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Step bunching on TaC(910) due to attractive step-step interactions

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Using scanning tunneling microscopy, we study the step configuration on TaC(910) which is vicinal to the (100) plane, miscut 6.34° toward the [010] direction. After annealing at ~2100 °C, the surface is dominated by double-height steps which are bunched between relatively long intervening (100) terraces. The step-separation distribution is very skewed and sharply peaked. Monte Carlo simulations show that a strong, medium-range, repulsive step interaction A/x^2 must be combined with a weak, long-range, attractive interaction, $-B/x^{1.0\pm0.5}$ to fit the measured distribution. Possible physical origins for these interactions are discussed.

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When cooled below a roughening temperature T_R, a vicinal surface can undergo a step-bunching (or faceting) transition in which a number of steps bunch closely or coalesce to become a multiheight step.[1–7] Based on x-ray scattering data from the vicinal Si(310) surface,[6] Song and Mochrie thought that such step bunching could involve step-step attraction. This work recently inspired much theoretical interest, and the faceting was predicted to arise from a competition between *short-range attraction and long-range repulsion* between steps,[8–10] where the *short-range spacing is about one atomic spacing* (hereafter referred to as an atomic range attraction). Earlier, short-range repulsion (1–2 atomic rows), in combination with a medium-range attraction (3–5 atomic rows), was also suggested by Frohn *et al.*[11] to explain the step-separation distribution measured from Cu(1,1,19). More recently, Pai *et al.*[12] observed evidence of interactions that oscillate between attractive and repulsive as a function of distance in the terrace width distributions on vicinal Ag(110). This observation was attributed to surface states, and may also serve to explain the Cu(1,1,19) data. Despite these observations, the existence of an attractive interaction still remains speculative, because there is no clear understanding of how the combination of attractive and repulsive interactions can lead to the experimentally observed step-separation distributions. Step-step interactions can be shown to arise from several possible mechanisms.[13–17] For example, elastic force dipoles due to strain relaxation at steps can produce repulsion between identical steps and attraction between different steps.[14] Electric dipoles at charged steps could also produce either repulsive or attractive step-step interaction depending on the orientation of dipoles at neighboring steps.[15] The potentials from these dipolar origins all vary as x^{-2}, where x is the step separation. In addition, ''force monopoles'' at steps that result from a strained surface layer lead to a much longer-range step-step attractive potential, varying as $\ln(x)$,[16,17] which is predicted to result in step bunching as well. However, the microscopic origin of the atomic range step-step attraction as assumed by theories[8–10] to explain the multi-height-step bunching is unknown. Based on the introduction above, the questions naturally raised are the following: (1) What is the microscopic origin of the atomic range attraction? (2) Could a competition between a *medium-range repulsion* and a *long-range attraction* between steps lead to step bunching on a vicinal surface? (3) If yes, what are the forms of the repulsive interaction and especially the attractive interaction, as well as their physical origins? (4) What is the manifestation of these interactions for a measurable quantity such as a step-separation distribution?

In this study, we gain insight into the above questions through a study of the step-step interactions on TaC(910) using scanning tunneling microscopy (STM) and Monte Carlo simulations. In particular, we show that a weak, long-range, attractive step interaction must be combined with a strong, medium-range, repulsive interaction to fit the measured step separation distribution. The physical origin of the atomic-range attractive interaction that leads to multiheight steps is also discussed.

Experiments were performed in an ultrahigh-vacuum chamber with a base pressure 1.0×10^{-10} Torr. The chamber is equipped with a STM system, low-energy electron-diffraction (LEED) optics, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), and an ion-sputter gun. TaC is an ionic crystal with a sodium chloride structure, and has *an extremely high melting point*, ~3983 °C. TaC(910), vicinal to the (100) plane, was cut 6.34° from the [100] direction toward the [010] direction, and polished to the desired orientation to within 0.25°. The surface was routinely cleaned by heating to ~2100 °C using electron bombardment. During the heating, the sample housing was cooled by liquid nitrogen to maintain a good vacuum. After cleaning, no impurities were detected with AES, and a LEED pattern with a spot splitting energy dependence indicative of dominant double-height steps was observed. Note that high-temperature heating also served as an activation process for faceting. All STM images were taken at room temperature (RT) in the constant-current mode, with a typical sample bias of 1–2 V and a tunneling current of ~1.0 nA.

First we determined a minimum annealing temperature ($T_{\min}$) at which obvious mass transport occurs on the surface. Below $T_{\min}$ the morphology is essentially frozen in when the sample is cooled slowly from higher annealing temperatures, and this is the morphology that is imaged at RT. A slow cooling is required in order to reach the well-ordered face-

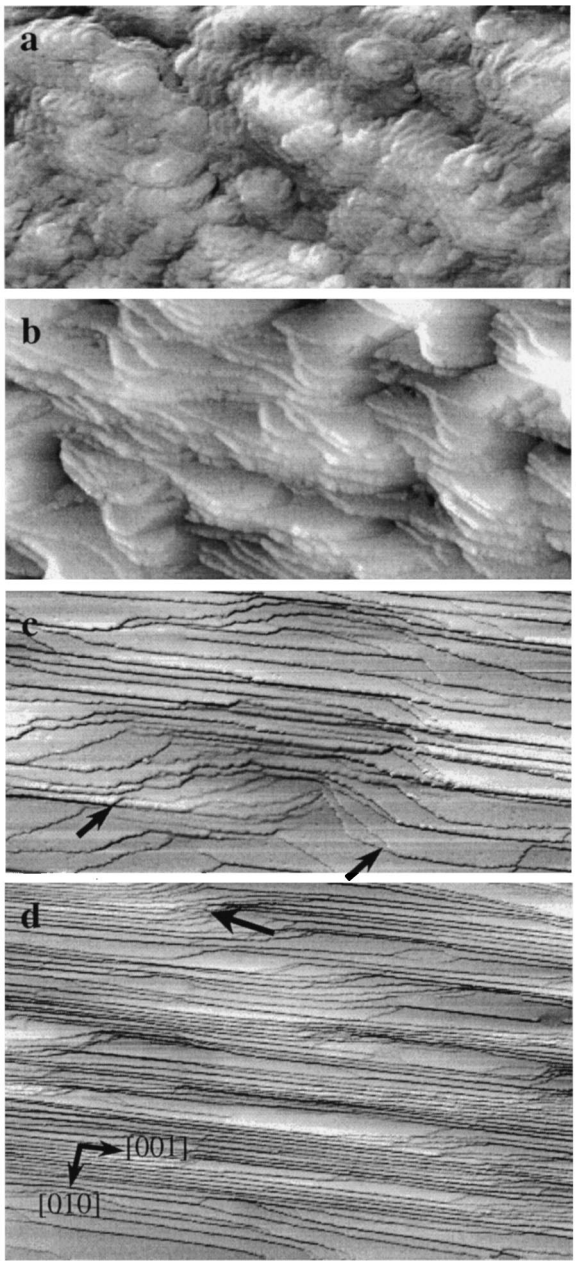

FIG. 1. The STM topographs for TaC(910) annealed at different temperatures and imaged at RT. The size in (a)–(c) is 1000 $\times 500$ Å^2 and that in (d) is 3000×2000 Å^2. The annealing temperatures are (a) $T=1000$ °C, (b) $T=1500$ °C, (c) $T=1750$ °C, and (d) $T=2100$ °C.

ting phase below T_R. Figure 1 shows the morphological evolution post annealed at different temperatures (T) after the surface is disordered by sputtering with Ne^+ ions at RT. The dwell time during each annealing process is ~60 sec for $T < 1500$ °C, and ~30 sec for $T \geqslant 1500$ °C. (Note that for $T \sim 2100$ °C, 30-sec annealing is long enough for the surface to reach a steady state.) As can be seen, the ordering begins to be indicated by the appearance of single-height steps after annealing at ~1000 °C [Fig. 1(a)], indicating that obvious mass transport occurs on the surface at this annealing temperature ($T_{\min}$). Other, more important, features in Fig. 1 are the following. (1) Single-height steps appear first, and are dominant after lower temperature annealing ($T \leqslant 1500$ °C), and merge from off-[001] directions to become multiheight steps along the [001] direction as T increases [see the arrows in Fig. 1(c)]. At $T \geqslant 2000$ °C [Fig. 1(d)], the step distribution is stabilized and consists of 12% single-, 56% double-, 31% triple-, and 1% quadruple-height steps. (2) These multiheight steps along the [001] direction are very straight, which implies a high kink excitation energy (or very strong bonding), and the step meandering is suppressed. This phenomenon was also observed on TaC(n10) ($n=1$, 2, and 3), where even higher multiheight steps are formed,[3–5] revealing the step faces to be (010) facets. The fact that these multiheight steps are only activated at high temperatures is consistent with the existence of atomic-range attraction between steps as suggested by theories.[8–10] We suggest that an attraction of such short range could originate from the orbital affinity between broken bonds or electron-density spillout at steps.[13] When a sample is cooled from above T_R, where step fluctuations can cause neighboring single steps to randomly move together, this short-range attraction can overcome a medium-range repulsion ($2 < x < 13$ atomic rows; see the discussion below) to make neighboring steps coalesce. The formation of multiheight steps reduces the repulsive interaction energies among the single steps,[3–5] since the average step separation must be increased to preserve the net surface orientation. Also, the step-edge energy is lowered by creation of a low-index step-wall facet owing to a reduction in the number of broken bonds at steps. On the other hand, the configurational entropy, due to kinks, would favor the existence of single-layer steps, particularly since the single-layer steps meander more than the multilayer steps. However, entropic kink generation is a minor factor in this system because of the exceptional straightness of the steps in general. Thus the total energy of the multiheight steps is more energetically favorable than the collection of purely single-height steps. This picture is not only consistent with the trend observed for vicinal Si (Refs. 1, 2, 6, 7, 18 and 19) and TaC surfaces,[3–5] where higher multiheight steps form with increasingly miscut angles, but also supports a very recent effective-medium-theory calculation by Frenken and Stoltze.[20] They predicted that, due to a very short-range step-step attraction, many metallic vicinal surfaces should be faceted into low-index planes; however, because of the entropic contribution of step vibrations (even at RT) to the surface free energy, the faceting of these surfaces will usually not be observed. However, as noted above for TaC surfaces, the step meandering is small [as can be observed from the straightness of the steps in Figs. 1(c) and 1(d)] due to very strong ionic bonding (as indicated by the extremely high melting point of 3983 °C). This suggests relatively small step vibrations. In addition, the orbital affinity responsible for this atomic range attraction is strongly orientation dependent, which is the general character of ionic bonding. Because of these special properties the entropy contribution to the free energy of TaC surfaces may be neglected; thus it is possible that the multiheight step facet can be stabilized by atomic-range step-step attractions.

Next we focus on the step-separation distribution for the steady-state images for a sample annealed at $T \sim 2100$ °C for

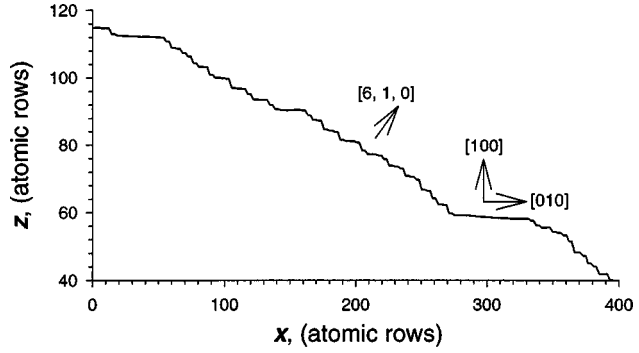

FIG. 2. A line-cut profile from Fig. 1(d) to show the cross section of the step configuration.

30 sec [Fig. 1(d)]. We can see a landscape of alternating step bunches and relatively wide terraces with irregular sizes. The step separation [(100) terrace width] within *these step bunches* is measured to be 13 atomic rows on average, where the atomic-row spacing $a=2.228\,\text{Å}$. Although these step bunches are composed of a mixture of single-, double-, triple-, and quadruple-height steps, they consistently display an orientation close to (6, 1, 0), which is different from the overall orientation (9, 1, 0) of the surface. A representative line-cut profile from Fig. 1(d) in the [010] direction shows the steps bunched into *pseudofacets* with intervening broader terraces that are required to produce the (9, 1, 0) orientation in Fig. 2. From systematic measurements of the step separations along the [010] direction, the probability distribution $P(x)$ is plotted in Fig. 3. This distribution assumes a highly skewed shape with a very sharp peak at $x_p \sim 13$ atomic rows and a mean step separation at $x_m \sim 18.6$ atomic rows. The sharp peak position x_p represents the most probable step separation within the step bunches, and the mean step separation x_m is close to the mean (100) terrace width of 18 rows

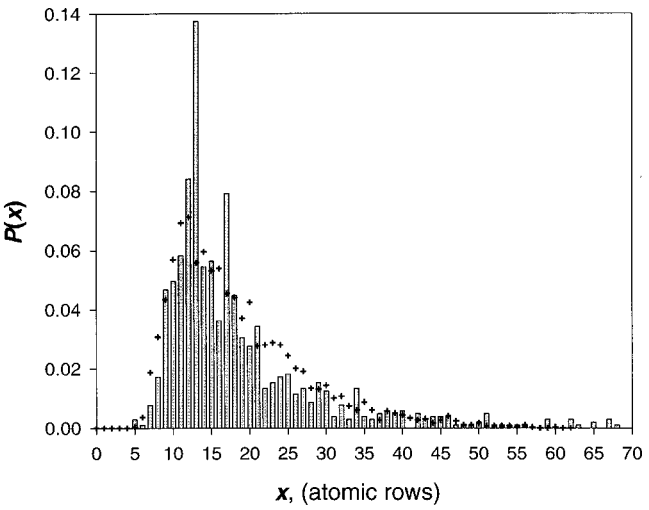

FIG. 3. The measured step-separation distribution for TaC(910) after annealing at $T\sim 2100\,°\text{C}$. Monte Carlo simulation results using the step-step potential in Eq. (1) are indicated by symbols (+). The experimental distribution represents 1012 data points. While the largest step separation measured is 67 atomic rows, the data above 55 rows are insufficient for reliability.

expected for dominant double-height steps with the (910) orientation.

The observed step-separation distribution is quite different from those reported from vicinal silicon surfaces,[18,19] and even from the TaC(n10) surfaces ($n=1$, 2, and 3),[3–5] where the Gaussian-like step-separation distributions observed result from a strong step-step repulsion varying as x^{-2}. The skewed shape observed is qualitatively more like the noninteracting terrace-step-kink model,[18] which is skewed by a weak entropic repulsion. However, the much more rapid decay for $x<x_p$ in the present case and the approach to zero for $x<5$ indicates the existence of a strong step-step repulsion in this range, so that the distribution of narrow terraces within step bunches is highly restricted. The decay for $x>x_p$ is much slower, and indicates a large variation in the width of the (100) terraces between the (6, 1, 0) pseudofacets. The skewed shape of the distribution indicates that only a medium-range repulsive potential between steps is unlikely to account for the observed distribution, which is confirmed by our Monte Carlo simulations discussed below. A weak but longer-range attractive potential must be introduced. One can expect that, if we cut a vicinal surface with the (100) terrace much smaller than that of the (910) surface, the step-separation distribution will be determined predominantly by the repulsive step-step interaction, so that the distribution will be Gaussian when the repulsive interaction varies as x^{-2}.[18] This is exactly what has been previously observed on the TaC(310) surface.[3,4] The origin of the repulsive interaction is believed to come from the elastic dipolar effect because from a LEED I-V study,[21] the TaC(100) terrace is slightly buckled with C atoms displaced outward (~0.2 Å) relative to Ta atoms. This obvious surface strain may be relieved at steps, resulting in a force dipole at steps.

To see quantitatively how the competition between the *medium-range repulsion and long-range attraction* between steps leads to such a skewed step-separation distribution, we have performed a Monte Carlo simulation. In the simulation, a one-dimensional (1D) array of 300 sites is initially given a uniform distribution, and then starts to approach equilibrium as the simulation time proceeds under the influence of a step-step potential,

$$V(x)=\frac{A}{x^2}-\frac{B}{x^{\alpha}}, \tag{1}$$

in which A, B, and α are positive parameters, and the first term represents medium-range repulsion and the second term long-range attraction. The 1D approximation is justified by observation of straight steps along the [001] direction due to a very high kink excitation energy. In order to reduce the fitting parameters, the first repulsive term in Eq. (1) is determined from the Gaussian distribution of step separations observed for the TaC(310) surface since, in this case, the step-step repulsion dominates. This can only be an approximation, since the repulsive interaction between steps is expected to be proportional to the product of the torques of the two interacting steps, where torque is proportional to step height.[22] The parameters B and α in the second attractive term are adjusted in simulations to fit the measured step-

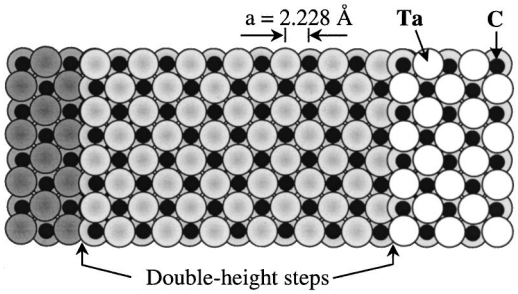

FIG. 4. Schematic view of a TaC(910) surface showing double-height steps with separation of 13 atomic rows corresponding to the average spacing observed in step bunches.

separation distribution in Fig. 3. *Note that a repulsive term alone cannot produce the observed skewed distribution*. We found that for $B/A \sim 0.11 \pm 0.03$ and $\alpha \sim 1.0 \pm 0.5$, the simulated distribution (''crosses'' in Fig. 3), is a good fit to the measured one, although we cannot precisely determine the value of α. This indicates that the attractive interaction strength B is much weaker than the repulsive interaction strength A, but the former is of longer range than the latter. It should be noted that the final result is rather insensitive to the errors expected from our approximation of A.

Finally, we want to comment briefly on a possible physical origin of the long-range attraction between steps. In Fig. 4 we show that with dominant double-height steps, Ta-C atomic pairs along the step edge at neighboring steps, separated by a (100) terrace with an odd number of atomic rows, are shifted by a. This is the case in the step bunches ($x_p \sim 13$ atomic rows), and makes the neighboring steps different. Therefore, some charge distribution in Ta-C pairs along steps could produce such an attractive interaction. A quantitative analysis will be left for future work.

In summary, using STM, step bunching is observed on TaC(910) with dominant double-height steps. Three ranges of interactions are introduced to account for the experimental observations. Based on the temperature dependence of the observed step structure, we propose a microscopic origin for an approximately one-atomic spacing step-step attraction as assumed by theories. The step-separation distribution measured between the double-height steps is very skewed and sharply peaked at $x_p \sim 13$ atomic rows, which represents the most probable step separation within step bunches. Monte Carlo simulations indicate that a weaker long-range attractive step-step interaction, $-B/x^{1.0\pm0.5}$, must be added to a medium-range repulsive interaction A/x^2 to fit the distribution. The nature of these interactions arises from the elastic dipolar effect for the repulsion and possible charge redistribution at steps for the attraction.

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