surface with the sample doped with 10^{19} cm^{-3} Si, and (b) a p-type GaAs(001)-(2×4)/c(2×8) surface with the sample doped with 10^{19} cm^{-3} Be.

fore a sample voltage of 0 V in Fig. 3 corresponds to the Fermi level on the GaAs(001) surface. In the case of n-type GaAs(001), this was found to be at midgap ($E_v+0.7$ eV).[2] The equivalent spectrum for the surface of the p-type sample shown in Fig. 2 is plotted in Fig. 3(b). Again, the observed band gap is 1.4 eV. The clear difference between the spectra obtained from n- and p-type samples is in the position of the Fermi level. On the p-type sample the Fermi level is close to the valence-band maximum (VBM). We determine the Fermi level on p-type samples doped at 10^{19} cm^{-3} with Be to be (0.15±0.1) eV above the VBM. In contrast to n-type GaAs(001), the surface Fermi level on these p-type samples is not pinned at midgap.

We can take advantage of the behavior of the p-type surface to provide an independent confirmation that kink formation depends upon the net donor concentration and not on the concentration of Si. To do this, a co-doped sample was grown doped with both Si and Be at approximately 10^{19} cm^{-3}, but with the Be concentration slightly in excess of the Si concentration. LEED and STM showed the kink density to be very low on this sample, similar to that seen on the p-type sample shown in Fig. 2. The formation of kinks on n-doped GaAs(001) therefore depends upon the net donor concentration and not on the Si concentration.

We have shown that the Fermi level on these p-type samples is not pinned at midgap as in the case of the n-type samples. However, the spectrum does indicate some band bending at the surface. Tunneling spectroscopy studies by Feenstra and Stroscio[5] on the clean p-type GaAs(110) surface, which is flat band, show a clear dopant-induced current arising from tunneling into empty valence-band states. This current is pinched off if a small amount of band bending occurs as a result of, for example, oxygen adsorption on the surface. In the spectra of the p-type GaAs(001) surface [Fig. 3(b)], there is no evidence of a similar dopant-induced current, indicating that there is some surface band bending. In addition, if there were no surface band bending, the Fermi level would be closer to E_v than is observed in the spectrum shown in Fig. 3(b).

The STM images of the surfaces of both n- and p-type GaAs(001) show a considerable number of defects of various types on the surface, including "missing" unit cells and step edges. No detailed studies have been made of the electronic properties of these defects, but it is likely that these will introduce some states within the band gap. This is supported by the fact that no step-edge structure consistent with STM images has been proposed which satisfies the electron-counting condition.[7] The density of these states is hard to quantify without a more detailed knowledge of their structure, but STM images indicate that it can be at least 10^{12} cm^{-2} on many of the samples. The density of these "intrinsic" defects is found to be very dependent on growth conditions and sample preparation technique. The presence of these intrinsic defect states will influence the Fermi-level position on the GaAs(001) surface.

The minimum surface-state density (acceptor states on n-type material and donor states on p-type material) that is required to bring the Fermi level to midgap can be determined by assuming that the surface charge density must equal the total number of donors (or acceptors) per unit area within the depletion width (see Ref. 8). This is plotted as a function of doping level in Fig. 4(a). Also plotted is the density of intrinsic surface states, which is assumed to be constant at all doping levels, and in this case assumed to be 3×10^{12} cm^{-2}. For simplicity we as-

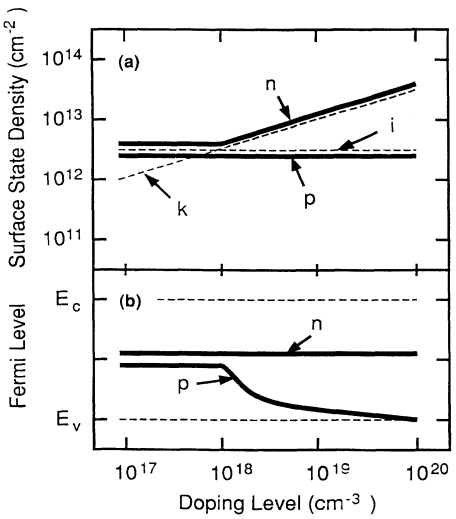

FIG. 4. The Fermi-level pinning behavior of n- and p-type GaAs(001) showing (a) the surface-state density and (b) the Fermi level as a function of doping level. Also plotted are the intrinsic defect-state density (i) and the surface-state density required to keep the Fermi level at midgap (k).

sume these intrinsic states all to be located close to midgap, although, more realistically, the states are distributed throughout the gap.[9] From this we can explain the different Fermi-level pinning behavior of n- and p-type GaAs(001) that we have observed. On n-type material, kinks form so as to maintain enough surface states to keep the Fermi level at midgap. So, for high doping levels, the intrinsic defects play no role (see Fig. 4). At lower doping levels the intrinsic defects provide enough surface states to pin the Fermi level. It is assumed that under these conditions there should be no energetic reason for kink formation. The Fermi level is pinned at midgap for all doping levels.

In the case of p-type material, it is only the intrinsic defects that provide surface states to pin the Fermi level. At low doping, the Fermi level will be pinned close to midgap as indicated in Fig. 4(b), although not necessarily at exactly the same position as for n-type material.[10] At higher doping levels the density is insufficient to bring the Fermi level up to midgap. The Fermi level will therefore "float" and be dependent upon the intrinsic defect density. As the doping level increases, the Fermi level moves down toward E_v. In the p-type samples discussed above with 10^{19} cm^{-3} Be doping, the Fermi level was found to be close to the valence band, consistent with an intrinsic defect density of about 3×10^{12} cm^{-2}. Recently published photoemission results[11] for p-type GaAs(001) doped with approximately 10^{18} cm^{-3} Be show the Fermi level to vary between $E_v+0.4$ eV and $E_v+0.6$ eV, consistent with an intrinsic defect density in the low 10^{12} cm^{-2} range [Fig. 4(b)].

The question remains: why is it that surface donors do not form on the p-type surface in the same way that surface acceptors form on the n-type surface? The formation of surface acceptors (kinks) on n-type GaAs(001) occurs in order to reduce the total energy of the surface region.[1] Energy is gained when electrons drop from the conduction band into acceptor states within the band gap. The energy cost is the formation of the charged acceptor, which is clearly small since they form in large numbers on the surface of n-type material. This mechanism should occur equally with any n-type dopant, as the actual dopant atom is not directly involved in the formation of the surface acceptor. Since we do not see the formation of similar surface donors on p-type material, we must conclude that the formation energy of a charged surface donor is much higher. The reason for this must relate to the details of the (2×4) surface reconstruction—surface donors require a reduction in the ratio of As dangling-bond states to Ga dangling-bond states at the surface, which is more difficult on an As-terminated surface.

The description of Fermi-level pinning on both n- and p-type GaAs(001) shown in Fig. 4 illustrates the important differences between n- and p-type GaAs(001) surfaces. Further investigation of the state density that is derived from the intrinsic defects and of the Fermi-level position as a function of doping level on p-type material remains to be done.

In summary, we have shown that the Fermi-level pinning behavior on p-type GaAs(001) is different from that on n-type GaAs(001). On n-type GaAs(001), the Fermi level is pinned at midgap for all doping levels due to the formation of surface acceptor states by a self-compensation mechanism. On p-type GaAs(001), the Fermi-level position is controlled by intrinsic defects (i.e., steps, missing unit cells, etc.). As a result the Fermi level will be pinned close to midgap at low doping levels, but at high doping levels the Fermi level is seen to be close to the valence-band maximum. On p-type GaAs(001), it is possible to move the surface Fermi level too close to the valence band by changing the doping level.

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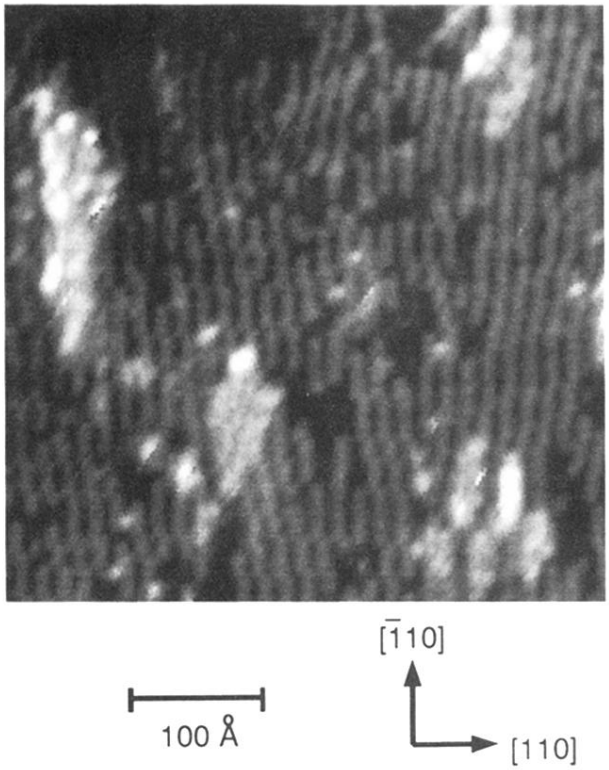

FIG. 1. A filled-state STM image of the $(2\times4)/c(2\times8)$ GaAs(001) surface of an n-type sample doped with 10^{19} cm^{-3} Si. After growth, the sample was capped with As and transferred through air to the STM system.

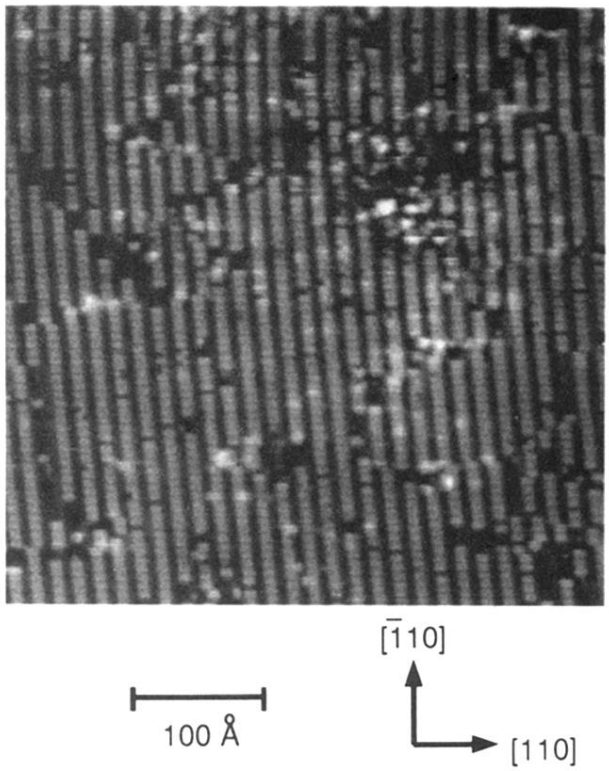

FIG. 2. A filled-state STM image of the $(2\times4)/c(2\times8)$ GaAs(001) surface of a p-type sample doped with 10^{19} cm^{-3} Be.