Scanning Tunneling Microscopy Studies of Si Donors (Si_{Ga}) in GaAs

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We report scanning tunneling microscopy (STM) studies of Si substitutional donors (Si_{Ga}) in GaAs that reveal delocalized and localized electronic features corresponding to Si_{Ga} in the top few layers of the (110) cleavage surface. The delocalized features appear as protrusions a few nm in size, superimposed on the background lattice. These features are attributed to enhanced tunneling due to the local perturbation of the band bending by the Coulomb potential of subsurface Si_{Ga}. In contrast, STM images of surface Si_{Ga} show very localized electronic structures, in good agreement with a recent theoretical prediction [J. Wang *et al.*, Phys. Rev. B **47**, 10329 (1993)].

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Shallow impurities in semiconductors, such as Si substitutional donors (Si_{Ga}) in GaAs, are of scientific and technological importance. These dopants are well described by the hydrogenic model. They are among the best understood imperfections in semiconductors. They are widely employed to control the electrical properties of semiconductors and play a dominant role in transistors, Schottky diodes, and doping superlattices. Despite extensive studies, these impurities have never been directly investigated on an atomic scale, due to the lack of a suitable technique.

We report here the first direct atomic scale investigation of the electronic structure associated with individual dopant atoms in a semiconductor. Our results demonstrate a general potential to study other shallow dopant impurities using scanning tunneling microscopy (STM). This can lead to a better understanding of dopant distribution and mutual interactions in the host semiconductor crystals.

In the last 10 years, STM has been widely used to study the geometric and electronic structure of semiconductor surfaces [1]. These studies [2] have focused on the properties of the topmost layer of the crystal surface, such as reconstruction, surface point defects and steps, adsorption, and epitaxy. Recently, STM techniques have been used to study the geometry and electronic structure of bulk imperfections, as opposed to surface, in the study of antisite defects in low-temperature-grown GaAs by Feenstra, Woodall, and Pettit [3]. Up to date, however, few STM studies related to shallow impurities in semiconductors have been carried out [4,5]. It has been suggested that Si induces fluctuations on the GaAs (110) surface in STM studies of doping superlattices [4]. On the theoretical side, Wang *et al.* recently predicted the electronic and spatial structure of features induced by Si on a GaAs (110) surface [6].

In this work, we identify and characterize Si shallow donors in Ga substitutional positions (Si_{Ga}) in GaAs using STM. STM spectroscopic images reveal characteristic delocalized and localized electronic features corresponding to Si_{Ga} located in the top five layers of the crystal and on the top (110) cleavage surface, respectively.

Samples used for the present study were Si doped GaAs grown by the liquid encapsulated Czochralski technique. Samples with different doping concentrations, n^+ GaAs (Si:2×10^{18}/cm^3) and n^- GaAs (Si:5×10^{16}/cm^3) and from different sources were investigated. The STM head is homemade and similar to that developed by Frohn *et al.* [7], which allows the STM tip to move over a large area on the sample surface. The electronic control is commercially made by RHK [8]. The samples were cleaved *in situ* in an ultrahigh vacuum STM chamber with a base pressure of 8×10^{-11} Torr. Electrochemically etched Pt-Rh tips were used. All STM images were taken in the constant current mode with a tunneling current of 0.5 nA.

Figure 1 is an STM image on the (110) surface of n^+ GaAs taken at a sample bias of -1.5 V. Bright (*D*) and dark (*B*) features are clearly observed. The *D* features

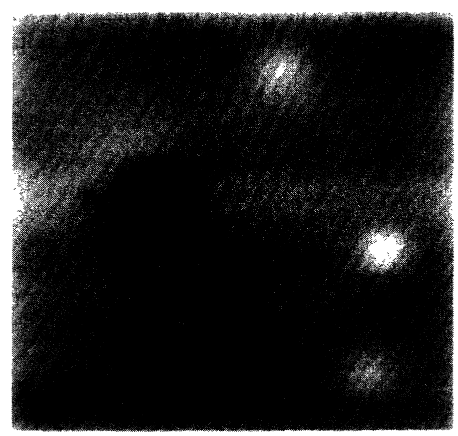

FIG. 1. 250 Å×250 Å STM image of the cleaved GaAs (110) surface, acquired with 0.5 nA tunneling current at a sample voltage of -1.5 V. Two types of features marked as *D* (donor) and *B* (black) are seen. The *D* features appear as bright protrusions of different apparent heights. They correspond to Si_{Ga} in various subsurface layers that enhance the local tunneling probability.

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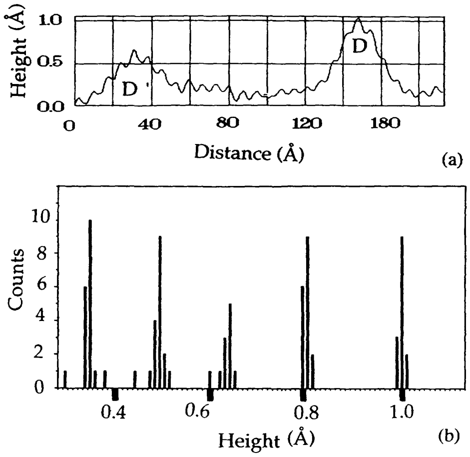

FIG. 2. (a) Surface profile across the centers of features D and D' in Fig. 1. (b) Histogram of different heights of D features measured at a sample bias of -1.5 V and tunneling current of 0.5 nA. The data are acquired from many images of D features in a large area of a (110) cleaved surface.

are attributed to subsurface Si_{Ga}, based on the following observations. First, their density is constant during several days of STM observations. Hence contamination is not the origin of the features. Second, their density is proportional to the Si doping concentration in the n^+ and n^- GaAs samples studied. For the n^+ GaAs shown in Fig. 1, the surface density of the D features is measured to be $(2\text{–}3)\times 10^{11}$ cm^{-2} based on a large number of images, in agreement with the expected Si concentration for a doping level of 2×10^{18} cm^{-3} [9]. For the n^- sample, the measured density is $(0.5\text{–}1)\times 10^{10}$/cm^2, which scales with the doping level of 5×10^{16}/cm^3. The B features in Fig. 1 are basically surface depressions superimposed on the perfect lattice. They are also bias dependent, and mobile during the observation. We attribute these features to Ga vacancies, which will be discussed in detail in a future publication.

Figure 2 shows that different subsurface Si_{Ga} features imaged at the same bias can have different apparent heights, as indicated by the profile across the centers of the D and D' (see arrows in Fig. 1). The apparent heights were measured over a large number of features imaged at -1.5 V sample bias. We observed at least five discrete values of the height, as shown in the histogram of Fig. 2(b). We believe the different heights correspond to the Si_{Ga} donors at different subsurface layers [from the first to the fifth (110) subsurface layer]. The approximately equal numbers of subsurface Si_{Ga} features counted for each layer indicate a uniform distribution of Si_{Ga} in the bulk. We believe that the largest height corresponds to Si_{Ga} in the first subsurface layer because this Si_{Ga} should have the strongest influence on the tunneling.

Figure 3 illustrates a spectroscopic study of the subsurface Si_{Ga} features imaged at various sample voltages. It indicates that their origin is electronic rather than topographic. In every case the protrusion is superimposed on the background atomic lattice for both the positive and negative sample bias [10]. The protrusion has a spatial extension of approximately 25 Å (FWHM), almost independent of the sample bias. The apparent height of the protrusions, however, is strongly bias dependent. Figures

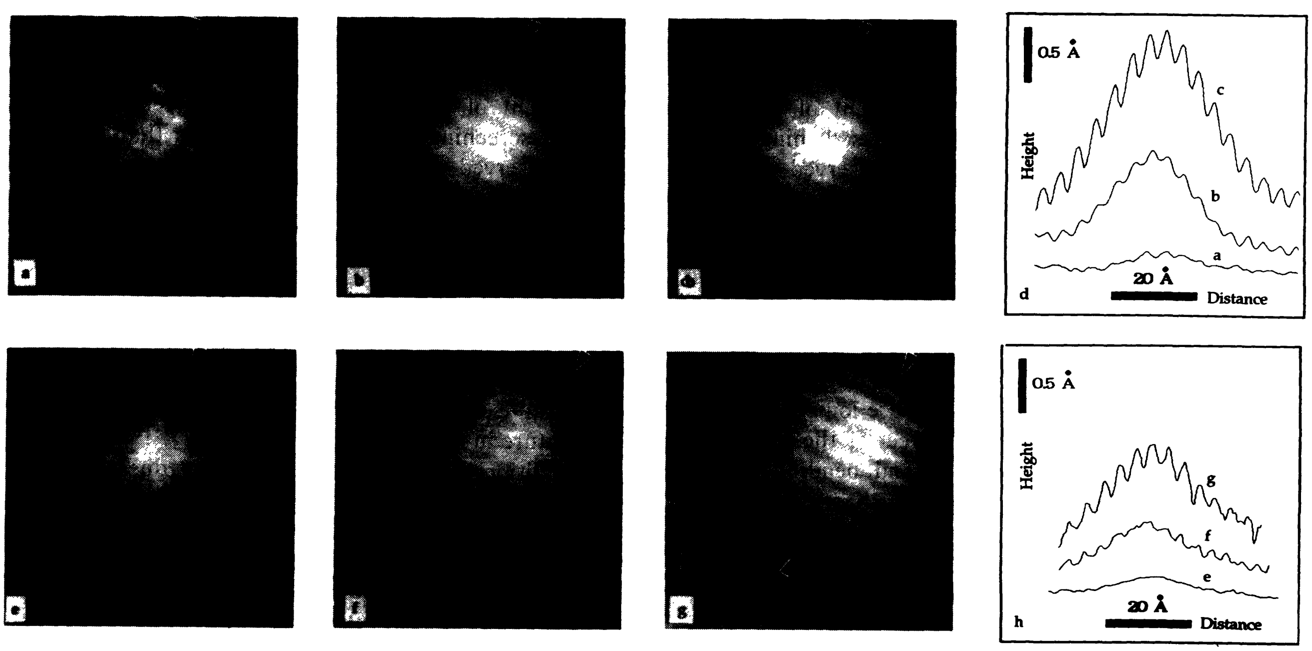

FIG. 3. STM images of the protrusion region D in Fig. 1 taken with tunneling current of 0.5 nA at various sample voltages. The sample voltages are (a) -3 V; (b) -2.0 V, (c) -1.5 V; (e) $+3.0$ V; (f) $+2.0$ V; and (g) $+1.5$ V. The topographic profiles along the $[1\bar{1}0]$ direction (indicated by the arrows) across the features are shown in (d) and (h). All images are 60 Å×60 Å in size.

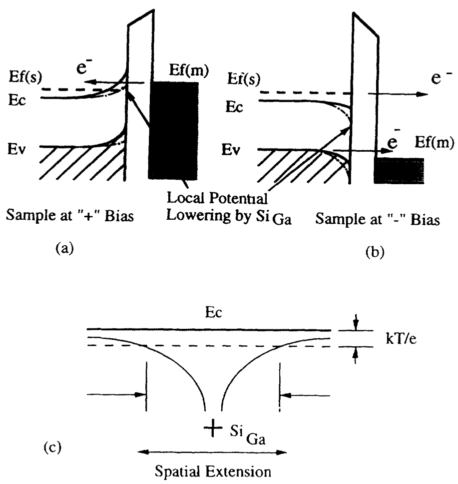

FIG. 4. Energy band diagram illustrating the electron tunneling process between metal tip and GaAs (110) surface in the presence of tip-induced band bending: (a) positive sample voltage; (b) negative sample voltage; and (c) schematic illustration of the Coulomb potential around the Si atom that causes a local lowering of the band. The dash-dotted lines in (a) and (b) indicate the local band bending perturbed by the subsurface Si_{Ga}.

3(a)–3(c) are filled state images, corresponding to electrons tunneling from the sample to the tip. The apparent heights of the features are 0.1, 0.7, and 1.0 Å at sample biases of −3.0, −2.0, and −1.5 V, respectively. The profiles of the features measured along the [110] direction (arrows in the image) across the center are shown in Fig. 2(d). The results at positive bias voltages of +3.0, +2.0, and +1.5 V are qualitatively similar to those at negative bias, but the heights of the protrusion are smaller [Figs. 2(e)–2(h)].

We believe that these protrusions are due to the Si_{Ga} donor in the subsurface layers of GaAs, which perturb the local band bending in the presence of the metal tip, as illustrated by the model in Fig. 4. The tip-induced band bending in the semiconductor and tunneling through the space charge region must be taken into account [10,11]. This is analogous to band bending in the metal-insulator-semiconductor system. At a positive sample bias [Fig. 4(a)], the subsurface region under the tip is depleted of electrons due to the tip-induced band bending. In this depletion region the shallow Si_{Ga} donors are ionized and are positively charged. The collective effect of the positively charged Si_{Ga} results in parabolic band bending in the semiconductor, which forms a potential barrier for electrons tunneling from the tip to the sample. On the atomic scale, the effect of individual ionized donors can be seen. Close to the core of each Si_{Ga} ion, its Coulomb potential locally decreases the band bending and effectively increases the density of states available for tunneling [Fig. 4(a)]. To compensate the enhanced tunneling current, the STM tip moves away from the surface, producing a protrusion superimposed on the lattice corrugation. The height of the protrusion decreases with increasing bias, since at high bias more conduction band states can contribute to the tunneling current, and the relative effect of the perturbation of the Si_{Ga} donor is reduced.

At negative sample bias, on the other hand, the tip-induced band bending causes electrons to accumulate in the near surface region as shown in Fig. 4(b). Electrons are tunneling out of the valence band states, and filled states near the conduction band edge in the accumulation layer. Although the subsurface Si_{Ga} Coulomb potential is now screened by conduction electrons in the accumulation layer, it still perturbs the local band structure. By further bending down the band, this produces a local increase of the filled states near the conduction band edge and a decrease of states near the top of the valence band edge [see Fig. 4(b)]. Since the donor states at the conduction band edge are closer to the Fermi level, their contribution dominates in the tunneling [12]. The net result is an enhanced tunneling near the core of the Si_{Ga} giving rise to the protrusion observed at negative bias. At high negative bias, the contribution to the tunneling current from the valence electrons increases, and the contrast of the feature therefore decreases.

The spatial extension of the imaged subsurface Si_{Ga} reflects the range over which the Coulomb potential exceeds kT/e [see Fig. 3(c)]. In the case of accumulation at negative sample bias, it might be expected that the observed spatial extension should decrease due to screening by conduction electrons. The screening length due to conduction electrons in the bulk crystal is calculated to be ~44 Å for an electron concentration of $2\times10^{18}/cm^3$ [13]. Since the high concentration of electrons in strong accumulation at high negative bias (e.g., −3 V) is mostly within a thin layer at the surface, considering a two dimensional limit, the screening length becomes ~45 Å, independent of conduction electron concentration [14]. Thus the screening length is always larger than the extent of the observed subsurface Si_{Ga} feature [see Figs. 2(d) and 2(h)] and therefore screening does not strongly affect the part of the Coulomb potential perturbing the local band bending. A similar spatial extension of the perturbed tunneling due to the screened Coulomb potential has been observed for adsorbed oxygen on n^+ GaAs (110) surface, where the tunneling current was enhanced within a radius of ~20 Å [15]. This is consistent with the spatial extension of 25 Å (FWHM) of the subsurface Si_{Ga} feature in our experiments.

In addition to the delocalized features due to the bulk Si_{Ga} donor discussed, localized features were also observed. Figures 5(a) and 5(b) are filled state and empty state STM images of the localized feature obtained at sample bias of −2.5 and +2.5 V, respectively. This localized feature is attributed to surface Si_{Ga} based on the comparison of its characteristic structure with a recent theoretical prediction [6]. When the Si_{Ga} is located on the cleaved GaAs (110) surface, its electronic structure is modified due to the dangling bond. According to Wang

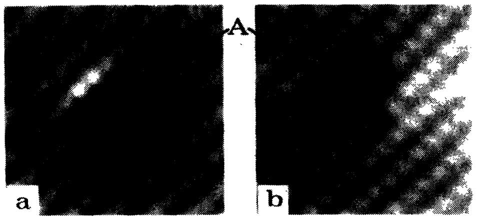

FIG. 5. Images of a substitutional donor Si at Ga site (Si_{Ga}) on the top layer GaAs (110) cleavage surface. (a) Filled states image acquired with 0.5 nA tunneling current and at -2.5 V sample bias. (b) Empty states image acquired with 0.5 nA tunneling current and at $+2.5$ V sample bias. The location of the Si dangling bond state is marked by the letter A. The defect structure is localized to a couple of nearest neighbors.

et al., this introduces a localized midgap level, which traps the donor electron and forms a half-filled localized dangling bond. In the filled state image, the half-filled surface dangling bond is imaged as a local maximum (bright spot marked as A). In addition, the filled dangling bond states of the As atoms bonded to this Si are pushed 0.4 eV downward from their normal position near the top of the valence band. As a result, these two As atoms appear dark because of reduced local tunneling. It is interesting to notice that the two next neighboring As atom positions appear brighter. In the empty state image, the Si dangling bond appears dark because the electron trapped in the dangling bond reduces tunneling compared to the completely empty states of the neighboring Ga dangling bonds. The details of the two images fit very well with the theoretically predicted images of Si_{Ga} on the GaAs (110) surface for bias voltages of -1.2 and $+1.9$ V, respectively. We compare experimental images at ± 2.5 V to theoretical images at -1.2 and $+1.9$ since the Fermi level of our sample is in the conduction band while the theoretical calculation used a Fermi level in the middle of the gap without corrections for band bending. We counted 5–8 surface Si_{Ga} features in ~ 100 images covering a total area of about 1500 Å×1500 Å on n^+ GaAs, while only one was observed in a similar number of images of n^- GaAs. We would expect 9.3 surface Si_{Ga} atoms on the (110) surface for n^+ GaAs and 0.2 Si_{Ga} atoms for n^- GaAs based on bulk Si concentration.

In conclusion, we have identified and characterized substitutional donor Si at Ga sites (Si_{Ga}) in GaAs by STM. The subsurface Si_{Ga} donor has a delocalized electronic structure that gives rise to a protrusion in the STM image with a typical spatial extension of about 25 Å (FWHM), and height from tenths of Å to a few Å depending on the sample bias and its location under the surface. Si_{Ga} has been probed down to at least the fifth layer of the subsurface. The delocalized subsurface Si_{Ga} features can be understood based on the perturbation of the local band bending by the Coulomb potential of the Si_{Ga} donor. Si_{Ga} on the (110) cleavage surface, however, shows a localized electronic structure due to its dangling bond.

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Note added.—After we submitted our original manuscript, another publication appeared on the observation of acceptors in GaAs by Johnson *et al.* [16].

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[9] For Si doping concentration of $2\times10^{18}/cm^3$, the estimated number of substitutional Si atoms in a (110) plane is $4\times10^{10}/cm^2$. Assuming that we simultaneously probe Si_{Ga} within five layers in the subsurface, the expected density of D features is $2\times10^{11}/cm^2$.

[10] Delocalized features had been observed previously but were not identified as subsurface Si_{Ga} donors on n^+ GaAs (it was suggested as a native defect). See Joseph A. Stroscio and R. M. Feenstra, in *Scanning Tunneling Microscopy*, Methods in Experimental Physics Vol. 27 (Academic, New York, 1993), pp. 126 and 127.

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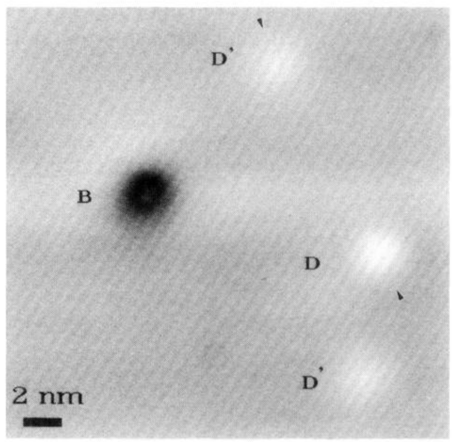

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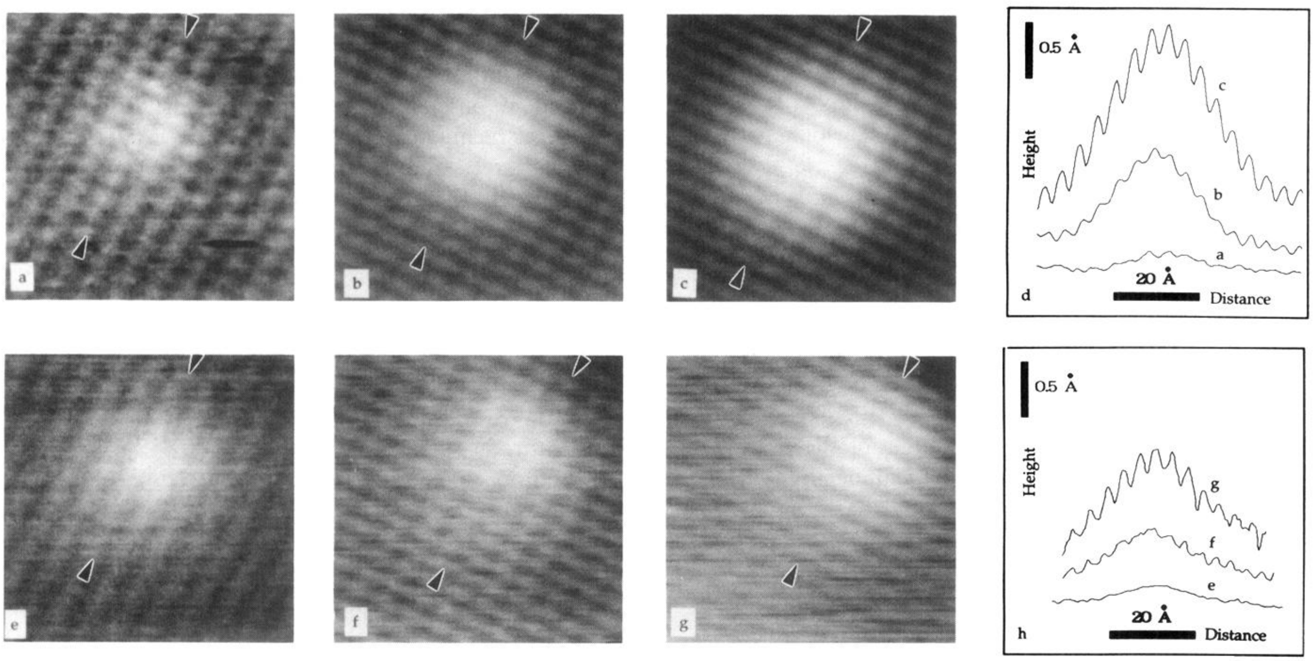

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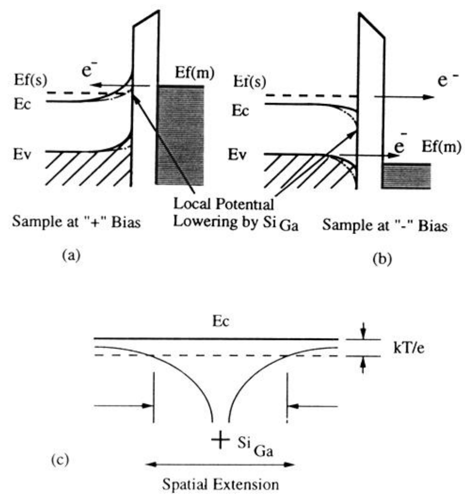

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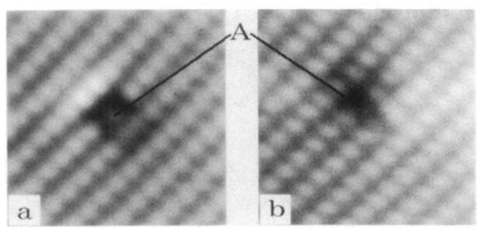

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