Surface induced asymmetry of acceptor wave functions

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Surface Induced Asymmetry of Acceptor Wave Functions

C. Çelebi, J. K. Garleff, A. Yu. Silov, A. M. Yakunin, and P. M. Koenraad

COBRA Inter-University Research Institute, Department of Applied Physics, Eindhoven University of Technology,
P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands

W. Van Roy
IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

J.-M. Tang
Department of Physics, University of New Hampshire, Durham, New Hampshire 03824, USA

M. E. Flatté
Optical Science and Technology Center and Department of Physics and Astronomy, University of Iowa, Iowa City, Iowa 52242, USA
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Measurements of the local density of states of individual acceptors in III–V semiconductors show that the symmetry of the acceptor states strongly depends on the depth of the atom below a (110) surface. Tight-binding calculations performed for a uniformly strained bulk material demonstrate that strain induced by the surface relaxation is responsible for the observed depth-dependent symmetry breaking of acceptor wave functions. As this effect is strongest for weakly bound acceptors, it explains within a unified approach the commonly observed triangular shapes of shallow acceptors and the crosslike shapes of deeply bound acceptor states in III–V materials.

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In the past decade many groups have scrutinized at the atomic scale the electronic and spectroscopic details of individual impurities, such as Si, Zn, and Mn, embedded in the topmost layers of a cleaved semiconductor crystal like GaAs or InAs [1–6]. A correct interpretation of these atomistic properties is essential for a proper understanding of the macroscopic properties of doped materials. For example, present models of impurity band formation and ferromagnetism [7] in GaMnAs require a proper description of the atomic scale properties of individual Mn acceptors. The surface, however, is known to strongly influence the properties of an impurity close to the surface [8], and thus a central question for all such surface measurements via cross-sectional scanning tunneling microscopy (XSTM) is how closely the local density of states (LDOS) is related to properties of an impurity in the bulk. Several groups have interpreted the XSTM contrast of acceptors as being directly related to the wave function of the impurity state [2,3,5,6], while others have proposed that highly asymmetric observed acceptor shapes arise from hybridization of the impurity state with excited states [4] or intrinsic surface states [9].

Here we report measurements and calculations of the LDOS of individual Mn acceptors in GaAs as a function of their distance below the reconstructed surface, and show that the XSTM contrast can be fully understood from the wave function of the impurity state. The contrast changes from a highly asymmetric shape, for Mn acceptors in the topmost layers, to a symmetric shape, for Mn acceptors at 8 atomic layers (AL) below the surface. By comparison of measurements with theoretical calculations we identify strain, induced by the surface reconstruction, as the dominant cause of the depth-dependent asymmetry of the LDOS for these energetically deep Mn acceptors in GaAs (E_a = 113 meV). We conclude that the LDOS of a Mn acceptor deep enough below the surface reflects the properties of the unperturbed acceptor state. For shallowly bound impurities like Zn in GaAs (E_a = 31 meV), with larger Bohr radii, this situation is never reached, and thus the observed LDOS of shallowly bound impurities is always strongly affected by the surface strain. Thus we resolve the longstanding controversy of XSTM contrast as due to the acceptor wave function, and simultaneously resolve the source of the very asymmetric LDOS of shallowly bound acceptors [10].

The XSTM experiments are performed on molecular-beam-epitaxy grown Mn doped GaAs and liquid-encapsulated Czochralski grown Zn doped GaP and Cd doped GaP samples. The concentration of Mn in the GaAs epilayer was 2 × 10^{18} cm^{-3}. The bulk concentration of Zn in GaP and Cd in GaP was close to 5 × 10^{17} cm^{-3}. A clean and atomically flat surface was obtained by cleaving the samples inside the ultrahigh vacuum STM chamber with a base pressure P < 2 × 10^{-11} torr. The topography scans were carried out on the (110) sample surface by using electrochemically etched polycrystalline tungsten tips that were further treated in vacuum as described in [11]. The measurement presented in Fig. 1 was acquired at T = 5 K in constant-current mode and the tunnel setpoint V_s = +1.55 V, I_t = 50 pA.

The topography image of Mn doped GaAs (Fig. 1) shows a number of Mn induced contrasts at the
GaAs(110) cleavage surface. The numbers in the image correspond with the position of Mn acceptors below the GaAs(110) surface, where 1 indicates the surface layer. The depth determination and hence the labeling are done according to the relative intensity and symmetry of the Mn induced contrasts. The structure p displays the typical shape of a Mn atom that is coupled to an adsorbate in the GaAs surface layer. The characteristics of the LDOS of these Mn related features were studied in detail elsewhere [11, 12]. Similar to the Mn acceptors in InAs [5], we observe that Mn displays a contrast which changes from a trapezoidal to a crosslike pattern as a function of the depth below the GaAs(110) surface. Unlike deeply buried Mn, the contrast of a Mn acceptor close to the surface has a smaller extension and is more asymmetric in the GaAs(110) mirror plane. The contrast of the Mn acceptor located deeper than 8 AL below the surface (corresponding to the label 9 in Fig. 1) has a highly extended profile which is asymmetric only around the topography maximum. A similar profile of the Mn wave functions has been found in tight-binding (TB) calculations [13].

A pronounced quantitative depth dependence in the (001)-reflection asymmetry of the Mn acceptors can be seen in Fig. 2 where Fig. 2(a) depicts the measured height profiles of the Mn acceptors that are located between 2 and 8 AL below the surface. The profiles shown in Fig. 2(a) were obtained by averaging a number of parallel STM traces taken in the [001] direction across the center of the Mn acceptor contrast. The width of the box, in which the parallel [001] traces are averaged, is typically 0.5 nm in the [110] direction. To quantify the observed trends in the depth-dependent change of the Mn symmetry, the background atomic corrugation is filtered out from the topography line profiles by a fast Fourier transform (FFT) technique, and shown in Fig. 2(b).

The asymmetry (skewness) of these envelope profiles is quantified by a standardized third moment, $\mu_3 = \left[\int_{-\infty}^{\infty} (r - \bar{r})^3 Z(r)dr\right]/\sigma^3$, where $Z(r)$ corresponds to the envelope profile and $\sigma$ is the standard deviation of this profile. The third moment and thus the degree of asymmetry increase substantially for the Mn atoms closer to the GaAs(110) surface. Figure 2(c) shows the transition from the symmetric bulklike behavior to a strongly asymmetric shape for near surface Mn acceptors, with an interesting alternation between the Mn acceptors located in an odd or even layer.

Previously we have shown that multiband TB calculations are extremely useful to understand the spatial properties of acceptor states in III–V semiconductor materials [3, 14] and therefore we use again the approach developed in [15]. The results of the TB calculations for an unstrained bulk GaAs lattice, as presented in Fig. 3(b), show also an even or odd alternation which varies between $\mu_3 = 0.07$ and $\mu_3 = 0.08$ for even and odd layers, respectively. The measured $\mu_3$ for the calculated wave function is somewhat smaller than the experimentally obtained results which vary from 0.12 to 0.2 on average for deeply buried Mn acceptors. This demonstrates that, for depths greater than 8 AL below the surface, the asymmetry of the bulk calculations is similar to that found experimentally. This observation is in contradiction with the prediction in Ref. [9]. The errors in modeling in [9] can likely be traced to the neglect of the $p-d$ exchange interaction and the resulting error in the relative weight between the $T_2$–like and the $E$–like envelope functions [3].
In Fig. 3 we compare the topography images of the Mn acceptors located at different depths [Fig. 3(a)] with the corresponding TB calculations either in the absence [Fig. 3(b)] or in the presence [Fig. 3(c)] of a uniform strain. The TB calculations for an unstrained bulk lattice are sufficient to explain the spatial structure of Mn acceptors deep below the surface [3,5], but obviously fail for the acceptor states located near the surface. Recently we have shown that the shape of an acceptor wave function is highly sensitive to the local strain around an InAs quantum dot in GaAs [16]. The (110) surface of III–V semiconductors such as GaAs and InAs is relaxed and the shift in the lattice near the surface [17,18] is described by a depth-dependent strain. To approximate the case of a relaxed GaAs surface within the TB model, the Ga lattice is shifted by 1.4 pm (0.25% of the GaAs lattice constant) with respect to the As lattice along the [110] direction. The displacement between the two lattices is relatively small and corresponds to 10% of the actual vertical displacement between the Ga and As sites in the first subsurface layer below the GaAs(110) relaxed surface [17]. The applied shift in TB calculations induces a homogeneous internal strain in the GaAs(110) relaxed surface [17]. The applied shift in TB calculations induces a homogeneous internal strain in the GaAs(110) relaxed surface [17]. The applied shift in TB calculations induces a homogeneous internal strain in the GaAs(110) relaxed surface [17]. The applied shift in TB calculations induces a homogeneous internal strain in the GaAs(110) relaxed surface [17]. The applied shift in TB calculations induces a homogeneous internal strain in the GaAs(110) relaxed surface [17]. The applied shift in TB calculations induces a homogeneous internal strain in the GaAs(110) relaxed surface [17]. 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FIG. 3 (color online). (a) (5 × 5 nm²) XSTM topography images of single Mn acceptors located between 2 and 4 AL underneath the GaAs(110) surface. Calculated (5 × 5 nm²) cross-sectional TB view of Mn LDOS either in (b) the absence or in (c) the presence of a homogeneously strained Ga(Mn)As unit cell. The position of the Mn atom is indicated by a white spot. All the TB cross-sectional images retain a spin polarization oriented along [001] direction.
The excited states retaining the zinc blende tetrahedral ($T_d$) symmetry show a different angular appearance from its previously reported triangular appearance near the (110) surface. Cd showing this peculiar LDOS in GaP is very different from Cd state in GaP. The Zn LDOS is highly extended over the GaP(110) surface and shows a strong asymmetry in the [001] direction. For a fixed depth of an acceptor below the surface, the interaction of the bound hole with the surface relaxation induced strain changes the shape of the Mn wave function symmetry near the surface of III–V materials. With respect to the calculations presented in [9], which predicts the wrong asymmetry for acceptors deep below the surface, we argue that contrary to their explanation we image the acceptor wave function directly and that the surface relaxation related strain is the key component which explains the broken symmetry of both energetically shallow and near surface energetically deep impurities and the depth dependence of the symmetry breaking of deep acceptors in a unified approach.

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FIG. 4 (color online). (6.5 × 6.5 nm$^2$) topography images of single (a) Mn:GaAs, (b) Cd:GaP, and (c) Zn:GaP acceptors located at 5 ÅL below the (110) surface of the corresponding host crystal. The tunneling setpoint is the same for all the measurements ($V_g = +1.55$ V, $I_t = 50$ pA).

major contribution from the ($T_d$) symmetry of the bulk crystal.

We now extend this analysis to other acceptors and hosts. Observations of the asymmetry of true Coulombic impurities like C, Be, and Zn [with ground state binding energies ($E_a$) around 30 meV in InP and GaAs] show much more pronounced triangular shapes than Mn. It is known that these shallow acceptors display a triangular contrast which extends laterally ~5 lattice constants on the cleavage surface [2,4,6,10]. Proposed explanations for the triangular appearance of the shallow acceptors include the electronic configuration of the outer shell d electrons of different acceptor species [10], wave function mapping of the excited states retaining the zinc blende tetrahedral ($T_d$) symmetry [4], and a resonant tunneling process involving evanescent states [6].

In Fig. 4 we compare the XSTM topography images of three acceptors with different binding energies [20] in GaAs and GaP. Each acceptor is located at 5 ÅL below the (110) surface of the respective host crystal. The acceptors with relatively large binding energy such as Mn:GaAs ($E_a = 113$ meV) [Fig. 4(a)] and Cd:GaP ($E_a = 102$ meV) [Fig. 4(b)] display identical crosslike LDOS at the (110) surface. Cd showing this peculiar LDOS in GaP is very different from its previously reported triangular appearance in GaAs ($E_a = 35$ meV) [2]. This clearly indicates that the shape is related to the acceptor state and is not determined by the intrinsic property of the dopant. The response of the hole bound to Zn, with a binding energy of 70 meV in GaP [Fig. 4(c)], to the same strain field, is rather different from Cd state in GaP. The Zn LDOS is highly extended over the GaP(110) surface and shows a strong asymmetry in the [001] direction. For a fixed depth of an acceptor below the surface, the interaction of the bound hole with the surface relaxation induced strain changes with acceptor binding energy. The reduction of the LDOS symmetry with the binding energy is thus somewhat analogous with the depth-dependent change of the contrast symmetry. Acceptors with a smaller binding energy have a larger effective Bohr radius and thus their wave functions couple more strongly with the surface strain than the energetically deep acceptor states which are more spatially localized. This argument addresses why all the shallow acceptors such as C, Zn, and Be in GaAs appear as triangular features in STM measurements [2,4,6,10].

XSTM has been used to investigate the LDOS of various acceptor states near the (110) semiconductor surface on the atomic scale. The experimentally observed depth-dependent change of the Mn wave function symmetry was characterized quantitatively and interpreted successfully by TB calculations. We were able to show within the TB model that, without a detailed description of the reconstruction of the near surface layers and a vacuum half-sphere, the strain due to the relative displacement between the cation (Ga) and the anion (As) sublattices is responsible for the experimentally observed reduction of the bulk acceptor wave function symmetry near the surface of III–V materials. With respect to the calculations presented in [9], which predicts the wrong asymmetry for acceptors deep below the surface, we argue that contrary to their explanation we image the acceptor wave function directly and that the surface relaxation related strain is the key component which explains the broken symmetry of both energetically shallow and near surface energetically deep impurities and the depth dependence of the symmetry breaking of deep acceptors in a unified approach.

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