Structure of YSi₂ nanowires from scanning tunneling spectroscopy and first principles

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Exceptionally long and uniform YSi₂ nanowires are formed via self-assembly on Si(001). The in-plane width of the thinnest wires is known to be quantized in odd multiples of the silicon lattice constant. Here, we identify a class of nanowires that violates the “odd multiple” rule. The structure of the thinnest wire in this category is determined by comparing scanning tunneling spectroscopy measurements with the calculated surface density of states of candidate models by means of the Pendry *R*-factor analysis. The relative stability of the odd and even wire systems is analyzed via first-principles calculations. © 2009 American Institute of Physics. [doi:10.1063/1.3236778]

Individual nanometer-sized objects have been the focus of many experimental and theoretical studies in recent years because of their special appeal to fundamental science and because of their interesting chemical and physical properties that may one day find their use in nanotechnology.^{1–4} Metallic nanowires embedded in a Si platform are particularly interesting because they might be used as metallic interconnects in Si-based nanodevices.^{2,5–9} For this matter, it is crucially important to elucidate their structural and electronic properties.

Epitaxial YSi₂ nanowires represent an interesting case in point. These nanowires are formed via self-assembly after depositing approximately 0.5 ML (monolayer) of Y onto an atomically clean Si(001) surface in ultrahigh vacuum (UHV). Most of the Y is incorporated into a (2×7) wetting layer reconstruction while isolated nanowires can be found on top.¹⁰ The wires have extraordinary aspect ratios and can grow up to microns long. The reported cross sections of the thinnest¹¹ wires are $0.4ma_0$ nm², where *m* represents an odd integer (*m*=3, 5, 7, 9) and *a*₀=0.384 nm the lattice constant of the Si(001) plane.² We refer to these nanowires in terms of their width, i.e., 3*a*₀ for 1.15 nm wide and 5*a*₀ for 1.92 nm wide wires. Although many metals can be used to create silicide nanowires,^{5–9} YSi₂ wires have the highest aspect ratio so far, probably because of the large anisotropic mismatch between the silicides AlB₂ structure and Si substrate and the near-perfect lattice match along the Si direction [1 $\bar{1}$ 0].

In this letter, we report on the existence of YSi₂ nanowires that violate the odd-multiple rule for stable wire widths. We investigate the structure and electronic properties of the thinnest nanowire in the even-multiple category by adopting a reliability or *R*-factor analysis for comparing scanning tunneling spectroscopy (STS) data with first-principles calculations. The formation enthalpies of the 3*a*₀, 4*a*₀, and 5*a*₀ wires are also computed.

These extremely thin nanowires are too small and fragile to be subjected to *ex situ* sample processing for, e.g., transmission electron microscopy, while their number density is

far too low for structure determination via surface x-ray diffraction or low energy electron diffraction (LEED). Therefore, scanning tunneling microscopy (STM) remains the most powerful tool for *in situ* investigation of their structure and electronic properties. However, STM images contain both topographical and electronic structure information¹² and therefore the image interpretation necessarily relies on supporting electronic structure calculations and theoretical image simulations, for a given structure model. In the present case of YSi₂, the competing models of the nanowires produce theoretical STM images that are qualitatively very similar. To determine the most likely structure, we introduce a reliability factor or *R* factor to quantify the agreement between the normalized *dI/dV* spectra from STS and the density functional theory (DFT) calculated surface projected density of states (PDOS), and apply this method to determine the structure of the 4*a*₀ YSi₂ nanowires.

Experiments were performed in a UHV system with a base pressure of 1×10^{-10} mbar. Y was deposited through e-beam evaporation onto an atomically clean Si(001)2×1 substrate held at 625 ± 25 °C. All STM/STS measurements were carried out using an Omicron VT-STM operated at room temperature. Spectroscopy was performed by recording the tunneling current (*I*) while ramping the tunneling bias (*V*) at specific locations on the nanowires. The differential conductance (*dI/dV*) was obtained by numerical differentiation of the *I-V* curves and subsequent normalization to the *I/V* ratio to remove the contribution of the transmission function.¹³

To assess the possible YSi₂ nanowires structures, we performed total energy calculations. We used DFT, implemented in the plane-wave projector augmented wave method^{14–16} and the local density approximation.¹⁷ We used supercells containing a slab with nine layers of Si atoms. Hydrogen atoms passivated the rear surface. The bottom two layers of atoms were held fixed at the theoretical bulk lattice positions. All other atoms were allowed to fully relax. Supercell dimensions were up to $16 \times 2 \times 8.48a_0$, containing up to 378 atoms. The $16a_0$ width allows for the study of relatively isolated nanowires. We used the same basis set and conver-

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FIG. 1. (Color online) STM characterization of the thinnest YSi_2 nanowires. (a) STM images (-1.7 V, 60 pA) of YSi_2 nanowires showing the junctions between $4a_0$ and $5a_0$ wire segments and between $3a_0$ and $4a_0$ segments (inset) inside the green circles. The 2×7 wetting layer reconstruction, which incorporates most of the Y, can be seen in the background (Ref. 10). The scale bar corresponds to 10 nm. (b) Line profiles of the $3a_0$, $4a_0$, and $5a_0$ wires. [(c) and (d)] High resolution STM images of the $3a_0$ and $4a_0$ wires.

gence criteria as for our previous calculations on $3a_0$ nanowires which yielded accurate results.²

Figure 1(a) illustrates two STM images of YSi_2 nanowires on the Si(001) surface. Due to the fourfold symmetry of the Si(001) substrate, the nanowires grow in two orthogonal directions. Most wires have uniform widths along their entire length but some wires contain segments of different widths that are separated by abrupt junctions. Two such junctions are shown in Fig. 1(a) where the green dotted circles highlight the junction between $4a_0$ and $5a_0$ wire segments and between $3a_0$ and $4a_0$ wire segments. The $4a_0$ wire width has not been seen before. Topographic line profiles of these wire segments are shown in Fig. 1(b). We occasionally observed $6a_0$ and $8a_0$ nanowires.

Atomic resolution STM images of the $3a_0$ and $4a_0$ wires in Figs. 1(c) and 1(d) indicate the presence of Si dimers on the surface, as was established in previous studies.^{2,5-9} The odd-multiple wires have mirror plane symmetry where the mirror plane is defined by the wire direction ($[11\bar{2}0]$ of the silicide²) and surface normal. On the other hand, the even-multiple wires do not have mirror plane symmetry. To determine the structure of the $4a_0$ nanowires, we performed DFT calculations considering various possible atomic arrangements for the smallest YSi_2 units on the Si(001) surface. The absence of a mirror plane greatly increases the number of possible candidates. DFT studies of unsupported nanowires have previously found many stable structures.¹⁸

Figure 2 shows the cross-sectional views of four plausible structures (labeled I–IV) whose atomic coordinates are fully relaxed via DFT. Each structure contains a different number of Y and/or Si atoms. The panels on the right show the simulated filled-state STM images (1.2 eV). The simulated images all agree at least qualitatively with the experimental image meaning that we cannot rule out any of these structures based on topographic images alone. The main features in the simulated images originate from the Si dimer rows that terminate the nanowire surfaces and which are similar in all of these models. The topographic details distinguishing these structures are mostly related to the structure inside the channels between the two dimer rows, which will

FIG. 2. (Color online) [(a)–(d)] Cross-sectional views of total-energy-minimized structures for $4a_0$ wires with varying composition, obtained from DFT (structures I–IV), along with the simulated filled state STM images (1.2 eV). The Si atoms are shown in yellow and the Y atoms are shown in red.

be very difficult to assess with STM because the imaging resolution is limited by the tip convolution.

To identify the likely composition of the channel between the dimer rows we performed a series of calculations comparing the energies of candidate structures with those where atoms in the channel were moved to a midpoint on the Si surface, away from the wire. We found that the additional Si and Y atoms of structure I were always preferred over the more open structures II–IV. For instance, converting structure I into structure II by removing a single Si atom from the channel results in a total energy increase of 0.1 eV. This result suggests that in the absence of kinetic barriers, model I is the preferred structure although absolute confirmation is not possible due to the large number of competing structures.

Since the $4a_0$ wires coexist with odd width wires on the Si surface, we also performed a thermodynamic analysis of their relative stability. We computed the enthalpy of formation (ΔH_f) of $m=3,4,5$ wires relative to the clean surface energy via the formula $H_f = E_0 - \mu_{\text{Si}}N_{\text{Si}} - \mu_{\text{Y}}N_{\text{Y}}$. Here E_0 is the total energy of the wire structure, μ_{Si} is the chemical potential of silicon atoms, μ_{Y} is the chemical potential of Y atoms, and N is the number of added atoms of the respective species. In the Si rich limit, $\mu_{\text{Si}}=0$ and $\mu_{\text{Y}} = \Delta H_f(\text{YSi}_2) = -1.96$ eV, we find that the $5a_0$ wire is most stable, while the $3a_0$ and $4a_0$ wires are 0.11 and 0.32 eV higher in energy, respectively. The higher energy of the $4a_0$ wire (structure I; measured in eV per Y atom) is likely due to the existence of dangling bonds. However, calculations using smaller supercells found that the $3a_0$ wires are preferred, indicating that surface strain and wire-wire interactions can stabilize these wires at higher coverage. While the computational result indicates that in the thermodynamic limit,

FIG. 3. (Color online) Electronic properties of the $4a_0$ wires. (a) Surface PDOS for structures I–IV. (b) Comparison between the normalized differential conductance from STS (red) and the calculated surface PDOS for structure I (blue).

yttrium adatoms prefer to be incorporated into existing $5a_0$ wires at low coverage, the existence of exceptionally long $3a_0$ wires in the experimental samples² indicates that the kinetic barriers are strongly anisotropic.

To verify that we have found the best structure in model I, we computed the DOS of each structure and compared it to the normalized differential conductance measured by STS. The calculated surface PDOSs of the structures discussed above are presented in Fig. 3(a). Peaks around the Fermi energy result primarily from Si states with modest Y hybridization. The normalized differential conductance $[dI/dV/(I/V)]$ measured by STS is proportional to the local DOS, displaying both the occupied and unoccupied states of the sample.¹³ The normalized differential conductance of the $4a_0$ wire is shown in Fig. 3(b), together with the PDOS of structure I, which seems to agree best with the experimental spectrum as judged by visual inspection. In the following, we will substantiate this conclusion using a more objective quality indicator.

The fairly sharp peaks in the spectrum are reminiscent of the Van Hove singularities characteristic to one-dimensional (1D) systems, similar to those observed in carbon nanotubes and other quasi-1D systems.^{19,20} The peak positions are thus considered to be a fingerprint on the electronic structure of the YSi_2 wire. On the other hand, the peak intensities are affected by many other factors such as the tunneling matrix elements and conditions of the tip. In light of the fact that the peaks are reasonably well separated, we can perform an R -factor analysis to judge the level of agreement between the experimental and theoretical peak positions. Specifically, we use the Pendry R factor²¹ because it emphasizes peak positions rather than peak intensities. The Pendry R -factor analysis was first introduced in LEED I - V analysis to quantify the agreement between the experimental and calculated positions of Lorentzian diffraction profiles. It can also be applied to

other line profiles, however, provided that the peaks are reasonably well separated. Good agreement between the theory and the experiment will give a small R factor while the R factor approaches unity when there is no correlation between the experimental and theoretical data sets. The computed R factors for the four structures are $R_I=0.5$, $R_{II}=1.2$, $R_{III}=1$, and $R_{IV}=1.1$.²² Indeed, structure I shows the best agreement with experiment. For comparison, we calculated the R factor for the $3a_0$ wire, whose structure and electronic properties have been reported elsewhere.² In that case, we obtained $R_{3a_0}=0.4$ for the currently accepted structure model. The higher R factor of the $4a_0$ is due to peak overlapping at biases approaching 1 V. While in LEED crystallography, a Pendry R factor of 0.5 would be considered rather poor, there is no clear benchmark yet for the R -factor analysis of STS spectra.

In conclusion, we observed a class of even-multiple YSi_2 nanowires and determined the structure of the thinnest $4a_0$ wire using STM/STS along in conjunction with total energy minimization and electronic structure calculations using DFT. The Pendry R factor appears to be a useful indicator for selecting the most promising structure model from experimental tunneling spectra and first-principles calculations.

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¹¹The expression “thinnest wires” refers to wires that have the smallest widths; all of them are ≈ 0.4 nm high.

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²²The R factor was computed for all the considered structures using a line-width (half width at half maximum) equal to 0.2 eV.