Ordering Kinetics at the $Cu_3Au(110)$ Surface

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The evolution of $Cu_3Au(110)$ surface order from 10^2 to 10^5 s after disordering anneals has been monitored by low-energy electron diffraction. On the basis of refined observations of the profiles of diffracted beams, it is concluded that the early stage of surface ordering consists of the nucleation of compositionally ordered microclusters prior to bulk ordering.

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Though the bulk ordering kinetics of the prototypical compositionally ordering alloy[1] Cu_3Au and other alloys has been studied for a long time and is a topic of current interest,[2-5] the surface ordering kinetics of alloys has received scant attention.[6] Yet surface ordering kinetics has a bearing on a larger question of the evolution of crystalline order, namely, the sequence of surface versus bulk ordering. In a highly plausible theoretical picture[7,8] that has received experimental support,[6,8] the disordering of a crystal starts at the surface and proceeds by the thickening of a layer of disordered material. The obverse of this picture is that ordering starts in the bulk, and the ordered bulk crystal acts as a template mediating the subsequent surface ordering. In this paper we report observations of the kinetics of the surface transition associated with the bulk compositional order-disorder transition of the Cu_3Au alloy at temperature T_0 near 663 K. For the late stage of ordering following a high-temperature disordering anneal, our results are in accord with the conventional picture. But we have also observed an earlier ordering regime resembling the nucleation of ordered microclusters on top of the still-disordered substrate. This is an unprecedented instance of purely two-dimensional compositional ordering, where the surface orders without an underlying ordered substrate to serve as a template.

We have used low-energy electron diffraction with position-sensitive detection[9] (LEED-PSD) to monitor the evolution of surface order by measuring the diffraction-beam profiles, i.e., by measuring the intensity versus surface-parallel momentum transfer relative to the beam center. The profiles were determined after annealing the crystal at a temperature T_A above the surface compositional-disordering temperature T_1, and then quenching rapidly to a lower temperature T_Q. We present results obtained for several values of quench depth $T_1 - T_Q$ ranging from 15 to 85 K, and for ordering times from 10^2 to 10^5 s. The results are presented in two series corresponding to opposite initial conditions of bulk disorder. The initial conditions (IC) were selected, taking advantage of the circumstance that T_1 lies slightly ($\sim$6 K) below T_0,[10] by choosing T_A between T_1 and T_0 [IC (1), initially ordered bulk] and above T_0 [IC (2), initially disordered bulk]. These results provide a quantitative description of surface ordering rates, including their dependence on the temperature T_Q and the initial state of subsurface bulk ordering, and permit evaluation of models of compositional ordering of Cu_3Au.

In the conventional picture of compositional surface ordering at Cu_3Au surfaces,[11] the long-range-ordered substrate acts as a template in establishing an array of "right" (energetically favored) and "wrong" sites for the surface Cu and Au atoms. The ordering is described statistically by a long-range-order parameter M equal to the excess number of surface atoms in right compared to wrong sites, and by a short-range correlation length ρ representing the range of the positional pair-correlation function for surface atoms. The profiles of fractional-order beams, such as $(\frac{1}{2},0)$ in the case of $Cu_3Au(110)$, contain different contributions associated, respectively, with the long- and short-range order: a narrow (ideally δ-function) contribution of integrated intensity proportional to M^2, and a broader contribution of half-width approximately equal to $1/\rho$. In the other picture of surface ordering introduced in this paper, there is no long-range-ordered substrate to provide a template. The fractional-order beam can grow in as a result of surface self-ordering, but because $M=0$ the beam profile initially contains only the relatively broad short-range-order contribution. Thus it is possible in principle to distinguish between the two pictures of surface ordering — respectively, with and without template — on the basis of observations of the evolution of beam profiles.

In order to measure LEED beam profiles with the accuracy required to determine the nature and degree of ordering, we have used a novel method involving integration of intensity over progressively larger squares in surface-parallel-momentum-transfer space, centered at the center of the beam. The relative values of the intensity integrals as a function of square side are then fitted by an intensity profile function. One form of profile function that we have found useful is

$$F(q) = [q_0^2/(q_0^2 + c^2 q^2)]^{3/2}, \qquad (1)$$

where q is the surface-parallel momentum transfer relative to the beam center, and

$$q_0 = q_1\{1 + q_2[\exp(-\tfrac{1}{2}q^2/q_1^2) - \exp(-\tfrac{1}{2})]\}. \qquad (2)$$

The value of the constant c is such that $F(q_1) = \exp(-\frac{1}{2})$, i.e., $c^2 = \exp(\frac{1}{3}) - 1$. The parameter q_1 is the half-width of the beam, and q_2 is a shape parameter. The meaning of these parameters is easiest to discuss for the case of relatively weak ordering where the long-range-order parameter M is small or zero, and the short-range correlation length ρ is large. This applies to the early stage of ordering discussed in this paper. When $q_2 = 0$, the profile function $F(q)$ is a Lorentzian to the power $\frac{3}{2}$ (L-$\frac{3}{2}$). L-$\frac{3}{2}$ is the profile shape that would be obtained for a fractional-order beam from $Cu_3Au(110)$ if, e.g., the narrow (long-range-order) component were absent and the pair-correlation function were exponential; q_1 is related to the correlation length by $q_1 = c/\rho$. When $q_2 > 0$, the profile function is flat topped relative to L-$\frac{3}{2}$. A flat-topped profile can be obtained in the absence of the narrow (long-range-order) component. The meaning of q_1 is still expressed approximately by $q_1 = c/\rho$. When $q_2 < 0$, the profile is pointy topped relative to L-$\frac{3}{2}$. Aside from pathological forms of the pair-correlation function, a pointy topped profile can arise only if there is a significant contribution from the narrow (long-range-order) component. In this case $q_1 < c/\rho$. The details of the fitting procedure, e.g., the background subtraction, are important and will be described elsewhere.[12]

All observations were made on a crystal that had been initially annealed for at least 100 h at 625 K. The crystal was cut from the same ingot as used previously,[11] and its mounting, surface preparation, temperature measurement, and monitoring by Auger-electron spectroscopy (AES) were as previously described.[10,11] No surface impurities were detected by AES. Our profile measurements refer to the $(\frac{1}{2},0)$ beam in diffraction of 23-eV electrons incident on the crystal in the (10) azimuth, and with an angle of 45° between the incident and diffraction beams. The detector was positioned so that each detection-channel width corresponded to a surface-parallel-momentum-transfer increment of 0.0020 Å^{-1}. The parallel-momentum resolution of the observations was limited mainly by the ±0.1° mosaic spread and was about 0.01 Å^{-1}. During the disordering anneal and kinetics runs, the crystal temperature was controlled within ±1 K of nominal values by manual adjustments of the heater power. After the disordering anneal, the sample heater power was temporarily reduced to allow the temperature to drop rapidly (< 150 s) to the ordering temperature T_Q while LEED-PSD measurements were made at the maximum rate used in these experiments (one frame per 75 s). Frames recorded for sample temperatures greater than 3 K above the ultimate value of T_Q were discarded, and the ordering time corresponding to the first accepted frame was taken to be 38 s. The disordering anneal temperatures were 657 and 673 K for IC's (1) and (2), respectively.

Our results show that ordering at the $Cu_3Au(110)$ surface proceeds in at least two distinct regimes, as illustrated for one value of T_Q in Figs. 1 and 2 for IC (1) and IC (2), respectively. In both regimes the beam width q_1 decreases with time t in proportion to t^{-a}, where a is a constant [Figs. 1(a) and 2(a)]. For all values of T_Q for which it is present in the experimental range of ordering time, the early regime is characterized by a small exponent ($a < 0.05$) relative to the later one ($a > 0.15$). For IC (1) ($T_A = 657$ K), there is a third distinct regime, which resembles saturation and will be so designated, in which again $q_1 \propto t^{-a}$ is obeyed with $a < 0.05$. Unlike q_1, the profile shape parameter q_2 has qualitatively different time dependences for the two initial conditions [Figs. 1(b) and 2(b)]. For IC (1) ($T_A = 657$ K), the profile is pointy topped [$q_2 < 0$, see Fig. 1(b) inset for an example] throughout the early regime, reverts to L-$\frac{3}{2}$ ($q_2 = 0$ within error) during the later regime, and remains L-$\frac{3}{2}$ in the saturation regime.

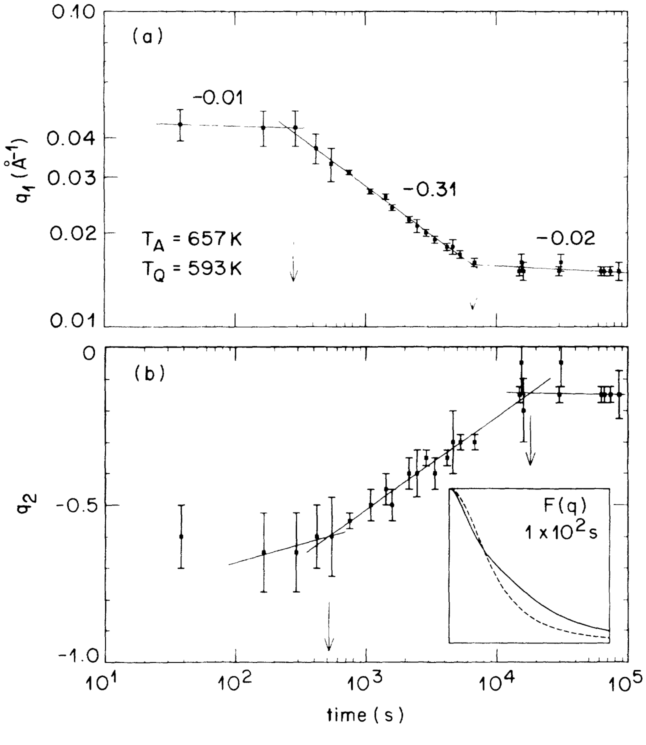

FIG. 1. Dependence of the $(\frac{1}{2},0)$-beam profile parameters on ordering time, for an initially ordered bulk crystal [IC (1), see text]. T_A and T_Q denote the anneal and ordering temperatures, respectively. The error bars indicate for each data point the extrema of the 95% confidence contour. Arrows indicate times at crossovers of ordered regimes. The straight lines are fits to the data in the ranges represented. (a) Profile width parameter q_1. The numbers are the slopes of the lines. (b) Profile shape parameter q_2. Inset: Profile function $F(q)$ corresponding to the values of the parameters (q_1, q_2) at the time indicated (solid line) in comparison with the L-$\frac{3}{2}$ profile for the same value of q_1 (dashed line). The range of surface-parallel momentum transfer represented is 0.2 Å^{-1}.

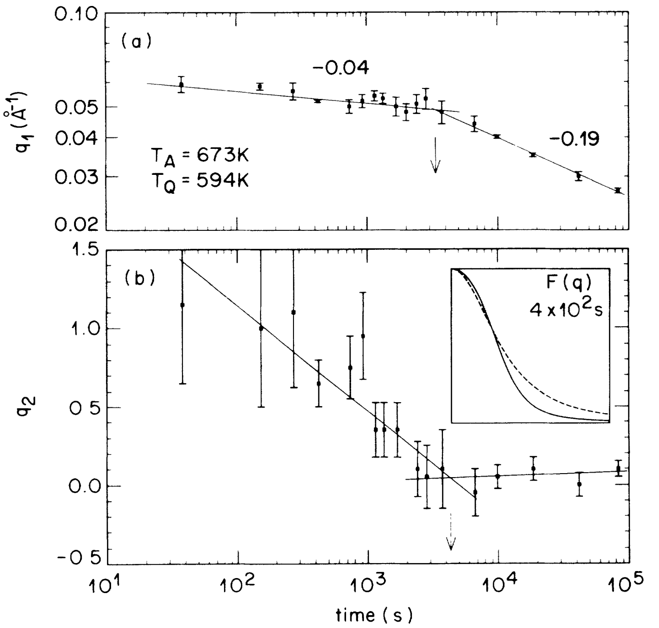

FIG. 2. Same as Fig. 1 for an initially disordered bulk crystal [IC (2), see text].

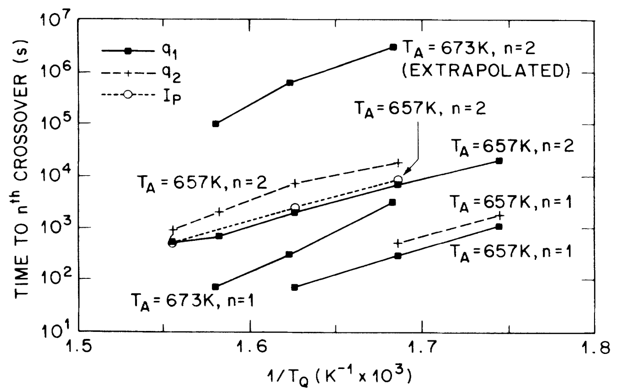

FIG. 3. Dependence of the times of crossover between different regimes on the ordering temperature T_Q. $n=1$ denotes the end of the early regime and $n=2$ the end of the later regime. T_A denotes the disordering anneal temperature. The legend shows the data used in determining the crossovers.

For IC (2) ($T_A=673$ K), the profile goes from flat topped [$q_2>0$, see Fig. 2(b) inset for an example] to L-$\frac{3}{2}$ during the early regime, and remains L-$\frac{3}{2}$ during the later regime. The peak intensity I_P was also measured, and the I_P vs t plot was found to have distinct breaks terminating an initial linear increase.

Distinct regimes like those illustrated in Figs. 1(a) and 2(a) are also present at other values of ordering temperature T_Q, but with different durations. In a good approximation the ordering time t_n corresponding to the crossover at the end of the nth regime ($n=1,2$), determined from q_1 vs t data, has an exponential dependence on $1/T_Q$, namely,

$$t_n=A_n\exp(B_n/T_Q)\,, \tag{3}$$

where A_n and B_n are constants. This regularity is displayed in Fig. 3. Also displayed in Fig. 3 are similar but less nearly perfect regularities for crossovers determined from other data comprising q_2 vs t, extrapolated q_1 vs t for $T_A=673$ K, and I_P vs t. If t_n is interpreted as the reciprocal of a rate constant for ordering in the regime ending at the nth crossover, then A_n^{-1} and B_nk_B (k_B is Boltzmann's constant) must be identified with the frequency factor and the activation energy, respectively, of ordering in that regime. The values obtained from fits of q_1 vs t data by Eq. (1) are shown in Table I.

Our results may be interpreted to determine early sequences of ordering at the Cu$_3$Au(110) surface and the nature of the early regime. In the case of the initially ordered bulk crystal [IC (1)] the early ordering regime is characterized by pointy topped profiles evidencing long-range order at the surface relative to the (2×1) substrate periodicity. Thus the surface orders on the already ordered substrate, as on a template. This is just as expected in this case. But in the case of the initially disordered bulk [IC (2)] the early regime is characterized by the flat-topped profile which is the signature of purely short-range ordering. X-ray observations[4] of Cu$_3$Au bulk ordering kinetics, for crystal temperature and time resolution similar to the present observations, do not give any hint of a distinct bulk-ordering regime comparable with the early surface-ordering regime reported here. Since the surface ordering is purely short ranged and does not have an analog in bulk ordering, we conclude that it develops prior to the bulk ordering. The same interpretation permits a rationalization of the dependences on T_Q summarized in Fig. 3 and Table I. For IC (1), the value of the apparent activation energy of ordering (Table I) is like those for diffusion in Cu$_3$Au.[13] This is as expected for ordering by a diffusion mechanism on the already ordered substrate. But for IC (2) the value of the activation energy is double that for diffusion. This is consistent with surface ordering prior to bulk ordering, since in the absence of an ordered substrate the initial development of (2×1) order requires the correlated motion of pairs of atoms. The observation of a flat-topped profile implies not only a disordered substrate but also a pair-

TABLE I. Frequency factors and activation energies.

T_A (K)[a]	n[b]	A_n^{-1} (s^{-1})[c]	B_nk_B (eV)[d]
657	1	9×10^{12}	1.8
657	2	8×10^{9}	1.6
673	1	1×10^{25}	3.4

[a] Disordering anneal temperature.
[b] Crossover.
[c] Apparent frequency factor.
[d] Apparent activation energy of ordering.

correlation function narrower than the exponential one. In view of these results, together with the observation of a linear initial increase of the peak intensity, we picture the early regime as the nucleation and slow growth of ordered domains of average effective radius equal approximately to the correlation length $c/q_1 \sim 10$ Å.

The later ordering regime occurs on a time scale similar to that for the later ordering of bulk Cu_3Au.[2] The surface ordering is faster in the initially ordered bulk case, indicating that the surface ordering lags behind the bulk ordering in the later regime.

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