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Nanoscale Periodicity in Stripe-Forming Systems at High Temperature: Au/W(110)

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We observe using low-energy electron microscopy the self-assembly of monolayer-thick stripes of Au on W(110) near the transition temperature between stripes and the nonpatterned (homogeneous) phase. We demonstrate that the amplitude of this Au-stripe phase decreases with increasing temperature and vanishes at the order-disorder transition (ODT). The wavelength varies much more slowly with temperature and coverage than theories of stress-domain patterns with sharp boundaries would predict, and maintains a finite value of about 100 nm at the ODT. We argue that such nanometer-scale stripes should often appear near the ODT.

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The theory that ordered patterns can occur on solid surfaces to relax stress was proposed many years ago [1,2]. These patterns in principle offer a way of controlling the structure and hence functionality of surfaces. "Stress-domain" patterns arise from the competition between the short-range attractive interaction between atoms, leading to a phase-boundary energy, and a long-range repulsive interaction between boundaries, due to the difference in surface stress between the two phases. This repulsion is mediated by elastic deformations of the substrate. So far, such stress-domain patterns have been observed and quantified in the low-temperature, sharp-interface regime, where the interfaces between the two separated phases are abrupt. (See for example [3–5].) However, as the temperature is increased, the amplitude of the modulated pattern should decrease. At sufficiently high temperature a transition to a homogeneous phase occurs, which we call the order-disorder transition (ODT). As the ODT is approached, the interface width is expected to increase, eventually becoming of the order of the stripe periodicity, making the sharp-boundary theory [1,2] inappropriate.

Our present experimental study of Au on W(110) explicitly shows this breakdown near an ODT and the large impact it has on the pattern periodicity. The Au-stripe periodicity varies much more slowly with temperature and coverage than sharp-boundary theories would predict, and maintains a finite value of about 100 nm at the ODT. In contrast, we find that the mean-field description of patterns with diffuse interfaces well describes the measured temperature dependence. Based on this agreement, we suggest that nanometer-scale periodicities should be much more common in pattern-forming systems at their high-temperature limit than one would expect from the low-T, sharp-interface theory.

Quantitative observations near the ODT are difficult because thermal fluctuations of boundaries typically destroy the pattern's long-range order. As first observed by Duden and Bauer [6,7], Au on W(110) self-assembles into

stripes of monolayer-thick Au islands [see Fig. 1(a)]. Because of strong surface anisotropy, the stripes form with long-range order along a particular crystallographic direction, $[1\bar{1}0]$. Thus, we are able to use low-energy electron microscopy (LEEM) to measure the pattern's amplitude (related to the Au density [8]) and wavelength approaching the ODT. The amplitude decreases steadily with increasing temperature and vanishes at the ODT. The pattern's wavelength also decreases with temperature but has a finite value of 100 nm at the ODT.

Our experimental setup and sample preparation are described in detail in Ref. [8]. Our estimated error in the absolute temperature is 10 K with a precision of 1 K. The total Au coverages, given as the fraction of a complete condensed Au layer in monolayers (ML), were determined by the elapsed deposition time from a calibrated Au flux.

We first establish the location of the pattern formation in the Au on W(110) phase diagram. Small amounts of Au form a two-dimensional adatom gas. At higher densities,
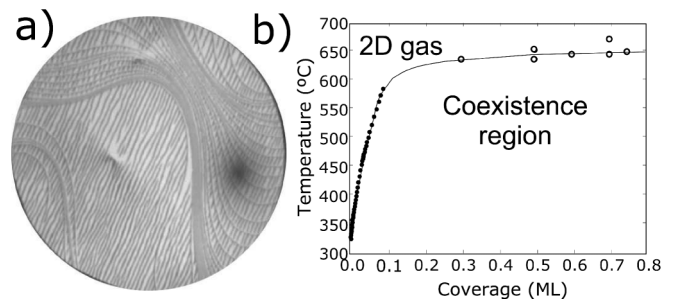

FIG. 1. (a) LEEM image of Au stripes, which appear dark at 10 eV electron energy, on W(110) at 619 °C. The field of view is 7 μm. (b) Measured phase diagram of Au on W(110). The solid line is a guide to the eye to show when the Au-adatom gas and the Au islands are in equilibrium. Closed circles are data from reflectivity measurements [8]. Open circles are determined from loss of contrast in LEEM images. Stripes were observed at temperatures near but below the open circles.

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the Au adatoms condense into monolayer-thick Au islands. Because Au and W do not alloy, the system has long been used to evaluate phase diagrams of condensates and ad-atom gases [10,9]. Figure 1(b) shows the phase diagram measured using LEEM. At low temperatures, we deter-mine the Au adatom concentration in equilibrium with condensed Au using the linear decrease in electron reflec-tivity with coverage [8]. As seen in Fig. 1(b) (closed circles), the adatom density in equilibrium with condensed Au increases with temperature. At higher temperatures and coverages, we find that the system self-assembles into a lamellar phase consisting of stripes of condensed Au sepa-rated by stripes of the Au-adatom gas [Fig. 1(a)].

In the sharp-interface limit, the stripes can be considered as being composed of two coexisting phases. In this limit, the density of the Au-adatom gas region of the stripes as well as the density of the condensed Au islands at any temperature should be that given by the phase diagram partially shown in Fig. 1(b). The relative areas of the two phases should be determined by the lever rule [see sche-matic of Fig. 2(a)]. In particular, at constant temperature the densities of both phases should be independent of the total Au coverage.

As shown in Fig. 2, our observations are inconsistent with the sharp-interface limit. Figures 2(b)–2(e) show images when the total Au coverage is varied from 0.2 ML to 0.5 ML. The uniform decrease in image intensity with increasing coverage indicates [8] that the atomic density of both the dilute and dense regions of the stripes

is changing with Au coverage. The changing density of the stripes is shown more directly in Fig. 2(f), which gives profiles across these images where we have converted image intensity to Au density, following [8]. Rather than the relative area of the two phases changing with overall coverage, the relative area is constant and the density of both phases changes. For example, the density of the gas-phase Au regions changes from about 0.25 to 0.4 ML when the total Au coverage is varied from 0.2 to 0.5 ML.

We next show that the pattern's wavelength and ampli-tude as temperature approaches the ODT are markedly different from the behavior expected from the sharp-interface limit. As seen in Fig. 3, with increasing tempera-ture the stripe density increases and the pattern contrast decreases. To quantify the amplitude and wavelength of the stripe phase, we used a Fourier analysis approach [11]. Results of this procedure applied to a sequence of images at different temperatures are shown in Fig. 4. As tempera-ture increases, the amplitude of the pattern decreases steadily until it vanishes at the ODT. While the periodicity of the pattern also initially decreases with increasing tem-perature, it does not approach zero at the ODT. Instead, the wavelength reaches a constant value of about 100 nm.

This striking coverage and temperature dependence and the fact that the stripes form near temperatures where the gas phase and condensed Au become indistinguishable suggest that a diffuse-interface limit of stress-domain pat-terns is appropriate. We adopt a continuum diffuse-interface model with a spatially varying order parameter $\phi = (2\rho - \rho_0)/\rho_0$, where ρ is the spatially dependent Au density and ρ_0 is the density of the condensed Au phase at low temperature. The free energy of the system is a sum of short-range and long-range contributions, $F = F_{sr} + F_{lr}$. The short-range energy per unit stripe length is

$$F_{sr} = \int dx \left[-\frac{r}{2} \phi^2 + \frac{u}{4} \phi^4 + \frac{c}{2} \left(\frac{d\phi}{dx}\right)^2 \right]. \quad (1)$$
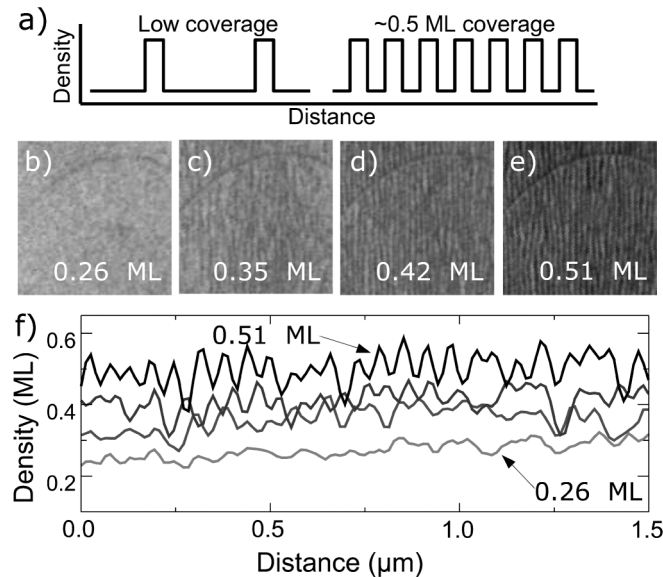

FIG. 2. (a) Schematic of the expected changes in the stripe pattern with coverage in the sharp-interface limit. In contrast, (b)–(e) show LEEM images at constant temperature (620 °C) while continuously depositing Au on the W(110) surface. The images are 4 μm wide. All frames use the same intensity scale. (f) Representative intensity profiles (averaging 10 lines of pixels for 1 s) at each coverage.
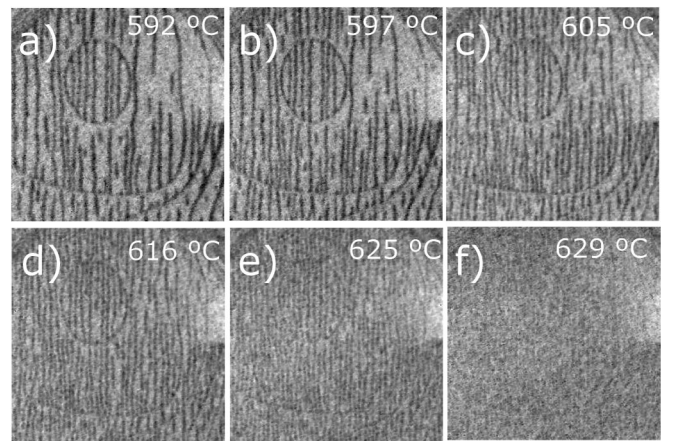
FIG. 3. (a)–(f) Sequence of LEEM images taken while chang-ing the temperature at a constant Au coverage. The images are 4 μm wide.
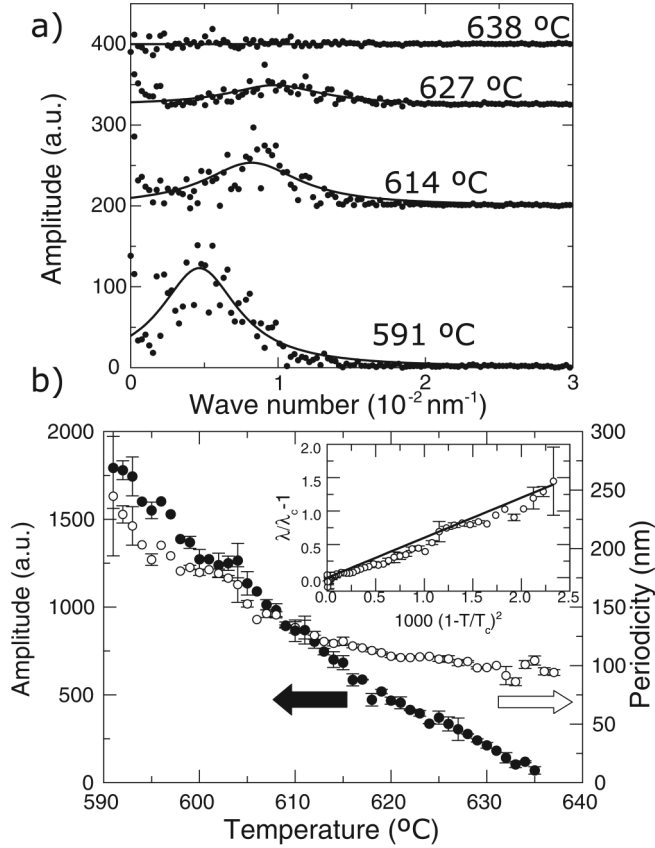
FIG. 4. (a) Plot of the Fourier spectra, offset for clarity, along the x direction at different temperatures. (b) Temperature dependence of the stripe amplitude and periodicity. Inset: Stripe periodicity showing the scaling as described in Eq. (4).

Here x is the coordinate perpendicular to the stripes, $r = r_0(T_c^0 - T)$ with T_c^0 the bare transition temperature (i.e., before renormalization by the long-range interaction), r_0 and u are phenomenological parameters and c determines the boundary energy. This form for the short-range free energy is the standard Landau expression representing a phase diagram with a low-temperature miscibility gap and a critical point at T_c^0.

The long-range interaction comes from the elastic fields in the substrate due to the presence of surface atomic stress dipoles. We assume that the local surface stress τ is proportional to the adatom concentration: $\tau = \phi \Delta \tau / 2$, with $\Delta \tau = \rho_0(\partial \tau / \partial \rho)$. Then the total long-range energy per unit stripe length is

$$F_{\text{lr}} = 2g \int dx dx' \frac{\phi(x)\phi(x')}{(x - x')^2 + a^2}. \tag{2}$$

Here $g = (\Delta \tau)^2 M / 2\pi$, where M is a combination of elastic constants [12], and a is on the order of an atomic lattice constant. Far from the ODT, $\phi = \pm 1$, with sharp interfaces separating the stripes. In this regime, the equilibrium

wavelength λ is obtained from the above free energy by standard methods [1,2]: $\lambda = 2\pi a e^{(1+(\beta/g))}$, where β is the boundary energy in the sharp-boundary limit. Near the ODT, however, the amplitude of the modulation is small, and a single-mode analysis is appropriate. Assuming a profile for the order parameter $\phi(x) = A\cos(2\pi x/\lambda)$, and minimizing the free energy as a function of λ, we find that at the renormalized ODT temperature, $T_c = T_c^0 - g/(r_0 a)$ [13,14]:

$$\lambda_c = \frac{2c}{g}. \tag{3}$$

This wavelength does not depend on coverage, exactly as we observe in Fig. 2 [15].

In contrast to the sharp-boundary approach, with its exponential dependence on the ratio of boundary to elastic energies, the wavelength at the ODT has a much milder linear dependence. Although we have neglected fluctuations in the stripes in deriving this equation, we expect the proportionality to c/g to be independent of this assumption. On dimensional grounds c/g defines a length scale that sets a lower limit for the periodicity of stress domains at high temperature.

To determine if Eq. (3) quantitatively explains the observed λ, we must estimate the parameters g and c. To calculate g, values for the stress difference between the two phases and the constant M are needed. Fortunately, previous work on stripe phases at solid surfaces has calculated the value of $M = 4.5 \times 10^{-12}$ m^2/N for stripes oriented along the $[1\bar{1}0]$ direction on the W(110) surface [12]. To provide a value for $\Delta \tau$, we performed density functional theory (DFT) calculations within the local density approximation (LDA) and the generalized gradient approximation (GGA) [16] of the excess stress of Au adatoms on W(110). The difference between LDA and GGA values is an estimate of the unknown errors introduced by the approximations to DFT. We use the VASP code [17] for our supercell calculations [18]. As shown in Fig. 5, the calculated surface stress perpendicular to the stripe direction depends linearly on the adatom coverage, providing the value $\Delta \tau = 3.7$ N/m. The value for g is thus $9.8 \times 10^{-12} J/m$.
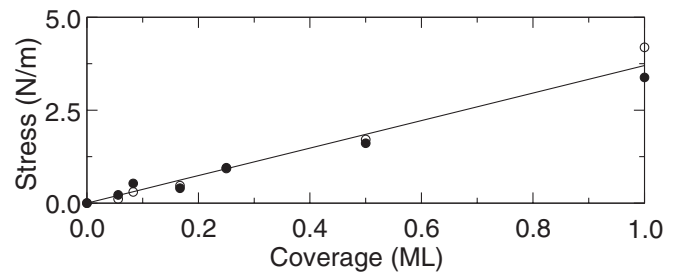

FIG. 5. Excess stress of Au adatoms on W(110) obtained from DFT calculations. (Open circles, GGA; closed circles, LDA).

Estimating c is more difficult because it depends on the detailed nature of the short-ranged attractions between Au adatoms. In general one expects c to scale with T_c. For example, in the simple nearest-neighbor Ising model on a square lattice $c = kT_c/2$. To make a more refined estimate we consider the temperature dependence of λ close to the ODT. To do so, we extend the single-mode analysis to two modes, and apply a perturbation analysis [19] to calculate the amplitudes of the two modes at equilibrium. Minimizing the free energy with respect to λ using the calculated amplitudes gives

$$\lambda = \lambda_c \left[1 + \frac{\lambda_c^4 a^4 r_0^2 T_c^2}{384 \pi^4 c^2} \left(1 - \frac{T}{T_c} \right)^2 \right]. \quad (4)$$

A plot of $\lambda/\lambda_c - 1$ versus $(1 - T/T_c)^2$ should give a straight line. Using the measured values $\lambda_c = 100$ nm and $T_c = 908$ K, the inset in Fig. 4 shows that our experimental data follows this prediction. A numerical fit gives the ratio $a^2 r_0 T_c/c \approx 0.5$. From the regular solution model [20], we have $a^2 r_0 = 4k_B$ giving $c \approx 8k_B T_c$. With this c value and the g given above, the stripe periodicity at the ODT predicted by Eq. (3) is then 20 nm. Given our approximations, this number is in reasonable agreement with the experimental result, $\lambda_c = 100$ nm.

Although accurately calculating values of c and g in any particular system is difficult, there is nothing special about Au/W(110). T_c is typical for metal monolayers, as is the calculated surface stress of the condensed overlayer. Thus we expect that the equilibrium structure of metal monolayers at high temperature will often have density modulations with a similar length scale. This is in striking contrast to the sharp-interface limit of stress domains, where the domain periodicity is extremely sensitive to interaction strengths.

In summary, we have presented experimental evidence that Au stripes observed on W(110) at high temperature are in the diffuse-interface limit of surface-stress domains, with a temperature and coverage dependence qualitatively different from the oft-applied sharp-interface limit. By comparing our results with theoretical calculations of the stripe periodicity, we predict that nanometer-scale stripe patterns should be common near two-dimensional critical points.

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