Charge State Dependent Structural Relaxation around Anion Vacancies on InP(110) and GaP(110) Surfaces

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The dependence of the structural relaxation around phosphorous vacancies in InP(110) and GaP(110) surfaces on their charge state was investigated by scanning tunneling microscopy. Two charge transition levels were localized within the band gap. The symmetry of the vacancies is lowered with an increasing number of electrons bonded in the electronic defect states. The vacancies on InP(110) and GaP(110) surfaces have essentially the same structure.

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The applicability of semiconductors in electronic or optoelectronic devices is influenced to a considerable degree by the presence of point defects such as vacancies, antisite defects, or dopant impurities. Dopant atoms, with energy levels near to the band edges, increase the conductivity of a crystal by several orders of magnitude and shift the Fermi energy depending on their concentration. In contrast, point defects such as vacancies and antisite defects may induce deep-lying electrical states in the band gap. At high concentrations these states can counteract the desired properties obtained by dopant atoms. Furthermore, a point defect may in general have several electronic levels and may have a net charge that depends on the number of electrons trapped in it. The energies of the electronic levels of the defect can depend strongly on structural distortions of the adjacent crystal lattice, which arise to minimize the free energy of the defect. The local lattice symmetry may thus be a function of the charge on the defect and the consequent occupancy of the defect energy levels [1,2].

Despite the recognition that structural relaxation can have significant consequences for the modification of electrical properties of point defects, few experiments have been performed and present knowledge rests principally on theoretical considerations [1–3]. The dearth of experimental results is in all likelihood due to the difficulty of making detailed atomic-scale measurements. Because of its atomic resolution and its ability to probe the surface electronic structure as well as the morphology, the scanning tunneling microscope (STM) is ideal for investigations of surface defects. To the extent that one can assume that the behavior of defects on surfaces is equivalent to that of bulk defects, one can make from surface measurements predictions about the general properties of defects in solids.

In this Letter we report on simultaneous STM studies of the morphology and the charge of anion (phosphorous) vacancies in InP(110) and GaP(110) surfaces. We demonstrate the ability to investigate structural relaxation around individual defects. We show that each vacancy has charge-transition levels that are localized within the band gap. The structural symmetry of a vacancy is lowered as the number of electrons trapped in it increases.

Vacancies on (110) surfaces of III-V semiconductors are particularly well suited for structural-relaxation studies, as their relaxation can be atomically resolved and their charge determined using the STM [4,5]. Defect-free (110) surfaces show only a relaxation of the surface bonds coupled with a charge transfer from the cation-derived dangling bond to the dangling bond localized above the anion. Thus the empty and occupied states correspond, respectively, to the cation (group III) and anion (group V) positions [6–8]. The expected structure of an anion vacancy on such a surface is shown schematically in Fig. 1. In order to remove one atom three bonds must be broken. The resulting dangling bonds rehybridize to form the defect states. The occupied surface state associated with the missing atom is absent. Thus in the STM images of an anion vacancy one can expect one missing

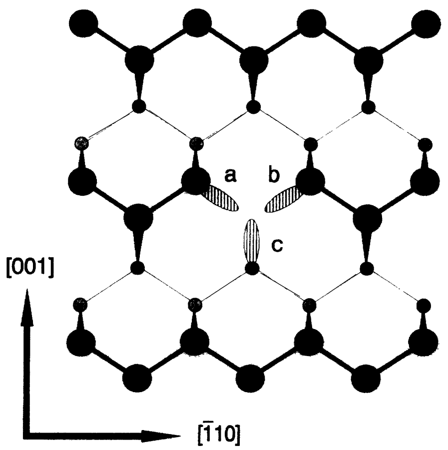

FIG. 1. Schematic image of an anion vacancy on a III-V semiconductor (110) surface. Three dangling bonds (*a*, *b*, and *c*) are created during the formation of a vacancy. They rehybridize to form the new defect states. Small circles correspond to atoms in the second layer. Dark circles represent cations.

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occupied surface state and no missing empty surface states [4].

The magnitude and sign of the charge of the vacancy may be influenced by the doping of the crystal if an electronic energy level of the vacancy exists in the band gap. The defect state can be either filled or empty, depending on the relative position of the Fermi energy with respect to the charge-transition level: If the Fermi energy lies below the charge-transition level the defect has one electron less than if the Fermi energy is above it. In highly *p*- and *n*-doped material the Fermi energy is, respectively, below and above all possible charge-transition levels in the band gap. Thus comparing *n*- and *p*-doped surfaces allows us to determine the existence of charge transition levels in the band gap. In our experiments *n*- and *p*-doped InP and GaP crystals were cleaved in UHV at room temperature. Under these conditions both the dopant atoms and the surface vacancies are immobile, and therefore the bulk dopant concentration fixes the position of the Fermi energy at the surface. The doping concentrations of $(0.9\text{-}1.8)\times 10^{18}$ cm^{-3} Sn for *n*-type InP, $(1.3\text{-}2.1)\times 10^{18}$ cm^{-3} Zn for *p*-type InP, $(5.6\text{-}6.0)\times 10^{17}$ cm^{-3} S for *n*-type GaP, and $(1.7\text{-}5.8)\times 10^{17}$ cm^{-3} Zn for *p*-type GaP, were chosen to give Fermi levels very close to the band edges in order to allow a search in the whole gap for possible defect states.

Point defects were produced nearly exclusively near steps and their density did not change with time. We identify the defects as vacancies on the basis of their filled and empty states. Dopant atoms, cation vacancies, or antisite defects can be excluded, as they have different structures [4,5]. If the defects were, e.g., due to hydrogen atoms adsorbed from the background gas (total pressure below 1×10^{-8} Pa), their density would be uniform and increase with time. We took care to keep gauge filaments off during cleavage and subsequent measurement, so that no atomic H was produced.

The sign of the charge of a vacancy can be deduced from elevations or depressions observed in the STM images, caused by an upward or a downward band bending, respectively [4,9,10]. Table I shows the sign of the observed charges of P vacancies on *n*- and *p*-doped surfaces. In all cases the charge-induced band bending was relatively weak, suggesting that the vacancies have a net charge of at most one electron [11]. The vacancies show a charge change from positive to negative when the Fermi energy is moved by doping from the valence band edge to the conduction band edge, indicating the existence of charge-transition levels in the fundamental gap. On both the InP(110) and GaP(110) surfaces we can conclude that the charge-transition levels from positive to uncharged states (+/0) and from uncharged to negative charge states (0/−) are situated in the band gap. The existence of both uncharged and negatively charged vacancies on *n*-doped GaP(110) surfaces indicates that the charge-transition level (0/−) must be close to the Fermi energy, which is pinned in the upper part of the gap due to the empty C_3 surface states of the defect-free surface. Hence that charge-transition level must be in the upper part of the gap.

TABLE I. Charges of P vacancies on *n*- and *p*-doped (110) surfaces of GaP and InP.

Doping	Charge on GaP(110)	Charge on InP(110)
p	+	+
n	0/−	−

We now compare the morphologies observed for P vacancies with different charge states. Figure 2 shows constant-current images of the occupied states of vacancies on GaP(110) [Figs. 2(a)-2(c)] and InP(110) [Figs. 2(d) and 2(e)]. The comparison demonstrates that the symmetry is reduced in going from positively to negatively charged vacancies. Figures 2(a) and 2(d) show the positively charged and Figs. 2(c) and 2(e) the negatively charged vacancies on GaP(110) and InP(110), respectively. Height profiles through the positively and negatively charged vacancies on InP(110) are shown in Fig. 2(f). Figure 2(b) shows an uncharged P vacancy on *n*-doped GaP(110). All images show that one occupied dangling bond is missing, but the morphology and the electronic structure of the neighboring dangling bonds change considerably between the different charge states. The displacements of the dangling bonds of each of the respective charge states are, however, similar on InP(110) and GaP(110) surfaces.

The neighboring occupied dangling bonds along the $[1\bar{1}0]$ direction of the positively charged vacancy are localized 0.02 nm deeper into the surface and their state density maxima are slightly displaced laterally by about 0.02 nm in the [001] direction, while the two neighboring empty dangling bonds are displaced out of the surface. Other dangling bonds show no displacements [12]. These displacements are in addition to the depression observed in the STM images due to the charge-induced band bending [4,13]. In order to eliminate this latter effect we measured the displacements at high voltages (−3 to −3.5 V) at which the band bending is minimal.

The negatively charged vacancies have a much more complicated structure. The images exhibit no mirror symmetry with respect to the $(1\bar{1}0)$ plane [Figs. 2(c), 2(e), and 2(f)]. Some occupied dangling bonds appear brighter around the vacancies. Because III-V (110) surfaces have a mirror symmetry with respect to the $(1\bar{1}0)$ plane, it can be expected that for the negatively charged vacancies two types of mirror-related structures exist. This is indeed the case, as shown for *n*-doped InP(110) in Figs. 2(f) and 3.

The uncharged vacancy exhibits no visible dangling-bond displacements. Such a defect structure was also observed for the uncharged As vacancy on *n*-doped

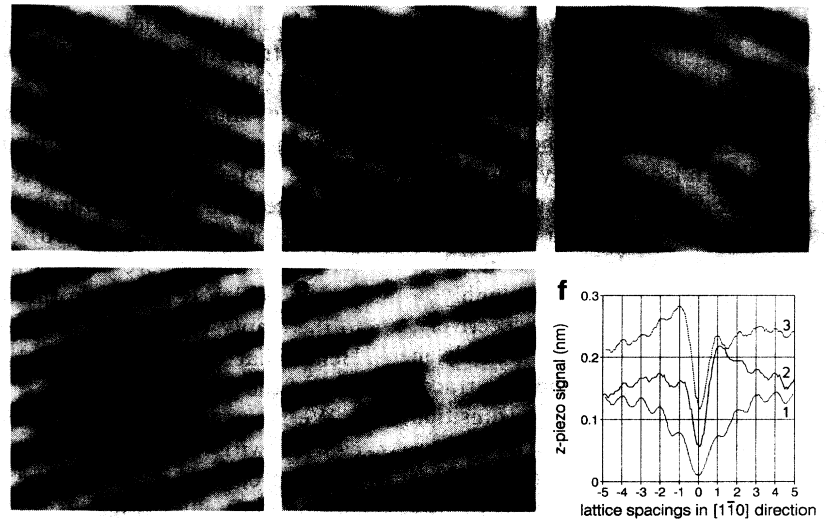

FIG. 2. Series of images of the occupied states of P vacancies on GaP(110) (a)-(c) and InP(110) (d),(e) measured with sample voltages relative to the tip between -2.7 and -3.4 V, at which the band bending effects are minimal. (a) and (d) show the positively charged, (b) the uncharged, and (c) and (e) the negatively charged states. The charge dependent structural relaxations of the vacancies are visible. The atomic rows are oriented in the [1$\bar{1}$0] direction. (f) Height profiles along the [1$\bar{1}$0] direction through a positively (1) and a negatively charged (2 and 3) P vacancy on InP show the defect symmetry. The profiles of the negatively charged vacancy correspond to two mirror-related configurations. The profiles have been shifted for clarity.

GaAs(110) [14]. In both cases the vacancies have a mirror symmetry with respect to the (1$\bar{1}$0) plane.

The rearrangement of the neighboring dangling bonds can be explained by structural relaxation of the atoms themselves. For the *positively* charged vacancy, the neighboring anions are moved into the surface, while the cations are displaced out of the surface. Such displacements are equivalent to a reduced buckling angle for atoms near the vacancy. The measured lateral and vertical displacements of the dangling bonds corroborate this interpretation. The area with the reduced buckling angle extends over two lattice spacings. In contrast, the lack of any relaxation around the *uncharged* vacancy suggests that the buckling is not affected by the presence of the vacancy. Finally, the complicated relaxation of the *negatively* charged vacancies affects a larger area and has no mirror symmetry. It is difficult to correlate the displacements of the dangling bonds in the image with geometric atom displacements. It is apparent, however, that the symmetry of the electronic states, and thus of the atomic structure, is lowered as compared to that of the positively charged and of the uncharged vacancies.

FIG. 3. Mirror-related configurations of negatively charged P vacancies on *n*-doped InP(110). The constant-current image was measured at -3.1 V. [See also profiles in Fig. 2(f).]

In order to explain the observed charge dependent changes of the morphology we refer to knowledge about bulk defects. In theoretical work on the symmetry/charge relation of vacancies in silicon a defect-molecule model has been successfully employed [1]. We shall apply a similar model to the anion vacancies here. Because the surface reconstruction consists basically of only a buckling, we start with a discussion of a vacancy on a nonreconstructed surface and then add the buckling. This rather simple model takes into account only the symmetry of the three nearest-neighbor atoms surrounding the missing atom and does not differentiate between different atom environments of the neighboring atoms. This appears justified [13] because there is experimental evidence that only the three broken bonds take part in the reconstruction process, as the STM images show no missing empty or occupied dangling bonds on the neighboring atoms [12,13,15]. Each nearest-neighbor atom has one broken bond (Fig. 1), which rehybridizes to form the new defect states. For the nonreconstructed surface with a local trigonal defect symmetry this procedure yields one

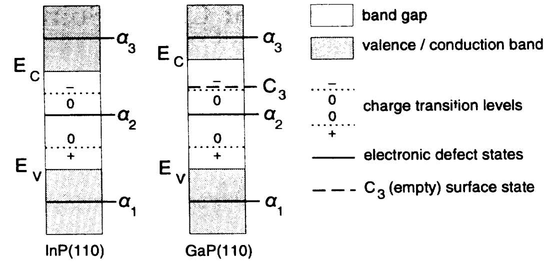

FIG. 4. Schematic representation of the locations of the charge transition levels (+/0 and 0/−) and the defect states (a_1,a_2,a_3) relative to the valence and conduction band edges (E_V and E_C) for P vacancies on GaP(110) and InP(110) surfaces.

lower energy level and two degenerate higher levels, in analogy to the calculation for the Si vacancy [1]. The latter ones will split as soon as the atoms are slightly displaced, e.g., as the surface relaxes. Thus a vacancy gives rise to three nondegenerate electronic levels.

For a *positively* charged P vacancy two electrons must fill the three available defect states and occupy the lowest state. As the two upper states are empty, only the energy of the lowest state must be minimized. Qualitative evaluation of the model indicates that there is a tendency to minimize the energy by locally reducing the buckling angle, as observed in the STM images. For an *uncharged* vacancy one electron is added and must now occupy the second defect level. For a *negatively* charged vacancy two electrons are in each the lowest and the second defect states. Minimization of the energy now involves all states and the vacancy is expected to reduce its energy by reducing its symmetry relative to the positively charged vacancy. It is, however, not possible to predict the detailed nature of the relaxation of any of these vacancies with this simple model.

We can now localize the positions of the defect states and the charge-transition levels in the band gap. Consider the positively charged vacancy. Because the vacancies appear to have a net charge of only one electron, the positively charged vacancy must have a completely filled lowest defect state. Because the vacancies occur on *p*-doped surfaces only, this state must be situated below the Fermi energy in the valence band. Similarly in *n*-doped GaP(110) we can localize the highest defect state in the conduction band or at least above the pinning level in the upper part of the gap. The positions of the charge-transition levels (+/0 and 0/−) and of the defect states (a_1, a_2, and a_3) relative to the band edges are summarized schematically in Fig. 4. It is only possible to localize energy levels as being either in the valence or conduction band or in the gap. Possible energy shifts between different charge states cannot be obtained.

Because of its simplicity the defect-molecule model cannot differentiate anion vacancies on (110) surfaces of different III-V semiconductors. On all materials the same type of symmetry for a given charge state is expected. This is indeed observed here for InP(110) and GaP(110) and also for GaAs(110) surfaces [12,14]. Only the locations in energy of the charge-transition levels and the defects states are slightly shifted from one surface to another.

In conclusion, we performed a direct imaging study, using STM, of the influence of the charge state on structural relaxations of P vacancies on InP(110) and GaP(110) surfaces. The number of electronic states and charge-transition levels in the band gap and the structural symmetry lowering as a function of the charge state have been determined. Theoretical comparisons of the electronic and structural properties of bulk and surface vacancies may form the basis for understanding the atomic structure of bulk defects through analogy with experimental data on surface defects.

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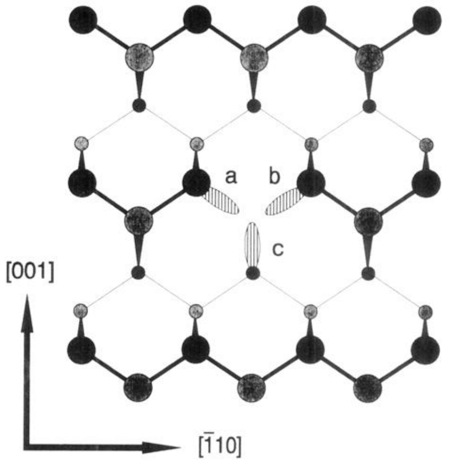

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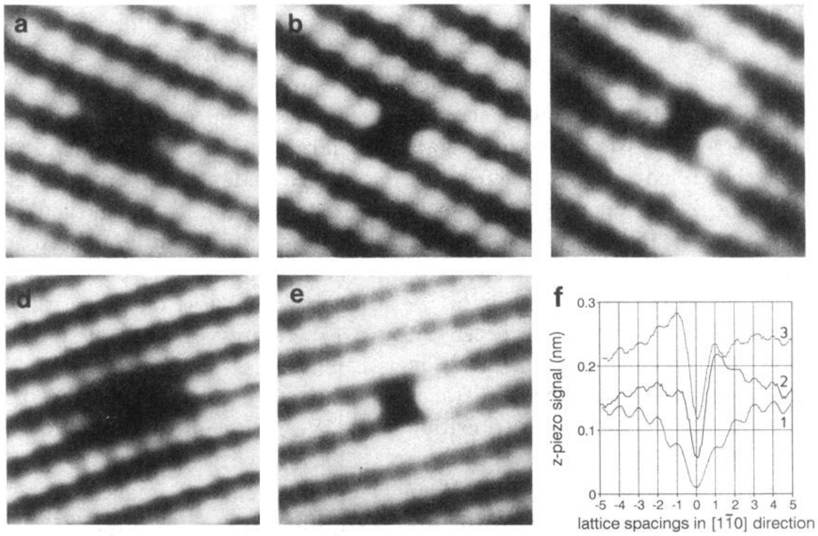

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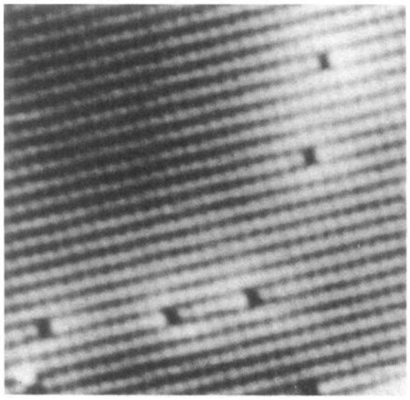

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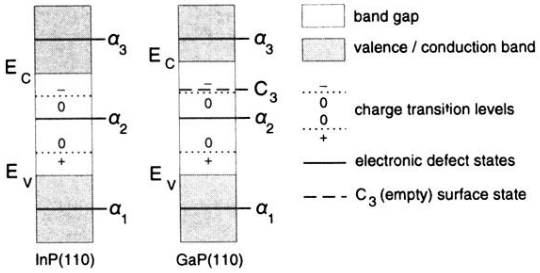

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