Self-Alignment of Co Adatoms on In Atomic Wires by Quasi-One-Dimensional Electron-Gas-Meditated Interactions

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Low-density Co atoms are found to self-align on the Si(111)-(4 × 1)-In surface in the direction of In atomic wires at incommensurate adsorption sites. Indirect interaction between a pair of Co adatoms is investigated through a site distribution function of adatoms determined with scanning tunneling microscopy. In the direction of self-alignment, the potential of the mean force between two Co adatoms is long-range and oscillatory with multiple frequencies, which correlate strongly to the electronic scattering vectors of the surface-state bands at the Fermi level. We thus attribute the Co-Co interaction to that mediated by a quasi-one-dimensional electron gas confined within the In atomic wires.

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The autonomous assembly of atoms and molecules on atomically well-defined surfaces is a promising route to a functional system with nanometer dimensions. Adatoms adsorbed on a metallic surface can interact with each other indirectly through electron scattering, resulting in a long-range interaction potential oscillating with a periodicity related to the Fermi wave vector of the substrate surface-state electrons [1–3]. Such surface-state-mediated interactions have been revealed to play significant roles in atomic self-assembly [4,5] and to influence sizes and shapes of nanostructures and distances between them on surfaces [6,7]. So far, all experimental studies on this issue have been performed only on the (111) surfaces of noble metals, where Shockley-type surface states provide two-dimensional (2D) nearly free-electron gas to mediate the interactions between adsorbates.

Two impurities embedded in a one-dimensional (1D) Fermi gas can also have a similar oscillatory interaction mediated by the host electrons, as predicted by previous theoretical reports [8]. In Au atomic wires formed on Si (111) and Si(557) surfaces, the distribution of inherent defects in lines shows a strong correlation to the Fermi surfaces of their quasi-1D electron gas [9,10], indicating the important roles of the electron scattering in the adatom alignment. Therefore, there is a good chance of developing a 1D self-assembly of adatoms by employing the 1D electron-gas-mediated interactions. Very recently, atomic Co and Fe strings have been created on the Ag(111) surface in an ingenious way based on the strongly anisotropic 2D electron scattering [5]. Here we demonstrate the self-alignment of Co atoms in a completely different way on the In-terminated Si(111) surface, which has an intrinsic quasi-1D surface-state electron gas to mediate the adsorbate-adsorbate interactions.

A periodically self-assembled array of In atomic wires, the Si(111)-(4 × 1)-In surface, was chosen as a template, since it has three metallic quasi-1D surface-state bands that have been extensively studied [11–14]. Low-density Co atoms [less than 0.04 monolayer (ML)] adsorbed on the template were revealed to be self-aligned on the In atomic wires with scanning tunneling microscopy (STM). By analyzing the site distribution of Co adatoms, we found that the potential of mean force between Co is oscillatory and extremely long-ranged in the direction of In atomic wire, which is in clear contrast to the previous work [5]. Furthermore, all frequencies of the oscillation correspond well to the electronic scattering vectors of the substrate surface-state bands at the Fermi level. This discovery evidences that this Co-Co interaction is mediated by the quasi-1D electron gas in the Si(111)-(4 × 1)-In template.

The experiments were performed in an UHV chamber with a base pressure lower than 10^{-10} Torr. The Si(111)-(4 × 1)-In surface was fabricated by depositing 1.5 ML of In on the Si(111)-7 × 7 surface at room temperature (RT), followed by a postannealing at ~340 °C. Co atoms were deposited on this template at RT or at lower temperatures between 150 and 220 K. The difference in the deposition temperature did not affect the experimental results. Both before and after Co deposition, the surface exhibited very clear 4 × 1 low-energy electron diffraction patterns. Finally, the sample was transferred to a cryogenic stage kept at 79 K to quench migration of Co adatoms, where STM observations were performed.

Figure 1(a) shows a typical STM image of In atomic wires covered with 0.02 ML of Co atoms, which are imaged as round protrusions. The almost identical apparent size of the protrusions suggests that the protrusions are individual Co adatoms. Notably, all adatoms are adsorbed on top of the In atomic wires, which thus play their roles as an excellent template. Increasing the Co coverage to 0.04 ML results in a higher density of Co adatoms that were still arranged in lines with irregular Co-Co spacing [Fig. 1(b)]. To quantitatively investigate the distribution of Co adatoms, we defined a Co occupation site function $\xi(r)$,

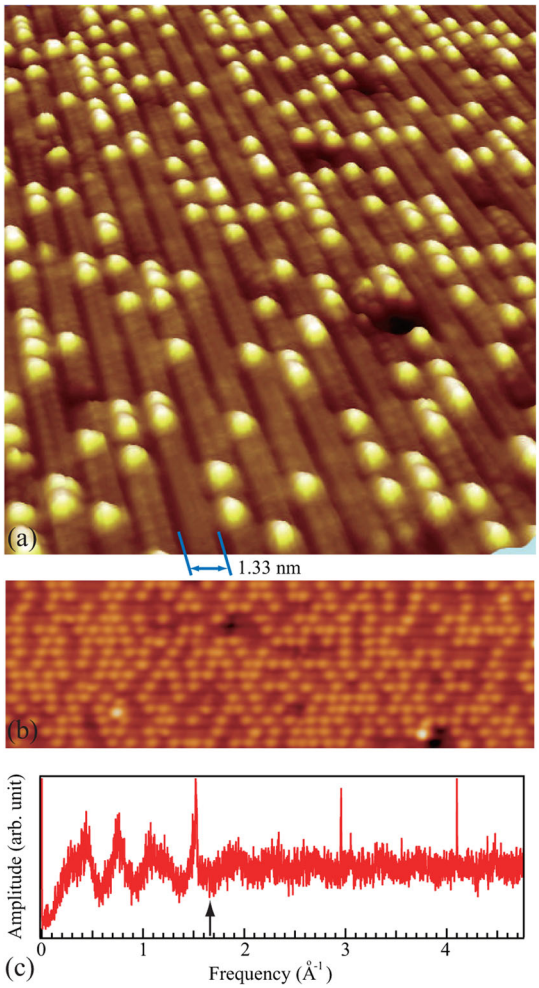

FIG. 1 (color online). (a) Bird's view of an STM image of the In atomic wire array covered with 0.02 ML of Co atoms. $V_s = -0.3$ V and $I = 0.1$ nA. (b) A typical STM image (60 nm × 19 nm) at the Co coverage of 0.04 ML. $V_s = -0.5$ V and $I = 0.1$ nA. Co adatoms (round protrusions) are self-aligned along the In atomic wires in array. (c) Fourier transform of the Co occupation site function $\xi(r)$ defined in the In wire direction.

where r is taken along the In wire direction; this function is equal to 1 or 0 corresponding to the presence or absence of Co adatoms at position r, respectively [15,16]. Figure 1(c) shows the 1D Fourier transform of $\xi(r)$, in which the presence of several distinctive peaks indicates the ordering of Co adatoms along the In atomic wires. The ordering is, however, not caused by the longitudinal lattice periodicity of In wires, since there is no peak observed at the frequency of $2\pi/a_0 = 1.64$ Å^{-1} [see the arrow in Fig. 1(c)], where $a_0 = 3.84$ Å is the length of the Si(111)-(1 × 1) surface unit vector. Additionally, the absence of the peak at $2\pi/a_0$ means that the Co adsorption site is incommensurate with the substrate.

A typical enlarged STM image (Fig. 2) shows that the bright protrusions have inequivalent adsorption sites with respect to the underlying In atomic wires, which agrees

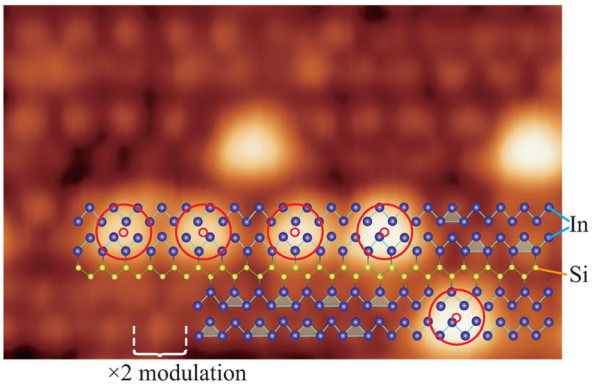

FIG. 2 (color online). Enlarged STM image showing the round protrusions of Co adatoms and ×2 modulation in the Co-free sections of In atomic wires. $V_s = -0.3$ V and $I = 0.1$ nA. A model of the Si(111)-(4 × 1)-In surface is superimposed to determine the registry of bright particles relative to the In wires.

with the above discussion. Before determining their positions on the STM image, we note that the pristine In atomic wires undergo a temperature-induced "×1 ↔ ×2" phase transition at $T_c \sim 130$ K [14,17,18]. A well-discussed driving force behind the transition is the formation of 1D charge density waves at low temperature due to the Peierls-like instability [11,14], which results in a periodic lattice distortion (PLD) of the In atoms and thus "×2" modulation in the local density of states along the wire direction, as the Co-free sections show in Fig. 2. We superimpose the ×1 phase model of the In atomic wires on the STM image and represent the negligible PLD with triangles on the ×2 modulation [19]. Since Co adatoms are mobile on the In atomic wire at RT (not shown here), coupling between Co and In atoms should be small, which indicates that the alteration of the In wire structure beneath the Co adatoms (bright protrusions in STM images) should be negligible. Concentric circles are superimposed on the bright protrusions in Fig. 2, from which one can see that the locations of the bright protrusions with respect to the In wires are not identical, so that the distance between Co adatoms can be any value besides integer times of a_0.

To reveal the origin of the observed frequencies of $\xi(r)$, we calculated the 1D pair correlation function $g(d)$ of Co adsorption sites along the In atomic wire by

$$g(d) = \frac{1}{n}\sum_i \frac{N\int \xi_i(r)\xi_i(r+d)dr}{[\int \xi_i(r)dr]^2}. \quad (1)$$

Here N is the total number of sites on each In atomic wire, n the total number of wires used in calculation, and $\xi_i(r)$ the Co occupation site function of the ith wire [15]. $g(d)$ is related to a probability of finding a particle at a distance d from another one and approaches unity as $d \to \infty$ in a system without long-range order. In Fig. 3(a), the obtained $g(d)$ varies intensively around unity without decaying even at $d = 20$ nm.

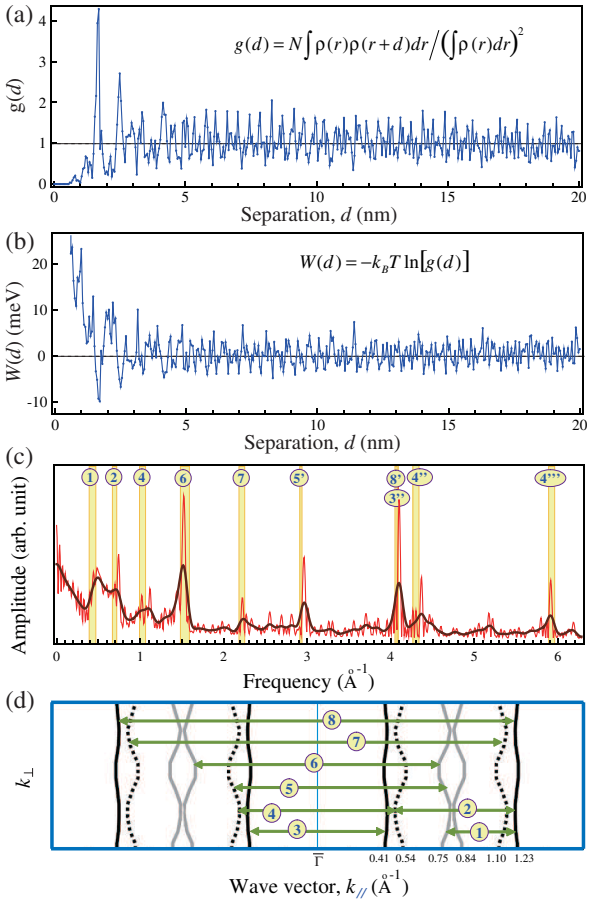

FIG. 3 (color online). (a) Pair correlation function $g(d)$ and (b) potential of mean force between Co adatoms $W(d)$; (c) Fourier transform of $W(d)$; (d) schematic diagram showing the Fermi surface of Si(111)-(4 × 1)-In together with the scattering vectors that have correspondent frequencies in (c).

The potential of mean force $W(d)$ between two Co adatoms is linked to $g(d)$ through [20]

$$g(d) = \exp[-W(d)/k_B T], \tag{2}$$

where k_B is the Boltzmann constant and T the temperature where Co adatoms cease to migrate on the Si(111)-(4 × 1)-In surface and finalize their site distribution. Since its exact temperature is unknown, we replace it with the observation temperature $T = 79$ K, which gives the lowest limit of $|W(d)|$ [Fig. 3(b)]. Although the absolute value of $W(d)$ is not precisely determined, this does not affect the following analysis. In Fig. 3(c), the Fourier transform of $W(d)$ shows many distinctive peaks, demonstrating the oscillatory behavior of $W(d)$. Beating among these oscillations makes the fluctuation so intensive that no obvious period can be directly recognized in Fig. 3(b).

The Fermi surface of the Si(111)-(4 × 1)-In substrate suggests a plausible explanation for the observed oscillations in the potential energy. Si(111)-(4 × 1)-In has three quasi-1D surface-state bands crossing E_F, resulting in a Fermi surface schematically shown in Fig. 3(d) [11]. All oscillation frequencies revealed in the Fourier transform of $W(d)$ [Fig. 3(c)] correspond very well to the scattering vectors of electrons at E_F [Fig. 3(d)]. Since the Fermi surface does not have an ideal 1D character, the scattering vectors take certain ranges that are represented by vertical bars in Fig. 3(c). Small frequencies labeled as 1, 2, 4, 6, and 7 directly correspond to the scattering vectors represented by arrows in Fig. 3(d). Large frequencies labeled as $5'$ and $8'$ correspond to the scattering vectors 5 and 8, respectively, added by $|\mathbf{k}| = 2\pi/a_0 = 1.64$ Å^{-1}, the value of the reciprocal lattice vector. Similarly, frequencies $3''$ and $4''$ correspond to those added by $2|\mathbf{k}|$ and $4'''$ to that added by $3|\mathbf{k}|$. Such a strong link between the potential energy and the electronic structure is thus clear evidence that the Co-Co interactions are mediated by the substrate quasi-1D surface-state electrons.

Indirect interaction $W_{ab}(d)$ between an isolated pair of impurity atoms in an electron gas has been theoretically studied with various continuum models [8,21–24]. The obtained asymptotic behavior of $W_{ab}(d)$ can be summarized to the general form [8]

$$\lim_{d\to\infty} W_{ab}(d) = W_{ab}^0 \frac{\cos(2k_F d - 2\eta)}{d^n}, \tag{3}$$

where n is an integer depending on the dimensionality of the metal band states that mediate the interaction and η the phase shift. In contrast to the decay feature represented by n in Eq. (3), the oscillation frequency in the numerator does not depend on a calculation model. In the previous model calculations, only one freelike electron band had been considered so that only a single scattering vector from $\mathbf{k}_F$ to $-\mathbf{k}_F$ contributes to W_{ab}, resulting in a single oscillation frequency $2|\mathbf{k}_F|$. In the present electron system, however, three metallic bands provide multiple scattering vectors at E_F due to intraband and interband excitations. In Fig. 3(d), we show only a part of the scattering vectors that contribute to the observed oscillations of the potential in Fig. 3(c). The absence of the other scattering vectors may be explained with the details of the matrix elements and wave functions, which critically determine the scattering vectors that contribute to the Co-Co interaction.

It is noted that $W(d)$ obtained through Eq. (2) approximates $W_{ab}(d)$ well only in the low atomic density limit [20]. In other words, $W(d) \approx W_{ab}$ requires finding Co adatom pairs well separated from others, which is in practice difficult even in an extremely low Co coverage. This is the reason that the potential energy $W(d)$ in Fig. 3 does not decay according to the power law as indicated in Eq. (3) ($n = 1$ for a 1D electron system), while only the oscillatory feature was observed.

The 1D feature of the substrate surface-state bands is expected to restrict the indirect Co-Co interaction only in the direction of the In atomic wires. To confirm it, we first calculated the mean force potential $W_{\mathrm{adj}}(d)$ between a pair

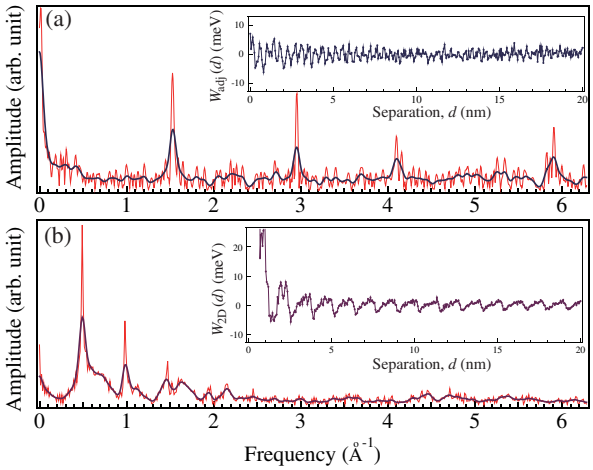

FIG. 4 (color online). Fourier transforms of mean force potentials shown in the respective inset. $W_{adj}(d)$ in (a) is defined between two Co adatoms on adjacent In atomic wires, while $W_{2D}(d)$ in (b) between arbitrary two Co adatoms in the STM images [15].

of Co adatoms on *adjacent* In atomic wires and its Fourier transform, as shown in Fig. 4(a). $W_{adj}(d)$ appears similar to $W(d)$ in Fig. 3(b), but its Fourier transform exhibits only four of the distinctive peaks observed in Fig. 3(c). The absence of other five peaks indicates that the surface-state-mediated Co pair interaction partly diminishes when the Co pairs are on different In wires. The remaining indirect interactions on adjacent In wires may be due to smearing of electron scattering. To testify the 1D feature of the indirect interactions, furthermore, we calculated the mean force potential $W_{2D}(d)$ and its Fourier transform for *arbitrary* Co adatoms on the surface, as shown in Fig. 4(b). Since Co pairs in all directions are considered, the contribution to $W_{2D}(d)$ from those in only one particular direction, e.g., the In atomic wire direction, is negligible. As expected, therefore, the electronic scattering vectors are not observed any more in the oscillations of the mean force potential W_{2D}. The distinctive frequencies in Fig. 4(b) originate from the transverse periodicity of the In wire array but have no concern with the electronic structure of the substrate.

In summary, we have realized the self-alignment of Co adatoms on an array of In atomic wires, in which Co-Co interaction is mediated by the substrate quasi-1D electron gas. The potential of mean force between Co adatoms in their alignment direction oscillates at frequencies determined by the electronic scattering vectors derived from the Fermi surface of the substrate surface-state electrons. The 1D feature of the electronic bands restricts the substrate-mediated Co-Co interaction in the In atomic wire direction. This work helps to understand the correlation between the distribution of defects on atomic wires and the Fermi surface of the substrate electron gas [9,10,25]. It also demonstrates how atomically well-defined surfaces with anisotropic electronic structure can be employed to create novel 1D nanostructures, which may exhibit exotic physical properties due to the reduction of dimensionality.

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