Direct Determination of the Interaction between Vacancies on InP(110) Surfaces

Ph. Ebert,[1,2] Xun Chen,[2] M. Heinrich,[1] M. Simon,[1] K. Urban,[1] and M. G. Lagally[2]
[1]*Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-5242, Jülich, Germany*
[2]*University of Wisconsin, Madison, Wisconsin 53706*

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The interaction potential between charged P vacancies on InP(110) surfaces is determined from scanning tunneling microscopy measurements of their correlation. It is found to have a functional form of a screened Coulomb potential except at very short distances. A vacancy charge of $+1e$ is derived from the measurements. The maximum repulsion is 65 meV and the range is 3 nm.

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The electronic properties of III-V compound semiconductors are to a significant part determined by defects. Point defects in the bulk, such as vacancies or antisite defects, can cause deep-level trap states that shift the Fermi energy and thus influence electronic and optical properties of the crystals. Similarly, interface defects and disorder can affect transport and luminescence, and defects at the surface can lead to localized states that bend bands and thus change the electrical properties of the surface. For example, the importance of surface defects in the formation of electrical contacts to compound semiconductors has long been recognized [1]. Scanning tunneling microscopy (STM) makes it possible to identify individual defects, providing the opportunity to explore their properties and consequently their influence on electronic and optical properties. Because of their simple reconstruction and reproducibility by cleavage, (110) surfaces of III-V semiconductors lend themselves well to model studies of defects. On such surfaces it has been possible to establish a direct correlation between their structural and electronic properties of vacancies [2,3]. The vacancies have localized electronic defect states in the band gap that are filled to the Fermi energy. Depending on the position of the Fermi energy the vacancies can have one of several charges [4,5] and consequently a different effect on the surface electronic properties. For example, if a point defect is charged, it induces a change of the potential in its vicinity. Knowledge of this potential is crucial for understanding the Fermi level pinning at semiconductor surfaces and metal-semiconductor interfaces. Although Fermi level pinning has been extensively investigated, essentially nothing quantitative is known about the magnitude and functional form of the change of potential induced by the charge of surface defects. Generally, it is assumed that surface defects are screened similarly to defects in the bulk, but that their screening is less effective, because charge carriers are only present in a half space. Thus the screening length should be longer on the surface than in the bulk. This assumption has, however, never been experimentally proved nor does it have any theoretical foundation deeper than what we have just stated.

In addition, it is difficult to determine the charge of surface vacancies. Several existing techniques [6–9] cannot be applied to surface defects, because of their lack of surface sensitivity. On semiconductor surfaces until recently it has been possible only to deduce the sign of the charge of vacancies, but not its magnitude [10,11].

In this Letter we provide the first quantitative measurement of the potential change induced by charged vacancies on a semiconducting surface. We probe this change by measuring the interaction potential between charged defects. We find good agreement of the data with a screened Coulomb potential of a single point charge. This agreement suggests a method to deduce the magnitude of the charge of surface defects from measurements of the interaction potential. We demonstrate the methodology on positively charged P vacancies on InP(110).

In our experiments *p*-type InP single crystals with a Zn dopant concentration of $(1.3–2.1) \times 10^{18}$ cm^{-3} were cleaved in UHV to form reproducibly clean (110) surfaces with low vacancy concentrations. These samples were annealed between 395 and 480 K for more than 24 h at a pressure of 5×10^{-9} Pa to form always positively charged P vacancies [12] and studied at room temperature with the STM. Images like that in Fig. 1 were obtained at negative tunneling voltage between -2.0 and -2.8 V. Positive charges will be screened by the holes in the valence band, forming around each vacancy a hole depletion zone (screening cloud) that induces band bending. The depression (dark zone) around vacancies confirms that the vacancies are positively charged.

The primary measurement to determine the interaction potential is the determination of the positional distribution function of the P vacancies. At the densities studied here, the mean distance between the vacancies ranges between 4.5 and 6.3 nm. Under the same experimental conditions, steps are surrounded by vacancy denuded zones about 10 nm wide. The existence of such denuded zones demonstrates that vacancies have sufficient mobility to move at least 20 lattice constants. As this distance is larger than the mean separation between the vacancies on the terraces, we can assume that the distribution

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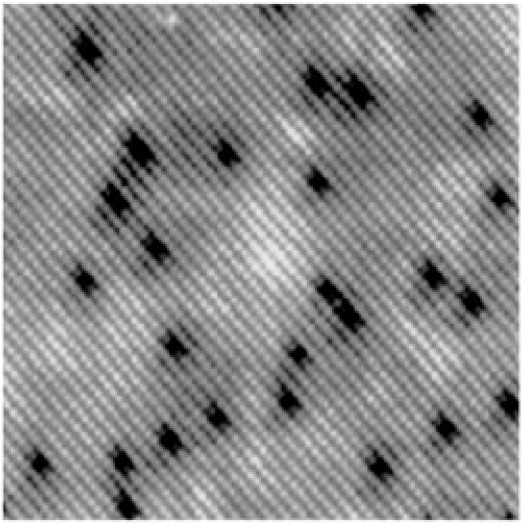

FIG. 1. Scanning tunneling microscope image of thermally formed P vacancies on an InP(110) surface. The image was acquired at −2.6 V tunneling voltage and shows the occupied surface states. The dark spots are the vacancies. Scan width 23×23 nm^2. If the tunneling voltage is changed, a dark zone appears around the vacancy. The magnitude of the depression is a function of the bias voltage and can be used to determine the surface screening length.

of vacancies far from steps is in thermal equilibrium. Results below will support this conclusion.

The interaction energy of the vacancies is obtained through a statistical analysis of the vacancy distributions. We calculated the distances between all possible pairs of vacancies to obtain a probability distribution of the pair distances, which we call the experimental pair distribution function. Dividing the experimental pair distribution function by one for noninteracting, randomly distributed vacancies results in the pair correlation function $c(r)$. This division is necessary to account for the increasing number of possible pair configurations with increasing separation. The pair correlation function $c(r)$ is related to the so-called mean force potential $W(r)$ through [13]

$$W(r) = -kT \ln[c(r)]. \qquad (1)$$

Using this procedure we determined the mean force potential for the P vacancies annealed at four different temperatures between 395 and 480 K, shown as data points in Fig. 2. For low vacancy densities the mean force potential equals the interaction energy between a pair of vacancies [13]. In the present case the vacancy density is $\sim 1\%$. Unless the interaction is very strong and long ranged, this concentration is low enough to obtain the pair interaction energy. We checked the validity of this low-density limit in a self-consistent manner by using the experimental probability distribution of pair distances and the deduced potential to calculate the total energy all other vacancies add on average to a vacancy pair. This additional energy is about 1 meV, lower than the achievable statistical error of the measurement. An estimation of the leading correction (or deviation) term in the relation between the pair interaction energy and the mean force potential [13] gives a similar result for the vacancy density used. Thus the potential in Fig. 2 corresponds with sufficient accuracy to the pair interaction energy.

Figure 2 shows that the vacancies have a repulsive interaction for distances up to 3 nm (about 5 to 8 lattice spacings depending on the crystallographic direction). The maximum repulsion of 65 meV is reached at distances between 1 and 2 bulk lattice spacings (0.6 to 1.2 nm). The results agree within errors for all measured temperatures, something that can be true only for equilibrium configurations.

An interaction between vacancies can have several origins, such as the formation of new defect states, structural relaxation, or a charge repulsion. The formation of new defect states by rehybridization can be excluded for the separations analyzed, because such effects are limited to directly adjacent vacancies. Lattice relaxations have been found theoretically [3] and experimentally [2] to extend to about the second-nearest-neighbor atoms. Figure 2 shows that an interaction exists up to 30 Å, which is definitively too far to be due to lattice relaxation. The charge of the vacancies will lead to a Coulomb repulsion. The strength of

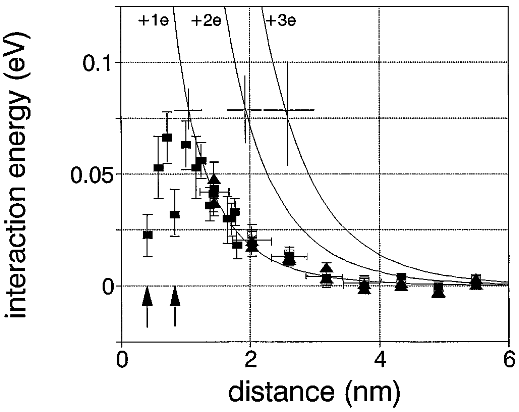

FIG. 2. Interaction energy between P vacancies like those in Fig. 1. The data points show the mean field potential $W(r)$, derived from the pair correlation function $c(r)$. The pair correlation function has been calculated from the vacancy positions measured in STM images. The y axis is the mean field potential derived using Eq. (1). It corresponds to the interaction energy between a pair of vacancies (see text), for annealing temperatures of (□) 395 K, (▲) 415 K, (∗) 455 K, and (■) 480 K. The error bars on these points reflect the experimental reproducibility. The solid lines correspond to the screened Coulomb pair interaction potential between vacancies that have one, two, or three positive screened charges. More than 7500 pairs are in the data points at distances below 3 nm, where the potential is larger than 0 (in total more than 130 000 vacancy pairs were considered). The bin size is ~ 0.6 nm for the data points at separation larger than 1.5 nm. The data points below 1.5 nm are for lattice sites. At very small separations, the deviation from the screened Coulomb potential of singly charged vacancies (solid line) is apparent. For distances equal to and larger than 2 lattice spacings the potential is isotropic and follows the screened charge repulsion. The crosses show the error bar of the calculated curves due to the measurement uncertainty of the screening length.

this interaction is governed by the magnitude of the charge and by its screening. As no theoretical support exists for screening of surface charges, we will first turn to the derivable case: screening in the bulk. In a semiconductor crystal the charge associated with point defects is screened by the electrons and/or holes [14]. In a semiclassical approximation the interaction potential of a screened point charge q acting on another with the same charge q has the form of a screened Coulomb potential [14]

$$V(r) = (1/4\pi\epsilon_0\epsilon_{r(\mathrm{eff})})\,(q^2/r)\exp(-r/R_B)\,, \qquad (2)$$

where r is the distance between the vacancies and R_B is the bulk screening length. The key question is whether this equation represents an acceptable approximation to the interaction potential between two charges on a surface. The screening at the surface should be between that in vacuum (no screening) and that in the bulk. The form of a screened Coulomb potential is valid in both cases. On the surface we are at the boundary of these two cases and we would expect that the potential has an ellipsoidal form. In our case the problem is, however, simplified by the fact that the vacancies interact in a two-dimensional plane and the spherical symmetry of the bulk screening and the cylindrical symmetry of the boundary problem cannot be distinguished.

In the absence of any theory for surface screening it appears natural to take the functional form of a screened Coulomb potential as a first trial assumption. The parameter r in Eq. (2) is then the *separation on the surface* and, most importantly, R_B must be replaced by the surface screening length R_S. Furthermore, we must use the dielectric constant of the surface, which we assume to have the classical electrodynamic form $\epsilon_{r(\mathrm{eff})} = \frac{1}{2}(\epsilon_{\mathrm{InP}} + \epsilon_{\mathrm{vac}})$ [15]. The magnitude of the interaction energy $V(r)$ and its range are governed by the charge q and by the screening length R_S. From the downward band bending in the STM images we already know that the vacancies are positively charged. Theory shows [3] that the vacancy has three possible positive charges: $+3e$, $+2e$, or $+1e$. We will need to consider all possibilities in determining $V(r)$.

The screening length R_S depends only on the concentration of the charge carriers and the dielectric constant (at least in the bulk) [14]. We can determine the screening length independently from the band-bending-induced height changes in the STM images [11]. The height change reflects the reduction, due to band bending, of the local density of surface states available for tunneling and thus the screening itself. The height change Δz in the image can be approximated by [11]

$$\Delta z = \Delta z_0 \exp(-r/R_S) + \text{ const}\,. \qquad (3)$$

It has been shown previously that this method yields good estimations of the screening length on GaAs(110) surfaces [16]. Fitting this equation to height profiles across vacancies yields a screening length of 1.05 ± 0.15 nm. A second way to obtain the screening length has been proposed by Stroscio and Feenstra [17]: If one solves the Poisson equation in cylindrical coordinates and uses the assumption that the variables are separable, the potential at the surface should have the functional form of the zeroth-order modified Bessel function $K_0(r/R_S)$. This Bessel function can be approximated by $r^{-1/2}\exp(-r/R_S)$. Applying this formulation to the measured potential yields a screening length of 1.2 ± 0.15 nm. These independently deduced values of the screening length agree well with each other; for the following analysis we will use their mean value (1.13 nm). It should be noted that for distances of $r > R_S$ all three normalized potentials (Bessel, approximation for Bessel, and screened Coulomb function) are very close to each other and it is difficult to discriminate between them. Deviations occur only at small separations, another indication that the screened Coulomb potential is a reasonable first approximation.

The screening length for the surface determined by the above methods is considerably smaller than the bulk screening length of 2.9 to 3.7 nm calculated for the dopant concentrations of the samples [14], in contrast to the intuitive expectation that the surface screening is less effective than screening in the bulk, due to the missing half space. The large difference suggests either that additional surface charge carriers (due to surface states) exist and add to the screening or that the effective mass of near-surface charge carriers differs from that of bulk charge carriers [18]. We provide here the experimental corroboration and an approximate description of the potential.

We proceed using Eq. (2) with parameters appropriate for the surface and calculate the interaction energy for the three possible different charge states $+1e$, $+2e$, and $+3e$. The results are shown as the solid lines in Fig. 2. There are no free fitting parameters. Agreement with the data (for separations larger than 1.2 nm) is found only for the potential calculated for a singly charged vacancy.

We can conclude that a repulsive screened Coulomb interaction is responsible for the long-range interaction between vacancies. There may, however, be other interactions that influence the potential at small separations. Figure 2 shows that for distances smaller than about 2 lattice constants (1.2 nm) the measured values lie below the screened Coulomb potential. The deviation goes toward a lower repulsion. Two specific lattice separations (0.7 and 1.4 bulk lattice constants, marked by arrows), which correspond to vacancies aligned along the $[1\bar{1}0]$ direction (the closed-packed atomic rows), have a particularly low interaction energy. Positively charged P vacancies on InP(110) have measurable lattice relaxations that reduce the buckling of the surrounding surface up to the second-nearest atom [2,3]. STM images show that similar lattice relaxation exists also between two close vacancies in the $[1\bar{1}0]$ direction for separations of up to about 3 lattice spacings or about 1.2 nm. These results suggest that at least part of the deviation from the screened Coulomb potential is due to lattice relaxation. The range of reduced repulsion is ~1.2 nm, which is similar to that of structural-relaxation-induced interactions of dimer vacancies on Ge-covered Si(001) [19]. No systematic deviation from isotropy (within the error margin) exists for distances above about 2 lattice constants (1.2 nm), as expected from the isotropic nature of the screened Coulomb interaction.

The vacancies may also have a non-point-like charge distribution. A deviation from the screened Coulomb potential for such a charge distribution would have its largest effect at small distances. A recent analysis of tip-induced migration events showed, however, that the states of the vacancy are spatially quite localized [20], suggesting that the charge connected with these states is similarly confined. Thus the approximation of a point charge is sufficient for distances larger than one unit cell from the vacancy.

The determination that the vacancy charge is $+1e$ makes it possible to draw conclusions about the position of charge transition levels and defect states. The energy of a charge transition level, $[n - 1/n]$, is the value of the chemical potential at which the charge of the vacancy changes from $(n - 1)e$ to ne [4,5]. The P vacancy has three two-electron defect levels, into which 2 electrons must be filled to have a single positive charge. Thus the charge transition levels $(1+/2+)$ and $(2+/3+)$ are both below the Fermi energy. Because the Fermi energy in our crystals is very close to the valence band maximum, the two mentioned charge transition states must lie in the valence band. Furthermore the lowest defect state must be in the valance band, otherwise it could not be completely filled. Combining these results with a previous measurement [2] we can also state that the only charge transition level in the band gap involving positively charged vacancies is that from uncharged to single positive charge $(0/+)$.

In summary, we have shown that it is possible to determine directly the interaction energy between vacancies on the surface and its dependence on the vacancy separation from correlation functions of their positions obtained from STM images. For P vacancies on InP(110), the interaction is repulsive with a maximum value of 65 ± 15 meV at a separation of 1.2 nm. Below this separation we observe a reduced repulsion, which we attribute to structural relaxation. The reduction in repulsion is anisotropic, being greatest in the low-index direction, in which the relaxation is easiest. The repulsion falls to zero at about 3 nm.

For P vacancies in InP(110) the interaction potential can be fitted with a screened Coulomb potential for distances above two lattice constants. A vacancy charge of $+1e$ is determined. A measured screening length of 1.13 ± 0.15 nm and a surface dielectric constant taken as the mean of the bulk InP and vacuum values are used in the potential. The surface screening length is smaller than that of the bulk, suggesting either that additional charge carriers above the bulk doping level exist in the surface region due to surface states or that the effective mass of the near-surface charge carriers differs from those in the bulk.

We believe that the use of STM-based determinations of positional correlation functions is a quite general way to obtain point defect interaction energies and interaction potentials. Such measurements may also serve as the basis for comprehensive first-principles theoretical treatments of surface screening, which are so far unavailable.

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Note added.—After the initial submission of this paper a different method to determine the charge of a vacancy was proposed by Chao, Smith, and Shih[21], based on charge compensation between charged vacancies and dopant atoms. It yields a charge of $+1e$, corroborating our result.

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