Charged steps on III-V compound semiconductor surfaces

M. Heinrich, C. Domke, Ph. Ebert, and K. Urban
Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

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The electrical charge of steps on (110) surfaces of InP, GaP, and GaAs is probed by scanning tunneling microscopy. It is demonstrated that step edges, with and without kinks, are charged and have localized defect states in the band gap. The charge of indium-terminated step edges on *p*-type doped InP(110) after annealing is found to be independent of the step orientation, while a strong orientation dependence is observed for phosphorus-terminated steps. This is explained by a partial compensation of the charge due to rebonding after phosphorus desorption. The magnitude of charge is estimated to be in the range of $+1e$ to $+3e$ per lattice spacing.

The surface phenomena controlling the growth and roughness of thin epitaxial semiconducting films have attracted considerable interest because of their technological importance. Several epitaxy methods have been developed in order to control the growth morphology in potential semiconductor devices. The epitaxy leads under certain conditions to layer-by-layer growth proceeding by the flow of steps across the surface and consequently yielding smooth interfaces.[1] Other growth conditions form three-dimensional islands,[2] resulting in rough interfaces. For specific applications interfaces with particular electrical, optical, or mechanical properties have to be fabricated. The desired interface properties are governed by the competing microscopic mechanisms involved in growth, such as diffusion of adatoms on terraces, diffusion over step edges, and sticking and binding at step edges. The latter two mechanisms are controlled by the atomistic and electronic structures as well as the energetics of the steps. Therefore considerable effort, both experimental and theoretical, has been devoted to the understanding of step properties, such as kink and step energies,[3] step dynamics,[4] step interaction,[5] or the reconstruction of step edges.[6] In particular, reconstructions of step edges can locally change the electronic properties and lead to states in the gap and thus, e.g., to charged kinks.[7] These charges have a pronounced influence on the physics of the microscopic mechanisms of diffusion and sticking of charged adatoms[8] and vacancies[9,10] at the step edges. Therefore, knowledge of the existence of charges along steps is important for the optimization of growth parameters and interface properties.

In this paper we report a direct observation by scanning tunneling microscopy (STM) of step charges not only at kinks but also along kink-free steps. The charge is observed through a localized band bending that is visible in constant-current STM images of InP, GaP, and GaAs (110) surfaces. Furthermore, the relative magnitude of the step charge is explored indirectly as a function of step type and orientation by the interaction of charged vacancies with the steps. We demonstrate this analysis for charged steps on InP. The charge is found to be an intrinsic property: the charge of indium (In) -terminated steps is independent of their orientation. However, after phosphorus desorption the charge of nominally phosphorus (P) -terminated [001] steps[11] is found to be reduced. The magnitude of the charge is estimated.

All three III-V semiconductors investigated were cleaved in UHV (5×10^{-9} Pa). This yielded nearly perfect (110) surfaces with large terraces separated by nonequilibrium *cleavage-induced* steps of arbitrary orientation. In order to test whether these cleavage steps are charged, the height signal perpendicular to the steps was measured in STM images of the occupied states. Figure 1 shows such height profiles across *kink-free* parts of $\langle 001\rangle$-oriented steps on *p*-type doped InP, *p*-type doped GaP, and *n*-type doped GaAs (110) surfaces. The steps on the *p*-type samples are surrounded by a depression zone, whereas steps on *n*-type doped GaAs

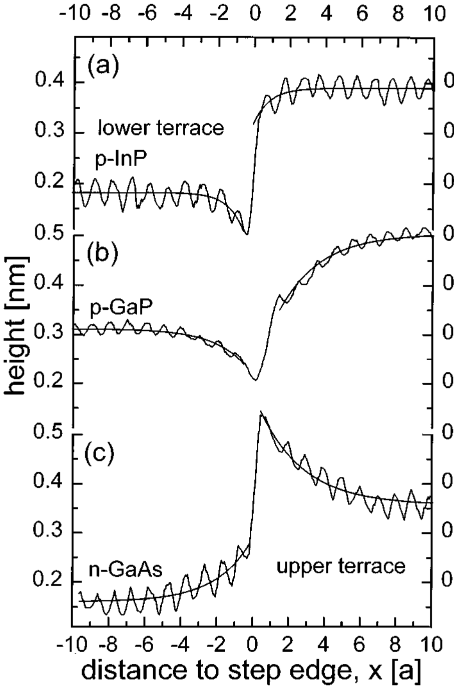

FIG. 1. Height profiles through kink-free parts of steps along the $[\bar{1}10]$ direction (normal vector $\langle 001\rangle$) for (a) Zn-doped InP [carrier concentration equal to $(1\text{–}2)\times10^{18}$ cm^{-3}], (b) Zn-doped GaP [carrier concentration equal to $(2\text{–}6)\times10^{17}$ cm^{-3}], and (c) Si-doped GaAs [carrier concentration approximately equal to 3×10^{18} cm^{-3}], respectively. The profiles were obtained from constant current images of the occupied states measured at -3 V sample voltage.

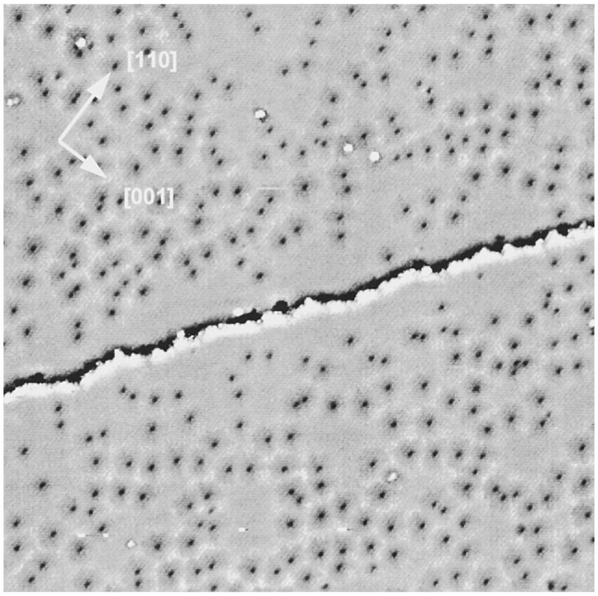

FIG. 2. STM image of a step on InP(110) after annealing at 480 K for 43 h. The localized dark spots are $+1e$ charged P vacancies. A denuded zone appears around the step. The scan width is 75×75 nm^2.

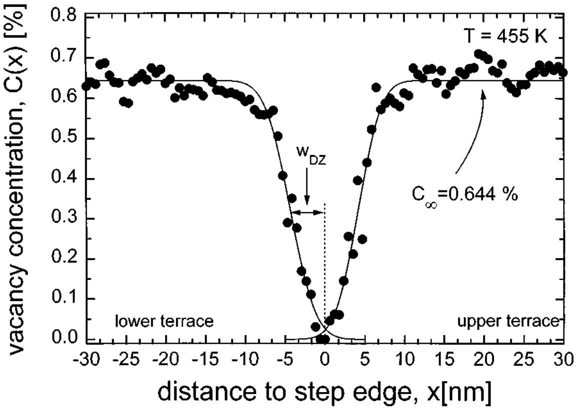

FIG. 3. Example of the dependence of the vacancy concentration $c(x)$ on the distance x to the step edge on InP(110). c_∞ is the concentration of vacancies on step-free surface areas. The solid line indicates the fitted error function used to deduce the width of the denuded zone w_{DZ}. Other functions, e.g., normal distribution, lead to the same values for w_{DZ}.

(110) show an elevation around the step edge. This observation is due to a reduced and an increased density of occupied states, respectively. The reverse effect is observed for the empty states. The height of the depressions and elevations diminishes with increasing magnitude of the sample voltage. This behavior is similar to that found for charged point defects.[12,13] This indicates that the steps are the source of a localized charge-induced downward or upward band bending. Thus, on the samples investigated the steps are found to be positively charged on p-type doped [Figs. 1(a) and 1(b)] and negatively charged on n-type doped [Fig. 1(c)] materials and give rise to localized defect states. It was already suspected that steps have electronic states in the band gap that are responsible for the Fermi-level pinning observed on badly cleaved samples.[14] However, the origin of the states in the band gap has never been shown directly. Scanning tunneling microscopy now allows us to distinguish between steps and point defects and thus to assign the charges to specific defects.

In the following analysis we will focus on one example: steps on p-type doped InP(110). The most direct measurement of the charge localized at steps would be to use a probe charge and measure the potential at a certain distance x from the step. However, this cannot be done as it is. In order to approximate this ideal measurement, charged vacancies are used as probes and we analyze their interaction with the charged steps. Positively charged P vacancies are formed during annealing of the samples at temperatures between 395 and 480 K.[13] At these temperatures the vacancies are mobile enough that we can assume their distribution on the surface to be in equilibrium.[10] For all temperatures and heating times a vacancy-denuded zone is observed around step edges (Fig. 2). Figure 3 shows a vacancy concentration profile across the step. The vacancy density is zero at the step edge and within typically 10 nm reaches the vacancy density c_∞ present on step-free surface areas.[13] For all steps the profiles turn out to be symmetric for the upper and the lower terrace. We determined a width of the denuded zone w_{DZ} by fitting an error function to the profiles of each terrace (Fig. 3). In the temperature range investigated the width w_{DZ} is independent of the vacancy concentration c_∞ and the temperature, but is dependent on the step type (Fig. 4).

At this stage we have to clarify the parameters determining the step type. Certainly, the step orientation, given by the smallest angle between the normal vector of the step and the [001] direction, is one parameter describing the step. However, this alone does not unambiguously fix the type of the step. On the (110) surface of a compound semiconductor a step edge can be terminated by anions and cations. Steps along the [110] direction [Fig. 5(a)] can be terminated either only by In atoms (normal vector [001]) or only by P atoms-(normal vector [001]). Therefore, equally oriented steps may have a different chemical character. Every kink site can, however, be P terminated as well as In terminated indepen-

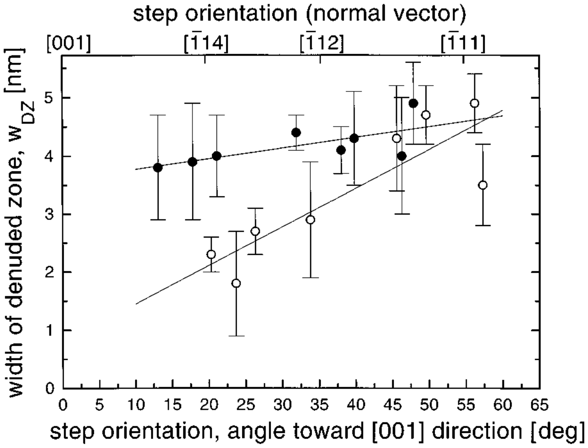

FIG. 4. Width of denuded zone as a function of step orientation and termination on InP(110). In-(P-) terminated step edges are indicated by solid (open) circles. The crystallographic orientations are given for the In-terminated steps. For P-terminated steps the opposite directions apply.

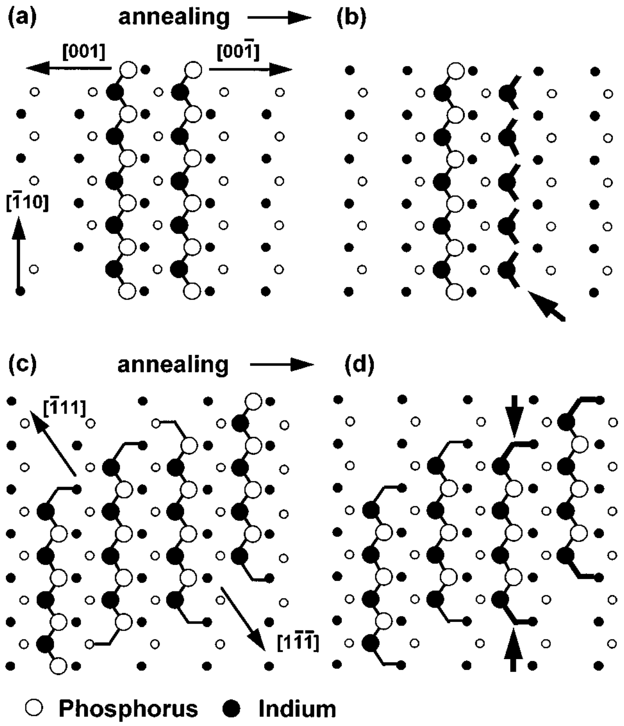

FIG. 5. Schematic drawing of step edges on InP(110); the upper (lower) terrace is indicated by large (small) circles. (a) In-terminated step edge ([001] step) right and P-terminated ([001] step) left. (b) Step edges of frame (a) after annealing and P desorption. The arrow points toward the created dangling bonds. (c) Nominally In-terminated step edge ([111] step) top and nominally P-terminated ([11 1] step) bottom. Both step edges are actually terminated by both atoms. (d) Step edges of frame (c) after annealing and P desorption. Both step edges are In terminated. The arrows indicate the mirror-related structures.

dent of the overall termination of the step edge. Steps with orientations deviating from this ideal [001] or [001] orientation therefore lose their anionic or cationic character with increasing deviation angle. Finally, steps with normal vectors [111] or [11 1] have on average no resulting anionic or cationic character [Fig. 5(c)].

The width of the denuded zone was found to remain nearly constant [$w_{DZ}=(4.2\pm0.8)$ nm] for In-terminated step edges. It is, however, smaller and orientation dependent for P-terminated step edges (Fig. 4). The largest difference between the two types of terminations exists at small angles and vanishes for [111] and [11 1] steps.

Several mechanisms can lead to a vacancy-denuded zone. We will discuss the diffusion of vacancies toward step edges, the annihilation of vacancies by adatoms, a strain-induced repulsion of vacancies, and a charge interaction. Vacancies can diffuse toward and annihilate at step edges and thus a vacancy-denuded zone appears.[15,16] However, this mechanism can be ruled out in our case since it strongly depends on the temperature and results in asymmetric denuded zones on the upper and the lower terrace (Schwoebel barrier for vacancies). Furthermore, it is known that diffusion on (110) surfaces is anisotropic.[15] This should result in a much larger variation of the width of the denuded zone with the step orientation.[15,16] Finally, on an InP(110) surface the continuous annihilation of P vacancies will leave a surplus of In atoms at the step edge, which was not observed.

Adatoms may leave step edges, annihilate vacancies, and thus create a denuded zone. The resulting profiles have characteristics similar to those discussed above for the vacancy annihilation at step edges. Both mechanisms result in step flow, which does not occur in that temperature range.[13] Moreover, step flow yields an asymmetric vacancy concentration profile since a moving step exposes a fresh, defect-free surface on the lower terrace. Thus annihilation of vacancies or step flow can both be ruled out.

A strain field along the step[5] may cause a denuded zone. However, this assumption cannot explain all the experimental results. The observed interaction length extends up to 10 nm, which is much longer than, e.g., the range of strain-induced repulsions on Ge-covered Si(001) surfaces.[17] Furthermore, the strain on the upper and the lower terrace is expected to differ and to be anisotropic, since the elastic relaxations and rebonding of the step should depend on the step orientation.[5] In addition, the band bending observed at the steps (Fig. 1) does not agree with the idea of a strain field because the apparent elevation switches to a depression if the polarity of the voltage is changed. This behavior is assigned to a charge.[12]

There exists, however, a model that can explain the experimental results: a charge repulsion between vacancies and the step. This is supported by the fact that both the step and the vacancies are positively charged. In addition, as will be discussed below, an estimate of the width of the denuded zone yields values similar to those observed if the measured Coulomb potential between charged vacancies[10] is used. The width of the denuded zone can be viewed as the signature of the relative magnitudes of the interaction and thus of the charge along different steps. In order to explain the data in Fig. 4 it is necessary to take into account the fact that during annealing P desorbs from terraces as well as at steps.[13] The effect of the desorption on the step structure depends on the chemical composition since In-terminated step edges are not affected by P desorption. Therefore, differences with the step orientation are expected.

P desorption from P-terminated step edges creates many dangling bonds per lattice spacing. Their reconstruction depends on the step type: Figs. 5(c) and 5(d) show [111]- and [11 1]-oriented step edges before and after P desorption. P desorption changes the step edges into purely In-terminated ones [Fig. 5(d)]. After P desorption both types of steps have the same reconstruction because their unit cells are mirror-related structures [Fig. 5(d)]. Both step edges will have the same electronic properties and consequently carry the same charge. This gives a reasonable explanation for the equal width of the denuded zone observed for In- and P-terminated steps oriented close to [111] and [11 1], respectively (Fig. 4). For [001]- and [001]-oriented steps the situation is different [Figs. 5(a) and 5(b)]. No desorption occurs at In-terminated step edges. P desorption creates many dangling bonds at initially P-terminated steps. The resulting step edge has no similarities with the In-terminated one [Fig. 5(b)]. We suggest that the rebonding results in defect states compensating local step charges. This is in agreement with a general behavior of charged point-defect formation in III-V compound semiconductors due to the Fermi-level effect.[18] For example, newly generated positively charged defects tend to compensate existing negatively charged doping atoms.[19] The observed significantly smaller width of the denuded zone reflects the reduced charge.

In order to obtain a rough estimate of the charge density at the step edges, we modeled the step charge by a chain of equally spaced point charges. The step potential is obtained by the superposition of all potentials of the aligned point charges. The potential of a point charge $V_{PC}(r)=1/(4\pi\epsilon_0 6.8)(qe/r)\exp(-r/1.2\ \mathrm{nm})$ is taken from a measurement of the Coulomb repulsion between charged vacancies on the InP(110) surface.[10] The width of the denuded zone for different charge densities is then deduced from the superposed potentials using $V(x)=-kT\ln[c(x)/c_\infty]$. For a charge density of $+1e$ per lattice spacing a width of the denuded zone of 2.6–3.1 nm is obtained. Electron counting based on a defect molecule model yields an upper limit of the step charge of $+3e$ per lattice spacing. With this charge density the potential yields a width of 4.1–4.6 nm. From the comparison of the computed values with the data in Fig. 4 we can conclude that the step charge is most likely in the range of $+1e$ to $+3e$ per lattice spacing. The computed width of the denuded zone depends only very weakly on temperature. It changes by 0.3 nm if the temperature is raised from 395 to 480 K. This is below our experimental resolution. Finally, in order to obtain the smaller width of the denuded zone for the P-terminated steps close to [001] only $\frac{1}{3}$ of the charge density necessary to obtain the width for the In-terminated step was needed. This suggests that approximately two-thirds of the charge has to be compensated.

The charge cannot be localized only at kink sites, as suggested earlier.[7] Smooth step edges with very few kinks would have to carry an enormous charge at the kink sites to produce the observed width of the denuded zone. In addition, the direct observation of a charge-induced band bending in Fig. 1 was made for kink-free ⟨001⟩-oriented steps. No correlation of the width of the denuded zone with the kink density was found. Therefore the charge is localized along kink-free steps as well as at kink sites.

In summary, we have shown that cleavage steps on III-V(110) compound semiconductor surfaces carry charges and have localized defect states in the band gap before and after annealing. The magnitude of the charge is a function of the orientation and atomic termination of the step. Indium-terminated steps have a nearly constant charge independent of their orientation. Charges of phosphorus-terminated step edges vary strongly with their orientation. This is traced back to a partial compensation of the step charge by phosphorus desorption during annealing modulated by the geometric structure of the step. The existence of a charge along steps suggests that the present understanding of the influence of steps on growth should be reviewed in the light of possibly charged adatoms.

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