Energetics of Ni-Induced Vacancy Line Defects on Si(001)

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Vacancy line defects on the Si(001) surface induced by small traces of Ni are analyzed with a scanning tunneling microscope. The domain structure that is found obeys the size relation derived by Zeppenfeld *et al.* [Phys. Rev. Lett. **72**, 2737 (1994)] for surface systems with long-range interactions, decaying as L^{-2}. From the thermally induced wandering of the vacancy line defects we extract the strength of this long-range repulsive interaction as well as the short-range attractive interaction between the vacancies in adjacent dimer rows.

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Since the advent of the scanning tunneling microscope (STM), surface defects like steps, kinks, vacancies, etc., have been actively studied on the atomic scale. These surface defects often play a key role in thin film growth processes. Because of its technological importance as well as its relatively simple structure, the Si(001) surface has been a model system for equilibrium structures. It is well known that missing-dimer vacancies are always present on the Si(001) surface. They are created during cleaning and a fair fraction survives after annealing. However, controlled amounts can be created by sputtering with noble gases (Xe^+, Ar^+) [1–6] or etching (O_2, H_2, Br_2, I_2, etc.) [7–11]. The motion of these relatively mobile vacancies [12] makes that, at elevated temperatures, they coalesce into vacancy islands. The equilibrium structure of these vacancy islands is, at least for low vacancy concentrations, elongated in a direction perpendicular to the dimer rows [13]. We refer to them as vacancy line defects (VLDs). It is interesting to note that also small traces of Ni contamination give rise to VLDs [14]. The atomic arrangement of Ni-induced VLD network was first imaged in real space by Niehus *et al.* [14]. The VLD structure was found in their STM images at both positive and negative sample bias voltages, confirming the geometric origin of the VLDs. Line scans across the Ni-induced VLDs even reveal that they are actually deeper than one atomic layer. It is interesting to note that at the present time there is no evidence that the VLDs induced by sputtering or etching are deeper than one atomic layer. Furthermore, there is another remarkable difference between the two different types of VLDs: When the etched or sputtered surfaces are flash annealed for a few seconds at temperatures around 1500 K, the surfaces are completely restored without any trace of VLDs, whereas the Ni-induced VLDs cannot be annealed away [4]. Because of these salient differences one cannot compare the two types of VLD networks *a priori*. We, therefore, focus our attention on one type only, namely, the Ni-induced VLDs. The ordering of the missing-dimer vacancies into VLDs is driven by an attractive interaction between vacancies in adjacent rows and a long-range repulsive interaction between the VLDs. First, we will demonstrate that the long-range interaction decays as L^{-2} and is probably a consequence of surface strain relief. Second, the strength of this interaction as well as the short-range attractive interaction between the vacancies in adjacent dimer rows will be determined from the thermally induced wandering of the VLDs.

The base pressure in the ultrahigh-vacuum (UHV) chamber during the STM experiments was $<1 \times 10^{-10}$ Torr. The Si(001) surfaces were cleaned by several times annealing the sample at 1500 K for several seconds followed by quenching to room temperature. During annealing, the chamber pressure did not rise above 2×10^{-9} Torr. After the annealing treatment, the sample was transferred to the scanning tunneling microscope where the usual 2×1 reconstructed Si(001) surface was observed. The Si samples were mounted on a Mo/Ta sample holder containing only one stainless steel screw in order to introduce the Ni contamination. In this way the amount of Ni contamination increases slightly after each flash.

In Fig. 1(a) a high-resolution STM image of a Ni contaminated Si(001) surface is displayed. Diluted (isolated) dimers are frequently observed in the VLDs and the missing-dimer defects around these "diluted dimers" often occur in a particular sequence, namely, missing-dimer defect, diluted dimer followed by two missing-dimer defects [14]. A schematic diagram of a VLD with a width of two dimer vacancies is depicted in Fig. 1(b). With increasing Ni contamination the averaged width ℓ of the VLDs increases only slightly, whereas the averaged spacing between them L decreases much more rapidly. We first compare these results with a model recently proposed by Zeppenfeld *et al.* [15]. This model is based on the energy balance between the creation of domain walls and the repulsive L^{-2} interaction between these walls. We consider here the quasi-one-dimensional (i.e., striped) domain structure. The energy E per unit length can, following Ref. [15], be written as

$$E = \frac{2\gamma}{\ell + L} - \frac{2\sigma}{\ell + L} \ln\left[\frac{\ell + L}{2\pi a_0} \sin\left(\frac{\pi \ell}{\ell + L}\right)\right], \quad (1)$$

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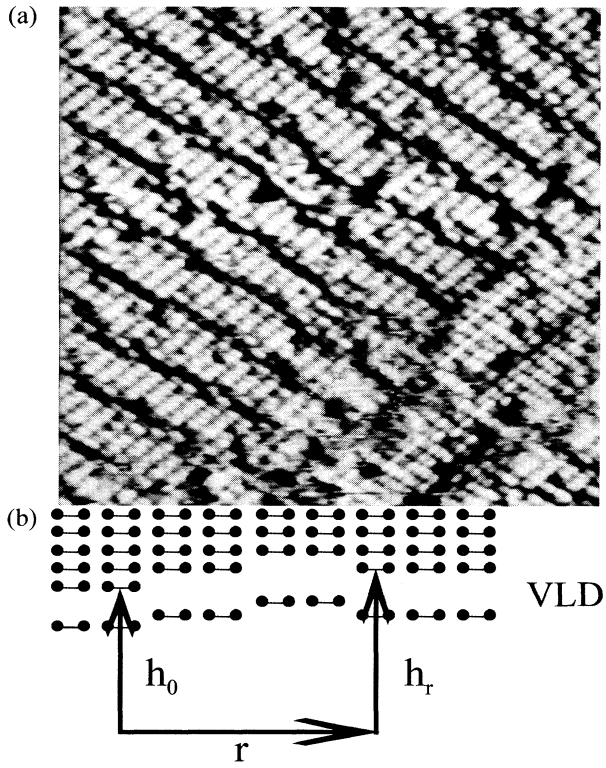

FIG. 1. (a) High-resolution STM image of a Ni (a few percent of a monolayer) contaminated Si(001) surface. The scan size is 25 nm × 25 nm, the sample bias −2 V and the tunneling current 0.5 nA. (b) Schematic representation of a VLD. h and r are measured in units of a and $2a$, respectively (a = 3.84 Å).

where γ is associated with the creation of the domain boundaries between the minority domain of width ℓ and the majority domain of width L. The second term describes the elastic relaxation: a_0 is a microscopic cutoff (e.g., the lattice constant) and σ is a function of the elastic constants and of the difference of the surface stress within the two types of domains (if the logarithmic term ln[..] in Eq. (1) is expanded for small displacements δL around the minimum-energy configuration, one finds that the leading term, which mimics the long-range interaction between the domain walls, is proportional to L^{-2}). From the minimalization of the energy of surface systems governed by an effective long-range interaction decaying as L^{-2}, Zeppenfeld *et al.* found that, independent of the actual values of γ and σ, the following relation between the size of the minority domain ℓ at a certain coverage $\theta = \ell/(L + \ell)$ and the minimal size of the minority at a coverage approaching zero, i.e., ℓ_0 must hold:

$$\ell = \ell_0 \frac{\pi\theta}{\sin(\pi\theta)}. \tag{2}$$

In Fig. 2 a plot of the periodicity $\ell + L$ of the VLDs pattern as well as the width ℓ of the VLDs in units of the dimer-dimer spacing versus coverage is shown. Because

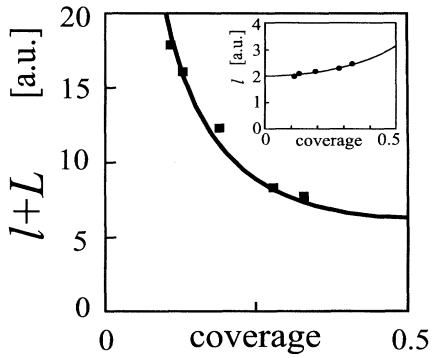

FIG. 2. Periodicity, $\ell + L$, in units of a (= 3.84 Å) of the VLD pattern versus coverage [$= \ell/(\ell + L)$] Solid line: $\ell_0\pi/\sin(\pi\theta)$. Inset: width ℓ in units of a of the VLD versus coverage. Solid line: $\ell_0\pi\theta/\sin(\pi\theta)$.

the Zeppenfeld *et al.* size relation is obeyed so well, we conclude that the VLD structure is indeed stabilized by an effective long-range interaction decaying as L^{-2}. In Fig. 3 a large scale STM image containing several monatomic step edges is displayed. The characteristic VLD network rotates at each monatomic step edge and does not give rise to a reversal of the step edge roughness, as has recently been observed for Ge-covered Si(001) [16].

Next we move to the determination of the strength of this long-range interaction as well as the determination of the short-range attractive interaction between the vacancies within the VLDs. We will extract these energetic parameters from the thermally induced wandering of the VLDs. The thermally, induced wandering of a VLD is most easily characterized by the deviation-deviation correlation function $\langle(h_0 - h_r)^2\rangle$ where r is the distance measured parallel to the VLD and h_r is the deviation measured perpendicular to the VLD with respect to a fixed reference [see Fig. 1(b)]. r and h_r are measured in units $2a$ and a, respectively (a is the dimer-dimer distance = 3.84 Å). For a single isolated VLD, the deviation-deviation correlation function diverges linearly with r. This results follows immediately from the random distribution of kinks in the VLDs under equilibrium. One can write

$$\langle(h_0 - h_r)^2\rangle = \langle k^2\rangle r \tag{3}$$

and $\langle k^2\rangle$ is the mean square displacement of the VLD,

$$\langle k^2\rangle = \frac{\sum_{-\infty}^{\infty} k^2 \exp(-E_k/k_bT)}{\sum_{-\infty}^{\infty} \exp(-E_k/k_bT)}, \tag{4}$$

where k is the kink length (again in units of 3.84 Å) and E_k the corresponding kink creation energy. The single kink formation energy E_1 can immediately be extracted from the distribution of single kinks and no kinks. According to the Burton-Cabrera-Frank (BCF) theory, one has [17,18]

$$E_1 = -k_BT \ln\left[\frac{n_1}{2n_0}\right], \tag{5}$$

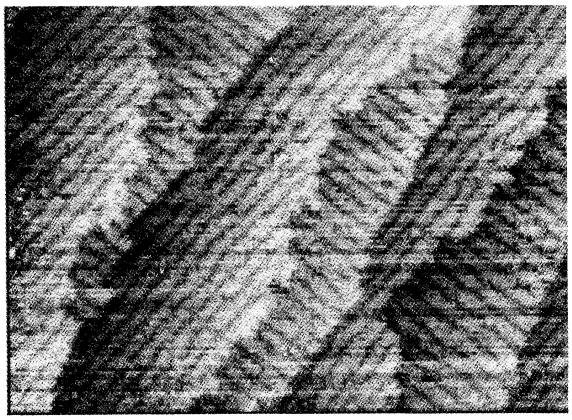

FIG. 3. Large scale STM image (60 nm × 80 nm) of a Ni contaminated Si(001) surface containing several monoatomic step edges. The sample bias is −2 V and the tunneling current 1 nA.

where $n_{0,1}$ is the probability of finding no kink and a single kink, respectively. From STM images like Fig. 1 we found $n_0 = 0.47$ and $n_1 = 0.41$ resulting in a value for E_1/k_BT of about 0.83. Taking a reasonable estimate of 750 ± 100 K for the freeze-out temperature [17] one finds a value of 0.055 ± 0.01 eV/a for the energy of the creation of a single kink in a VLD. Hence the short-range attractive interaction between vacancies in adjacent dimer rows is twice this value, i.e., 0.11 ± 0.02 eV/a. Interestingly, Weakliem, Zhang, and Metiu [19] use the Stillinger-Weber potential to calculate the interaction energy between missing dimer vacancies on the clean Si(001) surface. They found a long-range repulsion between missing-dimer vacancies located in the same dimer row and an attractive interaction of about 0.1 eV between missing-dimer vacancies in adjacent rows, which is in remarkably good agreement with our experiments.

When the VLDs begin to approach each other, i.e., when the mean square displacement becomes a significant fraction of the VLD-VLD width L deviations from the linear, "diffusive" behavior [see Eq. (3)] must occur. The repulsive interaction between the VLD results in a flattening out of the deviation-deviation correlation function. The simplest scheme to account for this is to take the continuum limit in the r direction, which reduces the problem to solving the one-dimensional Schrödinger equation for a harmonic oscillator [if the $\sigma \ln(L)$ term in Eq. (1) is expanded for small δL around the minimum-energy configuration, the leading harmonic term $\sim \sigma(\delta L)^2/L^2$]. Using path-integral arguments [20], one finally finds

$$\langle (h_0 - h_r)^2 \rangle \approx \left(\frac{k_B T \langle k^2 \rangle L^2}{2\sigma} \right)^{1/2} \times \left[1 - \exp\left(-r\sqrt{2\sigma \langle k^2 \rangle / k_B T L^2} \right) \right]. \quad (6)$$

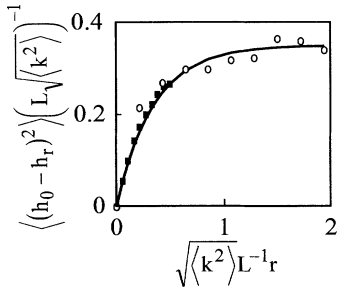

FIG. 4. Scaled mean square displacement of the VLD versus scaled position measured along the VLD. Squares: $L = 15.9a$ ($\ell = 2.0a$); circles: $L = 5.2a$ ($\ell = 2.5a$).

For small r, the linear behavior, noted earlier, is of course reproduced by Eq. (6). The saturation of $\langle (h_0 - h_r)^2 \rangle$ with increasing r is clearly an artifact of the fixed-wall approximation (neighboring VLDs are assumed to be fixed walls). One can go beyond the single wandering VLD and let all the VLDs wander simultaneously. For large r the deviation-deviation correlation function should diverge. However, this behavior becomes important only on length scales much larger than the typical VLD-VLD collision distance, i.e., $L^2/\langle k^2 \rangle$. By plotting $\langle (h_0 - h_r)^2 \rangle (L\sqrt{\langle k^2 \rangle})^{-1}$ vs $rL^{-1}\sqrt{\langle k^2 \rangle}$, a universal curve is found, independent of the actual values of L and $\langle k^2 \rangle$. In Fig. 4 a plot of this universal curve (with $\sigma = 0.27$ eV per dimer row) and the experimental data is shown. The error in the only free parameter σ is estimated to be less than 0.03 eV per dimer row.

In conclusion, the missing-dimer vacancies on Si(001) interact strongly with each other, and the interaction is highly anisotropic. The interaction between the VLDs is long-range repulsive and behaves as σL^{-2}, where σ is 0.27 ± 0.03 eV per dimer row. On the other hand, a short-range attractive interaction exists between vacancies located on adjacent dimer rows. Their binding energy is 0.11 ± 0.02 eV/a. In contrast to the VLD network on the Ge covered Si(001) surface we did not observe a reversal of the step edge roughness.

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[13] At first sight the appearance of VLDs oriented perpendicular to the dimer rows seems to be the opposite of what one should expect: The anisotropy of the nearest neighbor interaction between dimers, i.e., a strong interaction for neighbor dimers in the same row versus a much weaker interaction between neighbor dimers in adjacent rows, should favor vacancy islands oriented with their long axis along the dimer rows. This puzzle is reinforced by the fact that under specific experimental conditions (low temperature and high supersaturation of vacancies [1]) vacancy islands elongated along the dimer rows are indeed observed. However, as has been pointed out correctly by these authors [1], there is a strong difference in the step edge retraction speed of the two different edges on Si(001). The fact that the SB edges retract faster than the SA edges makes the vacancy island expand much faster along the dimer rows than perpendicular to the dimer rows. After thus having made plausible that the vacancy islands oriented along the dimer rows are controlled by kinetic effects, it remains to be seen whether the VLD configuration represents the thermodynamic equilibrium situation. However, the simple experimental observation that (at least for low vacancy concentrations up to about 0.2 monolayer) the VLD network emerges only after high temperature sputtering or etching (>900 K) and subsequent annealing supports strong evidence for this assumption.
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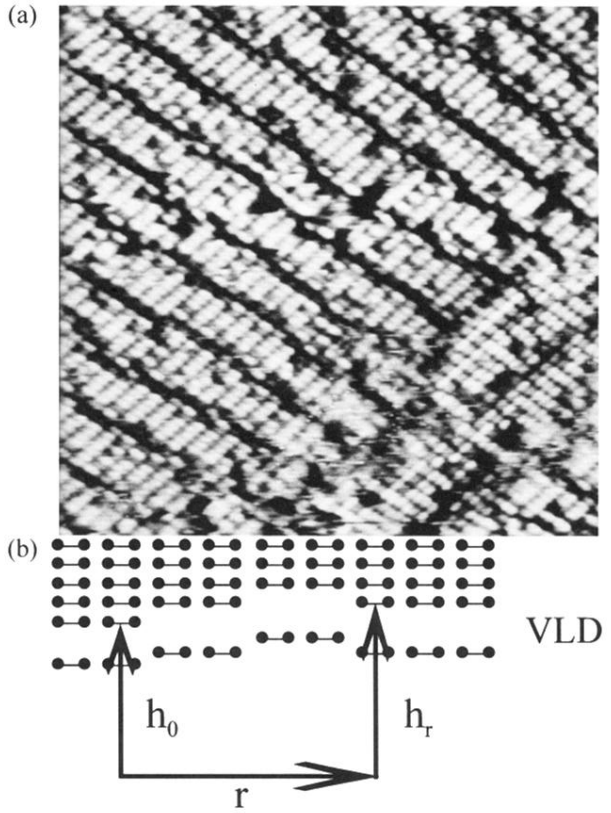

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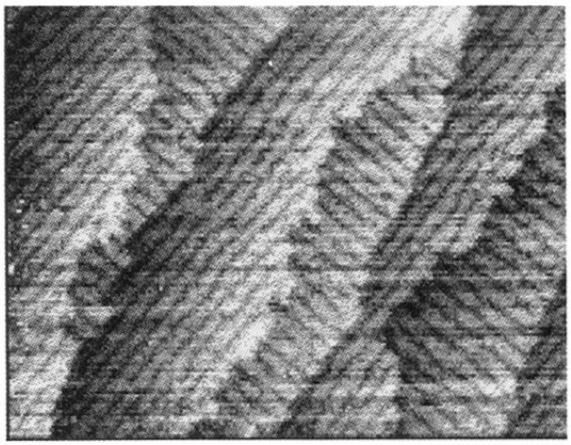

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