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Enhanced Donor Binding Energy Close to a Semiconductor Surface

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We measured the ionization threshold voltage of individual impurities close to a semiconductor-vacuum interface, where we use the STM tip to ionize individual donors. We observe a reversed order of ionization with depth below the surface, which proves that the binding energy is enhanced towards the surface. This is in contrast to the predicted reduction for a Coulombic impurity in the effective mass approach. We can estimate the binding energy from the ionization threshold and show experimentally that in the case of silicon doped gallium arsenide the binding energy gradually increases over the last 1.2 nm below the (110) surface.

The big success of semiconductors started as soon as it became possible to prepare clean materials that allowed one to dope the material in a controlled way and to tailor the electronic properties to create functional devices. Since then the study of dopants in semiconductors has been the subject of major attention. A main goal of research was to find impurities with a sufficiently low binding energy E_b, such that they act as donors and acceptors, which can easily be ionized at room temperature. They provide free carriers in the conduction band (CB) or the valence band (VB), respectively. Even though it can still be a challenge to find good doping elements especially for new semiconductor materials, e.g., a shallow acceptor for gallium nitride [1] and magnetic impurities [2], appropriate bulk dopants have been found for the commonly used materials such as silicon (Si) and gallium arsenide (GaAs). Having large binding energies, deep level defects were a problem because they act as traps that reduce the carrier density. Therefore the binding energy is of crucial importance to characterize a dopant atom. The binding energy in nanoscale devices has become a matter of research in recent years. Experimental efforts have been taken to measure E_b of dopants as a function of the device dimensions [3–5] revealing a slight increase for nanoscale devices. In these experiments, the precise positions of the dopants with respect to the interfaces were not known.

Effective mass theory of Coulomb impurities predicts a reduction of E_b close to a barrier [6]. However, for low dimensional systems an enhancement is expected due to image charges, as was shown by the tight binding method for quantum rods [7] and by density functional theory (DFT) calculations for nanocrystals [8]. However, in the case of the semi-infinite semiconductor-vacuum interface, the image charges cause a minor effect, and our calculations show the expected reduction of the binding energy

towards the surface. In contrast DFT calculations that include the surface reconstruction predict a deep state for Si donors in the first layer of GaAs(110), corresponding to $E_b \approx 0.5$ eV [9], which was attributed to the dangling bond of the surface donor. These calculations are only done for Si donors *in* the surface layer and not for subsurface layers.

In this Letter we present a method to measure the binding energy of individual dopants close to a semiconductor surface. We measure the threshold gate voltage V_{th} that is needed to ionize individual silicon donors close to the GaAs surface with the STM tip [10]. From V_{th} we can estimate the binding energy and show that it gradually increases towards the surface. In contrast to transport experiments [3,4] we have full knowledge of the position of the addressed impurity on the atomic scale. Our result is important for the functionality of devices, because the scanning tunneling microscope (STM), especially on a semiconductor surface, resembles the geometry of a metal-oxide-semiconductor field-effect transistor (MOSFET) structure. Both consist of a metal (gate or tip) on top of an insulating layer (oxide or vacuum) that induces a field in the semiconductor underneath, used to control the charge density. Following this analogy, the electrostatic potential that is induced by the STM tip, known as tip-induced band bending (TIBB) [11,12], corresponds to the gate depletion potential in a MOSFET.

In our experiment we use the GaAs(110) cleavage surface. Among the dopant atoms of technical importance, we chose the Si donor in GaAs because its properties and contrast in STM and scanning tunneling spectroscopy (STS) are well understood [13–15]. Furthermore Si in GaAs is *the* model hydrogenic donor. The depth of individual Si donors below the GaAs(110) surface can be extracted from STM topographies [16]. Furthermore, we

have recently shown that STM provides full control over the charge state of individual Si donors below the GaAs surface [10]. STM and STS provide unrivaled sensitivity to surface properties, which is crucial for studying the ionization of donors at different depths below the surface. For the investigations we used a low temperature STM operated at 5 K and a base pressure of 10^{-11} mbar. The tips were electrochemically etched from polycrystalline tungsten wire. Further preparation in UHV [17] guaranteed sharp tips of atomic resolution and stability over days in STS use at low temperature. We cleaved samples from commercially available Si-doped GaAs wafers with an average doping level of 3×10^{18} cm^{-3}.

Because of the unpinned Fermi level E_F at the GaAs(110) surface, the metallic STM tip modifies the electronic bands in the semiconductor [11,12]. A depletion area is formed underneath the tip when a positive sample voltage is applied, which decays both laterally and into the bulk. The decay of the TIBB as a function of depth below the surface is schematically shown in Fig. 1(d). As a result of the sharp tips that we use, the lateral extension of the depletion area is only a few nanometers. Because of the absence of surface states in the band gap [18], the bands are not intrinsically bent [10]. Therefore the donor will be neutral when the tip is laterally removed from it. When the tip approaches the donor, the bands at the donor position are lifted by the TIBB. When a sufficiently high sample voltage is applied, the electron is repelled from the donor core and released into the bulk CB. The remaining positive core charge causes a sudden local drop of the bands at the donor position. This ionization process is visible as rings in the dI/dV maps; see, for example, Figs. 1(a)–1(c).

The ionization process has recently been characterized quantitatively with respect to the sample voltage and tip-sample distance [10], and was also observed for Mn acceptors in InAs [19]. It was shown that each donor ionizes at a specific TIBB of $\sim$150 meV, which varies from donor to donor. We extracted the voltage dependent diameter of the rings surrounding the donors. The result in Fig. 2(b) shows that the ring diameter increases with voltage. The error bars reflect the spectroscopic resolution. When the sample voltage is smaller than the threshold voltage V_{th}, the TIBB is not sufficient to ionize the donor even when the tip is located directly on top of the donor.

In order to experimentally investigate the depth dependence of the binding energy, we first determined the depth of each donor below the surface. The contrast amplitude of the donors in constant current images and the odd-even symmetry [13,16] of the donor contrast with respect to the underlying GaAs lattice is used to determine the depth. Applying this to the donors in our measurements, as shown in Figs. 1 and 2, we find that donors deeper below the surface have a lower V_{th}. This is clearly seen in the dI/dV maps taken at different voltages shown in Figs. 1(a) and 1(c). The rings of ionization for the donors in layers 5 and 6 [Fig. 1(a)] appear already at 0.09 V, but a much higher voltage, up to $\sim$1 V, is needed to ionize the donors closer to the surface [Fig. 1(c)]. The same dependence of V_{th} on depth is experimentally observed in Fig. 2(c). V_{th} differs between Figs. 1 and 2 by $\sim$1 V for donors at the same depths due to differences in the flat band
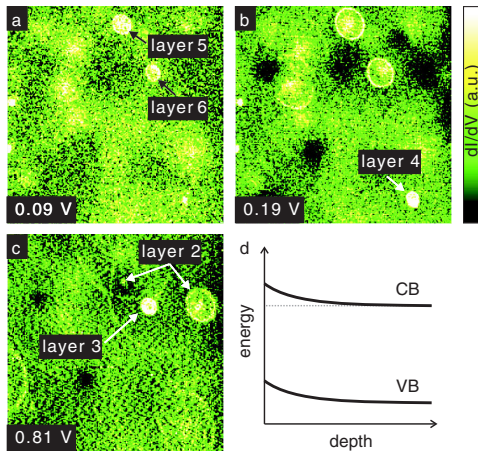

FIG. 1 (color online).   (a)–(c) Voltage dependent dI/dV maps obtained on the (110) surface of Si-GaAs showing the rings of ionization around the Si donors. All three images are of the same area of the sample. The image size is 48×48 nm^2. The layer in which the donor is situated is indicated, counting the surface layer as 1. The rings of ionization clearly appear at lower voltages for donors deeper below the surface. (d) Schematic energy diagram including the TIBB in the homogeneous approach.
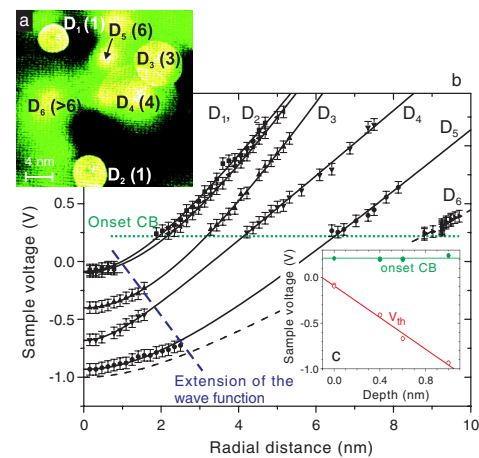

FIG. 2 (color online).   (a) dI/dV map at 0.24 V. This measurement is obtained with a different tip than the one shown in Fig. 1. The numbers in brackets refer to the layer in which the donor is situated, counting the surface as 1. (b) Voltage dependence of the ring radius. The lines are added to guide the eye. (c) V_{th} (open red dots) and the onset of tunneling into the bulk CB (solid green dots) for D_1 to D_5, where the horizontal axis represents the depth of the donor below the surface.

condition. Note that the onset of tunneling into the bulk CB (green dots) is at a constant voltage for all donors.

We interpret our data in the following way based on two assumptions. First the TIBB decays monotonically into the sample. Second, the vacuum barrier pushes the wave function toward the bulk, especially for donors close to the surface. However, effective mass calculations confirm that the center of mass of the wave function comes closer to the surface with decreasing depth of the donor impurity. Therefore the effect of the TIBB is always stronger for donors closer to the surface than for donors deeper in the material. Based on this we expect that a donor close to the surface should ionize at a lower TIBB, i.e., a lower sample voltage, than a donor that is located deeper below the surface. As we observe the opposite in our experiment, the binding energy must be enhanced for donors close to the surface. In a homogeneous model, where the donor level is rigidly shifted with the bands, the binding energy would correspond to the TIBB at the donor position. A large fraction of the externally applied voltage drops across the vacuum barrier; a sample voltage of ~ 1 V corresponds to a TIBB of ~ 150 meV as is shown in Figs. 3(a) and 3(b) [12]. The spreading of the data points in Fig. 3 is due to the Coulomb interaction of the randomly distributed donors, giving rise to local fluctuations of the potential. In the next
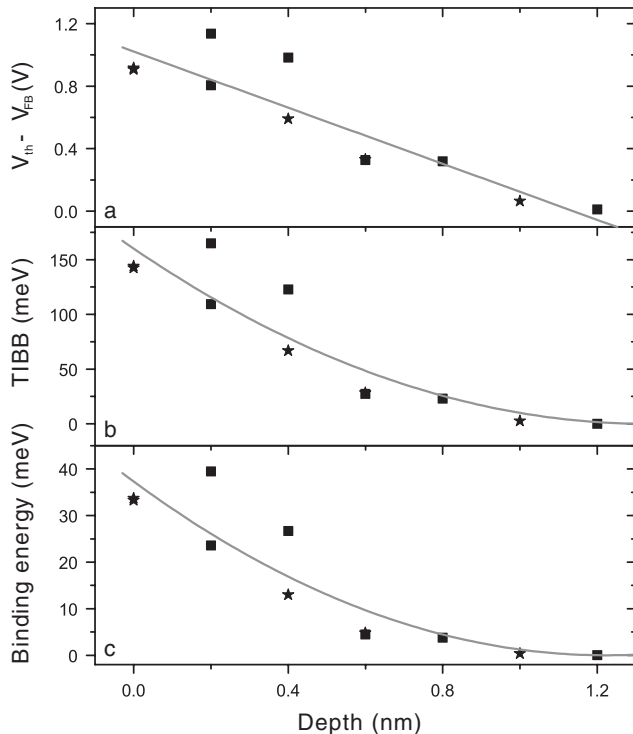
paragraph we discuss how to derive the binding energy [Fig. 3(c)] from the TIBB.

Because of the ultrasharp tips that we use [10], the TIBB extends in the bulk less than the bulk Bohr radius of Si in GaAs of 10.3 nm. Instead of a rigid shift of the donor level, the TIBB "squeezes" the Coulomb potential of the donor, as shown in Fig. 4. The red dotted line represents the TIBB and the solid black line depicts the bare Coulomb potential. The superposition of the TIBB and the Coulomb potential is represented by the blue dash-dotted line, and is shown in 3D in the inset. The donor potential is squeezed by the TIBB, and therefore its energy level is shifted upward. When this shift equals the binding energy and the state becomes resonant with the conduction band in the bulk, the donor ionizes. The magnitude of this shift can be estimated by the overlap between the wave function of the donor and the TIBB: $\Delta E = \int \Psi \times (\text{TIBB}) \times \Psi^* d^3 r$ [20]. The TIBB calculation contains a number of assumptions (e.g., tip shape, tip-sample distance) resulting in an uncertainty on the order of a factor of 2. The bigger challenge is to find the correct Ψ. As a first guess, we use the 1 s wave function of the bulk donor and modify the Bohr radius according to our measurements as described in the following paragraph.

The extension of the LDOS of the donors as observed in our STS data is indicated by the dashed blue line in Fig. 2(b). It decreases by a factor of ~ 2 for donors closer to the surface, corroborating the enhanced binding energy. The donor LDOS as measured in the STS is a projection of the real 3D wave function—where the real wave function as well as the details of the projection are not known. Thus the measured extension does not directly equal the Bohr radius, but we assume that the extension of the 3D wave function scales similarly as the contrast we observe experimentally, and thus reduces by a factor of ~ 2 for donors near the surface. The deepest donors that are visible ionize at a low TIBB, see Fig. 3(b), as expected for a bulklike donor. We therefore assume that those donors have the bulk Bohr radius of 10.3 nm. We scale the Bohr radius by a factor of up to 2 for donors closer to the surface to extract an *estimate* of the binding energy as a function of depth

FIG. 3. (a) V_{th} relative to the flat band voltage (V_{FB}), (b) the corresponding TIBB at the donor position and (c) the estimated binding energy (see text for details). The squares and stars refer to the measurement shown in Fig. 1 and 2 respectively. The solid lines are added to guide the eye.
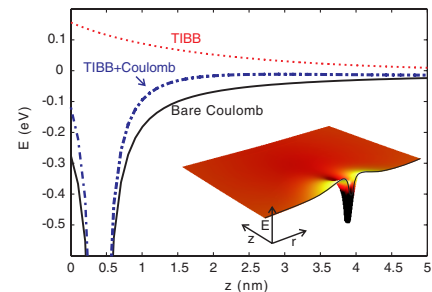

FIG. 4 (color online). Comparison of a bare Coulomb potential (solid black line) with the TIBB (red dotted line), where the tip is located on top of the donor. The blue dash-dotted line represents the superposition of the Coulomb potential and the TIBB, which is shown in 3D in the inset.

below the surface. The result is plotted in Fig. 3(c). Keeping the discussed limitations of our approach in mind, we find that the estimated binding energy increases from a bulklike value (within the spectroscopic resolution of our instrument of a few meV) for donors located 1.2 nm below the surface to ~40 meV for the donors close to the surface.

The enhanced binding energy towards to surface is surprising. Effective mass theory of Coulomb impurities near a vacuum barrier predicts a reduction of the binding energy, and thus does not describe donors close to surface particularly well. Since it is a powerful approximation to calculate shallow donors in the bulk we have used it to discuss trends in the binding energy by artificially modifying the dielectric constant ϵ_r and the effective mass m^* in a plausible way. DFT calculations show that the dielectric constant is reduced near the surface [21]. The broken symmetry and buckling distort the lattice at the surface, which might invalidate single-band effective mass theory and require a multiband theory. Both effects are expected to increase the binding energy for donors close to the surface [5,22]. We can only speculate whether these are the true reasons for the enhanced binding energy or that other effects are involved. DFT calculations predict $E_b \approx$ 0.5 eV [9] for a Si atom in the surface layer of GaAs(110). This was attributed to the half-filled dangling bond. Therefore this calculation does not explain the observed gradual increase. The observed enhanced binding energy could also be caused by the strain field near the surface [23,24], which is induced by the buckling and decays into the material on a roughly similar length scale as the enhanced binding energy.

In summary, we have presented a method for estimating the binding energy as a function of depth below the surface. In the case of Si-GaAs we find an enhancement of the binding energy, with an estimated value of ~40 meV, in contrast to the predicted reduction within the effective mass model. We conclude that the effective mass approach fails for Si in GaAs, which is a model hydrogenic donor in bulk GaAs, and we expect the same failure for all hydrogenic donors close to a semiconductor surface.

The enhanced binding energy will have strong implications for devices. Current device simulations [25] take the random distribution of the dopant atoms into account to calculate the microscopic potential, but adopt E_b as determined in the bulk [1]. The enhanced binding energy close to the surface leads to freezing out of the carriers. Also the observed reverse order of the ionization, which starts with

dopants that are located ~1.5 nm below the surface and propagates towards the surface, modifies the operation of a nanoscale device.

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