Broken Even-Odd Symmetry in Self-Selection of Distances between Nanoclusters due to the Presence or Absence of Topological Solitons

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Depositing particles randomly on a 1D lattice is expected to result in an equal number of particle pairs separated by even or odd lattice units. Unexpectedly, the even-odd symmetry is broken in the self-selection of distances between indium magic-number clusters on a Si(100)-2 × 1 reconstructed surface. Cluster pairs separated by even units are less abundant because they are linked by silicon atomic chains carrying topological solitons, which induce local strain and create localized electronic states with higher energy. Our findings reveal a unique particle-particle interaction mediated by the presence or absence of topological solitons on alternate lattices.

Self-assembly of atoms into particles is a promising approach for growing nanomaterials on surfaces. Particle-particle interactions affect the kinetics of self-assembly and lead to different particle size and spatial distributions, therefore influence the material properties. The interaction can be mediated by surface lattice that carries elastic strains induced by particles; and minimization of the strain energies leads to adjustments of distances between particles and sometimes results in an ordered array of particles [1]. Although lattice-mediated interactions have been intensively studied, detailed investigations on the atomic scale remain scarce, primarily because of our inability to precisely control the sizes of particles. The recent discovery of self-assembled clusters with enhanced stabilities on a surface [2–5], i.e., surface magic clusters (SMC), allows the growth of particles with identical size, thereby facilitating such investigations. Here we report studies of lattice-mediated interaction between indium SMCs (In-SMC) on a Si(100)-2 × 1 surface [3,6,7]. We discovered a very subtle regularity in a seemingly random distribution of clusters, namely, a pair of indium SMCs is less likely to be at distances spanning even number of lattice units. The chains of alternatively buckled silicon dimers (Si dimer) linking such cluster pairs carry topological solitons and therefore have higher energies than their odd counterparts. This first observation of even-odd symmetry breaking in the self-selection of atomic distances between cluster pairs contradicts our common expectation about random clustering processes. The symmetry is broken because of a particle-particle interaction mediated by the presence or absence of topological solitons on the alternate lattices.

Our study was conducted on a Si(100)-2 × 1 surface covered by Si-dimer chains. At temperatures around 900 K

[8], the Si-dimer chains undergo a Peierls-type transition [9] and result in alternate buckling of the Si dimers. Below 200 K, the alternately buckled Si dimers show static structures and appear as a zigzag chain of round spots in scanning tunneling microscopy (STM) images [9]. While at room temperature, the Si dimers flipped back and forth between two buckling orientations [10] and appear as a straight chain of oval spots in STM images. Despite its tendency to oscillate, a Si dimer can be locked in a particular orientation by the presence of a particle at its neighboring site [11]. This locking can then be passed on from one Si dimer to the next, creating a chain of alternately buckled Si dimers. The existence of interaction between a Si-dimer chain and its neighboring particles suggests it could act as a quasi-one-dimensional medium for particle-particle interaction.

Deposition of indium atoms on a Si(100)-2 × 1 surface at 820 K lead to the self-assembly of In-SMC with identical size and atomic structure [3,6,7], as shown by the bright spots in Fig. 1(a). Previously we had studied two-dimensional cooperative phenomena in the nucleation of In-SMCs and found that, for a pair of clusters located within certain range, the formation probability is enhanced or suppressed depending on their relative positions [7]. Now we investigate one-dimensional interaction between In-SMCs along Si-dimer rows. An In-SMC affects the Si dimers on the two rows it occupies while leaving no apparent strain to its adjacent rows. As shown in Fig. 1(b), an In-SMC locks its nearest neighboring Si dimers to opposite buckling orientations such that the two Si-dimer chains exhibit mirror-symmetry. The effect of orientation locking vanishes at a distance of ~20 lattice units. Since an In-SMC occupies two rows, a pair of In-SMCs can be
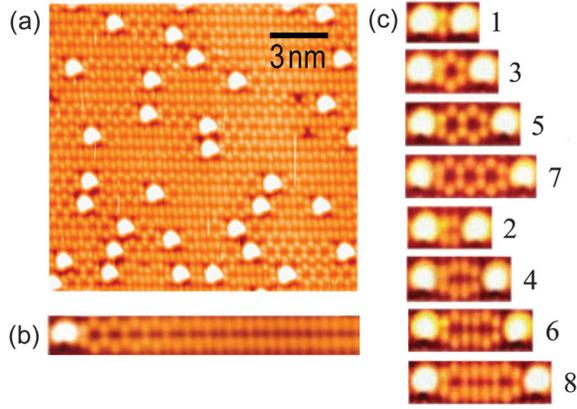
FIG. 1 (color). (a) Room temperature STM images (taken at sample bias of -2.1 V) of In-SMCs (bright spots) on a Si(100)-2×1 surface. (b) An In-SMC at one end of two Si-dimer chains. (c) D_n-cluster pairs with $n = 1$–8.

FIG. 2 (color). (a) Experimental histogram of D_n-cluster pairs. The gray line is a histogram derived from Monte Carlo simulation of cluster deposition. (b) Red symbols are second derivative of the populations N_n of D_n-cluster pairs. Yellow symbols are second derivative of the calculated energy E_n of a system containing a D_n-cluster pair.

linked by either two or one Si-dimer chains. In this work we focus on cluster pairs linked by two chains because particle-particle interaction mediated by two chains is expected to be doubled and its effect is easier to detect. For convenience, a cluster pair linked by two chains spanning n Si dimers will be called a D_n-cluster pair hereafter. Figure 1(c) shows various D_n-cluster pairs of different n. For D_n-cluster pairs with odd n, the Si-dimer chains appear like zigzag chains of round spots, indicating fixed buckling orientations of the Si dimers. In contrast, for D_n-cluster pairs with even n, only the Si dimers near In-SMCs appear like round spots, while those near chain centers become oval spots, indicating their oscillation between two buckling orientations.

The observations that chains with even n are more susceptible to thermal fluctuation suggests that, based on thermodynamic arguments, D_n-cluster pairs with even n should be less abundant than that with odd n. To verify the speculation, statistics of D_n-cluster pairs (N_n) is carried out as shown in Fig. 2(a). There are more D_n-cluster pairs with odd n than even n, indicating the enhanced stability of cluster pairs located at distances spanning odd number of Si dimers. It should be noted that, enhanced stability of nanostructures containing specific "magic" numbers of constituents like atoms [2], atomic wires [12], and atomic layers [13] have been observed on surfaces, but none of the reported cases is referred to the existence of such "magic" atomic distances between nanostructures. This is also the first observation where enhanced stability is conferred by a pair of nanostructures, as opposed to a single nanostructure.

The populations N_n of cluster pairs show a general trend to decrease with increasing n. To help understand the trend, Monte Carlo simulations of particles randomly deposited onto a system similar to an array of Si-dimer rows are carried out [14]. The simulation includes neither particle-particle nor particle-substrate interaction energy.
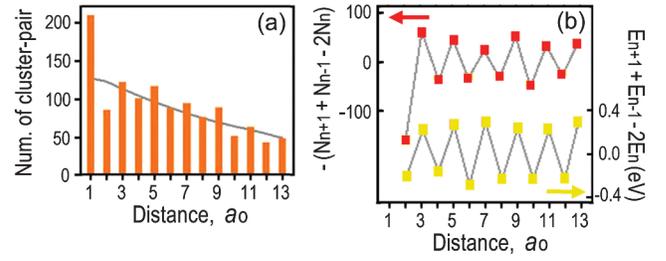
Therefore, the simulated result, as shown by the gray line in Fig. 2(a), reflects the probability to find a pair of non-interacting particles indeed tends to decrease with their distance. Such a slow monotonic decrease of N_n is removed if the second difference of the populations, $N_{n+1} + N_{n-1} - 2N_n$, is plotted against n, as shown by red symbols in Fig. 2(b), which better illustrates the even-odd alternation in the relative numbers of D_n-cluster pairs.

Theoretical calculation, as detailed in Ref. [14], using the Vienna *ab initio* simulation package based on density functional theory with projector-augmented wave pseudo-potentials is conducted to reveal the origin of the even-odd alternation. The energy E_n of a system containing a D_n-cluster-pair is found to depend linearly on n. Since E_n includes large contributions from background substrate, we choose to plot its second difference, $E_{n+1} + E_{n-1} - 2E_n$, to highlight the relative energy of D_n-cluster pairs. As shown by yellow symbols in Fig. 2(b), the result exhibits similar even-odd alternation as N_n, clearly demonstrating the energetic origin of the alternation in the distribution of distances between cluster pairs. The alternation has a uniform amplitude of 240 meV, indicating a constant energy difference of 120 meV between E_n and $(E_{n+1} + E_{n-1})/2$. In other words, there is additional 120 meV stored in D_n-cluster pairs with even n.

To further understand the origin of additional energy in D_n-cluster pairs with even n, we need to examine their detailed atomic structures. On the Si-dimer chains connecting a cluster-pair, two alternately buckling sequence originated from each In-SMC reach a deadlock to form topological solitons. Such topological solitons are slightly different from those theoretically predicted to exist on the dangling bond wires created on Si(100) surfaces [15]. Figures 3(a) and 3(b) shows an atomic model and simulated STM image of a D_{10}-cluster-pair with solitons at the centers of chains. Careful examinations of bond lengths reveal that Si-Si bonds near the topological solitons, as shown by 8 green lines in the insert of Fig. 3(a), are slightly different. They are either shorter or longer than those away from the solitons by as much as 1.5%. The corresponding
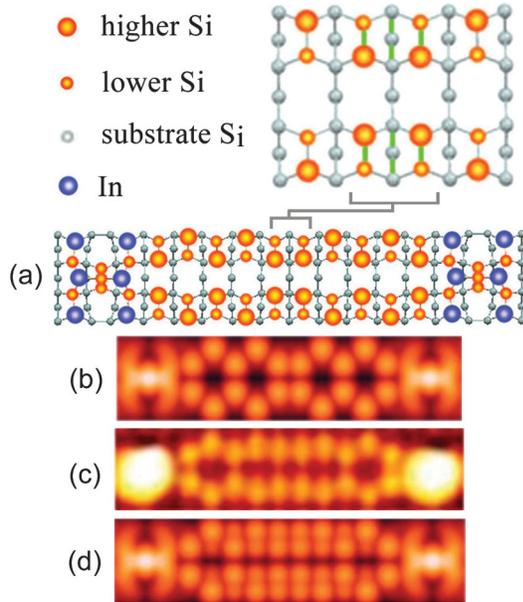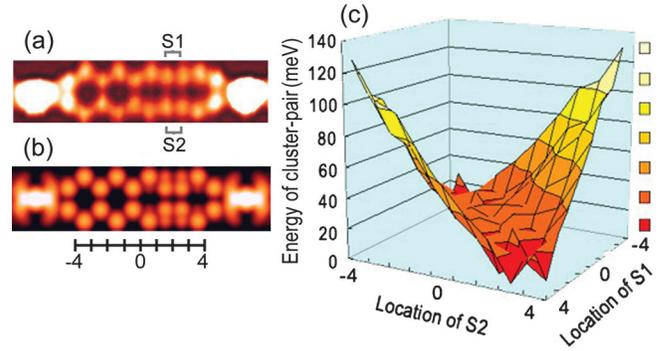
FIG. 4 (color). (a) Low temperature (110 K) STM image shows frozen topological solitons, as marked by $S1$ and $S2$, on two Si-dimer chains of a D_{10}-cluster pair. (b) Simulated STM image corresponding to (a). (c) Calculated energy of a D_{10}-cluster pair as function of the locations of two topological solitons.

FIG. 3 (color). (a) Top-view schematic of an atomic model of D_{10}-cluster pairs, with two topological solitons located at the centers of chains. Inset shows top 8 most distorted Si-Si bonds, marked by green sticks, around topological solitons. (b) Simulated STM image corresponding to (a). (c) Observed STM image at room temperature. (d) Simulated STM image corresponding to (c).

total strain energy of the 8 Si-Si bonds is estimated be ~ 160 meV, based on our calculated energies of a Si_2 molecule in free space. The energy is rather close to the additional energy of 120 meV stored in Si-dimer chains with even n as derived by *ab inito* calculation, suggesting that distortion of the Si-Si bonds near the topological solitons is the main cause for the energy increase.

Although similar, there are subtle differences in the simulated STM image [Fig. 3(b)] and observed STM image [Fig. 3(c)], which shows similar round spots for Si dimers close to the In-SMCs but dissimilar oval spots for Si dimers near the centers of chains. Intuitively, the two topological solitons on two chains with even n are expected to locate at the centers. However, *ab initio* calculations indicate that the energy of the system is independent (within 10 meV of calculation accuracy) of the locations of two solitons as long as they are aligned. Such degeneracy suggests that all of the nine degenerate structures with topological solitons on different locations are likely to contribute to the observed image. Therefore, the superposition of these nine structures' electron densities, as shown in Fig. 3(d), is to be compared to the observed STM image. The close similarity between two images indicates that the solitons are mobile on the two Si-dimer chains.

To verify if motion of solitons is thermally activated, STM imaging at 110 K was conducted. Solitons frozen at different locations were observed. As shown in Fig. 4(a), two solitons marked by $S1$ and $S2$ appear to be "fixed" on

the chains of a D_{10}-cluster-pair. Moreover, two solitons on the two chains appear aligned, suggesting there must be some attractive interactions between two solitons. To shed some lights on the observation, the energy of a D_{10}-cluster pair with its two solitons at different locations are calculated. As shown in Fig. 4(c), the diagonal band corresponding to two closest solitons have the lowest energy, while the two points at the corners corresponding to two farthest solitons have the highest energy. Between the two extremes, the energy increases linearly as a function of distance, indicating two solitons are bound together by an unusual V-shaped potential well. The origin of soliton-soliton attraction can be traced back to the fact that, on a Si(100) surface, $c(4 \times 2)$ reconstruction with mirror-symmetric Si-dimer chains has lower energy than $p(2 \times 2)$ reconstruction with parallel Si-dimer chains [16].

According to the potential energy surface shown in Fig. 4(c), the five series of states, i.e., $S_1 - S_2 = 0, 1, -1, 2, -2$, in the bottom of the valley, which corresponds to two solitons aligned within two lattice units, have energy differences of ~ 20 meV. These differences are comparable to the thermal energy at 110 K. Therefore, the two solitons are expected to fluctuate with an amplitude of two lattice units for STM images acquired at such a temperature. Indeed, the simulated STM image [Fig. 4(b)] including such localized motion of solitons is significantly different from that of a single degenerate structure [Fig. 3(b)]; and it is almost identical to the experimental result shown in Fig. 4(a). To be noted, the two solitons are confined in certain part of the potential valley rather than smeared into all positions within the valley as suggested by the flat bottom of the valley [Fig. 4(c)]. This apparent discrepancy between experiment and theory could be due to the fact that the calculation does not include the interaction between the atomic chains connecting a pair of In-SMCs also with their neighboring chains. Depending on the relative position between the chains, such interaction
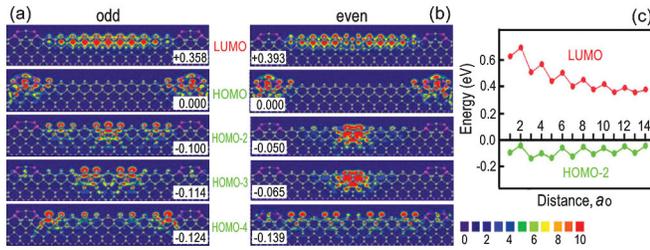
FIG. 5 (color). (a) and (b) Projected charge density distributions of electronic states near HOMO for D_{11}- and D_{12}-cluster pair, respectively. Energies (eV) of these states with respects to HOMO are labeled beside the panels. (c) Energies of LUMO and HOMO-2 states of D_n-cluster pairs.

can slant the potential valley towards one of the In-SMC, creating preference for the position of the solitons [14]. Furthermore, the Fig. 4(c) only depicts the depths of the potential surface, much more elaborate calculations are needed to include all the kinetic barriers that affects the motion of solitons.

Ab initio calculation helps trace the energy difference between cluster pairs linked by odd and even Si-dimer chains back to their different electronic structures. Shown in Fig. 5(a) and 5(b) are electric states near the highest occupied molecular orbital (HOMO) in D_{11}- and D_{12}-cluster pairs, respectively. For both cases, HOMO and HOMO-1 are almost degenerate and localized on the In-SMCs. HOMO-2 and HOMO-3 in D_{11}-cluster pairs are distributed on several regions of the chains. In contrast, these states in D_{12}-cluster pairs are localized at topological solitons (thus they can be considered as soliton states), and distributed on surface layer as well as substrate layers where strained bonds occur, as described previously. The existence of higher-energy soliton states in D_{12}-cluster pairs (50 meV higher than their corresponding HOMO-2 and HOMO-3 states in D_{11}-cluster pairs) provides a quantum mechanical explanation for the reduced stabilities of D_n-cluster pair with even n. The energies of LUMO and HOMO-2 as a function of chain length are shown by the red and green symbols, respectively, in Fig. 5(c). Both energies show even-odd alternation. The energies of LUMO decrease with increasing chain length, reflecting the particle-in-a-box nature of free electrons confined between two In-SMCs [17]. The energy of HOMO-2 is not as sensitive to the chain length as LUMO. In cases with even n, it is essentially independent of chain length, reflecting the highly localized nature of soliton states.

In conclusion, we have discovered a subtle broken even-odd symmetry in the statistics of distances between neighboring In-SMCs that are connected by two alternately buckled Si-dimer chains. The symmetry is broken due to

the presence of topological solitons on the chains with even number of Si-dimers, which are accompanied by higher-energy localized electronic states. At room temperature, the two solitons are mobile while at low temperature they are frozen and bound together by a V-shape potential well. The essence of our discovery is a new type of interaction between two particles imbedded in a lattice composed of alternately arranged half unit cells. When the particle distance (odd or even lattice unit) forces the alternation sequences on the lattice in between to meet out of phase, a topological soliton is created and the energy of the particle pair is elevated.

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