SAND2007-6284P

Stripe formation near the order-disorder transition: Au on W(110)

J. de la Figuera,[1,2] N. C. Bartelt,[3] F. Léonard,[3] R. Stumpf,[3] and K. F. McCarty[3]

[1] *Insituto de Química-Física "Rocasolano", CSIC, Madrid 28006 Spain*
[2] *Universidad Autónoma de Madrid, Madrid 28049, Spain*
[3] *Sandia National Laboratories, Livermore, California 94550, USA*

(Dated: August 7, 2007)

Using low-energy electron microscopy we observe and quantify the self-assembly of monolayer-thick stripes of Au on W(110) around the transition temperature between stripes and the non-patterned (homogeneous) phase. We demonstrate that the amplitude of this Au stripe phase decreases with increasing temperature, eventually vanishing at the order-disorder temperature (ODT). The wavelength varies much more slowly with temperature than theories of stress-domain patterns with sharp-phase boundaries would predict, and maintains a finite value of about 100 nm at the ODT. We demostrate that a model of stress domains with diffuse boundaries well reproduces the temperature dependence of the pattern wavelenght near the ODT.

PACS numbers:

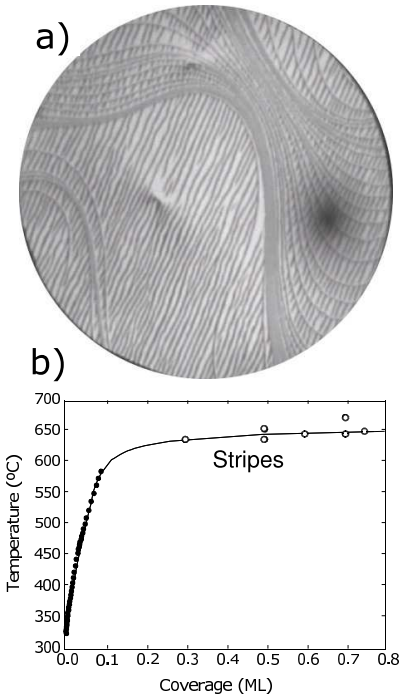
Equilibrium self-assembly into stripe or hexagonal patterns has been observed in systems as diverse as perpendicularly magnetized thin films[1] and diblock copolymers[2]. However, patterns formed by crystalline phases at solid surfaces are much less common [3]. These patterns typically arise from a short-range 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. At sufficiently low temperatures, the pattern consists of stripes or ordered droplets; at some higher temperature, however, a transition to the homogeneous phase occurs. We call this temperature the order-disorder transition (ODT). So far, such stress-domain patterns have been observed and quantified in the sharp-interface regime (low temperatures), where the interfaces between the two separated phases are abrupt. As a consequence, theories of pattern formation at crystalline surfaces have focused mainly on this sharp-interface regime[4, 5]. However, as the temperature is increased (i.e., as the ODT is approached) the amplitude of the modulated pattern decreases, the interfaces become broader, and the appropriateness of the sharp-boundary theory is unclear. Experimentally, quantitative observations near the ODT are difficult because thermal fluctuations of boundaries typically destroy the long-range order of the pattern.

Here we study stripe formation with long-range order in the system of Au on W(110). As first observed by Duden and Bauer[6, 7], submonolayer coverages of Au on W(110) self-assemble into stripe patterns, which consist of monolayer-thick stripes of condensed-phase Au in coexistence with stripes of a Au adatom gas (see Fig. 1a). Because of strong surface anisotropy, the stripes in this system form along a particular crystallographic direction, and we are able to use low-energy electron microscopy (LEEM) to quantitatively measure the amplitude (related to the Au density) and wavelength of the pattern as it approaches the ODT. We demonstrate that the amplitude decreases steadily with increasing temperature and vanishes at the ODT. The modulation wavelength also decreases with temperature, varying quadratically with the reduced temperature. But the wavelength has a finite value of 100 nm at the ODT.

The W(110) single-crystal substrate was cleaned by cycles of exposure to oxygen at 1300 K and brief flashes to 1800 K. Au was evaporated from a crucible heated by electron bombardment with active temperature control. The coverage was calibrated by the time required to grow a full layer of condensed-phase Au on W(110). The LEEM image magnification was calibrated using a grid of holes, whose separation was measured in a scanning electron microscope after machining with a focused ion beam. Temperatures above 400°C were measured using a two-color infrared pyrometer. Below 400°C, the temperature was measured with a W5%Re vs W26%Re (type-C) thermocouple[8] welded to a washer that was pressed against the sample. Our estimated error in absolute temperature is 10 K. The patterns in the Au films were imaged by LEEM both during Au deposition and as a function of temperature.

Before examining the details, we first establish the location of this pattern formation in the Au on W(110) phase diagram. Small amounts of Au on W(110) form a two-dimensional adatom gas. At higher coverage, the Au adatoms condense into monolayer-thick Au islands. Because Au and W do not alloy[9], the system has long been used to evaluate phase diagrams of condensates and adatom gases[10, 11]. Figure 1 shows the phase diagram measured using LEEM. At low coverages, we determine the Au adatom concentration in equilibrium with condensed Au from changes in electron reflectivity[12]. At intermediate coverages we find that the system self-organizes into a lamellar phase consisting of stripes of condensed Au separated by stripes of the Au adatom

FIG. 1: a) LEEM image of the W(110) surface at 619°C after Au deposition. The field of view is 7 μm. The islands of condensed-phase Au form stripes along the W[1$\bar{1}$0] direction and appear dark at the electron energy used (10 eV). b) Measured phase diagram of Au on W(110). The line shows when the Au adatom gas and the monoatomic Au islands are in equilibrium. Full circles indicate data obtained from reflectivity measurements. Open circles are determined from loss of contrast in the LEEM images. The solid line is a guide to the eye.



gas (Fig. 1a). In this coverage regime, we determine the phase boundary by measuring the temperature at which all contrast is lost between the two surface phases, i.e., the ODT. In Fig. 2, for example, the contrast between the Au stripes and the Au adatom gas disappears at about 635°C. We mark in Fig. 1b where well-ordered patterns were observed[17]. We next quantify how the wavelength and amplitude of the patterns change approaching the ODT.

The dependence with the temperature can be summarized in Fig. 2. Two effects are evident from the experimental data. First more stripes are seen when the temperature is increased. Furthermore, their spacing is far more uniform at high temperatures. While at low temperatures unequal area fractions of the two phases are accomodated by unequal stripe widths for the minority and majority phase (see lower profile in Fig. 2g), at high temperatures the stripe patterns are better described by a sinusoidal profile (see upper profile in Fig. 2g). Finally, the contrast of the pattern itself decreases with increasing temperature.

To quantify the amplitude and wavelength of the stripe phase, we rotated the images so the stripes were vertical and then removed the background by dividing by an unfocused image. We then Fourier transformed the center 256 pixels×256 pixels of the images, and after averaging several images in Fourier space (a minimum of 30 for the temperature-dependent observations and up to 400 for the coverage-dependent experiments), we extracted the periodicity and amplitude of the striped pattern by fitting the peak in Fourier space to a Lorentzian function. Results of this procedure applied to a sequence of images at different temperatures is shown in Fig. 3. As temperature 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 temperature, it does not approach zero at the ODT. Instead, the wavelength reaches a constant value of about 100 nm.

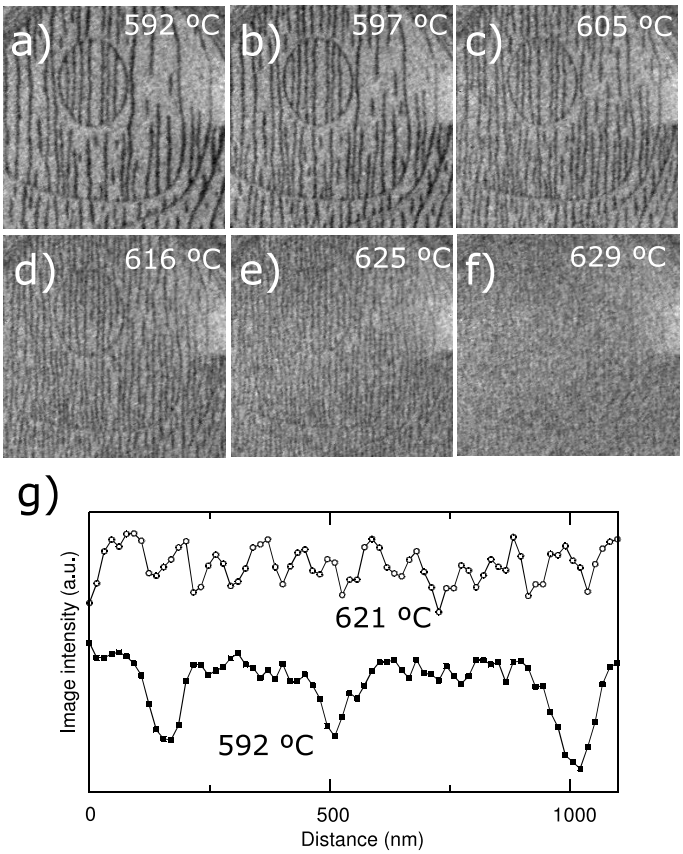


FIG. 2: a)-f) Sequence of LEEM images taken while changing the temperature at a constant Au coverage. The condensed Au appears dark, and the images are 4 μm wide. g) Representative profile of a single line of pixels averaged for 1 second at two temperatures.

The observation of a sinusoidal-like profile at high temperatures would imply diffuse boundaries between condensed and adatom gas Au phases. Additionally, we know from the phase diagram that the density of the adatom gas phase increases with temperature (see Fig.1), and the density difference between the two phases de-

creases. To treat this situation of varying densities of both phases, we employ a continuum model with a spatially varying order parameter $\phi = (2\rho - \rho_0)/\rho_0$ where ρ is the local Au density (ρ_0 is the density of the condensed Au islands 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 given by

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

In this equation 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 it is renormalized 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 Ginzburg-Landau expression representing a phase diagram with a low-temperature miscibility gap and a critical point at T_c^0.

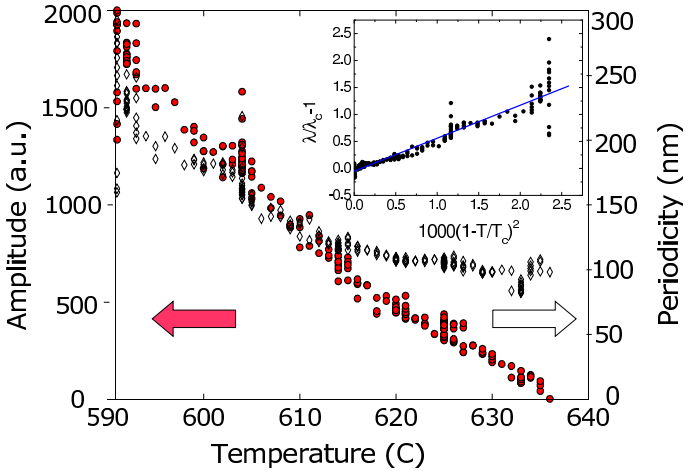


FIG. 3: Plot of the dependence of the stripe amplitude and periodicity on temperature. Inset: Plot of the stripe periodicity showing the scaling as described in Eq. (4).

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

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

Here $g = (\Delta\tau)^2 M/2\pi$ where M is a combination of elastic constants[13], 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[4, 5]: $\lambda = 2\pi a e^{\left(1+\frac{\beta}{g}\right)}$, 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 at $T = T_c$ that

$$\lambda_c = \frac{2c}{g}. \qquad (3)$$

The renormalized ODT temperature is $T_c = T_c^0 - g/(r_0 a)$. In contrast to the sharp-boundary approach with its exponential dependence of material parameters, the wavelength at the ODT has a much milder dependence on the ratio of boundary to elastic energies, and as will be discussed below, can be several tens of nanometers.

Our diffuse-interface model can be used to predict the temperature dependence of the stripe periodicity λ close to the ODT[18]. To do so, we extend the single-mode analysis to two modes, and we apply a perturbation analysis to calculate the amplitudes of the two modes at equilibrium [14]. Minimizing the free energy with respect to the wavelength using the calculated amplitudes gives the stripe periodicity:

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

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. 3 shows that our experimental data follows the prediction of Eq. (4).

To further support the appropriateness of the diffuse-interface model, we estimate the wavelength of the modulation at the ODT predicted from Eq. (3). To calculate the parameter 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[13]. To provide a value for the difference of surface stress between the condensed-phase Au stripes and the Au adatom phase, we performed density functional theory (DFT) calculations within the Local Density Approximation (LDA) and the Perdew-Burke-Ernzerhof (PBE) [15] generalized gradient approximation (GGA) of the excess stress of Au adatoms on W(110) using the VASP code[16]. Computational unit cells representing up to 18 surface atoms and eight layer slabs are used. For each coverage, to account for the configurational entropy several possible configurations (up to six at some coverages) were averaged with each configuration weighted by the Boltzmann factor, assuming a

measurement temperature of 540°C. As shown in Fig. 3, 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 9.8×10^{-12} J/m. To obtain a value for c, we perform a numerical fit of the data in the inset of Fig. 3; in combination with Eq. (4), this provides the ratio $a^2 r_0 T_c/c \approx 0.5$. From the regular solution model, we have $a^2 r_0 = 4k_B$ giving $c \approx 8k_B T_c$. The predicted stripe periodicity at the ODT from Eq. (3) is then 20 nm. This number is in reasonable agreement with the experimental result, λ_c =100 nm, given our approximations.

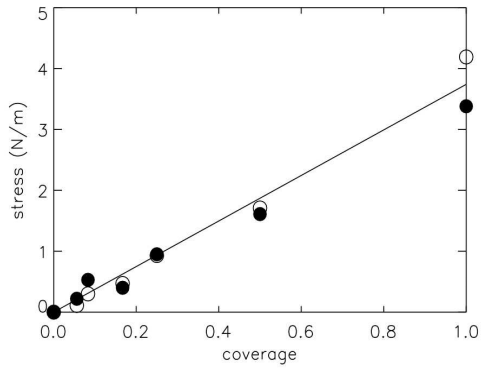


FIG. 4: Excess stress of Au adatoms on W(110) obtained from DFT calculations. (Open circles, GGA; filled circles, LDA).

In summary, we present observations of modulated patterns formed by the coexistence of condensed Au and Au adatom phases at the surface of W(110). The pattern can be explained in terms of a competition between a short-range attractive interaction due to boundary energy and a long-range elastic interactions due to stress dipoles. Our observations indicate that the traditional assumption of sharp, well-defined boundaries between the adatom gas and the condensed islands is incorrect close to the order-disorder transition. Relaxing that assumption, a continuum model with diffuse interfaces correctly predicts the observed dependence of the stripe periodicity versus temperature, and gives a reasonable agreement for the wavelength at the order-disorder transition when the surface stress is computed from DFT calculations.

We thank Thomas Duden for fruitful discussions. This research was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000, and by the Spanish Ministry of Science and Technology through Project No. MAT2006-13149-C02-02.

[1] T. Garel and S. Doniach, Phys. Rev. B **26**, 325 (1982).
[2] M. J. Fasolka and A. M. Mayes, Annual Review of Materials Research **31**, 323 (2001).
[3] R. Plass, J. A. Last, N. C. Bartelt, and G. L. Kellogg, Nature **412**, 875 (2001).
[4] O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Physical Review Letter **61**, 1973 (1988).
[5] V. I. Marchenko, Sov. Phys. JETP **54**, 605 (1981).
[6] T. Duden, Ph.D. thesis, Technischen Universität Clausthal, 1996.
[7] E. Bauer, in *The many facets of metal epitaxy*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1997), Vol. 3, Chap. 2, p. 46.
[8] K. Jacobi, V. S. Smentkowski, and J. T. Yates, J Vac Sci Technol A Vac Surf Films **14**, 260 (1996).
[9] *Binary Alloy Phase Diagrams*, 2nd ed., edited by T. B. Massalski (ASM International, Ohio, USA, 1990).
[10] J. Kolaczkiewicz and E. Bauer, Surface Science **155**, 700 (1985).
[11] J. Kolaczkiewicz and E. Bauer, Surface Science **151**, 333 (1985).
[12] J. de la Figuera, N. Bartelt, and K. McCarty, Surf. Sci. **600**, 4062 (2006).
[13] F. Léonard, N. C. Bartelt, and G. L. Kellogg, Physical Review B **71**, 045416 (2005).
[14] F. Léonard and R. C. Desai, Physical Review B **55**, 9990 (1997).
[15] J. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letter **77**, 3865 (1996).
[16] G. Kresse and D. Joubert, Physical Review B **59**, 1758 (1999).
[17] The pattern wavelength increases with decreasing temperature. But at low temperatures, as surface diffusion is reduced and the wavelength increases, it becomes more difficult to achieve equilibrium conditions. Experimentally we observe a transition from stripes to elongated islands at lower temperatures.
[18] The density of the Au adatom phase can be quantitatively measured with LEEM using electron reflectivity. However, measuring the density of the condensed-phase Au stripes as a function of temperature is not straightforward because of the complicated dependency between electron reflectivity and the density of the crystalline condensed phase. Thus, we do not compare our (uncalibrated) experimental values of the amplitude difference between the two phases to theory.