

Probing the internal structure of nanowires

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Abstract

Si(111)-In(4×1) is a fascinating quasi-1D system that contains a repeated nanowire motif. The nanowires contain only two rows of In atoms. We demonstrate that it is possible to infer the spacing between the rows from a study of the dispersion of the image state band, measured using inverse photoemission. Our analysis suggest that the rows of In atoms are separated by $4 \pm 0.5 \text{ \AA}$. This value is in excellent agreement with estimates of the spacing by both STM and surface x-ray diffraction.

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If a metal occupies the half space defined by $z < 0$, the image potential above the surface has the following asymptotic form $V(z) = -1/4z$. Furthermore, if the metal is infinitely repulsive at $z = 0$, the Schrödinger equation in the region above the surface ($z > 0$) reduces to the 1D analogue of the hydrogen atom and the electron energy eigenvalues, measured in eV, are described by $E_n = -0.85/n^2$. On semiconductor and insulator surfaces, the electrons do not screen external charges as effectively and consequently both the image potential^{1,2}

$$V(z) = -\frac{1}{4z} \left(\frac{\varepsilon - 1}{\varepsilon + 1} \right) \quad (1)$$

and the width of the energy spectrum, defined as $E_1 - E_\infty$ where

$$E_n = -\frac{0.85}{n^2} \left(\frac{\varepsilon - 1}{\varepsilon + 1} \right)^2, \quad (2)$$

are contracted. For example, the static dielectric constant of Si (ε) is 11.9, $(\varepsilon - 1)/(\varepsilon + 1) = 0.84$ and the width of the image state energy spectrum reduces from 0.85 to 0.61 eV. However, this is only a reduction of 28%. Both potentials are quite similar. Despite this, image states are not observed on semiconductor surfaces. This is because there are states in the semiconductor bandstructure, into which electrons outside the surface can scatter, at the binding energy of the image state. Consequently, states just below the vacuum level located just above the surface are not bound by the image potential. However, image states have been observed in Bi overlayers on GaAs(110)^{3,4} despite the fact that there are no image states on the GaAs(110) surface. This suggests that, in these cases, the interface between the metal overlayer and the semiconductor is sufficiently reflective to produce image states with long lifetimes in the metal overlayer.

In this paper, we report the results of a study of the image state in the Si(111)-In(4×1) (hereafter 4×1) system. The sample preparation details and a description of the inverse photoemission detector that was used in this study can be found elsewhere^{5,6,7,8,9,10}. Both photoemission¹¹, inverse photoemission^{7,8,9,10,12,13}, STM^{14,15,16,17} and surface x-ray diffraction studies¹⁸ have converged on the following picture of the 4×1 system. The In atoms order in rows which are only 2 atoms wide (fig.1). We will refer to these double rows as nanowires to make a clear distinction between the rows of atoms located within the nanowires and the nanowires themselves. The center-to-centre spacing of the nanowires is 13.3 Å and the STM^{14,15,16,17} has revealed that the nanowire motif is repeated to generate a surface structure

that resembles an atomic scale diffraction grating. In fact, low energy electron diffraction images⁷ do resemble their optical counterparts. The bands that comprise both the valence¹¹ and conduction bands⁷ are known to be quasi-1D, possessing negligible dispersion perpendicular to the nanowires ($\perp \equiv [\bar{1}\bar{1}2]$). This suggests that there is negligible wavefunction overlap between the nanowires. In contrast, parallel to the nanowires ($\parallel \equiv [\bar{1}10]$) there is a clear Fermi level crossing at $0.6 \bar{\Gamma}\bar{X}$ (rectangular cell⁹) indicating that there is sufficient wavefunction overlap along the nanowires to produce a dispersing energy band. Furthermore, it has recently been demonstrated¹⁹ that this quasi-1D surface structure has unique optical properties. For example, the reflectance anisotropy ($1.5 < \hbar\omega < 5.5eV$) is larger than that of any other semiconductor system.

In fig.2, two normal incidence inverse photoemission spectra collected from the (a) 4×1 and, for comparison, (b) the $\sqrt{7} \times \sqrt{3}$ (hereafter $\sqrt{7}$) systems are presented. The $\sqrt{7}$ system is a higher coverage system that is quasi-2D. The details of the $\sqrt{7}$ surface reconstruction are not pertinent to the argument developed in this paper. It is only important that the gaps between the In rows have been filled in and that the overlayer is not quasi-1D. Curve (a) has been rigidly shifted by $-0.1eV$ to line up the intense peak that dominates both spectra. In the 4×1 system, the peak is located $2.0eV$ above the Fermi level, whereas in the $\sqrt{7}$ system the peak is located $E_F + 1.9eV$. The dots represent the raw data and the smooth curves through the experimental points were generated by Gaussian averaging the spectra (FWHM= $0.18eV$) and then normalizing them to the peak maximum. Subsequently, the spectra were subtracted to yield a difference curve which is presented in the lower portion of the figure (c). The difference curve clearly illustrates that in the $4 \times 1 \rightarrow \sqrt{7}$ transition, intensity on either side of the main peak is suppressed causing the main peak to narrow. Apart from this, both spectra are quite similar at the $\bar{\Gamma}$ point. Both have an image state located $0.67eV$ below the vacuum level (VL). However, as we shall see later, the image states behave quite differently away from the zone center.

In fig.3, we have presented the measured dispersion of the $\sqrt{7}$ image state in both the \parallel and \perp directions. The band is clearly parabolic. The full line is a free electron parabola that has been matched to the experimental data at the $\bar{\Gamma}$ point. The parabola provides an excellent description of the experimental data. In fig.4, the measured dispersion of the image state in the 4×1 system is presented. In the \parallel direction the dispersion is once again parabolic. However, in the \perp direction the dispersion falls below the free electron parabola.

The break point in the curve can be correlated with the spacing of the nanowires. This result is important because on metal surfaces the image state effective mass is often measured to be much larger than unity²⁰. There has been a long standing discussion about the cause of the large effective mass²¹. Both the surface potential and many body effects have been ruled out as possible causes. Although it is known that a finite angular divergence in the electron beam could result in an overestimate of the image state effective mass²², the magnitude of the angular divergence required to reproduce the measured effective masses is unphysically large. However, here we have a clear cut detection of an image state band perturbation which can be correlated directly with the nanowire periodicity. Furthermore, poor momentum resolution can be ruled out as the source of the perturbation because the effective mass in the \parallel direction is measured to be unity. So this low-dimensional system provides us with a clear limiting case where the effect of a large surface corrugation can be unambiguously identified.

To get further information about the surface potential we solved the 1D Schrödinger equation by expressing the surface potential

$$V(\vec{r}) = \sum_l V(\vec{G}_l) e^{i\vec{G}_l \cdot \vec{r}}$$

and the surface Bloch function

$$|\Psi\rangle = \sum_m C(\vec{G}_m) |\vec{k} + \vec{G}_m\rangle$$

as a Fourier series. The central equation²³ was then used to generate the matrix equation $(\mathbf{M} - \varepsilon\mathbf{I})\mathbf{C} = 0$ where, using standard notation²³,

$$\mathbf{M} = \begin{bmatrix} \varepsilon_o & V_1 & V_2 & \cdots \\ V_1 & \varepsilon_1 & V_1 & \cdots \\ V_2 & V_1 & \varepsilon_2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}, \quad (3)$$

\mathbf{I} is the identity matrix and \mathbf{C} is the coefficient matrix of the Bloch function. As usual, for a unique solution $|\mathbf{M} - \varepsilon\mathbf{I}| = 0$. This equation was solved analytically for the image state energy bands ε using symbolic computer algebra²⁴. The potential was altered in an ad-hoc fashion until the calculated bands agreed with the experimental bands. The potential that we obtained from this analysis is

$$V(x) = 1.07 \sin G_3 x + 0.41 \cos G_4 x, \quad (4)$$

where $G_n = n2\pi/a$ and $a = 13.3 \text{ \AA}$. (A plot of the energy bands can be found elsewhere¹⁰. We will concentrate on the interpretation of the results here.) Our main finding is that although the first two minigaps are small, and below our detection threshold, the third and fourth are large. The fourth component corresponds to the $\times 1$ periodicity of the surface which is retained because the $\times 4$ symmetry is generated by a missing row structure. The two dominant components in the potential have been plotted in fig.5. The third and fourth components add to produce a potential with two deep minima separated by $\approx 4 \text{ \AA}$. STM line profiles taken perpendicular to the nanowires in positive bias¹⁴, probing the unoccupied states above the Fermi level but below the energy of the image state, possess two maxima that are also separated by $\approx 4 \text{ \AA}$. The STM line profile has been arbitrarily shifted to line up the maxima with the minima in $V(x)$. The maxima that are observed in positive bias have been associated with the In atom rows¹⁴, so it is likely that the minima in $V(x)$ are also associated with the presence of the In atom rows. Furthermore, recent surface x-ray diffraction studies¹⁸ have determined that the In atom rows are two atoms wide and the spacing between the rows is $4.4 \pm 0.2 \text{ \AA}$. All three experiments appear to be probing the internal structure of the In atom rows in different ways. All provide estimates of the row spacing that are in surprisingly good agreement.

In summary, we have demonstrated that the ordered array of In nanowires that comprise the Si(111)-In(4×1) system, strongly perturb the image state band. From the perturbation of the band it is possible to infer the internal spacing of the atoms within the nanowires. The spacing is consistent with the results of recent STM and surface x-ray diffraction studies. Furthermore, this quasi-1D system provides a clear cut example where it is possible to correlate the perturbation of the image state band with the spacing of the nanowires.

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FIGURES

FIG. 1. A structural model of the 4×1 system obtained from a recent surface x-ray diffraction study¹⁸. In atoms are black. Si atoms are gray. The dashed line is the oblique 4×1 unit cell.

FIG. 2. Inverse photoemission spectra collected from **(a)** 4×1 and **(b)** $\sqrt{7}$ are very similar. Both possess image states lying 0.67 eV below the vacuum level (VL). Both spectra were collected with the electron gun in normal incidence and they probe the $\bar{\Gamma}$ point of the surface Brillouin zone.

FIG. 3 $\sqrt{7}$: The dispersion of the most tightly bound $n = 1$ image state and a free electron parabola which has been matched to the experimental energy band at the $\bar{\Gamma}$ point. On the scale of the graph, the momentum uncertainty ($\pm 0.025 \text{ \AA}^{-1}$) is relatively unimportant compared to the $\pm 0.150 \text{ eV}$ energy uncertainty and, for clarity, it has not been added to the figure.

FIG. 4. 4×1 : The dispersion of the $n = 1$ image state and a free electron parabola which has been matched to the experimental energy band at the $\bar{\Gamma}$ point. Note the deviation from parabolicity in the \perp direction at $\approx \pi/13.3 = 0.24 \text{ \AA}^{-1}$

FIG. 5. The potential $V(x)$ plotted together with a constant current STM scan¹⁴. The curves have been shifted to arbitrarily line up the maxima in the STM scan with the minima in $V(x)$.

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