

Interpretation of orientational contrast in STM images of GaAs(1 1 0) cleavage surface

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Abstract

The electronic structure of GaAs(1 1 0) surface is analyzed using Density Functional Theory (DFT-GGA) in atomic orbital basis (LCAO). The surface orbitals and the corresponding local density of electronic states (LDOS) are calculated for purposes of interpreting STM images. We show how local atomic orbitals of surface atoms are related to tunneling channels for electrons in STM imaging. A destructive interference between orbitals of two neighbouring atoms increases the contrast between the two atoms, and this is reflected in directionality of STM patterns of GaAs(1 1 0) surfaces. We also discuss how the basic formalism of Tersoff–Hamann approach to STM simulation can be reformulated to reveal the role of phase difference between tunneling channels.

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1. Introduction

The geometry of semiconductor surfaces and their electronic structure in the neighbourhood of the band gap can be investigated using scanning tunneling microscopy (STM) with varying bias voltage. In practical applications of semiconductor physics, it is not only necessary to know the struc-

ture of the uppermost surface layer revealed by STM, but also the growth profile of the sample. Cross-sectional scanning tunneling microscopy (X-STM), where the sample is cleaved in a direction perpendicular to the growth direction, can be utilized to monitor the growth profile. This method allows one, in principle, to observe defects and segregation in MBE grown layers. Especially spatial irregularities require theoretical understanding for interpretation of STM images.

In practice, it is not straightforward to identify the elements of the sample, since STM image is a mapping of local density of electronic states

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(LDOS), i.e., the real atomic positions and the chemical configuration appear indirectly in an STM image. This problem calls for assistance from theoretical interpretation of STM images. Since the experimental patterns can be varied by changing bias voltage, a qualitative interpretation can be obtained from calculating LDOS at relevant energy windows. In the case of the electron density concentrated at certain atoms at the observed energies, it is evident that those atoms dominate the corresponding STM pattern. More sophisticated methods of analysis are necessary in studying the resolution and contrast changes within an STM image.

However, successful qualitative interpretation of bias dependence of STM images of compound semiconductors has been done. Ebert et al. [1], Jäger et al. [2] and Raad et al. [3] have considered the directionality of LDOS of a few dangling bond states and surface resonances. This kind of analysis is very well in accordance with experimental results. In this paper we take a step further, and consider existence of tunneling channels for electrons in STM experiment. The specific geometrical features of the LDOS can be reinterpreted as an interference effect between spacial tunneling channels opened by local atomic orbitals.

In this study, we analyze the STM images of the (110) cleavage surface of GaAs. The analysis is based on electronic structure calculations of the surface as linear combination of atomic orbitals (LCAO). The basic idea behind interpretation of the images is a decomposition into different interfering tunneling channels [4–6]. In an atomic orbital basis, it is rather straightforward to take each orbital of the surface atoms as a “terminal” of a localized tunneling channel. In this approach, the phase difference of localized orbitals at energies related to a chosen bias voltage determines, whether there is a constructive or destructive interference between the corresponding channels.

Although LCAO basis is utilized in our simulations, the electronic structure calculations could be done in any basis. Then the obtained wave functions should be projected into local basis orbitals in order to find the interference between local tunneling channels. The advantage of atomic or molecular orbital basis is the localization of the

basis functions. Thus, the tunneling channels are well defined in real space. In addition, such basis functions also have usually a well defined symmetry, which may be reflected in STM images.

2. Theory and hypotheses

Tersoff–Hamann (TH) formalism [7] is one of the most popular methods to apply DFT calculations in STM image simulations since it expresses the tunneling current in terms of the local density of states (LDOS) of the studied surface at the position of the microscope tip. In this approach, the STM image is a rather straightforward convolution of the surface LDOS and the tip geometry, which is assumed to be spherical. Resolution of the image is controlled by two parameters: the radius of the tip and the tip-sample distance.

TH approach is based on Bardeen’s [8] formalism

$$I = \frac{2\pi e}{\hbar} \sum_{\mu\nu} f(E_\mu) [1 - f(E_\nu + eV)] \times |M_{\mu\nu}|^2 \delta(E_\mu - E_\nu), \quad (1)$$

where $M_{\mu\nu}$ is the tunneling matrix element between states ψ_μ of the microscope tip and ψ_ν of the surface. Fermi functions, $f(E)$, determine the tunneling window for electrons, i.e., the range of energies, where elastic transport from an occupied state to an unoccupied state is possible. With a few simplifying approximations, Tersoff and Hamann derive an explicit mathematical form for the matrix element [7]:

$$M_{\mu\nu} \propto \kappa R e^{\kappa R} \psi_\nu(\mathbf{r}_0), \quad (2)$$

where R is the radius of the curvature of the tip and $\mathbf{r}_0$ is the position of its centre of the curvature.

From the formulae above, the following dependence between the current and the LDOS, $d(\mathbf{r}_0, E)$, is found:

$$I(E) \propto \sum_\nu |\psi_\nu(\mathbf{r}_0)|^2 \delta(E_\nu - E) = d(\mathbf{r}_0, E), \quad (3)$$

for a chosen energy within the tunneling window. It is useful to notice that the formula above can be written in terms of wave functions, and further,

as a linear combination of a chosen set of basis functions. In a localized basis, this eigenfunction expansion reveals, how individual atoms contribute to the STM image. This provides a very powerful interpretative tool for analysis of STM images.

In a localized basis, ψ_v is a linear combination of local orbitals and then it is possible to observe the phase difference between the dominant orbitals as a function of energy of the tunneling electrons. This idea is analogous to decomposition of total tunneling into interfering channels, as discussed in Ref. [6]. In this reference, the contrast changes in STM images of adsorbed molecules are explained by interference between direct through space tunneling and through adsorbate tunneling in terms of the atomic and molecular orbitals. This kind of analysis makes it possible to monitor and predict trends in observed patterns in STM images in case of varying imaging conditions.

Another interesting approach to expanding wave functions in atomic orbital basis is given by Jäger et al. [2]. They find that the two-dimensional translational symmetry of the sample implies well defined variation of the phase factor of the basis orbitals in $\mathbf{k}$ -space. This kind of utilization of symmetry arguments would be nicely complementary to our method which, in terms of symmetry, is more related to local point group properties of the surface.

In order to illustrate the idea of interference between two channels, let us consider a situation where the tip is above a point $\mathbf{r}_0$ between two surface atoms a and b with local orbitals ϕ_a and ϕ_b (see Fig. 1). At some tunneling energies the total wave function $\psi_v(\mathbf{r}_0)$ is proportional to

$$\psi_v^\pm(\mathbf{r}_0) \propto \phi_a \pm \phi_b \quad (4)$$

neglecting minor contribution from local orbitals of atoms further away from the position of the tip.

Let us assume that ψ_v^+ corresponds to states near the top of the valence band and ψ_v^- corresponds to states near the bottom of the conduction band. In the case of the basis orbitals in phase, the term $|\psi_v^+|^2 \propto |\phi_a + \phi_b|^2$ has a relatively large value (constructive interference). In the opposite case of the antiphase, the term $|\psi_v^-|^2 \propto |\phi_a - \phi_b|^2$ has a low value (destructive interference). If this kind

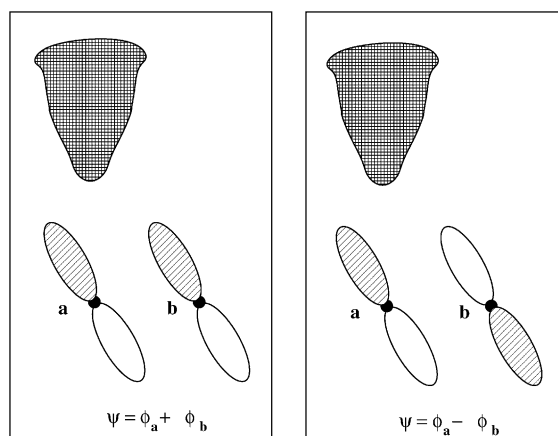


Fig. 1. Formation of constructive (left) and destructive (right) interference between two orbitals as the STM tip probes the area between two atoms. The shaded lobes of orbitals have the opposite sign to the unshaded lobes.

of rapid inversion of phase is seen between atoms in some direction, it is reflected as a clear contrast in this direction between the neighboring atoms in an STM image.

This kind of decomposition into tunneling channels through basis orbitals and their phase difference between arises more naturally in methods based on Green's functions, such as Todorov–Pendry approach [9]. Nevertheless, decomposition of surface wave functions into atomic orbitals is compatible with expressing transmission probabilities in terms of interorbital matrix elements of the Green's function, $G_{ab}(E)$, which contains the necessary phase information.

Even if the phase difference between two orbitals can be calculated as a function of energy, a precise mapping between electron energies and the bias voltages is not as straightforward in case of semiconductors as it is for metals. For metals, the Fermi energy is rather fixed, and the bias voltage can be related to the difference between the electron energy and the Fermi level. For semiconductors, doping of the sample shifts the Fermi level, and thus it shifts the tunneling window, i.e., the range of electron energies where tunneling takes place. A more complicated phenomenon is tip induced band bending, which takes place due to the voltage difference (electric field) between the tip and the sample. Contrary to metals,

semiconductors allow electric field to penetrate into the surface, which bends the bands in the surface region. Thus, it is either necessary to model band bending in some reasonable way or just seek qualitative trends, in comparing bias dependence of experimental and theoretical STM images.

3. Computational methods

For electronic structure calculations performed in this study we use first principles density-functional method with the generalized gradient approximation (GGA) using Perdew–Wang exchange-correlation functional [10]. We use all-electron atomic orbital basis and DMol³ code [11]. Apart from well defined tunneling channels in space, one advantage of the local orbital basis set is that core orbitals can be included in the basis. Another one is that increasing the vacuum thickness in slab model does not increase the computational work. For a proper description of conduction band we used an optimized double-numerical basis set including polarization functions (DNP) with 5.5 Å cut-off radius.

For bulk GaAs we obtained lattice constant 5.78 Å and band gap 0.67 eV. By comparison to plane wave pseudopotential (PWPP) calculations of bulk GaAs it turns out that both calculations give almost identical band structure, except for the band gap that is better reproduced (larger) by local-orbital and all-electron basis.

The (110) surface is modeled by a slab with a surface at both sides. The slab is mirror symmetric with respect to the centermost atomic layer or vacuum. Surface cell used in the slab is three times as wide as the primitive surface cell in $\langle\bar{1}10\rangle$ -direction and double in $\langle100\rangle$ -direction. The slab contains 15 atomic layers plus a vacuum region with a thickness larger than 11 Å, that is twice the length of the basis set cut-off radius. With such a large supercell we find the SCF Γ -point calculation sufficiently accurate to reproduce the bulk GaAs properties and to describe the (110) surface with the slab model. The lateral lattice constants and the centermost atomic layer structure are fixed to those of the bulk, otherwise allowing full relaxation of atomic geometry. Relaxed atomic geometry

of the surface, is in good agreement with previous calculations and low-energy electron-diffraction analysis [12]. In our calculations the buckling angle of the surface Ga–As bond is 29.7°.

We made an analysis of the electronic states in the range of –1.1 eV from the top of the valence band to +1.25 eV from the bottom of the conduction band. Our calculations show that the band gap of the slab is determined by bulk-type states. The gap is 0.84 eV for 15 layers used in our calculations, and it converges towards the bulk value as the number of layers is increased. In good agreement with previous calculations [1,13], the surface density of occupied states is dominated by occupied dangling-bond states, A_5 , which are localized on the anions, and energetically lie below –0.5 eV from valence band maximum. The surface density of unoccupied states is dominated by C_3 dangling bond states in range 0.5 → 1.0 eV from conduction band minimum and by C_4 resonant states above 1.0 eV. In our results, also the lowest unoccupied states around the Γ -point have nonvanishing density on the surface.

4. Observed STM images

In experiments of Raad et al. [3], STM images of (110) surface of a doped GaAs for different bias voltages are presented. We can assume that the doping itself does not affect much on the geometry or electronic structure of the surface, since the impurity states are rather local and the probability to probe an impurity atom on the surface is very low. Hence, we can compare these experimental images with images simulated for a clean surface. However, the impurities shift the Fermi-level upwards or downwards depending on the nature of impurities. Thus, the electron energy corresponding to a chosen bias voltage should be taken with respect to the chemical potential of the doped sample. In practice, however, it is difficult to match the experimental and theoretical bias voltages better than qualitatively. Thus, we are able to simulate trends rather than exact bias voltage dependences of STM patterns.

Three kind of patterns can be found in the experimental STM images for different bias

voltages. As is seen in Fig. 2, the dominant pattern is the one, where the surface atoms are seen as bright rows in $\langle \bar{1}10 \rangle$ direction. On the other hand, this can be seen as a strong contrast between atoms in $\langle 001 \rangle$ direction. At some voltages this pattern is decomposed into separate bright spots at the position of individual surface atoms. There are also voltages, where the pattern consists of bright rows in $\langle 001 \rangle$ direction, and there is a clear contrast between atoms in $\langle \bar{1}10 \rangle$ direction.

In Refs. [1,3] the origin of the directionality of the patterns has been analyzed in terms of partial LDOS projected on dangling bonds and resonance states. In the case of filled states, it is found that a dangling bond state A_5 and a resonance state A_4 have a corrugation in $\langle 001 \rangle$ direction in their LDOS. This is why the negative voltages invariably give patterns, where the bright rows point to $\langle \bar{1}10 \rangle$ direction. In the case of empty states, the dangling bond state C_3 has a corrugation in $\langle \bar{1}10 \rangle$ direction, whereas the resonance state C_4 is corrugated in $\langle 001 \rangle$ direction. This is a qualitative explanation to changes in the direction of the bright rows in STM images.

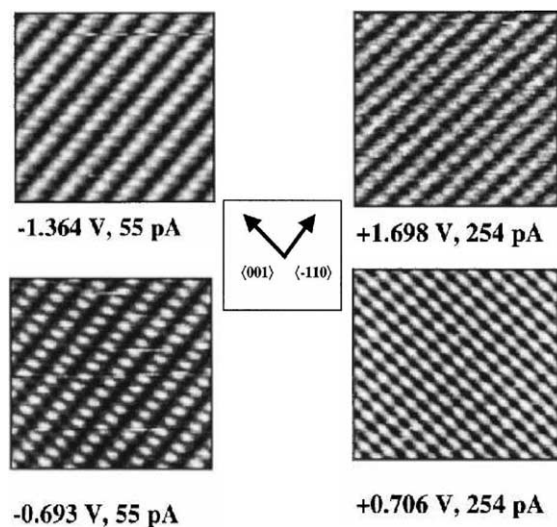


Fig. 2. Experimental STM images from Ref. [3]. Note especially patterns for -0.693 V and $+0.706$ V which corresponds to the directions in the theoretical images. Modified figure with permission from deRaad et al., Phys. Rev. B 66, 195306 (2002). Copyright 2002 by the American Physical Society.

The explanation in Refs. [1,3] is obviously a valid one. The analysis can be taken a step further, by considering the surface wave functions in terms of atomic orbitals of the surface atoms. As using the atomic orbitals in constructing the periodic Bloch functions, the bias dependence has its origin in the variation of the wave length of surface wave functions. Obviously two neighbouring atoms have a clear contrast if their local orbitals are in opposite phase, i.e., their distance is approximately a half wave length of the probed energy level.

5. Simulations and interpretations

We combine the idea of tunneling channels and the hypotheses of Refs. [1,3] in simulating bias dependent STM images. First, we consider tunneling through each surface atom as an individual tunneling channel, which interfere with neighbouring channels [6]. In order to demonstrate the contribution of individual tunneling channels, we consider only a couple of highest occupied and lowest unoccupied states. Especially, we consider the empty and filled dangling bond states. In other words, instead of integrating over the whole tunneling window in TH approximation, we restrict the tunneling window to the most dominant channels only.

In the case of GaAs, the minimum of the band gap occurs at the Γ -point, which implies that, for the corresponding states, each unit cell is in the same phase. Thus, the phase difference may take place between orbitals within a primitive cell. Hence, if the orbitals of two neighbouring atoms are in the opposite phase, there should be a clear contrast between these two atoms.

In Fig. 3 we show an example of energy and direction dependence of the wave length, and its effect on the STM image. The Fig. 3(b) and (c) show the total LDOS at two energies corresponding to states A_5 and C_3 , respectively. These images are not intended to represent STM images as themselves, but rather the contributions of the two levels, only. Thus, this is what the images would look like if the tunneling window could be restricted to include only one energy level. In our supercell calculations, these energies are doubly

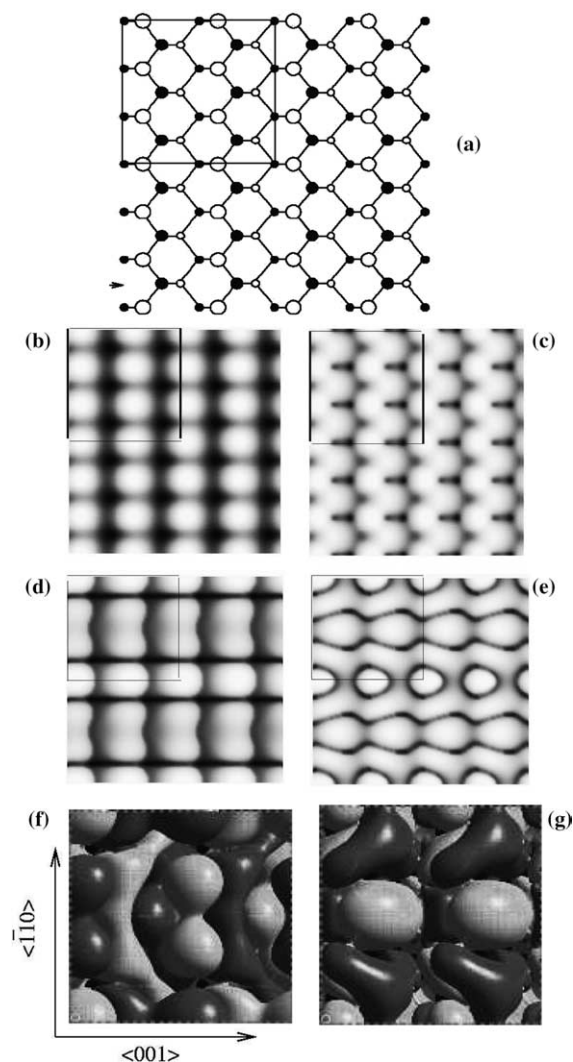


Fig. 3. Theoretical LDOS images and corresponding surface wave functions. The ball-stick model of the surface atomic layer depicted in (a). Total LDOS images combined from doubly degenerate dangling bond states at energies -0.75 eV (A_5) (b), and $+0.60$ eV (C_3) (c). The corresponding LDOS images ((d) and (e)) and wave functions ((f) and (g)) for one of the two degenerate orbitals are shown, respectively. The light areas have a positive and the dark areas have a negative sign. In figures (a)–(e), the rectangle in LDOS images indicates the computational cell for the wave functions which is used in the bottom row.

degenerate. In Fig. 3(d) and (e) are shown the LDOS of one of the two degenerate orbitals, for both energy levels. Note, that these individual

orbitals do not carry the periodicity of the lattice, but that of the supercell, only. Furthermore, the shape of the corresponding wave functions is shown in Fig. 3(f) and (g).

The LDOS and the wave function of the filled dangling bond state A_5 at the energy -0.75 eV are shown in Fig. 3(d) and (f). There is a relatively rapid change of sign of the wave function in $\langle 001 \rangle$ direction, which is reflected as a more continuous pattern in the total LDOS image in $\langle \bar{1}10 \rangle$ direction Fig. 3(b). Nevertheless, the wave function also changes its sign in $\langle \bar{1}10 \rangle$ direction, but with a longer wave length. If this calculated pattern is compared with the experiments, it is somewhere between continuous rows in $\langle \bar{1}10 \rangle$ direction and decomposition into separate bright spots (see Fig. 2). This decomposition could be further enhanced, if the matrix element $M_{\mu\nu}$ of Eq. (1) were selective to either of the degenerate orbitals, in which case the STM image would be more like Fig. 3(d). Hence, this calculated image has a qualitative accordance with the experimental image at $V = -0.693$ V.

The calculations for the empty dangling bond state C_3 at $+0.60$ eV seems to contribute to the pattern in $\langle 001 \rangle$ direction. The total LDOS of the energy level, the LDOS of an individual orbital and the wave function are shown in Fig. 3(b), (d) and (g), respectively. In this case the wave function has a rapid variation of phase in $\langle \bar{1}10 \rangle$ direction, whereas it is mainly the amplitude of the wave function changing in the perpendicular direction. This corresponds to a LDOS image of an individual orbital, where bright rows are formed in $\langle 001 \rangle$ direction. In total LDOS, this directionality is not that clear, but also in this case the tunneling matrix element $M_{\mu\nu}$ may be orbital dependent.

In experiments, the pattern in $\langle 001 \rangle$ direction is a more rare situation, seen at some positive voltages which probe the empty states. The experimental image in Fig. 2. for $V = +0.706$ V has the directionality of this image, and thus, we might conclude that the phase variation of the empty dangling bond is responsible for this image.

In our calculations, TH approach with direct integration over whole the tunneling window shows rows in $\langle \bar{1}10 \rangle$ direction only. In this case,

the other energy states apart from A_5 and C_3 give a too strong contribution in the STM simulation. Especially for empty states (positive voltages), C_3 is the only state that would lead to rows in $\langle 001 \rangle$ direction, and the other states above the gap contribute to the rows in the perpendicular direction. This is also in accordance with experiments, since increasing the bias voltage creates rows in $\langle \bar{1}10 \rangle$ direction.

6. Discussion and conclusions

Our simulations indicate that qualitative trends of the bias dependence of STM images can be found for semiconductor surfaces by studying phase differences of tunneling channels through different surface atoms. The band gap between the occupied and unoccupied states of semiconductor makes this analysis more straightforward than metal surfaces. In case of a band gap, it is possible to isolate the most dominant tunneling channels in terms of energy levels and atomic orbitals, especially at small bias voltages. In case of metals, there is a continuum of states with a wide energy range contributing to tunneling current at any energy.

In the case of a clean semiconductor surface, the decomposition into tunneling channels through surface atoms is rather simple since the geometrical and chemical configuration is regular. The existence of impurities or defects, however, would provide a less trivial test for this approach. Inspecting phase differences of orbitals of an impurity atom or a defect site and neighbouring substrate atoms would reveal, how strongly these special sites are in contrast with the neighbourhood.

Although TH approach was not systematically performed in the present study, our attempts to integrate over a finite tunneling window suggest, that TH approach may not be appropriate for semiconductor surfaces, as such. In this case the external field causes band bending at the surface. This complex effects of band bending in variously doped semiconductors have been studied in, e.g., Refs. [14,15]. The existence of a surface state at the tunneling energy does not necessarily allow

tunneling between the tip and the substrate. In addition to suitable surface states, conduction band states must exist further within the bulk for electrons tunneling from tip to surface, and valence states from which electrons can tunnel from sample to the tip.

As a future prospect, we intend to combine our tunneling channel analysis to symmetry studies such as discussed in Ref. [2]. On the other hand, this study rises suggestions to STM experiments. Since variation of the tunneling matrix element $M_{\mu\nu}$ in Bardeen's formula allows selectivity to different surface orbitals, it might be possible to establish orbital selectivity to STM by controlled variation of the geometrical of chemical structure of the tip. This kind of orbital selectivity has been found in studies of adsorbate molecules by functionalizing the STM tip with a molecule lifted from the surface [16,6]. Since the dominating surface orbitals are relatively easy to recognize in the case of semiconductors, this kind of orbital selective STM should be possible for semiconductor surfaces, as well.

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