Quantum size effects in competing charge and spin orderings of dangling bond wires on Si(001)

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Using spin-polarized density-functional theory calculations, we investigate the competition between charge and spin orderings in dangling-bond (DB) wires of increasing lengths fabricated on an H-terminated Si(001) surface. For wires containing less than ten DBs as studied in recent experiments, we find antiferromagnetic (AF) ordering to be energetically much more favorable than charge ordering. The energy preference of AF ordering shrinks in an oscillatory way as the wire length increases and preserves its sign even for DB wires of infinite length. The oscillatory behavior can be attributed to quantum size effects as the DB electrons fill discrete quantum levels. The predicted AF ordering is in startling contrast with the prevailing picture of charge ordering due to Jahn-Teller distortion or Peierls instability for wires of finite or infinite lengths, respectively.

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I. INTRODUCTION

The development of modern nanoelectronics relies crucially on the identification of various types of quantized structures such as quantum wells, quantum wires, quantum dots, and their assemblies.[1] These artificially synthesized quantum structures exhibit a variety of intriguing physical phenomena distinct from their bulk counterparts due to the confinement of electrons in only two, one, or zero directions. Especially, the coupling between spins within nanostructures is of central importance for the design of novel devices engineered at the level of individual atomic spins whose functionality is geared towards computing speed, storage capacity, and energy saving. In the present work, we demonstrates conclusively that the widely studied silicon dangling-bond (DB) wires actually exhibit spin ordering, thereby opening up unprecedented opportunities for atomic engineering of future spintronics and quantum information devices.

The DB wires[2,4] fabricated on an H-terminated Si(001) surface by removing H atoms along one side of a Si dimer row (see Fig. 1) provide an ideal 1D metallic system with a half-filled DB state crossing the Fermi level. Based on first-principles density-functional theory (DFT) calculations, Watanabe *et al.*[3] proposed that a DB wire of infinite length is unstable against metal-insulator transition, characterized by the Peierls instability, where the metallic system will move away from a geometrically symmetrical state to alternating up and down vertical displacements of the Si atoms composing the DB wire [see Fig. 1(c)], resulting in the formation of a charge density wave. Subsequently, Hitosugi *et al.*[2] performed a combination of low-temperature scanning tunneling microscopy (STM) and DFT calculations for DB wires of finite lengths [see Figs. 1(a) and 1(b)], and also interpreted the observed STM data in terms of a Jahn-Teller distortion with charge transfer from the down to the up Si atoms. Therefore, the prevailing structural models[2,3] for DB wires have so far been focused on charge ordering.

In this letter, we examine the influence of magnetism on DB wires where the electron-electron interaction of localized DB electrons may be competent with the electron-phonon coupling proposed in the prevailing structural models. Our spin-polarized DFT calculations predict the existence of a structural order for DB wires, where the spins of adjacent DBs are aligned antiferromagnetically. For wires of finite lengths, such an antiferromagnetic (AF) ordering is found to be energetically much more favorable than previously considered charge ordering due to Jahn-Teller distortion.[2] Furthermore, as the wire length increases, the energy difference $\Delta E_{\mathrm{NM-AF}}$ per dangling bond between the nonmagnetic (NM) and AF configurations decreases in an oscillatory way, and preserves its sign even for DB wires of infinite length. Our band-structure analysis shows that this quantum size effect is

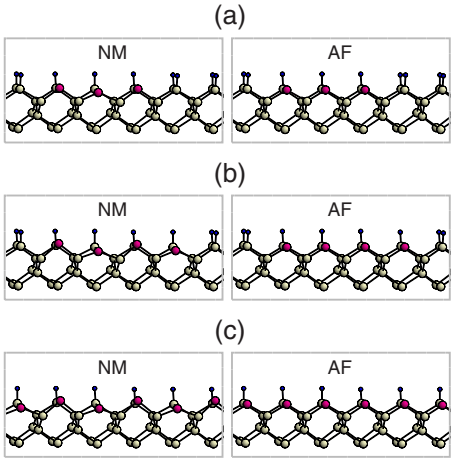

FIG. 1. (Color online) Optimized structures of (a) DB-3, (b) DB-4, and (c) DB-∞ within the NM and AF configurations. The large and small circles represent Si and H atoms, respectively. For distinction, the Si atoms composing the DB wire are drawn in dark color.

associated with half filling of the highest occupied quantum well state in the NM configuration of odd-numbered DB wires. We discuss these results in connection with recent experiments.[2]

II. CALCULATION METHOD

The total-energy and force calculations were performed using spin-polarized DFT within the generalized-gradient approximation,[5] together with norm-conserving pseudopotentials.[6] The surface was modeled by periodic slab geometry. Each slab contains six Si atomic layers plus one H atomic layer and the bottom Si layer is passivated by two H atoms per Si atom. For simulations of the DB wires, we used a 2×8 unit cell that includes eight Si dimers along the dimer row. The electronic wave functions were expanded in a plane-wave basis set with a cutoff of 20 Ry. The k-space integration was done with four k points in the 2×8 surface Brillouin zone. Our calculation scheme has been successfully applied for the adsorption of various molecules on Si(001).[7]

III. RESULTS

We first optimize the atomic structures for DB wires of infinite length (hereafter designated as DB-∞) and finite lengths containing up to seven DBs (designated as DB-2, DB-3, DB-4, DB-5, DB-6, and DB-7, respectively). For all these DB wires, we consider the NM, ferromagnetic (FM), and AF configurations. To obatin the energy gains caused by Jahn-Teller (or Peierls) distortion and magnetic orderings, we calculate the energies of the NM, FM, and AF configurations relative to the nonbuckled NM configuration (designated as NM_{sym}) where the Si atoms composing the DB wire are constrained to have an identical height. The results with respect to the wire length are plotted in Fig. 2(a). For each DB wire, the AF configuration is found to be more stable than the NM and FM ones, showing an AF ground state.[8] Here, the total spin of the AF configuration is zero ($1\ \mu_B$) for the even(odd)-numbered DB wires, while that of the FM configuration is $1\ \mu_B$ per dangling bond.

Figure 2(a) shows that for the even(odd)-numbered DB wires, the energy gain arising from a Jahn-Teller distortion increases as the wire length increases. The energy difference per dangling bond between the NM_{sym} and NM configurations is 10, 23, and 34 (13, 18, 23) meV for DB-2, DB-4, and DB-6 (DB-3, DB-5, DB-7), respectively. We obtain the largest Jahn-Teller energy gain of 49 meV in DB-∞. This may be ascribed to a decreased elastic-energy cost in DB-∞ compared to in DB wires of finite lengths, where the two ends give rise to a relatively larger elastic-energy cost for the alternating up and down lattice distortion.

The energy gain caused by spin polarization decreases with increasing the wire length [see Fig. 2(a)]. The energy difference per dangling bond between the NM_{sym} and AF (FM) configurations is 84 (56), 96 (59), 81 (39), 80 (35), 74 (27), 72 (22), and 57(−1) meV for the DB-2, DB-3, DB-4, DB-5, DB-6, DB-7, and DB-∞ wires, respectively. Thus, the AF configuration is more stable than the buckled NM configuration by ΔE_{NM-AF}=74, 83, 58, 62, 40, 49, and 8 meV

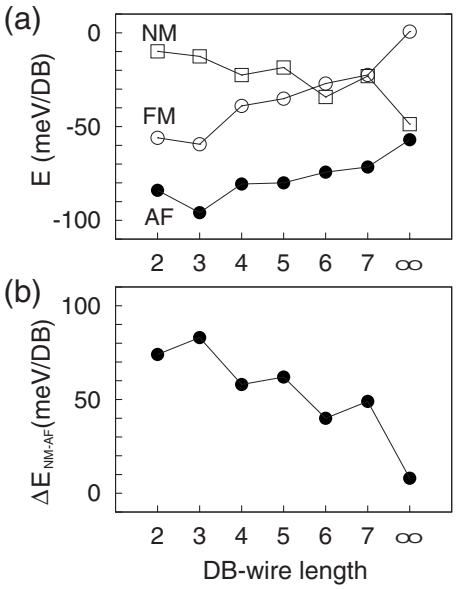

FIG. 2. (a) Calculated energies (per dangling bond) of the NM, FM, and AF configurations relative to the NM_{sym} configuration and (b) the energy difference ΔE_{NM-AM} between the NM and AF configurations as a function of the wire length.

for DB-2, DB-3, DB-4, DB-5, DB-6, DB-7,[9] and DB-∞, respectively. Here, it is worth emphasizing that ΔE_{NM-AF} for the odd-numbered DB wire (containing n dangling bonds) is larger than those of the even-numbered DB wires (containing $n-1$ and $n+1$ dangling bonds): see Fig. 2(b). This oscillatory behavior correlates with the variation in DB states with respect to the wire length, as discussed below.

Using the Heisenberg spin Hamiltonian $\hat{H}=\Sigma_{i,j}J\hat{S}_i\cdot\hat{S}_j$ where we assume only the existence of the nearest neighbor interactions in DB wires, we obtain the exchange-coupling constant J=56, 56, 56, 56, 56, 58, and 58 meV for the DB-2, DB-3, DB-4, DB-5, DB-6, DB-7, and DB-∞, respectively.[10] This result indicates that the exchange coupling constant between adjacent spins in DB wires is nearly independent of the wire length. Thus, we need to caution that, as the wire length increases, the decrease in the energy difference between the NM_{sym} and AF configurations is not due to the weakened AF ordering but to the enhanced stability of the NM_{sym} configuration.[11]

As shown in Fig. 1, the NM configuration exhibits alternating up and down displacements of the Si atoms composing DB wires. Thus, the NM configuration of DB-2, DB-3, DB-4, DB-5, DB-6, and DB-7 has the buckling patterns of UD, UDU, UDUD, UDUDU, UDUDUD, and UDUDUD, respectively,[12] where U (D) represents the up (down) Si atom. In Table I, we summarize the calculated heights of the up and down Si atoms relative to that of the H-terminated Si atoms. We find that for the even(odd)-numbered DB wires, the height difference $h_{up-down}$ between the up and down Si atoms increases as the wire length increases, taking the values of 0.49, 0.59∼0.69, and 0.70∼0.76 (0.41, 0.53∼0.66, 0.53∼0.74) Å for DB-2, DB-4, and DB-6 (DB-3, DB-5, DB-7), respectively. Especially, DB-∞ has the largest value (0.78 Å) for $h_{up-down}$, indicating that the up and down lattice distortion can be maximized by the absence of ends.

TABLE I. Calculated heights (in Å) of the Si atoms composing the DB wire. The values are given relative to the average height of the H-terminated Si atoms within the DB wire.

		Si atoms						
		1	2	3	4	5	6	7
NM	DB-2	0.18	−0.31					
	DB-3	0.07	−0.34	0.07				
	DB-4	0.23	−0.43	0.26	−0.33			
	DB-5	0.12	−0.41	0.25	−0.41	0.12		
	DB-6	0.27	−0.44	0.30	−0.46	0.30	−0.40	
	DB-7	0.12	−0.41	0.29	−0.45	0.29	−0.41	0.12
	DB-∞	0.32	−0.46					
AF	DB-2	−0.05	−0.05					
	DB-3	−0.04	−0.05	−0.04				
	DB-4	−0.04	−0.05	−0.05	−0.04			
	DB-5	−0.04	−0.05	−0.05	−0.05	−0.04		
	DB-6	−0.04	−0.05	−0.05	−0.05	−0.05	−0.04	
	DB-7	−0.04	−0.05	−0.05	−0.05	−0.05	−0.05	−0.04
	DB-∞	−0.05	−0.05					

In contrast with the NM configuration, the AF configuration gives rise to a nearly nonbuckled structure (see Table I), indicating the absence of spin-Peierls instability.

Next, we study the electronic band structures for various configurations of DB wires. In Fig. 3, we plot the results for DB-2, DB-3, DB-4, DB-5, and DB-∞ within the NM and AF configurations. We see that subbands due to the DB electrons appear in the band gap of bulk Si. The charge characters of these DB states, as displayed in Fig. 3, reveal that the NM configuration has a charge transfer from the down to the up Si atoms while the AF configuration involves an opposite spin orientation between adjacent dangling bonds. It is noticeable that, as the wire length increases, the subbands are lower in energy and their spacings decrease, representing the evolution of quantum well states. Especially, for the odd-numbered DB wires, the NM configuration has a half-filled subband, while the AF configuration shows a band-gap opening (i.e., 0.79, 0.73, and 0.66 eV for DB-3, DB-5, and DB-7, respectively: see Table II). This different feature of subbands between the NM and AF configurations of odd-numbered DB wires possibly gives rise to the above-mentioned oscillatory variation in $\Delta E_{\mathrm{NM-AF}}$ with respect to the wire length [see Fig. 2(b)]. Note that for the even-numbered DB wires of DB-2, DB-4, and DB-6, the AF configuration has the band gaps of 0.89, 0.79, and 0.72 eV, respectively, larger than the corresponding ones (0.45, 0.28, and 0.24 eV) of the NM configuration. For DB-∞, the band-gap difference between the NM and AF configurations is much reduced as 0.24 eV (see Table II), thereby resulting in a relatively smaller value of $\Delta E_{\mathrm{NM-AF}}$ compared to for DB wires of finite lengths. Our calculated band structures manifest that the electronic energy gain is enhanced by generating AF spin polarization, compared to by accompanying Jahan-Teller lattice distortion.

For DB wires fabricated on the H-terminated Si(001)-2×1 surface, Hitosugi *et al.*[2] performed STM studies at low temperatures ranging from 96 to 110 K. In their filled-state STM data, DB-2, DB-3, and DB-4 appear as two, three, and four bright protrusions, respectively, while DB-5 appears as three bright protrusions and DB-∞ appears as one bright protrusion per two DBs. Using the Tersoff-Hamann approximation,[13] we simulate the constant-current STM images for the filled states of DB-2, DB-3, DB-4, DB-5, and DB-∞ within the NM and AF configurations. The results are displayed in Fig. 4, together with their cross-sectional views

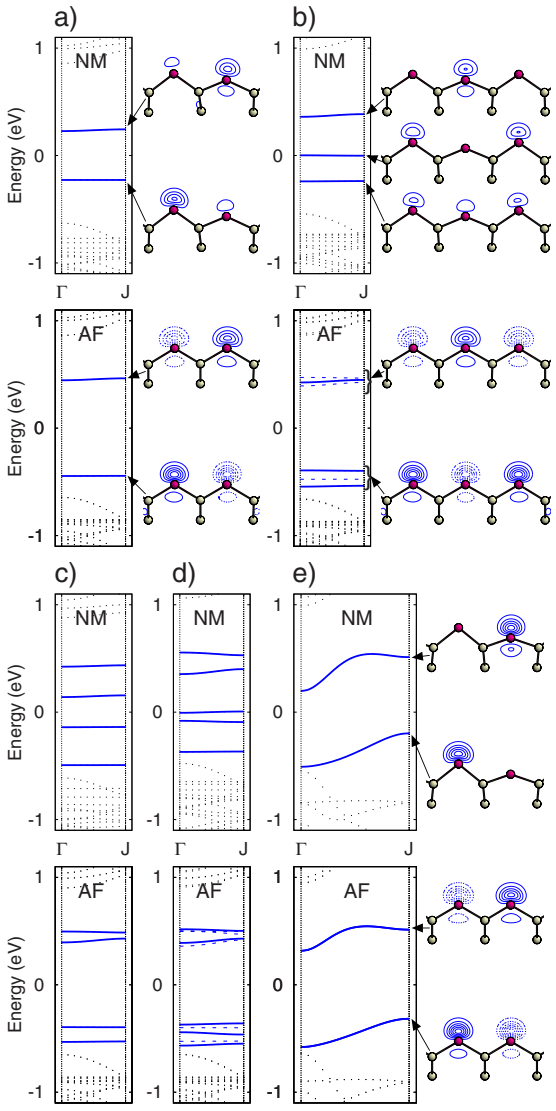

FIG. 3. (Color online) Calculated band structures of (a) DB-2, (b) DB-3, (c) DB-4, (d) DB-5, and (e) DB-∞ within the NM and AF configurations. The energy zero represents the Fermi level. The direction of Γ-J line is along the DB wire. In the NM configuration, the solid lines represent the subbands due to the dangling-bond electrons, while in the AF configuration the solid (dashed) lines represent the subbands of majority (minority) spin. In (a), (c), and (e), the subbands of the majority and minority spins are equal to each other. The charge characters of subbands at the *J* point are also given. The plots are drawn in the vertical plane containing the Si atoms of the DB wire. The first contour line and the line spacings are the same as 0.004 electron/bohr^3. In the AF configuration, the solid (dotted) line represents the majority (minority) spin density.

TABLE II. Calculated band gaps (in electron volts) for the DB-2, DB-3, DB-4, DB-5, DB-6, DB-7, and DB-∞ wires within the NM and AF configurations.

	DB-2	DB-3	DB-4	DB-5	DB-6	DB-7	DB-∞
NM	0.45		0.28		0.24		0.39
AF	0.89	0.79	0.79	0.73	0.72	0.66	0.63

along the wire direction. We find that the NM and AF configurations exhibit a conspicuous difference in the features of simulated STM images. The NM configuration composed of the alternating up and down Si atoms produces bright protrusions associated with the up Si atoms, whereas the AF configuration produces bright protrusions for all the Si atoms composing the DB wire. Thus, comparison of these simulation results with the STM measurements[2] implies that at ~100 K (used in the experiments of Hitosugi *et al.*) DB-2, DB-3, and DB-4 order in the AF configuration, whereas DB-5 and DB-∞ favor the NM configuration.

It is notable that the measured[2] cross-sectional view of the filled-state STM image of DB-2 gives a peak-to-valley height difference of ~0.26 Å, similar to the simulated value of 0.39 Å in the AF configuration [see Fig. 4(c)]. For DB-3, the measured STM image showed that the height of the center peak is lower than those of the two edge peaks by ~0.13 Å, in good agreement with a simulated value of 0.06 Å in the AF configuration. For DB-4, the measured image also showed that the two inner peaks are 0.06 ~0.11 Å lower than the edge peaks, close to 0.06 Å in the AF configuration [see Fig. 4(c)]. However, for DB-5 and DB-∞, the measured peak-to-valley height differences are much smaller than our zero-temperature simulated values in the NM configuration by a few tenths of factor, possibly due to a relatively larger thermal vibration effect of the up and down Si atoms.

Finally, we note that experimentally observed buckled NM configuration at ~100 K for DB wires longer than DB-4 could be due to vibrational contributions to the free energy, the minimum of which determines the equilibrium structure at a given temperature.[14] As the wire length increases, the vibrational effects will play a much bigger role in contributing to the internal energy and the vibrational entropy, thereby yielding a relatively lower free energy in the buckled NM configurations compared to the nonbuckled AF configurations. For more conclusive identification on this length-dependent AF-NM transition in DB wires, theoretical studies employing free-energy calculations as well as variable low-temperature STM experiments will be anticipated.

IV. SUMMARY

Our spin-polarized DFT calculations predicted that DB wires on an H-terminated Si(001) surface prefer the AF ordering rather than the prevailing picture of charge ordering due to Jahn-Teller distortion or Peierls instability. We further found that DB wires of finite lengths exhibit various quantum-size effects in their energetics, geometries, and electronic states. These predictions may help the design of silicon-based devices for storages and processing of quantum information.[15] Since our predictions are likely to hold for other semiconductor (C and Ge) materials, various DB wires may offer a unique way to device the spintronics on semiconductor substrates.

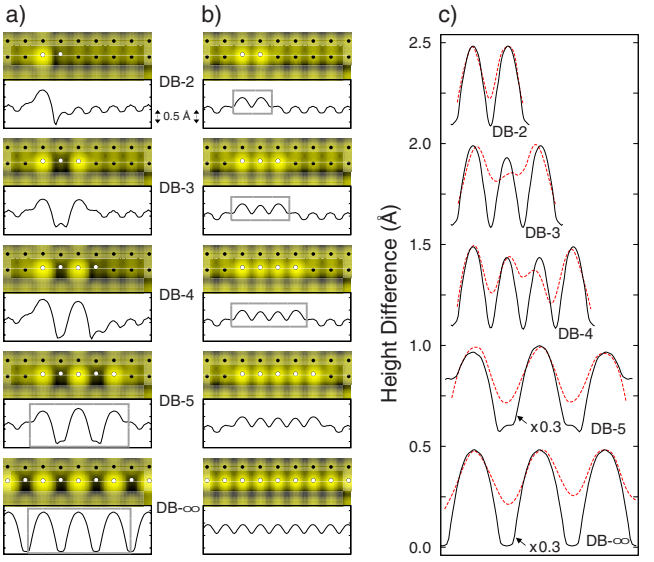

FIG. 4. (Color online) Simulated filled-state STM images of the (a) NM and (b) AF configurations for DB-2, DB-3, DB-4, DB-5, and DB-∞, including (c) the cross-sectional view along the line connecting dangling bonds. The images were obtained by integrating the charge from $E_F-2.0$ eV to E_F. All the images were taken at a charge density of 1.0×10^{-6} electron/bohr^3. Comparison of the cross-sectional views of simulated images with the experimental data (Ref. 2) is given in (c). The solid line represents the simulated data (multiplied by 0.3) taken from the boxes of (a) and (b), while the dashed line represents the experimental data.

ACKNOWLEDGMENTS

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[8] Spin-polarized DFT calculations of C. F. Bird and D. R. Bowler, Surf. Sci. **531**, L351 (2003) predicted the NM and AF ground states for even- and odd-numbered DBs, respectively. In order to explain the disparity between STM measurements and simulations for even-numbered DB wires, Bird and Bowler speculated the flipping motion of buckled dimers to produce time-averaging STM images However, noting that thermally activated flipping motion of buckled dimers becomes frozen at ~ 100 K [e.g., A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992)], it is most likely that the observed bright protrusion of each DB in even-number DB wires can be associated with their static geometries of the AF configuration rather than the flipping motion of buckled dimers of the NM configuration.

[9] Using the 2×10 unit-cell calculations with the plane-wave-basis cutoff of 30 Ry, we found that the energy difference between the NM and AF configurations and the heights of dangling bonds (in Table I) change by a few meV/DB and less than a hundredth of angstroms, respectively.

[10] The exchange coupling constant J for the DB-n wire can be evaluated by $J = E_{\mathrm{FM-AF}}/(n-1)$, where $E_{\mathrm{FM-AF}}$ is the energy difference per unit cell between the FM and AF configurations. For DB-∞, $n=2$.

[11] We found that the formation energy of $\mathrm{NM}_{\mathrm{sym}}$, defined as the energy cost of desorbing H atoms from the H-terminated Si(001) surface, is 3.426, 3.433, 3.414, 3.411, 3.404, 3.400, and 3.380 eV per dangling bond for DB-2, DB-3, DB-4, DB-5, Db-6, DB-7, and DB-∞, respectively.

[12] The buckling patterns of DUD, DUDUD, and DUDUDUD in DB-3, DB-5, and DB-7 are less stable than UDU, UDUDU, and UDUDUDU by 9, 5, 3 meV/DB, respectively.

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