Generalised effective mass theory of sub-surface scanning tunnelling microscopy: application to weakly bound impurity states

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Abstract. We apply our generalised effective mass theory of sub-surface scanning tunnelling microscopy (STM) (Phys. Rev. B 19, 195304 (2010)) to simulate STM images of electronic states localised around sub-surface Si dopant atoms in GaAs. In the case of these shallow impurity-states, we demonstrate that electrostatic effects from image-charges and from the STM tip have a strong influence on the sub-surface state and hence the simulated image.

1. Introduction
Scanning tunnelling microscopy (STM) samples the local density of states (LDOS) above a surface, but this is influenced by sub-surface structure, and there is growing interest in using STM to probe quantum states localised below a surface. States associated with near-surface shallow donors and cleaved dots have all been recently imaged [1, 2, 3].

To understand these experiments we must calculate the LDOS, but such calculations are challenging because the sub-surface states can be very broad, extending over millions of atoms. In such large systems an effective mass approach is appealing as it provides an excellent semi-quantitative description of shallow-impurity states in the bulk. However, because it is a bulk theory, a traditional effective mass approach cannot be used to find the LDOS above a surface.

Here we discuss a recent extension to the theory and its application to STM. In Ref. [1] we demonstrated that the LDOS above the surface can be written in terms of a simple weighted integral of the bulk envelope function. The resulting ‘surface envelope function’ contains the lateral information in the tail of the LDOS that is probed in STM. We apply this theory to simulate STM images of electronic states localised around sub-surface Si dopant atoms in GaAs.

We develop a detailed continuum model of the sub-surface impurity, including the band bending caused by the STM tip, and the effect of the image-charges. These electrostatic effects are important for the shallow impurity-states and contribute to the observed increase in binding energy with decreasing dopant depth [2].

2. Generalised effective mass theory
In a recent paper [1] we generalised effective mass theory to find the local density of states above a semiconductor surface in the presence of a sub-surface nanostructure or impurity. Here we quote the key results appropriate to GaAs (110): we give the single-band results for a crystal with an inversion plane parallel to the surface. Details and general results are given in Ref. [1].
In our model, a slab of semiconductor, of lattice constant $a_0$, extends from $-L$ to 0 in the $z$-direction and is of infinite extent parallel to the surface. We consider a slowly varying confinement potential, $v(\rho,z)$, that is generated by an impurity or nanostructure located below the surface, close to $z = 0$. The localised states, $\psi(\rho,z)$, associated with $v(\rho,z)$ then have some tail above the surface that can be probed in STM. The experimental tunnelling current is proportional to $|\psi(\rho,z)|^2$ at $(\rho_t,z_t)$, the position of the tip [4]. So, to compare to STM experiments, we simply need to calculate the localised states where $z > 0$.

The single-band wavefunction above the surface can be written [1],

$$\psi(\rho,z) = F_s(\rho)w_{00}(\rho,z),$$

where $F_s(\rho)$ is a surface envelope function that varies in the plane parallel to the surface and $w_{00}(\rho,z)$ is a Bloch-like function at the band edge, with wave vector $k_{||} = 0$, and $k_z = 0$. As in the traditional bulk effective mass theory, the Bloch part of $\psi$ describes the atomic scale variation that comes from the host semiconductor in the absence of $v(\rho,z)$. The surface envelope function then contains all the effects of the sub-surface nanostructure or impurity. It is given by

$$F_s(\rho) = \int_{-L}^{0} G(z)F(\rho,z)dz,$$  \hspace{1cm} (2)

where $F(\rho,z)$ is a bulk envelope function that can be found by diagonalising the usual bulk effective mass Hamiltonian with the additional boundary conditions that $F(\rho,z) = 0$ at the edges of the slab where $z = -L$ and $z = 0$. In the region $|z| \ll L$, where $F$ is large, the weighting function $G(z)$ is simply

$$G(z) = \frac{2}{z} \sin^2 \left( \frac{\pi z}{2a_0} \right).$$  \hspace{1cm} (3)

In an STM experiment, the tunnelling current is $I_{STM} \propto |F_s(\rho_t)|^2|w_{00}|^2 = I(\rho_t)|w_{00}|^2$. So, to calculate the atomic scale variation in tunnelling current we must find $w_{00}$ [5]. However, for qualitative or semi-quantitative analysis of the states associated with the sub-surface impurity or nanostructure it is often sufficient to calculate only the large scale variation in $I_{STM}$. In this case the procedure is very simple:

(i) calculate the bulk envelope function, $F(\rho,z)$, with the additional boundary conditions that $F = 0$ at the surfaces of the slab.

(ii) calculate the surface envelope function, $F_s(\rho)$, from Eq. (2).

(iii) calculate the tunnelling current $I(\rho_t) \propto |F_s(\rho)|^2$.

3. Effective mass model of a sub-surface Si in GaAs

We consider a Si dopant located at $z = -z_d$ in a semi-infinite GaAs slab that extends from $z = -\infty$ to $z = 0$. To find the bulk envelope function (step (i) from section 2) we solve the Schrödinger equation in cylindrical polar co-ordinates,

$$\left( \frac{-\hbar^2}{2m^*} \left[ \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) + \frac{\partial^2}{\partial z^2} \right] + v(\rho,z) \right) F(\rho,z) = EF(\rho,z),$$ \hspace{1cm} (4)

where $F(\rho,z) = 0$ at $z = 0$ and $F \to 0$ as $z \to -\infty$. Here we only consider systems with cylindrical symmetry and, in Eq. (4), $v$ is cylindrically symmetric in the absence of an STM tip and in the presence of a cylindrically symmetric tip centered at $\rho = 0$.

In the bulk, when $z_d \ll 0$, the potential associated with a Si dopant is simply the usual Coulomb potential screened by the macroscopic dielectric constant of GaAs,
\[ v_{\text{imp}}(\rho, z) = -e^2/(4\pi\varepsilon_0\varepsilon_r)/\sqrt{\rho^2 + (z - z_d)^2}, \] where \(\varepsilon_r = 13.1\). When \(z_d\) is close to zero, however, the surface affects the electric field and we include this effect using the classical method of images. The potential may also be affected by the STM tip, so that

\[ v(\rho, z) = v_{\text{imp}}(\rho, z) + v_{\text{di}}(\rho, z) + v_{\text{ei}}(\rho, z) + v_{\text{bb}}(\rho, z), \] (5)

where \(v_{\text{di}} = -e^2(\varepsilon_r - 1)/(4\pi\varepsilon_0\varepsilon_r(\varepsilon_r + 1))/\sqrt{\rho^2 + (z + z_d)^2}\) is the dopant image potential, and \(v_{\text{ei}} = e^2(\varepsilon_r - 1)/(16\pi\varepsilon_0\varepsilon_r(\varepsilon_r + 1))/|z|\) is the electron image potential [7]. In the presence of an STM tip centred at \(\rho_t = 0, v_{\text{bb}}(\rho, z)\) gives the effect of the tip induced band bending (TIBB).

We calculate the TIBB by solving Poisson’s equation using the standard finite-difference code of Feenstra [6]. We simulate an experimentally realistic [2, 3] ultrasharp tip of opening angle 19°, and tip radius 2.5 nm, with a tip voltage of \(V_{\text{tip}} = -0.5\) V. The tip is 0.5 nm from the GaAs surface and the GaAs has an average Si doping concentration of \(10^{18}\) cm\(^{-3}\).

We solve Eq. (4) by expanding \(F(\rho, z)\) in a basis of harmonic oscillator functions and then diagonalising the resultant Hamiltonian matrix [8].

\[ F(\rho, z) = \sum_{n} \sum_{m=0}^{m_{\text{max}}} a_{nm} Z_{2m+1}(z) R_{n0}(\rho), \] (6)

where \(Z_m(z) = \exp(-z^2/2z_0^2)H_m(z/z_0)/(2^{m}m!\sqrt{\pi}z_0)^{1/2}\) are the 1D oscillator functions, \(R_{n0}(\rho) = \exp(\rho^2/4\rho_0^2)L_n(\rho^2/2\rho_0^2)/\rho_0\) are 2D oscillator functions with zero angular momentum, and \(L_n\) and \(H_m\) are Laguerre and Hermite polynomials respectively. In the expansion in Eq. (6) we only include the 1D oscillator states with odd quantum number (and hence odd symmetry about \(z = 0\)) to ensure that \(F(\rho, z)\) goes to zero at the surface.

**4. Results and discussion**

Here we focus on a single silicon dopant at \(z_d = -0.6\) nm. To investigate the effect of the image charges and the TIBB on the localised state we calculate \(F(\rho, z)\) for 3 different cases: in (i) we neglect the image potentials and set \(v_{\text{bb}} = 0\); in (ii) we include the image potentials and set \(v_{\text{bb}} = 0\); in (iii) we include both image potentials and \(v_{\text{bb}}(\rho, z)\). In all 3 cases we converge the ground state energy to within 0.05 meV with 96 states in our expansion (\(n_{\text{max}} = 12, m_{\text{max}} = 16\)), using oscillator length scales of \(z_0 = 19\) nm, and \(\rho_0 = 11\) nm.

**Figure 1.** Components of \(v(\rho, z)\) shown at \(\rho = 0\) as a function of \(z\). The effect of the dopant image potential, \(v_{\text{di}}\), is to deepen the confinement generated by \(v_{\text{imp}}\), while the electron image potential, \(v_{\text{ei}}\), repels the state away from the surface. The TIBB \((v_{\text{bb}})\) \((V_{\text{tip}} = -0.5\) V\)) raises the total potential and acts to repel the state away from the tip at \(\rho_t = 0, z_t = 0.5\) nm.

Figure 1 shows line scans through \(v_{\text{imp}}(\rho, z), v_{\text{di}}(\rho, z), v_{\text{ei}}(\rho, z)\) and \(v_{\text{bb}}(\rho, z)\). Figure 2 shows \(|F(\rho, z)|^2\) as a function of \(\rho\) and \(z\) for the 3 different cases. In case (i) (left panel) we find a binding energy of \(E_b = |E| = 1.4\) meV; the presence of the surface reduces the binding energy below the well-known bulk value of 5.3 meV. In the centre panel of Fig. 2 we see that the result of including the image potentials (case (ii)) is to localise the state closer to \(z = 0, \rho = 0\), increasing the binding energy from 1.4 to 3.2 meV. However, although the effect on \(E_b\) is significant, it is
not large enough to explain the experiment [2] where $E_b$ was estimated to increase to $\sim 10$ meV, around twice the bulk value. The right panel shows $|F(\rho, z)|^2$ in case (iii). The TIBB pushes the state away from the surface, decreasing the binding energy to $E_b = 2.4$ meV.

Figure 2. $|F(\rho, z)|^2 \left( 10^{-5} \text{ nm}^{-3} \right)$ for a Si dopant at $z_d = -0.6$ nm. Left: calculation (i) without image potentials in the absence of a tip. Centre: calculation (ii) including image potentials in the absence of a tip. Right: calculation (iii) including image potentials and TIBB ($V_{\text{tip}} = -0.5$ V, $\rho_t = 0$, $z_t = 0.5$ nm).

In Fig. 3 we can see the effect of the TIBB on the simulated image is significant and this illustrates a challenge when interpreting STM images of weakly bound states: the state is affected by the tip and so the character of the state that is imaged will depend on the position of the tip as it scans across the image. In principle, to simulate the image we should recalculate $v_{bb}$, $|F(\rho, z)|^2$ and $|F_s|^2$ for each separate tip position.

In summary, we have simulated STM images of the state localised around an Si dopant 0.6 nm below a GaAs surface. We have shown that the tip induced band bending can have a significant effect on the imaged LDOS and find that the effect of the image potentials is to increase the binding energy of the sub-surface state from 1.4 to 3.2 meV. Although this increase in binding energy is significant it is not enough to explain the experimentally observed enhancement.

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