Controlled Coupling and Occupation of Silicon Atomic Quantum Dots at Room Temperature

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It is demonstrated that the silicon atom dangling bond (DB) state serves as a quantum dot. Coulomb repulsion causes DBs separated by $\lesssim 2$ nm to exhibit reduced localized charge, which enables electron tunnel coupling of DBs. Scanning tunneling microscopy measurements and theoretical modeling reveal that fabrication geometry of multi-DB assemblies determines net occupation and tunnel coupling strength among dots. Electron occupation of DB assemblies can be controlled at room temperature. Electrostatic control over charge distribution within assemblies is demonstrated.

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Interest in zero-dimensional electronic structures both for fundamental science and device application has exploded in recent years. Their rich electrical, magnetic, and optical properties offer appealing territory both for fundamental condensed matter investigations and for exploration of new device concepts. Examples include semiconductor quantum dots (QDs) [1,2], impurity-state tunneling systems [3–5], and single molecules [6].

QDs have been pursued in the context of nanoelectronics applications [7] (transistors, logic gates, spin devices, etc.), light emitting diodes and lasers [8], solar cells [9], ultradense memories [10], among other areas. Moreover, controlled coupling of the electronic states of QDs have been investigated as a basis for alternative computing approaches, such as quantum computing [11] and quantum cellular automata (QCA) schemes [12–14]. However, current miniaturization of QDs is far from reaching its limit. Present QD fabrication techniques render QD assemblies of a scale that requires cryogenic conditions to attain energy level spacings greater than k_BT—a key condition for enabling controlled electronic properties.

In this Letter, we report for the first time an experimentally observable tunnel coupling between zero-dimensional entities of atomic size: Si atom dangling bonds (DB) on an otherwise hydrogen terminated silicon crystal surface. Such DBs can serve as quantum dots, and due to their strong charge localization, circumvent key problems associated with QD charging. Indeed, we show here that the charging and the tunnel coupling behavior within DB assemblies can be controlled even at room temperature. In addition, due to the fundamental similarities with semiconductor QDs and to the common Si-based fabrication platform, our approach can bring important advances to many of the applications described above.

Unlike the delocalized valence and conduction band states in a silicon crystal, DB states exist within the silicon band gap. DBs are therefore substantially decoupled from the bulk and retain a degree of atomlike character. The distance-dependent coupling of two or more DBs via an electron tunneling interaction is observed. Working under conditions where individual DBs are ordinarily negatively charged, coupled DB assemblies are found to exhibit a ''self-biasing'' behavior—Coulombic repulsion acts to reduce electron filling and enable tunneling between DBs. The fabrication and room temperature electrostatic setting of the state of a ~1 nm-scale assembly of four coupled silicon DBs is demonstrated.

Scanning tunneling microscopy (STM) images of H-terminated silicon surfaces are shown in Fig. 1. Each surface silicon atom at the (100) surface shares in a surface-parallel Si-Si dimer bond and is capped by a single H atom (Fig. 1 inset). The diagonal barlike features in the images are rows of silicon dimers. Figure 1(a) shows a

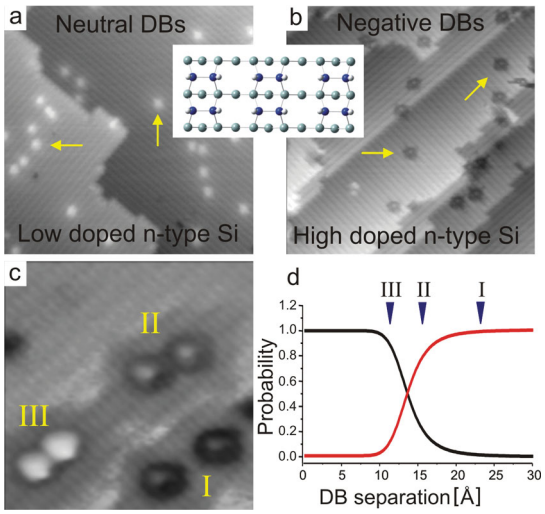

FIG. 1 (color). Si surface structure, inset (Si dimers = blue, H = white, subsurface Si = grey). (a) STM image of low doped n-type Si ($\sim 5 \times 10^{15}$ cm^{-3}). 35 × 35 nm, 2 V, 0.1 nA. DBs appear bright. (b) High doped n-type Si ($\sim 5 \times 10^{18}$ cm^{-3}) 35 × 35 nm, 2.2 V, 0.1 nA. DBs appear dark with a central spot. (c) 9 × 9 nm, 2 V, 0.2 nA. Three groups of DBs are prepared. A noncoupled DB pair at 2.32 nm (I). Coupled DB pairs at 1.56 nm (II) and 1.15 nm (III). (d) Calculated one- and two-electron occupation probabilities (black and red curves, respectively) corresponding to the DB pairs in (c).

distribution of DBs, silicon atoms that do not have a capping H atom. The low n-type dopant concentration results in DBs that tend to be neutral, corresponding to one electron in the DB state [15].

Figure 1(b) shows a distribution of DBs on a highly n-type doped H-terminated silicon crystal. The high Fermi level (~1.06 eV from the bulk valence band) causes DBs on this surface to contain a total of 2 electrons each, rendering them negatively charged [15]. The charged DBs bend bands upward, thereby locally inhibiting electron injection from the STM tip into the conduction band (CB), causing a dark halo around DBs in unoccupied state images [Fig. 1(b)] [16]. DBs show the dark halo regardless of whether they are created by single H atom removal with the STM tip [17] or are naturally occurring, as a result of incomplete H-termination. The imaging characteristics of dangling bond states are consistent with previous STM studies on surface states [15,16,18].

Figure 1(c) explores the effect of distance between DBs. An STM procedure [17] for removing single H atoms was used to make three pairs of DBs with varying separations. Both DBs of pair "I" image as individual, negatively charged DBs, that is, greater separation has no effect on DB appearance. However, pairs "II" and "III" display a distance-dependent brightness (a protrusion in STM image). This pronounced coupling effect has not previously been reported. In the following, we explain that this is a signature of tunnel-coupled DBs. A DB within approximately 15 Å of another DB will exhibit this coupling. It is apparent that the coupling between two sufficiently close DBs is mediated by the lattice, as through-space covalent bonding between DBs is negligible at separations greater than one dimer spacing. This is verified by hybrid density function theory (DFT) [19–21] calculations performed on a silicon cluster model. These calculations show that the DB state is partially localized in the vacuum region above the surface and has greater spatial breadth inside the Si medium. However, the state density does not substantially extend beyond a radius of approximately 3.8 Å. The extreme cases of two DBs on one silicon dimer [22] or on adjacent dimers in a row [23] (separations within 3.8 Å) are well known and qualitatively different than the weaker coupling considered here.

In Fig. 1(d), the calculated charging probabilities of a DB pair as a function of DB separation are shown, based on our statistical-mechanical treatment. A DB assembly (or cell) is a finite system in contact with a reservoir (the Si crystal) of constant temperature, T, and chemical potential, E_F. Thus, the (unnormalized) statistical weight of charging a DB cell with i electrons is

$$f_i = g_i \exp[-(E_i^{\mathrm{tot}} - iE_F)/k_B T], \quad (1)$$

where E_i^{tot} is the total energy of the n-DB cell with i extra electrons (including interactions), $k_B T$ is the temperature, E_F is the Fermi level, and g_i is the degeneracy of the charging state i. In order to obtain the probability of the charging state i [plot in Fig. 1(d)], the statistical weight f_i is divided by the partition function of the n-DB cell $Z_n(T, E_F) = \sum_{i=1,n} f_i$. The total energy is written in the lattice gas form as the sum of the self-energies and the Coulombic and tunneling interactions.

DB coupling is further explored in a theoretical model qualitatively illustrated in Fig. 2. DBs were modeled using a harmonic oscillator potential, as was previously done for coupled quantum dots [11]. The 2D potential well of a single DB is defined in a truncated harmonic form which allows for electron escape into the CB

$$V_{\mathrm{DB}}(r) = \frac{1}{2}\left(\frac{m\omega^2}{2} r^2 - V_0\right)\left[1 - \tanh\left(\frac{r - R_b}{w}\right)\right], \quad (2)$$

where ω is the classical electron oscillation frequency, m the electron mass, V_0 is potential depth from the CBM, R_b and w determine the location and the width of the truncation region, respectively. The isolated DB wave function has the form $\psi_0(r) = A \exp(-\alpha r^2)$, with normalization constant A, energy $E_0 = \hbar\omega$, and $\alpha = m\omega/2\hbar$. The binding energy (~0.32 eV) and the spatial extent of the wave function (3.8 Å) were determined from DFT calculations. The potential wells plateau at the CB energy. Figure 2(a) qualitatively depicts two potential wells, sufficiently separated laterally to be uncoupled. The horizontal line crossing each well represents the bound DB level capable of holding up to two electrons each. Figure 2(b) represents 2 DBs laterally separated by less than ~15 Å. As a result of Coulombic repulsion, the occupation state with 2 electrons per DB is destabilized (shifted upward in energy). Consequently, the two-DB entity is shown to be more stable if one electron is excluded from one of the DBs and put into a bulk energy level. This "self-biasing" effect is crucial to the coupling of closely spaced atomic quantum dots: The exclusion of one electron from the paired DBs

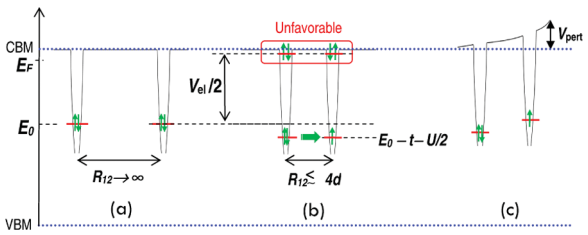

FIG. 2 (color). Qualitative diagram of paired DBs as variably spaced potential wells. (a) Isolated negatively charged DBs each occupied by two electrons at a ground state energy E_0. (b) Coulomb repulsion, V_{el}, excludes one electron from a pair of coupled DBs, resulting in a net charge of one electron. The occupation state in which each DB has one extra electron, enclosed in red, becomes increasingly unfavorable with decreasing distance. The repulsive Hubbard on-site pairing energy U and the tunnel splitting energy t are also indicated, and d is the nearest dimer-dimer distance. (c) A double-well potential for two tunnel-coupled DBs perturbed by a third, more distant DB that is negatively charged. CBM and VBM are the bulk conduction and valence band edges, respectively.

provides a partially empty state and therefore a destination for a tunneling electron. When close enough, the barrier separating the DBs is sufficiently narrow to permit substantial tunnel coupling between DBs. Our statistical treatment shows that the average electron occupation of coupled DBs shifts from just under 2 extra electrons on average for DBs spaced by approximately 23 Å, to 1 extra electron as DBs become closer than 10 Å, see Fig. 1(d). This accounts for the increasingly bright appearance of DB pairs with decreasing separation [Fig. 1(c)]: The exclusion of one of the two extra electrons reduces upward band bending and creates a partially empty state, enabling relatively easy injection of electrons from the STM tip and a brighter appearance in the STM image. Though the charge at coupled DBs is reduced and the appearance resembles that of neutral DBs [Fig. 1(a)], the pair-encircling dark halo due to an extra electron, distinguishes coupled DBs from neutral DBs.

The STM image in Fig. 1(c) represents the direct observation of tunnel coupling between DBs. We note that the tunnel-coupled pairs of Si DBs resemble charge qubits that are being considered for quantum computing architectures. However, the necessary coherence remains to be demonstrated.

Figures 3(a) and 3(b) show the tip-induced creation of one DB. Figure 3(c) demonstrates that an isolated negative DB (labeled DB1) will enter into a coupling arrangement when offered a sufficiently close partner (DB2). A third, negatively charged DB (DB3) was created at a distance where it cannot tunnel-couple with DB1 and DB2 [Fig. 3(d)]. However, the electrostatic repulsion due to DB3 causes the extra electron in the DB pair to favor occupation on DB2, as illustrated schematically in Fig. 2(c). This effect is clear in the line profiles shown in Fig. 3: An electrostatic perturbation has caused DB1 to become appreciably brighter, that is, less negative, than DB2. DB3 causes a breaking of symmetry leading to a dominance of one occupation over another. The self-biasing effect—the determination of occupation through control of DB separation—results in the 2 DB group having only one extra electron on average. This electron occupation control is achieved without the use of an external electrostatic perturbation or gate electrode.

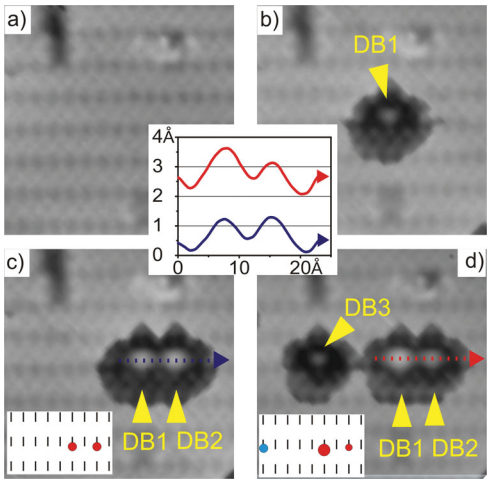

FIG. 3 (color). Formation and coupling of DBs and demonstration of an electrostatic perturbation on coupled DBs. STM images are 5 × 5 nm, 2.5 V, 0.1 nA: (a) H-terminated Si(100) 2 × 1 surface—no DBs. (b) DB1 is created. (c) DB2 created 0.768 nm from the DB1. These DBs are tunnel coupled. (d) DB3 is formed; it is negatively charged and not coupled to DB1 and DB2. DB1 now appears brighter as a result of its proximity to the negatively charged DB3. The insets show grids to represent the DB positions on the Si surface. Comparison of relative height profiles for the DB pair prior to (blue) and after (red) the addition of DB3 is overlaid on the STM images.

We now examine assemblies of more than two coupled DBs. Figure 4(a) shows 3 coupled DBs. The question of how many extra electrons are contained by such a structure is in part answered by our experimental observations: The encircling dark halo indicates that the entire assembly is negatively charged. The brightness variation among the DBs indicates that DB1 and DB3 are more negatively charged, on average, than DB2. This can only be caused by the presence of two extra electrons in the assembly. This is supported by calculations which show that Coulombic repulsion is too great for 3 electrons to be bound on the structure shown in Fig. 4(a).

In Fig. 4(b), a fourth DB (DB4) is created by STM tip-induced removal of a single H atom in a position close enough to couple to the first three DBs. The schematic in Fig. 4 shows that the four DB structure deviates from a regular rectangular arrangement. The most widely separated DBs in the group of four DBs (DB2 and DB4) are darkest in appearance. Note that DB2 was initially brighter than DB1 and DB3 in Fig. 4(a), then became darker than DBs 1 and 3 in Fig. 4(b). It is apparent that the approximately two extra electrons in this structure are predominantly located at the most distant DBs (DBs 2 and 4). This is consistent with the expectation that the greatest charge separation corresponds to the lowest energy configuration. Computation reveals that a net charge of −3 on this 4 DB

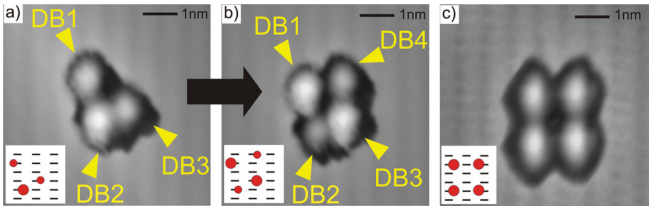

FIG. 4 (color). Coupling in asymmetric and symmetric DB arrangements. (a) 2 V, 0.1 nA. Three coupled DBs showing inequivalencies. DB2 is brightest. (b) 2 V, 0.1 nA. A fourth coupled DB was created. DB2 became less bright, DB1 and DB3 became most bright. Average height differences are ∼0.4 and ∼0.7 Å for (a) and (b), respectively. (c) 2 V, 0.08 nA. A separate experiment showing a symmetric group of 4 DBs of equal heights within 0.1 Å. Grids on the images represent DB positions.

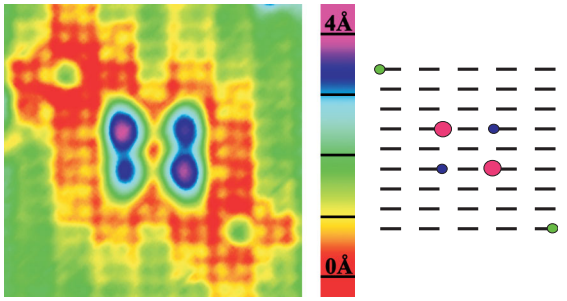

FIG. 5 (color). A color mapped STM image (6 × 6 nm, 2.5 V, 0.11 nA) of a rectangular 4-DB coupled entity with two additional electrostatically perturbing DBs diagonally placed. The 2 DBs nearest the negative perturbing DBs are relatively high in appearance as a result of unfavored electron occupation at those sites. The average height difference between the violet (higher) and blue colored (lower) DBs is ~0.4 Å. A grid represents the DB positions on the silicon surface.

assembly is prohibitive due to excessive Coulombic repulsion. The experimental observations are inconsistent with a charge state of −1 because a single electron is expected to be shared between the two most highly coupled DBs. This would result in adjacent (rather than opposite DBs) appearing darker. A charge state of −2 fits the experiment and computational results. Figure 4(c) shows a rectangular arrangement of 4 coupled DBs. In this case, the DBs heights are within 0.1 Å indicating that the approximately 2 extra electrons are close to being equally shared between all 4 DBs. This is in contrast to the case in Fig. 4(b) where the irregular structure causes the asymmetric distribution of electrons.

It is possible to induce an asymmetry in the electronic structure of the 4 DB system through the application of negatively charged DBs, as was demonstrated for a 2 DB system in Fig. 3(d). Figure 5 shows 4 coupled DBs and 2 diagonally placed perturbing DBs. The schematic shows the positions of all 6 DBs. Consistent with the expectation that a negative gating effect destabilizes electron occupation, it is seen that the two DBs within the cell that are nearest the perturbing DBs appear brighter, indicating less negative charge is localized there. The image shows a controlled electrostatic breaking of symmetry and setting of an antipodal state at room temperature. The structure shown in Fig. 5 is reminiscent of the central building block in the QCA scheme proposed by Lent and co-workers in 1993 [12]. The dynamic setting of such a state will require the introduction of suitable gates—a goal of ongoing work.

Within the coupled DB scheme, considerable latitude exists for control over electron occupation. Slightly more widely spaced configurations will reduce Coulombic repulsion to allow, and lead automatically to, a greater net charge. Similarly, closer spaced structures will naturally exhibit reduced charging. This self-biasing is most desirable as it removes the need for filling gates. A related result is notable: Fixed charges beyond ~30 Å are observed experimentally to be insignificant perturbations on the state and filling level of a Si DB-based QD assembly. This is in contrast to the acute sensitivity of some quantum dots to relatively distant unintended charges [24]. The robustness of the atomic system described here results from the relatively great energy level spacing of bound states. For this same reason, the coupling and controlled electron filling of assemblies of coupled DBs is achieved at room temperature rather than requiring cryogenic conditions. We assert that such DB states hold the prospect of a novel route to advancement in nanoelectronics and computing devices, offering extreme miniaturization and a well-understood route to fabrication.

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[1] C. B. Murray, C. R. Kagan, and M. G. Bawendi, Annu. Rev. Mater. Sci. **30**, 545 (2000).
[2] S. M. Reimann and M. Manninen, Rev. Mod. Phys. **74**, 1283 (2002).
[3] M. R. Deshpande *et al.*, Phys. Rev. B **62**, 8240 (2000).
[4] L. E. Calvet, R. G. Wheeler, and M. A. Reed, Phys. Rev. Lett. **98**, 096805 (2007).
[5] C. Flindt, N. A. Mortensen, and A.-P. Jauho, Nano Lett. **5**, 2515 (2005).
[6] J. V. Barth, G. Constatini, and K. Kern, Nature (London) **437**, 671 (2005).
[7] L. P. Kouwenhoven, D. G. Austing, and S. Tarucha, Rep. Prog. Phys. **64**, 701 (2001).
[8] A. D. Yoffe, Adv. Phys. **50**, 1 (2001).
[9] B. O'Regan and M. Gratzel, Nature (London) **353**, 737 (1991).
[10] J. J. Welser *et al.*, IEEE Electron Device Lett. **18**, 278 (1997).
[11] G. Burkard, D. Loss, and D. P. DiVincenzo, Phys. Rev. B **59**, 2070 (1999).
[12] C. S. Lent *et al.*, Nanotechnology **4**, 49 (1993).
[13] A. O. Orlov *et al.*, Science **277**, 928 (1997).
[14] *Quantum Cellular Automata*, edited by M. Macucci (Imperial College Press, London, UK, 2006).
[15] P. G. Piva *et al.*, Nature (London) **435**, 658 (2005).
[16] P. Ebert, Surf. Sci. Rep. **33**, 121 (1999).
[17] J. W. Lyding *et al.*, Appl. Phys. Lett. **64**, 2010 (1994).
[18] P. Ebert, Curr. Opin. Solid State Mater. Sci. **5**, 211 (2001).
[19] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[20] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[21] M. J. Frisch *et al.*, *Gaussian 03 Revision C.02* (Gaussian, Inc., Wallingford, Connecticut, 2004).
[22] J. J. Boland, J. Vac. Sci. Technol. A **10**, 2458 (1992).
[23] T. Hitosugi *et al.*, Phys. Rev. Lett. **82**, 4034 (1999).
[24] J. R. Tucker and T.-C. Shen, Int. J. Circuit Theory Appl. **28**, 553 (2000).