Terrace-width distributions on vicinal Ag(110): evidence of oscillatory interactions

W.W. Pai, J.S. Ozcomert, N.C. Bartelt, T.L. Einstein

Department of Physics, University of Maryland, College Park, MD 20742, USA

J.E. Reutt-Robey *

Department of Chemistry, University of Maryland, College Park, MD 20742, USA

Abstract

The distribution of terrace widths on vicinal Ag(110) surfaces is measured with scanning tunneling microscopy as a function of mean terrace width $\langle l \rangle$ and interpreted in terms of a step–step interaction potential. As previously observed on vicinal Cu(100) surfaces, but in contrast to reports involving semiconductor surfaces, the distribution does not scale simply with $\langle l \rangle$. For vicinal Ag(110) surfaces with $\langle l \rangle = 22$ Å, the distribution resembles that expected for noninteracting steps. For $\langle l \rangle = 30$ Å, the distribution narrows significantly, suggesting repulsive interactions. For $\langle l \rangle = 40$ Å, the distribution has a form expected for attractive interactions. The absence of simple scaling of this distribution reveals that the decay of step–step interactions is more complicated than the l^{-2} behavior expected for elastic or dipolar repulsions. A nonmonotonic potential is found to reproduce the observed terrace-width distributions, as demonstrated with Monte Carlo simulations of a terrace–step–kink model. According to this trial potential, step interactions are dominated by a repulsive l^{-2} term at short l and by an RKKY-like oscillatory term at longer l. The form of the latter term is reminiscent of indirect interactions between adsorbates.

1. Introduction

Although steps are known to play a major role in equilibrium crystal shapes, thin film growth, and catalysis, their essential properties remain poorly characterized. Even the interaction potential between steps is not well established in either

* Corresponding author. Fax: +1 (301) 314 9121; E-mail: rrobey@wam.umd.edu.

form or magnitude. Since these interactions govern step configurations and the manner in which steps respond to adsorption, stress, and other perturbations [1], the understanding of this potential is an important pursuit.

In many cases it has proved reasonable to describe the interaction potential between steps, $U(l)$, as repulsive and decaying by l^{-2}, where l denotes the distance between steps [2,3]. This form describes energetic interactions expected from both dipole–dipole [4,5] and elastic effects

[6,7]. Given the absence of direct experimental data to describe step–step interactions, there was little incentive to develop $U(l)$ further.

Recently, however, microscopic probes of surface structure, such as the scanning tunneling microscope (STM) and reflection electron microscope, have permitted detailed measurements of the configuration of steps on single crystal surfaces. In particular, measurements of the terrace-width distribution function $P(l)$ provide a sensitive probe of step–step interactions. In cases involving semiconductor surfaces, the form of $P(l)$ has generally proven consistent with steps which interact via a repulsive l^{-2} potential [8–12]. However, this form for the potential provides an inadequate description of the terrace-width distributions which have been measured on vicinal Cu(100) surfaces [13]. Although $P(l)$ for Cu(117) has the shape expected for a simple repulsive potential, the width and asymmetry of $P(l)$ for Cu(1,1,19) suggests attractive interactions between steps. Thus, on these two vicinal Cu(100) surfaces, the step–step interaction potential seems to be repulsive for small step separations and attractive at intermediate step separations.

Several possible sources of attractive step–step interactions have been identified [5,13]. Attractive interactions may result from surface stress relaxation in the vicinity of steps [3,5] or from dipole–dipole interactions [3,14] (if dominated by the in-plane orientation). More likely, indirect step–step interactions mediated by extended electron states in the substrate may introduce attractive step–step interactions at some step separations [5,13]. In order to establish the source and form of $U(l)$ on metal surfaces more generally, a more extensive data base must be obtained.

In this paper we report STM measurements of terrace-width distributions on vicinal Ag(110) surfaces with average terrace widths $\langle l \rangle = 22$, 30, and 40 Å. As in the previous study involving vicinal Cu(100) surfaces, the width of $P(l)$ is not simply proportional to $\langle l \rangle$, and plots of the scaled form $\langle l \rangle P(l)$ versus $l/\langle l \rangle$ depend even qualitatively on $\langle l \rangle$, both results indicating the potential is more complicated than l^{-2}. For these vicinal Ag(110) surfaces, steps appear noninteracting for

$\langle l \rangle = 22$ Å, repulsive for $\langle l \rangle = 30$ Å, and attractive for $\langle l \rangle = 40$ Å. Monte Carlo (MC) simulations based upon a terrace–step–kink (TSK) model of surface structure and using a rather ad hoc potential that contains an oscillatory term beyond the first six lattice spacings is found to reproduce the observed terrace-width distributions. While there is insufficient data to warrant confidence in the specific potential, it is nonetheless noteworthy that this potential, with reasonable parameters, can account for the three distributions. The physical basis of this potential is explored.

2. Experimental

Experiments were conducted in an ultrahigh-vacuum chamber (base pressure 6×10^{-11} Torr) equipped with a scanning tunneling microscope (Omicron STU-52), reverse-view LEED, and retarding field Auger. All STM measurements were performed at room temperature with a negative sample bias of ≤ 80 mV and a tunneling current of 1.0–1.5 nA.

The two macroscopic silver single crystals employed in this study were obtained from Monocrystals LTD and mechanically polished with alumina down to a 0.3 μm grit. One of the crystals was oriented and polished to expose the (110) surface and the other crystal to expose a surface miscut by 2.3° from (110) toward the (001) azimuth. The crystals were mounted on tantalum sample plates and suspended from the variable temperature (300–1200 K) sample manipulator. The samples were initially cleaned by many cycles of hot (600 K) argon ion sputtering (2 μA 500 eV Ar$^+$ cm^{-2}) and oxidation. After this procedure, surfaces showed sharp (1 × 1) LEED patterns, and no contaminants were detectable with AES.

Immediately prior to STM measurements, the samples were sputtered for 15 min at 300 K, flash-annealed at 875 K for 60 s, and then cooled to room temperature at a rate of ~ 5 K/s. For both crystals, this treatment produced sharp LEED spots. When probed with STM, the sample was found to consist of microscopic (~ 1 μm^2) regions with different local orientations,

but with well specified step orientations and densities. These local orientations were generated by this relatively high temperature (for silver) preparation, which introduces a low density (~ 1 site/5 μm^2) of pinning sites on the surface [15], thereby preventing the surface from attaining global equilibrium. Within these micron-sized regions, substantial fluctuations in the step position are observed, indicating that a local equilibrium is established. These local orientations are stable for times much longer than the time scale (48 h) in which contamination from background gases can be detected. Although such variations in local surface morphologies are not usually desirable, they prove convenient for the present study.

In order to perform a meaningful study of step–step interactions, terrace-width distributions were tabulated only for regions which contained close-packed steps running along [$1\bar{1}0$]. Distributions for $\langle l \rangle = 30$ Å and $\langle l \rangle = 40$ Å were measured on the macroscopic Ag(110) crystal and that for $\langle l \rangle = 22$ Å on the macroscopic Ag(110)-

(a)
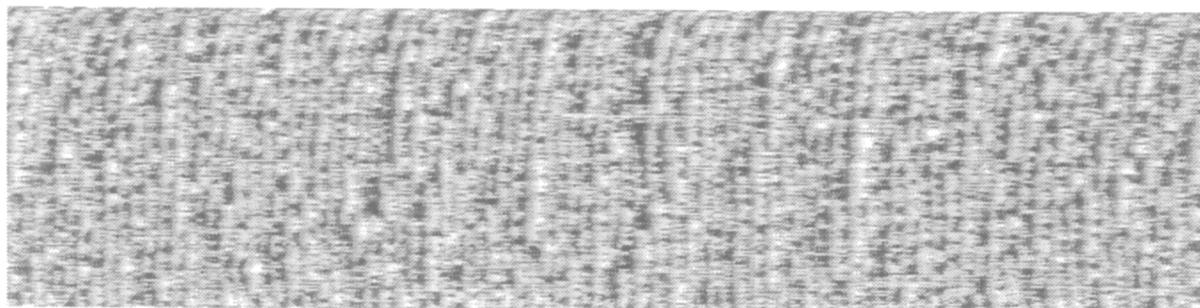
(b)
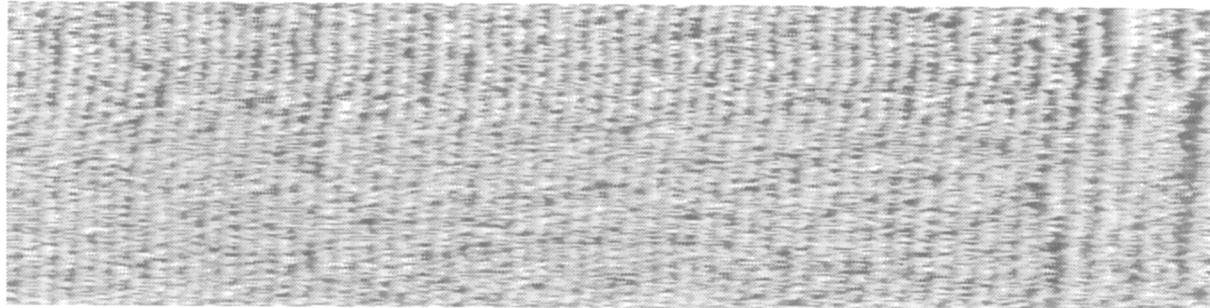
(c)
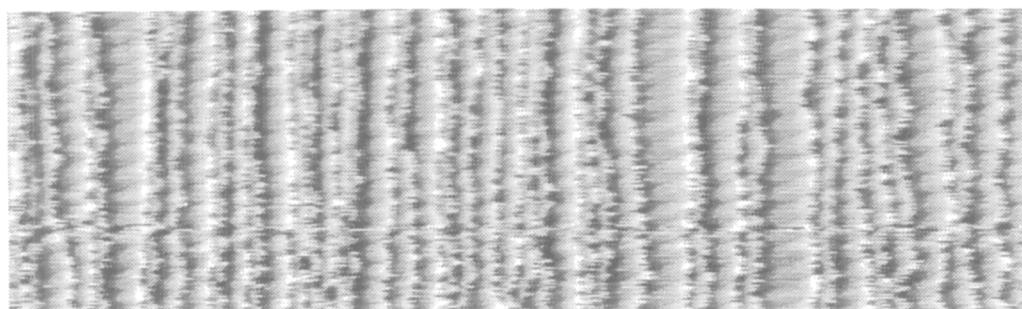
|———————| 250Å   ↑ [$1\bar{1}0$]

Fig. 1. Scanning tunneling microscopy images of vicinal Ag(110) surfaces at different mean terrace widths $\langle l \rangle$: (a) $\langle l \rangle = 22$ A, (b) $\langle l \rangle = 30$ Å, and (c) $\langle l \rangle = 40$ Å.

2.3° [001] surface. The $P(l)$ were derived from large-area (3000 Å × 3000 Å) scans, well separated (> 5000 Å) from any pinning site. Two such large-area scans on macroscopically different regions of the surface are incorporated into each $P(l)$.

A statistical analysis of terrace-width distributions was performed by first creating a grid of meshpoints on the STM images. (Since the steps wander significantly, more than one terrace length may be determined from two adjacent steps.) The meshpoints are the points of intersection between the step edge and an equi-spaced array of lines in the [001] direction. The spacing between the lines along [1$\bar{1}$0], 40–60 Å depending on mean step separation, was selected to maximize the statistical information which could be obtained from an image. Placing the lines closer than 40 Å does not improve the statistics, since correlations in the position along the step edge extend to distances of this order. Finally, we note that thermal fluctuations in the position of the step edge on the time scale of the STM measurement produce a characteristic frizzled step edge, as previously observed on vicinal Ag(111) [16], Cu(100) [13], and Cu(110) [17] surfaces. This frizziness introduces an uncertainty in determining the separation between two adjacent steps, but is effectively averaged out in the statistical analysis of a large number of mesh points.

3. Experimental results

Sections of STM images acquired for $\langle l \rangle = 22$, 30, and 40 Å are provided in Fig. 1. By inspection, the distribution of terrace widths on the surfaces with $\langle l \rangle = 22$ Å appears broad yet very regular. On surfaces with average terrace widths of $\langle l \rangle = 30$ Å, the distribution narrows significantly. Finally, on surfaces with average terrace widths of $\langle l \rangle = 40$ Å, the nature of the distribution no longer appears uniform. Rather, some steps appear much closer than those observed even on the surfaces with much smaller mean step separations, while other steps remain widely separated.

These qualitative observations of the terrace
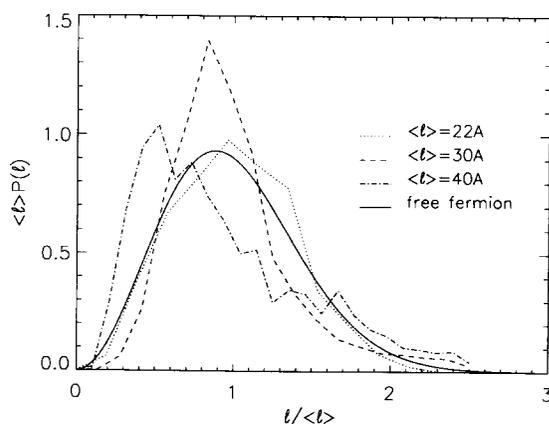
Fig. 2. Scaled terrace-width distributions measured for vicinal Ag(110) surfaces with mean terrace widths of $\langle l \rangle = 22$, 30, and 40 Å are plotted together with the universal distribution predicted by a free fermion model, which considers only entropic interactions between steps.

width distribution are confirmed in a statistical analysis of the data. In Fig. 2 a plot of the scaled terrace width distribution, $\langle l \rangle P(l)$ versus $l/\langle l \rangle$, reveals that the terrace-width distribution changes shape as a function of mean terrace width. In the case of $\langle l \rangle = 22$ Å, this distribution is similar to that expected [18] for steps without energetic interactions (i.e. the free fermion case). This distribution narrows for $\langle l \rangle = 30$ Å, as expected for steps with repulsive interactions. Finally, for $\langle l \rangle = 40$ Å, the distribution becomes broad and asymmetric with one peak in the distribution clearly evident at small separation $l/\langle l \rangle = 0.55$ and a second smaller peak in the tail of the distribution at $l/\langle l \rangle = 1.7$.

The sensitivity of these distributions to $\langle l \rangle$ can thus be used to characterize further the step–step interaction potential. Formally, the measured width (w) of the terrace-width distribution is defined via the second moment of the distribution:

$$w = \left[\frac{\sum (l - \langle l \rangle)^2}{N} \right]^{1/2}, \qquad (1)$$

where N is the total number of terrace widths included in the distribution. In Fig. 3, the experimentally derived widths are compared to those expected from potentials of the Al^{-n} form, which are evaluated using the MC method described
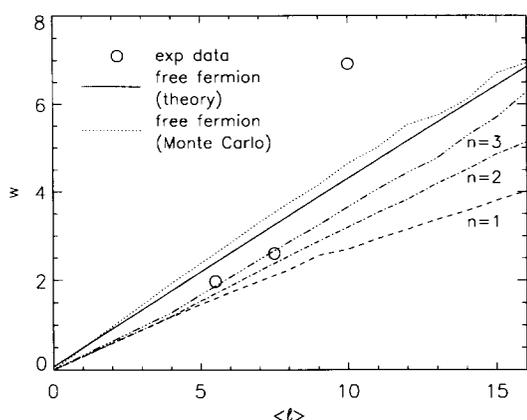
Fig. 3. Measured width w of the terrace-width distribution $P(l)$ is compared to theoretical predictions based upon potentials of the form Al^{-n} as a function of mean terrace width $\langle l \rangle$, for $n = 1$, 2, and 3, generated by MC in the TSK model, with $A = 4$. Data area presented as open circles. The solid line gives the result for the free fermion model [18] describing steps with no energetic interactions ($n = \infty$, in this scheme), with the dotted line showing the Monte Carlo values for noninteracting steps in the TSK model. The larger w in the MC results compared to the free fermion values is due to the moderately high temperature used in the simulation [19].

below. The abscissa in Fig. 3 is expressed in units of $a_\perp = 4.09$ Å (the lattice spacing in the [001] direction, perpendicular to the steps); thus, $\langle l \rangle = 22$, 30, and 40 Å correspond to $\langle l \rangle = 5.4$, 7.3, and 9.8, respectively. For both the noninteracting (free fermion) and inverse-square potentials, w increases linearly with $\langle l \rangle$. (In general, even for noninteracting steps, an effective l^{-2} interaction comes from entropic repulsions.) The proportionality constant decreases slowly, by $A^{-1/4}$, with increasing repulsive amplitude A, once this energetic contribution dominates the entropic repulsion. In general, for a repulsive l^{-n} potential, w is proportional to $l^{(n+2)/4}$ [19]. These three experimental distribution widths are inconsistent with any simple power form. The widths for $\langle l \rangle = 22$ and 30 Å are significantly narrower than expected for the noninteracting case, suggesting repulsive potentials. (This result is curious for the smaller-$\langle l \rangle$ case, which otherwise has the behavior of noninteracting steps.) However, the width for $\langle l \rangle = 40$ Å is much *larger* than it would be for noninteracting steps, suggesting attractive interactions.

We thus conclude that the variation in terrace-width distribution with $\langle l \rangle$ cannot be described by a potential with just a simple power form. The data strongly suggest there is an oscillatory RKKY-like term [20] in the potential to generate distributions characteristic of attractive, repulsive, and even noninteracting steps, depending upon the mean step separation. Such an oscillatory term in the interaction potential can arise from indirect "through metal" interactions via extended substrate electron states [21], and has been previously identified as a possible source of attraction between steps [5,13].

4. Model potential and simulations

We now show with MC simulations that the distributions observed on vicinal Ag(110) can be described by a potential with an RKKY-like form at $l > 6$ lattice spacings and a repulsive l^{-2}-like form at smaller step separations.

To obtain a potential for use in our simulations, we began with the general form

$$U(l) = \frac{A}{l^n} + \frac{B \cos(\kappa l + \delta)}{l^m}. \qquad (2)$$

The first term, with $n = 2$, is just the elastic or dipolar interaction. We recall that the l^{-n} behavior comes from the r^{-3} elastic repulsion between pairs of point defects, separated by r, on a surface. Approximating the steps as lines of independent points, we find the l^{-2} behavior by naively integrating along one of the steps [22].

The second term has the form expected for indirect interactions. On metals, the dominant interaction between chemisorbed atoms (or defects [23]), when there is little charge transfer, is typically the electronic indirect interaction. This interaction is insignificant on semiconductors, since all bands are essentially filled or empty. Indirect interactions can be attractive or repulsive, depending on whether the net coupling of the adatoms' wavefunctions is in-phase or out-of-phase. In the present case, we imagine that relaxations at step edges provide local perturbations of the substrate comparable to chemisorptive coupling.

At small separations, the r-dependence of indirect interactions can be quite complicated, since all occupied states contribute, but asymptotically the interaction is mediated by electrons at the Fermi level. In this limit, which should be reached once adatoms are several spacings apart [24], the interaction reduces to $r^{-p} \cos(2k_F r)$, where k_F is the Fermi wavevector pointing in the $\hat{r}$ direction. The exponent p depends strongly on the electronic states mediating the interaction. The integration along the step edge is complicated by the oscillatory factor [22]. Redfield and Zangwill [5] point out that, given site–site interactions of the form $r^{-p} \cos(\kappa r)$, the inter-row interaction has the form of the second term of Eq. (2), with $m = p - \frac{1}{2}$ and $\delta = \pi/4$ [25]. For bulk electronic states, $p = 5$, so $m = 9/2$ [5]. When mediated by (2D-isotropic) surface states, the interaction decays like r^{-2}, as reported by Lau and Kohn [26], leading by similar arguments [5,25] to $m = 3/2$ in Eq. (2). While there apparently are surface states on the highly anisotropic (110) faces of noble metals that may well mediate interactions in the [001] direction, these states exist only near $\overline{Y}$ [27], suggesting a small integration range along the step-edge direction [25], and m much closer to 2.

Lacking definitive information, we chose $m = 2$ as the best estimate in our trial empirical potential, which in any case should roughly approximate the actual interactions.

The MC method used to perform the simulations has been described previously [28]. Briefly, 20 steps are created on a square lattice by applying screw-periodic boundary conditions in the direction perpendicular to the steps. The lattice is first allowed 10^5 MC steps per site to equilibrate. Then, an additional 10^5 steps are run to obtain sufficient data to calculate the distribution curve with an acceptable signal to noise level. Since previous experiments [15] on this surface found a high density of thermally excited kinks, we set the temperature $T = \epsilon/k_B$, where ϵ is the energy of a unit kink and k_B is Boltzmann's constant. The potential is then expressed in units of ϵ, as a function of l in units of lattice spacing $a_\perp$.

Our goal in this part of the work was to concoct an interstep potential with a plausible form which would lead to $P(l)$'s similar to those measured. After many trial simulations involving different choices of parameters, we were able to reproduce our experimental observations with the
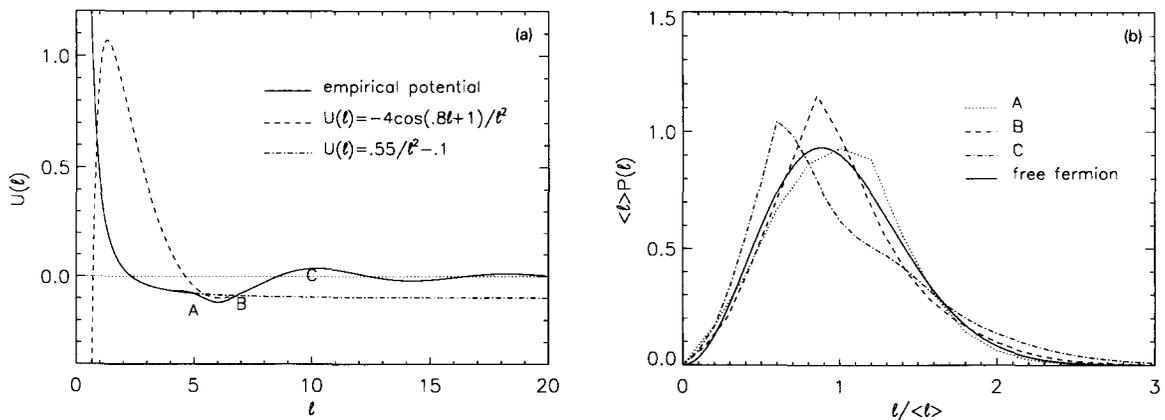
Fig. 4. (a) The form of a step–step interaction potential $U(l)$ which describes the terrace-width distributions observed on vicinal Ag(110) surfaces is shown (solid line) as a function of step separation l. At step separations $l > 6$, this potential is parameterized as $U(l) = -4 \cos(0.8\ l + 1)/l^2$. At step separations $l < 6$, this potential is parameterized as $U(l) = -0.1 + 0.55/l^2$. $U(6)$ is essentially a free paramater, but retains the minimum of the cosine form. MC simulations of terrace-width distributions were performed at points A, B, and C, where l matches the mean terrace widths of our data of $\langle l \rangle = 22$, 30, and 40 Å, respectively. (b) Scaled terrace-width distributions, $\langle l \rangle P(l)$ vs. $l/\langle l \rangle$, evaluated via MC methods for the empirical step–step interaction potential $U(l)$ of (a). Points A, B, and C denote surfaces with mean terrace widths of $\langle l \rangle = 22$, 30, and 40 Å, respectively. The free-fermion "universal" curve for noninteracting steps, is shown as a solid line for comparison. The calculated scaled terrace-width distributions are similar to those observed on vicinal Ag(110) surfaces.

functional form shown as the solid line in Fig. 4a. This form is $U(l) = -4 \cos(0.8l + 1)/l^2$ for $l > 6$. At short step–step separations, there is no reason to expect a simple cosine form. Indeed, for any reasonable choice of parameters, the strong oscillations in this form at small l lead to spurious terrace-width distributions inconsistent with the experimental data. Instead, for $l < 6$ we chose the form $U(l) = A/l^2 + U_0$ and picked $A = 0.55$ to set the strength of the repulsive wall and $U_0 = -0.1$ so that $U(l)$ joins the oscillatory form at $l = 7$. Finally, $U(6)$ is treated as a free parameter, which assumes a slightly deeper minimum than the cosine term evaluated at this l.

Terrace-width distributions obtained from MC simulations performed with $\langle l \rangle$ corresponding to points A (5 spacings or 20 Å), B (7 spacings or 29 Å), and C (10 spacings or 41 Å) are shown in Fig. 4b. The distribution simulated at point A exhibits a form similar to that of noninteracting steps. The distribution simulated at point B exhibits the narrow symmetric form expected for steps with repulsive interactions. These distributions closely match our experimental findings. Since points A and B are close to local minima in $U(l)$, the steps are constrained into narrow ("repulsive") distributions. Finally, the distributions simulated at point C exhibit the very broad asymmetric form observed experimentally. Since point C is a local maximum in $U(l)$, steps with this separation will redistribute to lower their energies, resulting in a broader distribution. To summarize, MC simulations of terrace-width distributions using the empirical potential of Fig. 4a are consistent with our experimental findings on vicinal Ag(110) surfaces. In particular, we note that the distribution maxima are reproduced remarkably well in the simulation.

Of course, to develop confidence in the existence of this oscillatory form, it is necessary to measure distributions on vicinal surfaces with larger $\langle l \rangle$ ($\langle l \rangle = 56$ Å, 72 Å, etc.).

5. Conclusion

We have measured the terrace-width distributions for three different (local) misorientations on vicinal Ag(110) surfaces. Our results confirm earlier reports of much richer behavior on noble-metal vicinal surfaces compared to that which has been observed on semiconductor surfaces.

Since the standard deviation of the terrace-width distribution does not scale simply with average width, we have evidence that step–step interactions have a more complicated form than the Al^{-2} form familiar from semiconductors. Since metals have partially filled bands, we suspect there is an additional contribution of indirect interactions between steps analogous to that between adatoms. However, data sets are still too limited for definitive conclusions.

While our results are tantalizing, it is clear that more data over a wider range of misorientations is needed if we are to characterize convincingly the form of the interaction potential between steps. While we were able to mimic our limited data with a potential of plausible form, we caution that we have made no checks regarding uniqueness. Even the decay power of the asymptotic oscillations, crucial to understanding which substrate electrons mediate the interaction, has not been adequately determined; the power of 2 that we used emerged from a limited empirical search for a viable form. Thus, our plans to acquire more data are essential if we are to clarify the nature of the interaction between steps on vicinal metal surfaces.

6. Addendum

We have also measured $P(l)$ for $\langle l \rangle = 35$ Å on the corresponding macroscopic orientation, Ag(110)-2.3° [001]. The asymmetric distribution, peaked at $l/\langle l \rangle = 0.8$, is consistent with our empirical potential.

7. Acknowledgements

8. References

[1] E.D. Williams, Surf. Sci. 300 (1994) 502.

[2] G.A. Somorjai, Chemistry in Two Dimensions (Cornell University Press, Ithaca, NY, 1981) p 156 ff.

[3] C. Jayaprakash, C. Rottman and W.F. Saam, Phys. Rev. B 30 (1984) 6549.

[4] V.V. Voronkov, Sov. Phys.-Crystallogr. 12 (1968) 728.

[5] A.C. Redfield and A. Zangwill, Phys. Rev. B 46 (1992) 4289.

[6] J.M. Blakely and R.L. Schwoebel, Surf. Sci. 26 (1971) 321.

[7] V.I. Marchenko and A.Ya. Parshin, JETP Lett. 52 (1980) 129; Zh. Eksp. Teor. Fiz. 79 (1980) 257 [Sov. Phys.-JETP 52 (1981) 129].

[8] C. Alfonso, J.M. Bermond, J.C. Heyraud and J.J. Métois, Surf. Sci. 262 (1992) 371.

[9] X.-S. Wang, J.L. Goldberg, N.C. Bartelt, T.L. Einstein and E.D. Williams, Phys. Rev. Lett. 65 (1990) 2430.

[10] B.S. Swartzentruber, Phys. Rev. 47 (1993) 13432.

[11] Y.-N. Yang, B.M. Trafas, R.L. Seifert and J.H. Weaver, Phys. Rev. B 44 (1991) 3218.

[12] A noteworthy exception is the case of vicinal Si{100}, on which anisotropic stress from alternating (2×1) and (1×2) terraces complicates the interaction. Cf. Ref. [10] and O.L. Alerhand, D. Vanderbilt, R.D. Meade and J.D. Joannopoulos, Phys. Rev. Lett. 61 (1988) 1973.

[13] J. Frohn, M. Giesen, M. Poensgen, J.F. Wolf and H. Ibach, Phys. Rev. Lett. 67 (1991) 3543.

[14] D.E. Wolf and J. Villain, Phys. Rev. B 41 (1990) 2434.

[15] J.S. Ozcomert, W.W. Pai, N.C. Bartelt and J.E. Reutt-Robey, Surf. Sci. 293 (1993) 183.

[16] M. Poensgen, J.F. Wolf, J. Frohn, M. Giesen and H. Ibach, Surf. Sci. 274 (1992) 430.

[17] S. Rousset, S. Gauthier, O. Siboulet, J.C. Girard, S. de Cheveigne, M. Huerta-Garnica, W. Sacks, M. Belin and J. Klein, Ultramicroscopy 42–44 (1992) 515; L. Kuipers and F.W.M. Frenken, private communication 1993.

[18] B. Joós, T.L. Einstein and N.C. Bartelt, Phys. Rev. B 43 (1991) 8153.

[19] N.C. Bartelt, T.L. Einstein and E.D. Williams, Surf. Sci. Lett. 240 (1990) L591.

[20] M.A. Ruderman and C. Kittel, Phys. Rev. 96 (1954) 99; K. Yosida, Phys. Rev. 106 (1957) 893; J.H. Van Vleck, Rev. Mod. Phys. 34 (1962) 681.

[21] T.L Einstein, in: Chemistry and Physics of Solid Surfaces II, Ed. R. Vanselow (CRC Press, Boca Raton, FL, 1979) p. 181; T.L. Einstein and J.R. Schrieffer, Phys. Rev. B 7 (1973) 3629; T.L. Einstein, in: Physical Structure, Ed. W.N. Unertl, Handbook of Surface Science, Eds. N.V. Richardson and S. Holloway (North-Holland, Amsterdam), to be published.

[22] Redfield and Zangwill [5] point out that this summation procedure is strictly valid only in the (weak) limit, when the local perturbation due to each site is independent of its neighbors.

[23] A. Yaniv, Phys. Rev. B 24 (1981) 7093, applied the same formalism to defects as used for chemisorbed atoms in Ref. [21].

[24] T.L. Einstein, Surf. Sci. 75 (1978) 161L. In nearest-neighbor tight-binding models, the asymptotic regime for indirect interactions via *bulk* states was reached in ~ 4 lattice spacings.

[25] The essence apparently is taking the leading term of

$$\int_0^\infty (x^2 + y^2)^{-p/2} \cos\left(\kappa\sqrt{x^2 + y^2}\right) dy \quad \text{to be}$$

$$\int_0^x x^{-p} \cos\left[\kappa(x + y^2/2x)\right] dx = x^{-(p-1/2)} f(\kappa x),$$

where $f(\kappa x)$ contains products of trigonometric functions and Fresnel integrals but has a simple asymptotic limit $\propto \cos[\kappa x + (\pi/4)]$.

[26] K.H. Lau and W. Kohn, Surf. Sci. 75 (1978) 69.

[27] A surface state in a gap near $\bar{Y}$ (the intersection of the [001] direction and the surface Brillouin zone boundary) has been observed often for (110) late-transition/noble fcc metals, about 2 eV above E_F. [Cf., e.g., E. Bertel and U. Bischler, Surf. Sci. 307–309 (1994) 947.] These states are probably too far from E_F to play an important role. However, calculations on Au(110) revealed a second surface state just below E_F, over a narrower range near $\bar{Y}$. [S.H. Liu, C. Hinnen, C.N. van Huong, N.R. de Tacconi and K.-M. Ho, J. Electroanal. Chem. 176 (1984) 325], and there is some calculational evidence of a similar state on Ag [K.-M. Ho, private communication]. Such a state was reported [R. Courths, H. Wern, U. Hau, B. Cord, V. Bachelier and S. Hüfner, J. Phys. F 14 (1984) 1559] in an angle-resolved photoemission (ARUPS) study of Ag: it was found to be dispersionless at 0.1 eV below E_F and sharply peaked in intensity at $\bar{Y}$, seemingly vanishing by 20% of the distance to $\bar{\Gamma}$. While the effect of steps and disorder are unclear, it is plausible that this state could be broadened or shifted to cross E_F in some small region near $\bar{Y}$.

[28] N.C. Bartelt, T.L. Einstein and E.D. Williams, Surf. Sci. 276 (1992) 308.