Self-Assembly of Paired Nanoribbons

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Self-assembly of surface phase domains is a promising route to fabricate stable nanometer-scale structures. This Letter reports a novel labyrinth structure of orthogonal nanoscale ribbons of Cu₄Pb₃ ordered-alloy on Cu(100) formed by electrochemical deposition. The labyrinth develops as loops of Cu₄Pb₃ ribbons elongate as closely spaced paired stripes. The structure is explained in terms of elastic interactions between anisotropic surface stress domains, wherein stripes of different phase variants form attractive dipoles. An energetic analysis determines the physical conditions necessary for the structure to form.

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Since the original work of Marchenko [1] and Alerhand et al. [2], numerous systems have been observed to form two-dimensional surface domains organized as thermodynamically stable arrays of dots or stripes [3,4]. Such structures have potential to serve as nanometer-scale device features or as templates for device fabrication. The formation of these domains is driven by elastic relaxation or electrostatic interactions while coarsening is limited by the self-energy of domain walls. It is this competition that sets a length scale for the self-assembly process.

Surprisingly, there have been no reports of domain organization in electrochemical systems designed to mimic the vacuum analogue, in spite of numerous similarities between these processes [5,6]. This Letter describes a unique self-assembled labyrinth structure in the electrochemical system Cu(100)/10⁻³M Pb²⁺ + 10⁻³M NaCl + 10⁻²M HClO₄. A similar structure was first observed by Moffat, who described it in terms of a templating process previously reported. Instead of domain walls of adjacent ribbons repelling one another, there is an apparent attractive interaction, which leads to smaller length scale structures than previously reported.

The morphology is likely driven by surface stress, as discussed by Alerhand et al. [2]. They, however, consider ordered Cu₄Pb₃, which form in closed loops that elongate as bunched pairs in the [010] or [001] directions [Figs. 1(b) and 1(c)].

FIG. 1 (color online). In situ STM images of the current system at 0.105 V versus Pb²⁺/Pb (Θ ≈ 0.3). In images (a)–(c) (80 × 80 nm), ordered Cu₄Pb₃ and c(2 × 2) Cl phases appear as a light and dark contrasts, respectively. The labyrinth structure (a) has a period on 2.2 nm and forms as closed loops of the Cu₄Pb₃ phase elongate. Arrows mark the elongation of a loop in (b) and (c). Atomic resolution (d) shows that paired Cu₄Pb₃ stripes are of different variants rotated by 90°. Dashed lines mark the 0.72 nm unit cell and the direction of Pb rows. The c(2 × 2) Cl phase boundaries are delimited by solid lines.
only two unique stress domains, while the current system generally has three, two Cu₄Pb₃ variants and one c(2 × 2) Cl phase. Figure 1(d) indicates that a bunched pair is composed of both variants of the ordered Cu₄Pb₃. It is expected that both must be present for ribbons to form stable bunched pairs. The Cu₄Pb₃ phase has an anisotropic surface stress, and as suggested by its atomic structure [Fig. 2(a)], the principle directions of surface stress lie tangent and perpendicular to the rows of Pb atoms. The c(2 × 2) Cl phase [Fig. 2(b)] has an isotropic surface stress. It is expected that the presence of bunched pairs suggests something about the character of surface stress. It is expected that both must be present for ribbons to form

energy and surface energy are functions of strain, and for surface energy, and domain wall excess energy. Bulk energy is taken to consist of bulk strain energy, surface energy, and domain wall excess energy. Bulk energy and surface energy are functions of strain, and for simplicity, the domain wall energy per unit length is taken to be a constant $\psi$. Surface stress is assumed to be independent of strain and is defined in terms of surface energy per unit of undeformed area, $\Gamma(\varepsilon)$, as $\tau = \partial \Gamma / \partial e$ where $\tau$ is surface strain. The surface stress tensors of phases $A$, $B$, and $C$ are respectively $\tau^A$, $\tau^B$, and $\tau^C$, and generally differ such that there is a jump in surface stress across each domain wall. The jumps give rise to a strain field, with strain energy stored in both the bulk and surface phases.

The total strain energy can be evaluated with reference to a fictitious unstrained state that is physically achieved through the application of certain forces on the domain walls. They are determined from a force balance as $f = (\tau - \tau^*) \hat{n}$ where $\tau$ is replaced by $\tau^A$ or $\tau^B$ for the walls of domains $A$ or $B$, respectively, and $\hat{n}$ is the outward unit normal to these domains. For the system of Fig. 2, the normal and tangential components of $f$ are, respectively,

$$f_n' = (\tau_1 - \tau^*) (\alpha \cos^2 \theta_j + \sin^2 \theta_j),$$

$$f_t' = (\tau_1 - \tau^*) (1 - \alpha) \cos \theta_j \sin \theta_j,$$

where $J = A$ or $B$ depending on the domain wall and

$$\alpha = (\tau_2 - \tau^*) / (\tau_1 - \tau^*)$$

characterizes the system anisotropy.

The internal energy of the unstrained reference state includes binding energy of the bulk, surface energy $\Gamma(\varepsilon = 0)$, and domain wall energy. For a fixed area fraction of domains $A + B$ (i.e., a fixed electrochemical potential of Pb), configurational energy varies as

$$E_0 = 4 \psi / \lambda,$$

which is the domain wall energy per unit area.

The difference in internal energy between the reference and deformed states is the strain energy. As the forces $f$ cause the strain energy to vanish and their effect is reversible, the strain energy must equal the negative of the work done as these forces are applied. The strain energy per unit area of the surface is, therefore, [2]

$$E_\epsilon = - \frac{1}{2L^2} \int_{\text{walls}} f(s) \cdot \int_{\text{walls}} f(p)G[x(s), y(p)]dpds$$

(5)

where $L$ is the system size which is taken to be indefinitely large, $G(x, y)$ is the linear elastic half-space Green’s function, and integrals are taken over all domain walls. The horizontal line through the integral denotes a cutoff that is needed to regularize the energy, which is unbounded otherwise. It is imposed by excluding points $|x(s) - y(p)| < r_0$ from the integral, where the radius $r_0$ is on the order of the lattice spacing.

The total free energy per area of the system in Fig. 2(c) is given by $E = E_0 + E_\epsilon$, which is evaluated as
\[ E = \frac{4\psi}{\lambda} + \frac{1}{\pi \mu \lambda} \left( f^A_1 f^A_1 + \beta f^A_n f^A_1 \right) \ln \frac{r_0}{w} \]
\[ + \frac{1}{\pi \mu \lambda} \left( f^B_1 f^B_1 + \beta f^B_n f^B_1 \right) \ln \frac{r_0}{w} \]
\[ + \frac{1}{\pi \mu \lambda} \left( f^A_1 f^A_1 + \beta f^A_n f^A_1 \right) \ln \left( \frac{\pi w}{\lambda} \csc \frac{\pi w}{\lambda} \right) \]
\[ + \frac{1}{\pi \mu \lambda} \left( f^B_1 f^B_1 + \beta f^B_n f^B_1 \right) \ln \left( \frac{2 \sin^2 \pi d/\lambda}{\cos 2 \pi w/\lambda - \cos 2 \pi d/\lambda} \right) \]

(6)

where \( \beta = 1 - \nu \) and \( \mu \) and \( \nu \) are, respectively, the shear modulus and Poisson ratio of the bulk material. The first three terms account for the self-energy of individual stripes. The first is the unrelaxed domain wall energy. The second and third terms contain the effect of elastic relaxation on the self-energy of the domain walls, as evident from the appearance of the cutoff \( r_0 \). Note that increasing \( r_0 \) has a similar effect as increasing \( \psi \). The second and third terms also include the interaction energy between walls of a given stripe. Both decrease with increasing stripe width \( w \), which indicates that domain walls of a stripe tend to repel. The fourth and fifth terms account for interactions between two stripes of the same variant. For fixed stripe width \( w \), these terms decrease as \( \lambda \) increases. Hence stripes of the same variant tend to repel irrespective of anisotropy. This implies bunches pairs cannot form unless the stripes are of different variants.

The last term in Eq. (6) accounts for the interaction between stripes of (possibly) different variants. It is the only term that depends on distance \( d \), and it alone discriminates between bunched and uniformly spaced stripes. If the prefactor of the logarithm is positive, the stripe spacing \( d = \lambda/2 \) minimizes the term and hence the total energy. If the prefactor is negative, \( d = \lambda/2 \) corresponds to a maximum and energy is reduced as the stripes form into bunched pairs; this can occur only if \( A \) and \( B \) are different variants. Using Eqs. (1) and (2) with \( \theta_B = \theta_A + \pi/2 \) for the variants of \( \text{Cu}_4\text{Pb}_3 \) in Eq. (6) and taking \( \nu > 0 \), energy \( E \) is found to be minimum for \( \theta_A = \pi/4 \) and \( 3\pi/4 \). The domain wall forces become \( f^A_1 = -f^B_1 = (\tau_1 - \tau^*) \times (1 - \alpha)/2 \) and \( f^A_n = f^B_n = (\tau_1 - \tau^*)(1 + \alpha)/2 \) and the prefactor of the last term in Eq. (6) becomes negative for anisotropies

\[ \alpha < \frac{\nu}{2 - \nu + 2\sqrt{1 - \nu}} \quad \text{or} \quad \alpha > \frac{2 - \nu + 2\sqrt{1 - \nu}}{\nu} \]

(7)

Equation (7) is a necessary condition for the formation of bunched pairs and implies a relatively high anisotropy factor. For example when \( \nu = 0.33 \), pair formation requires \( \alpha < 0.1 \) or \( \alpha > 10.0 \). Note that the tangential forces, \( f^A_1 \) and \( f^B_1 \) are equal but opposite in sign. They cause stripes of different variants to interact as dipoles of opposite and hence to attract. The normal forces are equivalent and cause the stripe to interact as dipoles of the same sign and repel. When Eq. (7) is satisfied, the tangential forces become dominant, resulting in a net attraction. Also note that the minimum energy occurs at two orthogonal orientations, \( \theta_A = \pi/4 \) and \( 3\pi/4 \), which relate the \( \text{Cu}_4\text{Pb}_3 \) structure to the domain wall. This is consistent with Fig. 1(d) and implies that bunched stripes are likely form in two orthogonal directions, as in the labyrinth structure of Fig. 1(a). Both the experiment and theory suggest that bunched stripes of \( \text{Cu}_4\text{Pb}_3 \) form in the [010] and [001] directions on Cu(100).

When bunching occurs the energy decreases without bound as the stripes approach each other, as \( d \to w \) or \( d \to \lambda - w \). This is because a short-ranged elastic interaction was omitted. Similar to surface steps, the domain walls induce an additional strain associated with a line force dipole [11]. The force dipole is analogous to the surface stress of a two-dimensional phase in that it arises when the wall energy \( \psi \) depends on strain [12]. The dipole interaction produces a strong close-ranged repulsion, which if included would determine a stable separation between bunched pairs. For simplicity it is assumed that the domain walls can come no closer than a few atomic spacings, \( N r_0 \) where \( N \) is a positive integer. Hence, for bunched stripes \( d = N r_0 + w \).

Fixing the area fraction \( \rho \) of domains \( A + B \) such that \( 2\rho = \rho \lambda \), a unique stripe width \( w \) is found to minimize energy. The width is found to be fairly insensitive to \( N \), \( A \), \( \nu \), and \( \rho \) but to depend strongly on \( \psi \) and \( r_0 \), which are both related to the domain wall self-energy. For fixed values of \( N \), \( A \), \( \nu \), and \( \rho \), stripe width scales with \( r_0 \) and grows as \( \exp(\psi) \) where \( \psi = \psi \mu c(\alpha, \nu)/(\tau_1 - \tau_2)^2 \) and \( c \) is function of \( \alpha \) and \( \nu \). The parameter \( \psi \) compares domain wall energy to the elastic relaxation, which compete to set the length scale of the morphology. In the case of \( \psi = 0 \) (\( r_0 \) alone accounts for wall self-energy), the stripe width ranges from about \( w = 2r_0 \) to \( 3r_0 \) (several lattice spacings) for physically meaningful values of \( N \), \( A \), \( \nu \), and \( \rho \). The width increases with increasing \( \psi \).

Equation (7) determines when equally spaced stripes of alternating variants become unstable and form bunched pairs, but does not imply the energy is lower than a single-variant system \( \theta_B = \theta_A \). The single-variant system is found to often have the lower energy, making the condition for bunched pairs more restrictive than Eq. (7).

The single-variant and two-variant cases are compared for asymptotically small \( \rho \) and with \( \psi = 0 \) (\( r_0 \) alone determines wall self-energy). Equilibrium of the single-variant system occurs with uniformly spaced stripes \( (d = \lambda/2) \), stripe width \( w = e r_0 \), and orientations \( (\theta_A = \theta_B) \) that depend on \( \alpha \) and \( \nu \). Equilibrium orientations versus \( \alpha \) are plotted in Fig. 3 for \( \nu = 0.33 \). Typically there
is one unique orientation. Exceptions are the isotropic case ($\alpha = 1$) where energy is independent of orientation and a range of negative anisotropies ($-3 < \alpha < -0.33$) where there are two different equilibrium orientations, which are orthogonal only in the case of $\alpha = -1$. It is noted that the behavior indicated by Fig. 3 has been observed in recent phase-field simulations [13]. Anisotropic elasticity introduces a similar orientational dependence [14].

Minimum free energy versus anisotropy is plotted in Fig. 4 for both single-variant and two-variant systems. The two-variant system has the lower free energy only for anisotropies in the range $0 < \alpha < 0.0133$, which corresponds to a single stripe for a given $\alpha$. As the tendency for self-assembly is strong in this system, the energy difference must be substantially larger than thermal fluctuations, which precludes small values of $(\tau_1 - \tau_2)^2$.

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FIG. 3. Equilibrium orientations of a single-variant system with $\nu = 0.33$. 

FIG. 4 (color online). Minimum energy plotted versus anisotropy for paired stripes of different variants and a single stripe for the case $\nu = 0.33$, $N = 2$, $\psi = 0$, and $\rho \rightarrow 0$. 

$$\tilde{\psi} = \psi \mu c / (\tau_1 - \tau_2)^2.$$  As stripe width grows exponentially with $\tilde{\psi}$, either $\psi$ is small or $(\tau_1 - \tau_2)^2$ is large for this system. Furthermore, it is observed from Fig. 4 that the difference in free energy between bunched and uniformly spaced stripes scales as $(\tau_1 - \tau_2)^2$, or equivalently as $(\tau_1 - \tau_2)^2$ for a given $\alpha$. As the tendency for self-assembly is strong in this system, the energy difference must be substantially larger than thermal fluctuations, which precludes small values of $(\tau_1 - \tau_2)^2$.