Entropic Step Doubling on W(430)

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We present high resolution low energy electron diffraction results for the W(430) surface. Unlike every other system studied to date, single atomic height steps on this surface become thermodynamically unfavorable at elevated temperatures. Above 940 K a new phase consisting of bound single and double height steps forms. The transition to double height steps is predicted on the basis of a simple model provided that kinks on the double height steps have a lower formation energy than kinks on single height steps. The new phase is stabilized by a step edge interaction between single-double pairs. [S0031-9007(96)00644-8]

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The thermodynamics of surface defect morphologies is an intriguing and rich area of surface physics. Within this field, the evolution of surface structure on vicinal surfaces (i.e., surfaces with a small misorientation from a high symmetry direction) has been extensively studied and is in general well understood [1,2]. Simple models that predict the surface free energy as a function of miscut angle and surface temperature have been extremely successful in predicting numerous phenomena such as surface roughening, faceting, and step doubling [3–5].

In the case of step doubling both experimental and theoretical work have shown that double height steps on vicinal surfaces are stable at sufficiently low temperatures or large miscut angles [5]. At higher temperatures, however, they spontaneously break up into single height steps. Physically, double height steps are stabilized by step-step repulsions that favor widely separated double height steps over closer spaced single height steps [2]. At higher temperatures, provided the kink energy for single height steps is similar to or less than the kink energy of double height steps, the entropy gain associated with step meandering always favors single height steps (i.e., there ate twice as many single height steps per unit area as double height steps). Numerous experimental examples support this picture [5].

In this Letter we present a counterintuitive experimental example where approximately half of the single height steps spontaneously double in height as the temperature is increases. Specifically, we will show that the W(430) surface undergoes a step doubling transition above 940 K, forming a new phase consisting of bound single-double height step pairs. We will further demonstrate that this result can be reconciled within current models, although long held views about the energies of steps must be significantly modified for bcc surfaces.

The W(430) sample was cut and oriented to within 0.2° of the (430) plane. Sample cleaning followed well described methods [6]. These include heating in a $P = 2 \times 10^{-6}$ torr O_2 atmosphere at 1600 K for 4 days to remove carbon, followed by repeated rapid flashes to 2100 K to remove excess oxygen. The sample was then slowly annealed from 1000 K to room temperature. The system pressure was kept below 1×10^{-10} torr for all experiments to prevent CO_2 contamination. Periodic flashing to 2100 K was sufficient to remove the excess CO_2 adsorbed during the course of the experiment. Temperatures were measured with a W–5% Re/W thermocouple spot welded to the sample. The thermocouple was calibrated against an optical pyrometer to give an absolute temperature error of ± 25 K; relative temperature errors are ± 2 K. All data presented here were obtained with a high q-resolution low energy electron diffraction (LEED) system [7]. The LEED transfer width was 2000 Å at the experimental geometry used in these experiments. Reciprocal space coordinates are given in terms of the conventional cubic unit cell with sides $a^* = 2\pi/a = 1.988$ Å^{-1}. The components of the momentum transfer $q_\parallel$ and $q_\perp$ are measured parallel and perpendicular to the (110) plane, respectively.

Tungsten crystallizes into a bcc lattice. The stepped W(430) surface is shown in the inset of Fig. 1. At low temperatures is consists of close packed (110) terraces (with width $L = 3.5a\sqrt{2} = 15.64$ Å) separated by monatomic steps running along the $[00\bar{1}]$ direction. Diffraction measurements of the peak widths at in-phase conditions indicate that the mosaic spread is less than 0.08° and that the crystal is well ordered over a distance of 1000 Å.

Below 940 K, LEED scans across the specular diffraction rod (with $q_\parallel$ in the $[1\bar{1}0]$ direction) at an out of phase condition, $q_\perp = (2.5, 2.5, 0)$, show the characteristic splitting of a vicinal surface with monatomic steps (see Fig. 1) [8]. The splitting corresponds exactly to $2\pi/L$ where L is the average distance between steps [measured in the (110) plane] for the (430) surface. Above a critical temperature $T_c = 940$ K, a new peak reversibly appears halfway between the split peaks at $q_\parallel = 0.0$. It is this peak that signals the formation of double height steps. If only single height steps were present, the intensity at $q_\parallel = 0.0$ would be near zero at the out-of-phase condition since scattered waves from two terraces separated by a monatomic step

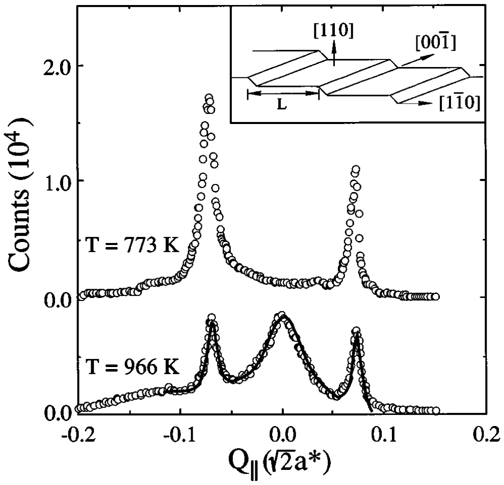

FIG. 1. Reflectivity scans across the specular rod above and below the transition temperature. Data are for the $q_\perp = (2.5, 2.5, 0)$ reflection with the incident e^- beam in the $[1\bar{1}0]$ direction (down the steps). The electron energy is 150 eV, and the detector angle is 111.86° relative to the incident direction. The inset shows a schematic of the W(430) surface. Solid line is a fit as described in the text.

are 180° out of phase [8]. If double height steps are present, the two terraces produce scattered waves 360° apart, or in phase, giving rise to the center peak. The conclusion that the center peak is due to double height steps was further confirmed by taking a series of scans across the specular rod for various $q_\perp$ between the (220) and (330) points. These scans reveal that the shift of the center peak position with $q_\perp$ is consistent with the prediction of kinematic calculations from a surface with double height steps [9].

There are two important conclusions that can be ascertained from the high temperature profile in Fig. 1. First, the positions of the low temperature split peaks (due to single height steps) do not change above T_c. Their positions, in fact, remain constant for all higher temperatures where they remain visible (up to 1100 K). This implies that there is no macroscopic faceting when the steps double [i.e., the surface maintains its (430) orientation]. Again, scans along the specular rod as a function of $q_\perp$ support this conclusion. Since no faceting occurs and the (430) orientation is preserved, the width of the (110) terraces must double as the step height doubles.

The second conclusion that can be drawn from the high temperature scans is that both single and double height steps coexist in the high temperature phase. This is supported simply by the fact that the original split peaks (derived from single height steps) persist above T_c. This is also demonstrated in Fig. 2 where the ratio of the split-to-central peak intensity is plotted (note that below T_c, the background intensity at $q_\parallel = 0$ is used to calculate the ratio in Fig. 2 since no resolvable central peak exists below this temperature). While the ratio in Fig. 2 becomes small above T_c, it is not zero. The split peaks still exist up to 1100 K which is the highest temperature that can be obtained before signal to noise problems become serious. If only double steps were present, a single peak at $q_\parallel = 0$ would be present. This observation has important implications for the nature of the high temperature phase that we will now discuss.

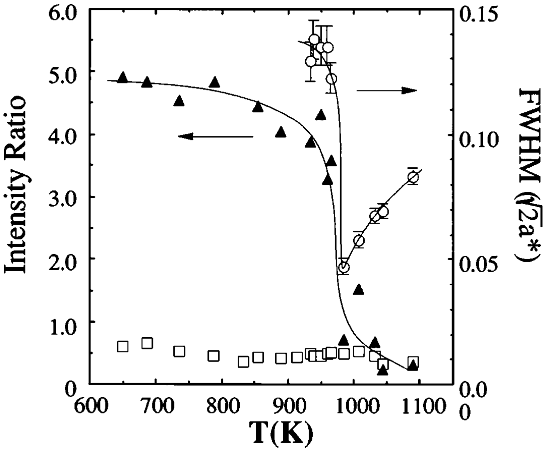

FIG. 2. Intensity ratio of single to double height peaks (▲), FWHM of the single (□) and double (○) height peaks vs temperature. Solid lines are guides to the eye.

The step doubling transition can be predicted within the framework of existing models (although this possibility has been previously overlooked). We start by writing the free energy per unit area for a surface miscut by an angle ϕ with respect to the (110) surface [3,4],

$$f(\phi, T) = f_{110}(T) + \frac{\eta(T)}{h} |\tan\phi| + \frac{B(T)}{a_\parallel h^3} |\tan\phi|^3, \tag{1}$$

where $f_{110}(T)$ is the free energy of the (110) surface, h is the height of a step ($h = a/\sqrt{2}$ for single height steps), and $a_\parallel$ is the smallest kink length along a step edge. For the (430) surface $a_\parallel = a = 3.16$ Å.

The second term in Eq. (1) is the free energy associated with making a step where $|\tan\phi|$ is proportional to the step density and $\eta(T)$ is the (free energy)/length of a step including the step meandering entropy. Provided that T_c is far from the roughening temperature, this term decreases with increasing temperature [2],

$$\eta(T) = \eta(0) - \frac{2kT}{a_\parallel} \exp(-\varepsilon/kT). \tag{2}$$

Here ε is the energy to make a kink.

The last term in Eq. (1) is due to step-step interactions which can be entropic or include a particular step interaction. As we will show, this term will be required to stabilize the high temperature phase.

In order to have a transition to a double height step phase consistent with the experimental data three conditions must be met. First, at $T = 0$ K the (free energy)/area of a double height step, $f_d(\phi_d, 0)$, must be more than a single step, $f_S(\phi_s, 0)$, so that single steps are preferred at low temperatures. This condition can be expressed as an inequality with the aid of the second term in Eq. (1), $\Delta\eta = (\eta_d |\tan\phi_d|/2h - \eta_s |\tan\phi_s|/h) > 0$, where η_s and η_d are the energy/length of a single and double step, respectively, at $T = 0$ K. The angles ϕ_s and ϕ_d are the misorientation angles from the (110) for surfaces composed of pure single steps and pure double steps, respectively.

In order to drive a transition from a single to a double step phase, a second condition is required so that entropy will favor double height steps at some higher temperature. A necessary requirement for this is that the energy to make a kink on a double height step must be less than the energy of a kink on a single height step, i.e., $\varepsilon_d < \varepsilon_s$. This allows for the possibility that kinks on double height steps can be thermally excited before kinks on single height steps. With these first two conditions, it is possible to find a set of energies, $\Delta\eta$, ε_d, and ε_s so that the meander entropy will favor double height steps for some finite temperature range where single height kinks are not excited to an appreciable density [10]. Note that at sufficiently high temperatures, when single height kinds are excited, a reentrant phase transition back to single height steps is possible. This is because there are twice as many ways of arranging two single height steps.

Finally, a third condition requiring single-double step-step interactions is necessary to stabilize the double-single coexistence phase. Without such an interaction, Eq. (1) would predict phase separation into regions of pure single and double steps with continuously varying misorientation angles ϕ_s and ϕ_d, respectively, as a function of temperature. This would be analogous to the continuous faceting observed on miscut Si(111) during the (7×7) to (1×1) transition [2]. Since such a phase separation would produce a temperature dependent splitting of the single step peaks that we do not observe, we infer that the interaction is sufficiently strong to stabilize that (430) orientation so that $\phi_d = \phi_s = 8.13°$, the angle between the (430) and (110) surfaces.

We denote the (interaction energy)/length between single pairs and single-double pairs as U_s and U_{sd}, respectively. For simplicity we ignore double-double step interaction since they must be significantly smaller (they interact over a range twice that of either single-single or single-double steps). If $U_s > U_{sd}$, regardless of whether or not the interactions are repulsive or attractive, then the free energy will favor single-double pairs over phase separation. Thus, the new phase formed will consist of a repeating array of single-double step pairs. The surface structure will resemble the one shown in Fig. 3(a) or its degenerate equivalent Fig. 3(b). In all of this discussion we have neglected any mixing entropy. Qualitatively this entropy term will allow mixtures of the two degenerate structures, giving rise to defects in the perfect periodicity. The actual surface structure would resemble Fig. 3(c).

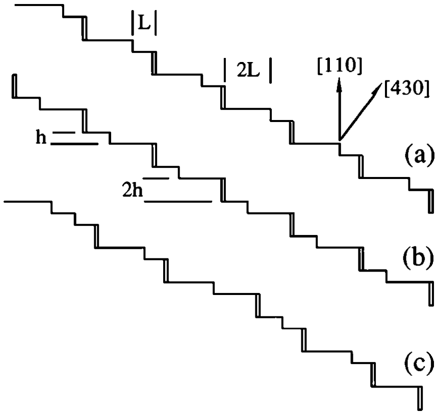

FIG. 3. Structural model of single-double step phase: (a) and (b) are two degenerate ordered phases, (c) is a disordered phase.

The high temperature diffraction results from the W(430) surface are consistent with this model. At T_c, when the central peak at $q_\perp = (2.5, 2.5, 0)$ becomes clearly resolvable, the width is very broad but narrows considerably by 980 K (see Fig. 2). We have performed fits to the line shapes using a model consisting of double height steps (terrace width $2L$) separated by single height steps (terrace width L). To simulate the disorder in a perfect single-double pair periodicity, the surface was constructed by assuming that the probability that a double height step occurs after N single steps is given by $P(N) = \gamma(N - 1)^{1-\gamma}$, where γ is the probability of making a double step. With this distribution the mean number of single steps between doubles is $(1 - \gamma)/\gamma$. For the surface model in Figs. 3(a) or 3(b) $\gamma = 0.5$ (i.e., 1 single step per double step). Kinematic diffraction calculations from surfaces constructed using $P(N)$ were fit to the experimental line shape at T_c (see Fig. 1). A best fit γ was determined to be 0.35 ± 0.05 (1.9 single steps per double step), which is in reasonable agreement with $\gamma = 0.5$ if fluctuations in the concentration due to mixing entropy are allowed.

Above 940 K the center peak broadens with little change in either the width or height of the satellite peaks which is presumably due to either a change in the structure, the structural order, or both. The former would result when single-double pairs break up at higher temperatures and the latter from mixing entropy. In addition, fluctuation of the double step edges due to their low kink energy will further destroy the step-step correlation in the diffraction measurement and also broaden the peak.

The two important assumptions that must be addressed for this model are the validity of the assertions that single height kinks cost more energy than double height kinks and that the inequality $U_s > U_{sd}$ is true. Also, if these energetics are correct, why are they true for tungsten and not for previously investigated metal surfaces? A strong case for the energetics can be made by considering the bcc geometry of W(430). Steps on the (430) surface have a (001) orientation which is not a close-packed face for a bcc crystal. Double height steps that expose a larger (001) facet would have a higher energy. On the other hand, a kink exposes a (111) facet which is a close-packed face. Therefore kinks on double height steps expose a larger (111) facet and may have a lower energy. There is theoretical support for this energy hierarchy. Fourth moment approximations to tight binding calculations for stepped W(110) surfaces show that $\eta_d \approx 2.5\eta_s$ while $\varepsilon_s \approx 2.4\varepsilon_d$ [11]. In addition, these same calculations predict an oscillatory interaction between step edges that is attractive for the W(430) step separation [12]. The depth of the attractive minimum is deeper for single-double step pairs, in agreement with the assertion of the proposed model. Note, however, the experimental data presented here are not sufficient to distinguish between repulsive or attractive forces between steps. It is only possible to conclude that an interaction of sufficient magnitude exists to stabilize double-single step pairs.

Diffusion measurements on the same family of vicinal tungsten surfaces also support a doubling transition. Gomer and Wang have studied diffusion on W(110) surfaces with both (001) and (111) oriented steps [13]. They found that the adatom diffusion coefficients for surfaces with (001) steps show a dramatic drop for $T > 700$ K. They suggest that the drop is not correlated with surface roughening since the diffusion remains one dimensional even at higher temperatures (surface roughening would lead to isotropic diffusion). The decrease in the diffusion coefficient is, however, consistent with a step doubling transition.

The reason is that double height steps have a larger rms fluctuation than single height steps because $\varepsilon_s > \varepsilon_d$ [2]. Once the doubling transition temperature is crossed, diffusion along the step edges must slow down because of the longer path around the meandering double height step edges.

In conclusion, we have shown that the W(430) surface undergoes a step doubling transition at 940 K. Based on the simple model represented by Eq. (1), entropy favors double height steps in an intermediate temperature range because kinks on double heights steps cost less energy than kinks on single height steps. Phase separation into single stepped and double stepped regions is prevented by an interaction between step edges that favors single-double pairs.

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