Size quantization of surface-state electrons on the Si(001) surface

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One-dimensional (1D) quantum wells are created on a Si(001)-$c(4\times2)$ surface. A pair of straight Al ad-dimer chains works as potential walls for the confinement of surface-state electrons on the Si(001) surface. The quantum properties of the 1D quantum wells are directly probed by low-temperature scanning tunneling microscopy and spectroscopy. They are well described by size quantization of electrons in the unoccupied π^* surface states of the Si(001)-$c(4\times2)$ surface, based on the ''1D particle-in-a-box'' model. [S0163-1829(99)11719-3]

Quantum properties of confined electrons have been extensively studied in semiconductor nanostructures like quantum wells, wires, or dots.[1] In contrast to such confinement systems, two-dimensional (2D) electron gas occupying surface states of noble metals can be confined in lateral closed structures like corrals,[2,3] narrow terraces,[4,5] and small islands.[4,6] It is remarkable that the lateral confinement of surface-state electrons allows real-space investigation of the quantum phenomena by using scanning tunneling microscopy (STM) and spectroscopy (STS). Contrary to the 2D electron gas on noble-metal surfaces, the Si(001)-$c(4\times2)$ surface has occupied π (π_1 and π_2) and unoccupied π^* (π_1^* and π_2^*) surface states in the bulk-band gap. In particular, the unoccupied π^* surface states disperse only along the dimer row, exhibiting quasi-one-dimensional (1D) character.[7–9] The study of the π^* surface states provides a unique opportunity to probe the 1D electron system using STM and STS.

In this paper, we report 1D confinement of the π^* surface electrons. A pair of long straight chains of Al ad-dimers used for potential walls creates a well-defined 1D quantum well. The quantitative analysis of the spectroscopic properties reveals that the 1D quantum well is well described by size quantization of the π^* surface states, based on the ''1D particle-in-a-box'' model.

The experiments were performed with a low-temperature STM in an ultra-high-vacuum chamber at 1×10^{-9} Pa.[10] The *p*-type Si(001) wafer (B doped with 0.01–0.02 Ω cm) was cleaned by heating at 1450 K and slowly cooled to room temperature. A small amount of Al (typically 0.05 monolayer coverage) was then deposited at room temperature on the surface using a tungsten filament. After the deposition, long straight chains of Al ad-dimers are formed on the Si(001) surface, perpendicular to the substrate dimer row:[11,12] Each Al ad-dimer is located between substrate dimer rows, and forms local bonds with dangling bonds of the neighboring Si dimers. The Si(001)-Al sample was then transferred to the low-temperature STM.

The dangling bonds on the Si(001)-$c(4\times2)$ surface generate occupied π and unoccupied π^* surface states in the bulk-band gap.[7–9] The π^* surface states exhibit quasi-1D character in the dimer-row direction because of the nearly flat dispersion in the perpendicular direction.[7–9] During STM observation at a positive sample bias voltage, electrons tunnel into the unoccupied π^* surface band from the STM tip, and propagate only in the dimer-row direction of the surface plane. If an Al ad-dimer chain is regarded as a 1D potential wall that scatters the π^* surface electrons, a pair of Al ad-dimer chains should confine the electron waves, leading to the formation of a 1D quantum well in the dimer-row direction.

The 1D quantum well, formed between Al ad-dimer chains, was directly investigated by STM with atomic resolution at a temperature of 63 K. Figures 1(a), 1(b), and 1(c) show constant-current STM images of a quantum well at sample bias voltages V_s of 0.9, 1.1, and 1.2 V, respectively. The distance L between the Al ad-dimer chains is 7.7 nm, corresponding to 20 times the unit cell dimension ($d=0.385$ nm) of the Si(001)-1×1 surface. In these STM images, the most remarkable feature is the drastic evolution of 1D standing wave patterns (spatial oscillations in the dimer-row direction), which changes with the sample bias voltage. As will be discussed later, the standing wave patterns are associated with the density distributions of the π^* surface electrons confined in the 1D quantum well. The standing wave patterns were also observed for quantum wells with $L=1.54$–8.47 nm at $V_s=0.85$–1.3 V.

The most distinguishing feature for the 1D quantum well should be the discrete energy levels E_n of the quantum states. We obtained such energy levels from tunneling spectra $[(dI/dV)/(I/V)]$, which almost represent the local density of states.[13] Figure 2 shows the tunneling spectra measured for the 1D quantum well with $L=6.16$ nm and for the Si(001)-$c(4\times2)$ clean surface. The first curve shows the spectrum obtained on the Si(001)-$c(4\times2)$ surface far from Al ad-dimer chains. This spectrum shows three characteristic peaks, *A*, *B*, and *C* at $V_s=-0.51$, 0.6, and 1.27 V, respectively. We obtained similar spectra on the Si(001)-$c(4\times2)$

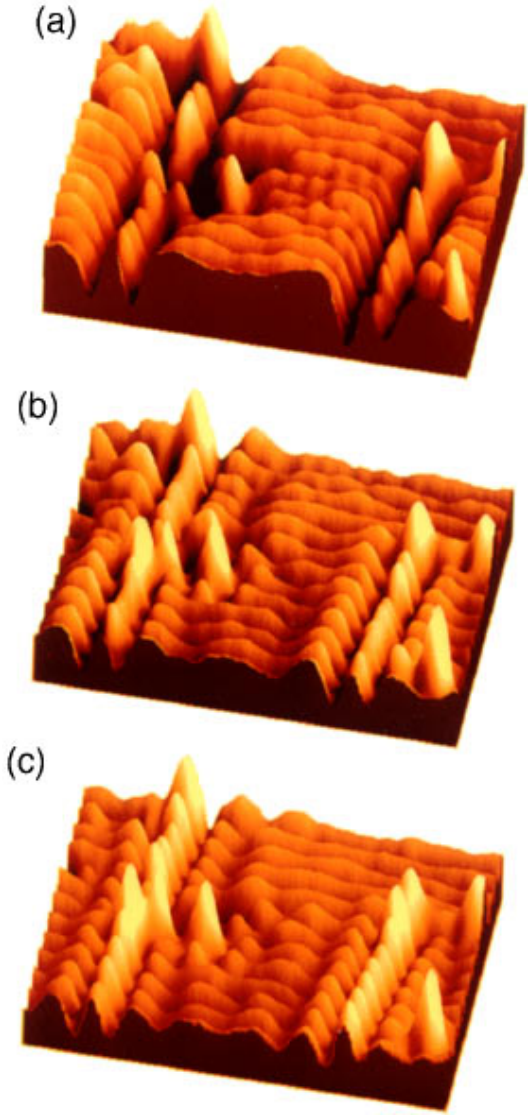

FIG. 1. (a)–(c) (Color) Constant-current STM topography of a series of standing wave patterns between a pair of Al ad-dimer chains at $V_s = 0.9$ V, 1.1 V, and 1.2 V ($I_t = 100$ pA) for $T = 63$ K. The Al ad-dimer chains are separated by 7.7 nm. In these STM images, the atomic corrugations for the $c(4\times2)$ periodicity have been filtered out. Standing-wave patterns exhibit two peaks between the Al ad-dimer chains at $V_s = 0.9$ V, three peaks at $V_s = 1.1$ V, and four peaks at $V_s = 1.2$ V.

clean surface before the deposition of Al. The second and third spectra were obtained at the center of the quantum well and at about 1 nm away from the center (about one third of the well width), respectively. The former has new spectral peaks at $V_s = 1.14$ and 1.41 V, while the latter has them at $V_s = 1.04$ and 1.33 V. These peaks correspond to energy levels E_n for the nth quantum states. The peaks in the second curve should exhibit only the odd quantum states ($n = 1,3,5$), since the even quantum states have a node at the center of the 1D quantum well. We identify the peaks at $V_s = 1.14$ and 1.41 V as E_3 and E_5, respectively, although the peak for E_1 appears as a shoulder of the peak B at $V_s \approx 0.8$ V. In the third curve, the peaks at $V_s = 1.04$ and 1.33 V correspond to E_2 and E_4, respectively. We also obtained the spectral peaks for E_n ($n = 1$–5) inside various sized quantum wells ($L = 1.93$–6.93 nm). Figure 3(a) shows the

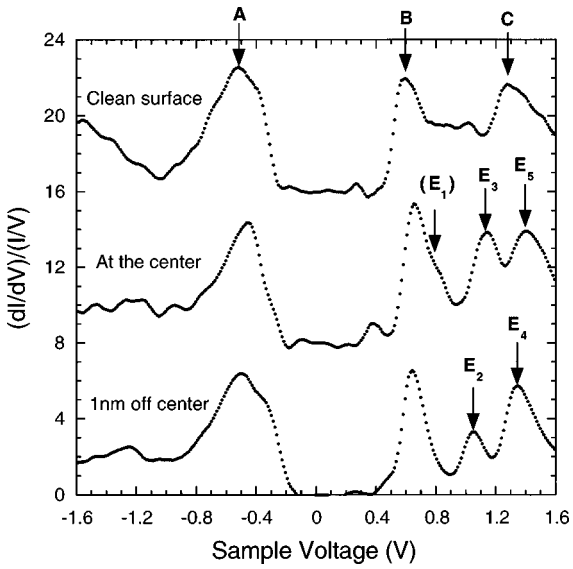

FIG. 2. Tunneling spectra $[(dI/dV)/(I/V)]$ measured with the STM tip far from Al ad-dimer chains (top curve), at the center of the $L = 6.16$ nm quantum well (second curve), and at about 1 nm away from the center of the well (third curve). The curves have been shifted vertically for better viewing. At each position, the tip was fixed at $V_s = 1.5$ V and $I_t = 100$ pA to obtain current-voltage (I-V) curves. In the top curve, characteristic peaks for the Si(001)-$c(4\times2)$ surface are labeled A, B, and C. The second and third curves show new peaks corresponding to the discrete energy levels E_n of the quantum states, whereas peaks A and B remain at the same levels.

peak levels as a function of L.

The relation between E_n and L can be interpreted using the 1D particle-in-a-box model along the dimer-row direction. Assuming that the Al ad-dimer chain works as an impenetrable square potential barrier of thickness a, the wave number k_n of the confined surface-state electrons is described by

$$k_n = n\frac{\pi}{L-a}. \tag{1}$$

To obtain the value of a, a dispersion relation $E(k)$ of the confined electrons is approached using the 1D tight-binding model. It gives

$$E(k) = \beta_0 - 2\beta_1 \cos(k2d), \tag{2}$$

where β_0 and β_1 are hopping integrals, and $2d = 0.77$ nm. From the results shown on Fig. 3(a), we obtained $a = 0.45$ nm ($\beta_0 = 1.25$ eV and $\beta_1 = 0.21$ eV). Although we examined a better fitting of the E_n–L relation by assuming a finite height V_B of the potential barrier, the obtained value of V_B stayed extremely large compared to the work function (other values, a, β_0, and β_1, were changed only slightly). This impenetrable hard wall potential of the Al ad-dimer chain is generated by the absence of unoccupied surface states at the Al-Si local bonds. Because each Al dimer is bonded with two neighboring Si dimers along the dimer-row direction,[11,12] our estimated barrier thickness a is slightly larger than the interdimer spacing ($d = 0.385$ nm). In addi-

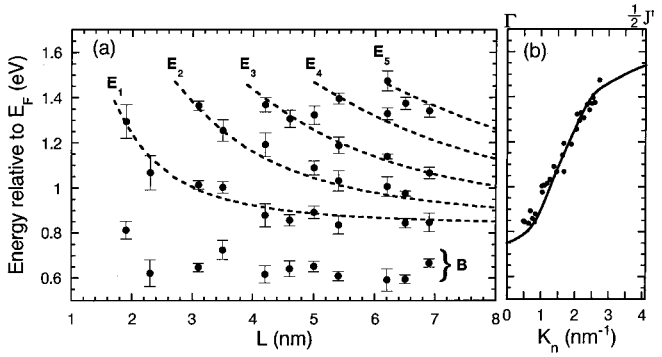

FIG. 3. (a) Plots of discrete energy levels E_n and peaks B for different L (1.93–6.93 nm). Peak positions (closed circles) are the mean values obtained from 5 to 20 spectra using four different STM tips, and the error bars for each plot are given by the standard deviation. Peaks B were at $V_s \approx 0.6$ V in quantum wells. Dashed lines: calculated energy levels for different L using Eqs. (1) and (2) ($\beta_0 = 1.25$ eV, $\beta_1 = 0.21$ eV, and $a = 0.45$ nm). (b) Plots of the relation between $k_n = n\pi/(L-a)$ and experimental E_n. Solid line: calculated dispersion relation for π_1^* surface states by Northrup in Ref. 9.

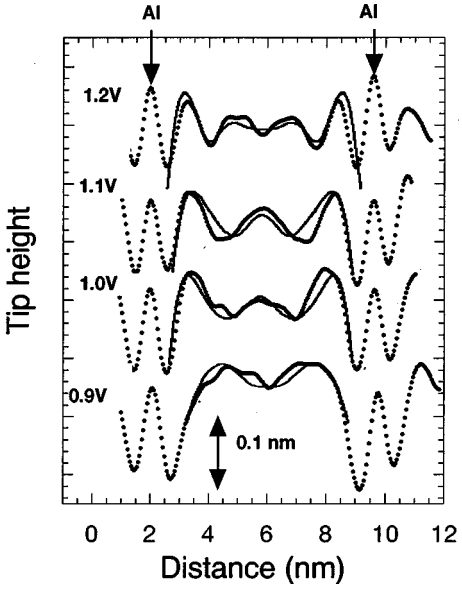

FIG. 4. Experimental data (dots) for cross sections of the standing wave patterns (the $L = 7.7$ nm quantum well shown in Fig. 1) at $V_s = 0.9$, 1.0, 1.1, and 1.2 V, and calculated tip-height variations (solid lines) at $V_s^{cal} = 0.95$, 1.05, 1.10, and 1.20 V. In the cross sections, the atomic corrugations for the $c(4\times2)$ periodicity have been filtered out. The calculations include the influence of the energy widths ΔE for quantum states. The tunneling coefficient from the STM tip to the surface is assumed to be $T(E, eV_s, z) = \exp\{-2z[2m/\hbar^2(\bar{\phi} + eV_s/2 - E)]^{1/2}\}$ based on the WKB approximation. Experimental and theoretical bias voltages are in agreement within experimental accuracy for E_n [see error bars in Fig. 3(a)].

tion, the barrier thickness is independent of the well size, and does not differ from that ($a = 0.45$ nm) for an isolated Al ad-dimer chain.[14]

To extract the quantum states of the confined electrons, we replot the relation between E_n and $k_n = n\pi/(L-a)$ ($a = 0.45$ nm) in Fig. 3(b). This plot gives a dispersion relation for the confined electrons along the dimer row (Γ-$\frac{1}{2}$ J line in the surface Brillouin zone), which agrees quantitatively with previous first-principle calculation [solid line in Fig. 3(b)] for the π_1^* surface states reported by Northrup.[9] Therefore, the discrete energy levels result from size quantization of electrons in the unoccupied π^* surface states. From this dispersion relation, the effective mass m^* of electrons in the π^* surface states is estimated to be $0.28m_e$ (m_e corresponds to free electrons) around the Γ point along the dimer-row direction.

The standing wave patterns are generated by the density distributions of the confined π^* electron waves. Following Eq. (2), the discrete energy levels E_n for the quantum well with $L = 7.7$ nm are equal to 0.92 ($n = 2$), 1.02 ($n = 3$), and 1.15 eV ($n = 4$). Figure 4 shows that cross sections of the standing wave patterns (the $L = 7.7$ nm quantum well shown in Fig. 1) exhibit two peaks ($n = 2$) between the Al ad-dimer chains at $V_s = 0.9$ V, three peaks ($n = 3$) at $V_s = 1.0$ V, and four peaks ($n = 4$) at $V_s = 1.2$ V, in agreement with the expected values for each quantum state. However, more detailed inspection of the standing wave patterns shows that the central peak at $V_s = 1.0$ V became more intense at $V_s = 1.1$ V, although both of them exhibit the $n = 3$ quantum state. To explain this discrepancy, we have considered the finite width ΔE of the spectral peaks. Assuming a Lorentzian distribution, the energy widths of our STS peaks were changed as a function of E_n, given by $\Delta E_n = 0.46E_n - 0.2$ (eV). Using the energy levels E_n ($n = 1$–5) and ΔE_n, the standing wave patterns were well reproduced by calculation (tip-height variations at a constant current) as shown in Fig. 4 (solid lines). Therefore, the energy broadening of the quantum states is important for quantitative analysis of the STM images.

Energy broadening of quantum states, which is much larger than the thermal broadening, has been reported for lateral closed structures on noble-metal surfaces.[2–4,6] Several theoretical accounts of the broadening mechanisms[3,15–17] are for partial lateral confinement and scattering into the bulk states. For the Si(001)-Al surface, the Al ad-dimer chain works as an impenetrable hard wall, and the dispersion curve of the π^* surface states is almost flat in the direction perpendicular to the Si dimer row.[7–9] These results exclude the lateral leakage of the confined electrons in the π^* surface states. Although the π^* surface states are orthogonal to bulk states, some coupling between these states at the Al-Si local bonds may allow scattering into the bulk states, limiting the lifetime of confined electrons.

In conclusion, we directly observed confined electron standing waves and their associated energy levels inside various sized quantum wells using low-temperature STM and STS. The quantum wells are generated by lateral confinement of the π^* surface states. Their quantum properties can be interpreted using the 1D particle-in-a-box model except for the energy broadening. The quantitative analysis of the spectroscopic properties provided detailed information about the dispersion relation for the π^* surface states, as well as about the confinement phenomena by the Al ad-dimer chains.

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