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FAST TRACK COMMUNICATION

Highly ordered nanoscale surface ripples produced by ion bombardment of binary compounds

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Abstract
Nanoscale surface ripples generated by oblique-incidence ion bombardment of a solid are generally full of defects, and this has prevented the widespread adoption of ion bombardment as a nanofabrication tool. We advance a theory that predicts that remarkably defect-free ripples can be produced by ion bombardment of a binary material if the ion species, energy and angle of incidence are appropriately chosen. This high degree of order results from the coupling between the surface height and composition, and cannot be achieved by bombarding an elemental material.

(Some figures may appear in colour only in the online journal)

Bombarding a nominally flat solid surface with a broad ion beam can produce an impressive variety of self-assembled nanoscale patterns with feature sizes that can be as small as 10 nm. These patterns include periodic height modulations or 'ripples' produced by oblique-incidence ion bombardment (OIIB) [1], as well as nanodots arranged in hexagonal arrays of astonishing regularity [2]. The spontaneous emergence of these patterns is not just fascinating in its own right: ion bombardment has the potential to become a cost-effective method to rapidly fabricate large-area nanostructures at length scales beyond the limits of conventional optical lithography.

A serious issue that has diminished the utility of ion-induced pattern formation as a nanoscale fabrication tool is the presence of numerous defects in the patterns that are typically produced. In the case of surface ripples, some ripples terminate, while others fuse with their neighbours. In contrast, penta- and hepta-defects are found in hexagonal arrays of nanodots produced by ion bombardment of binary materials. Limited progress has been made in reducing the number of defects in surface ripples—for example, experiments have shown that few defects form near the boundary of a region subjected to OIIB [3].

In this Communication, we demonstrate that ripples formed by OIIB of a *binary compound* can have a much higher degree of order than those formed by bombardment of an elemental material. This dramatic reduction in the number of defects is the result of the coupling between the topography and a surface layer of altered composition. Because the spatial oscillations in the surface height are mirrored in the variations of the composition at the surface, OIIB could be used to simultaneously achieve nearly defect-free nanoscale patterning of the surface topography and composition.

Ripples develop if $R(\boldsymbol{k})$, the growth rate of a low-amplitude sinusoidal surface disturbance of wave vector $\boldsymbol{k}$, is positive for some value of $\boldsymbol{k}$. Before nonlinear effects become important, the experimentally observed ripple wave vector is the one with the greatest growth rate.

The modern theory of pattern formation tells us that highly ordered ripples with the wave vector $\boldsymbol{k}_0$ develop only if $R(\boldsymbol{k})$ is positive only in the immediate vicinity of the points $\pm\boldsymbol{k}_0$ in $\boldsymbol{k}$-space [4]. If this condition is satisfied, the ripples with positive growth rates have wavelengths in a narrow range centred on $2\pi/|\boldsymbol{k}_0|$. Ripples of arbitrarily long wavelengths have a positive growth rate in the Bradley–Harper

(BH) theory of ripple formation on elemental materials [5], and so according to that theory, highly ordered ripples will not develop on single-component samples. This remains true if the BH theory is extended to include nonlinear terms [6, 7] and the effect of mass redistribution [8–12], i.e. the surface atomic current produced by momentum transfer from the incident ions to atoms near the solid surface.

When a binary material is bombarded with an ion beam, one of the atomic species is preferentially sputtered, and this leads to the formation of a surface layer of altered composition. As we shall demonstrate, a well-ordered pattern of wave vector $\boldsymbol{k}_0$ can emerge because the dynamics of the surface topography and the surface layer of altered composition are coupled. $R(\boldsymbol{k})$ is only positive close to the points $\pm\boldsymbol{k}_0$ if the ion species, energy and angle of incidence θ are appropriately chosen.

In ground breaking work, Shenoy, Chan and Chason studied the coupling between the surface topography and composition that arises during ion bombardment of a binary compound [13]. Bradley and Shipman (BS) extended this theory to include the effect of mass redistribution and the leading order nonlinear terms [14–16]. The BS equations of motion govern the behaviour of u and ϕ, the deviations of the surface height and surface composition from their steady-state values. They apply to normal-incidence bombardment, but are readily generalized to arbitrary angles of incidence θ [17]. A total of twelve dimensionless parameters appear in the resulting equations. Three of these parameters are eliminated by shifting our attention to a closely related problem in which two ion beams bombard the sample surface rather than one. In the dual-beam problem, both beams have an angle of incidence θ, but their azimuthal angles differ by 180°. Adopting the same notation, assumptions and rescaling as BS, we then obtain

$$u_t = \phi - (r_1 u_{xx} + u_{yy}) - \nabla^2\nabla^2 u + \lambda(r_3 u_x^2 + u_y^2) \qquad (1)$$

and

$$\phi_t = -a\phi + b(r_2 u_{xx} + u_{yy}) + c\nabla^2\phi + \nu\phi^2 + \eta\phi^3, \qquad (2)$$

where $u_t \equiv \partial u/\partial t$, $u_x \equiv \partial u/\partial x$ and so forth. Explicit expressions that relate the dimensionless constants a, b, c, λ, ν and η to the underlying physical parameters may be found in [16]. The corresponding expressions for r_1, r_2 and r_3 are lengthy and will be given elsewhere [17]. For normal incidence, $r_1 = r_2 = r_3 = 1$, and equations (1) and (2) reduce to the BS equations of motion.

If the term ϕ did not appear on the right-hand side of equation (1), this equation would be the usual anisotropic Kuramoto–Sivashinsky (AKS) equation for the surface height

$$u_t = -(r_1 u_{xx} + u_{yy}) - \nabla^2\nabla^2 u + \lambda(r_3 u_x^2 + u_y^2), \qquad (3)$$

and the dynamics of the topography would simply decouple from those of the surface composition. The differing sputter yields of the atomic species A and B give rise to the term ϕ in equation (1) and to the term $-a\phi + \nu\phi^2 + \eta\phi^3$ in equation (2) as well. The term $b(r_2 u_{xx} + u_{yy})$ on the right-hand side of equation (2), on the other hand, has mass redistribution as its origin. Finally, the term $c\nabla^2\phi$ describes surface diffusion's tendency to smooth out spatial variations in the surface composition.

In the case of an elemental material, $\phi = 0$, $b = 0$, and equations (1) and (2) reduce to the AKS equation (3). A remarkable feature of this equation is that the nonlinear terms stabilize the linear instability, leading to a state of bounded spatiotemporal chaos if $r_3 > \min(r_1, 0)$ [18]. A sample time series from a numerical integration of equation (3) for the case $r_1 = 2$, $r_3 = 1$ and $\lambda = -0.3$ is shown in figures 1(a)–(c); the initial state was low-amplitude spatial white noise. The ripple-dominated state that develops at early times is rife with defects. As time passes, it degenerates into a spatially and temporally chaotic state with a cellular structure.

Detailed analysis of the equations of motion (1) and (2) for oblique-incidence bombardment of a binary material reveals that the flat steady-state solution $u = \phi = 0$ becomes unstable as the parameter b is reduced below a critical value b_T which depends on the parameters a, c, r_1 and r_2. In [15], a linear stability analysis of the flat steady state was presented for the isotropic case $r_1 = r_2 = r_3 = 1$ which is valid for all possible values of the parameters a, b and c. The generalization of this analysis to the anisotropic case [17] is omitted here for the sake of brevity. It shows that for b just below b_T, the growth rate $R(\boldsymbol{k})$ is positive only in the immediate vicinity of two nonzero points $\pm\boldsymbol{k}_0$ in $\boldsymbol{k}$-space for a wide range of the parameters a, c, r_1, r_2 and r_3. As we have discussed, we expect a high degree of order to be attained in this case.

Let us restrict our attention to the region $\mathcal{R}$ in parameter space in which $cr_1 > a$, $r_1 > 1 > r_2$, and $4a$ is greater than $(r_1 - c)^2$ if c is less than r_1. The critical value of b is then $b_T = (cr_1 + a)^2/(4cr_2)$ and $\boldsymbol{k}_0$ lies on the k_x-axis. Moreover, $k_0 = \sqrt{(cr_1 - a)/(2c)}$. The growth rate $R(\boldsymbol{k})$ is positive only in the immediate vicinity of the points $\pm\boldsymbol{k}_0$ if b is just below b_T, as illustrated in figure 1(g). Our linear stability analysis therefore suggests that for b slightly smaller than b_T, nearly defect-free ripples with their crests aligned with the y-axis will emerge as time passes.

Numerical integrations of the equations of motion (1) and (2) bear these expectations out. A time series of greyscale plots of u for a set of parameter values in the region $\mathcal{R}$ of parameter space is shown in figures 1(d)–(f). The parameters r_1, r_3 and λ were taken to have the same values as in our simulation of the AKS equation, the initial condition was again low-amplitude spatial white noise, and snapshots were taken at the same times as in figure 1(a)–(c). We additionally chose the representative parameter values $a = 0.8$, $c = 0.9$, $b = 0.95b_T = 8.92$, $r_2 = 0.2$, $\nu = 0$ and $\gamma = 10$.

The contrast between the two simulations is striking: in the case of the binary compound, a defect-free rippled state has formed by time $t = 800$, whereas a very disordered, chaotic state is found at this time for the elemental material. This contrast is brought into even sharper focus by the Fourier transforms of the surface height that are shown in the insets of panels (a)–(f) in figure 1. By time $t = 800$, the Fourier spectrum of the topography of the elemental material is quite diffuse. Conversely, in the case of the binary material, the peaks in the Fourier spectrum are centred on points on the k_x-axis (which is consistent with our analysis) and the peaks

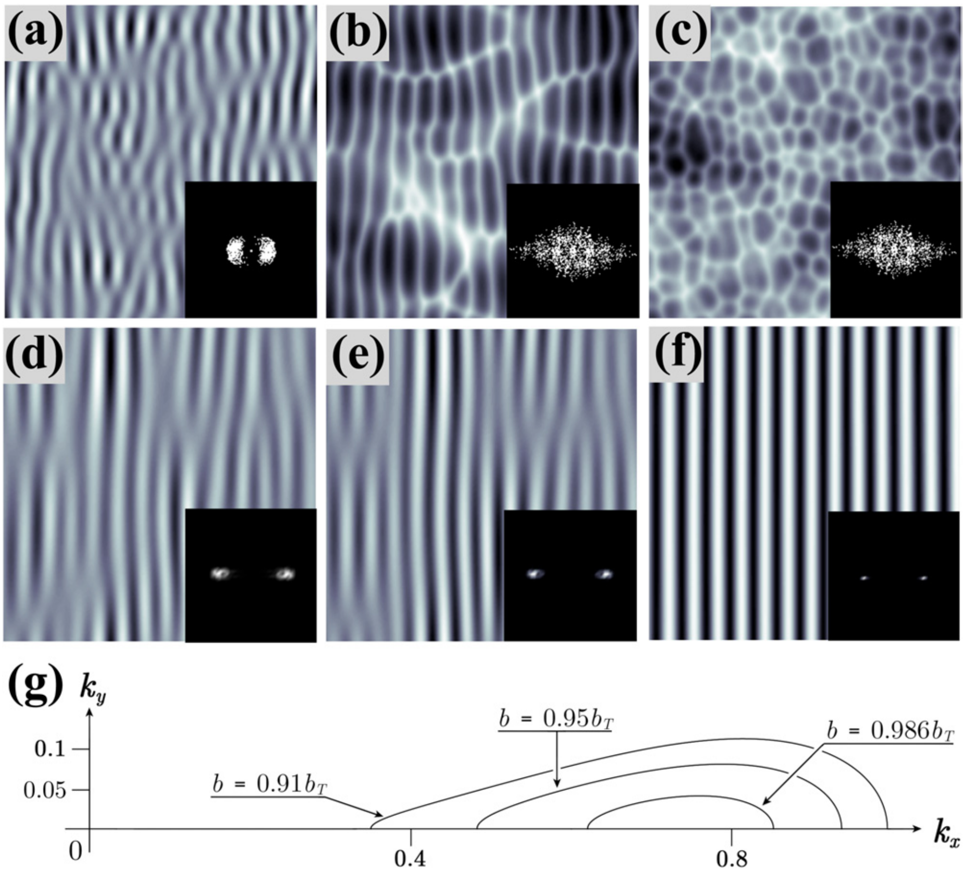

Figure 1. (*a*)–(*c*): greyscale plots of u resulting from a simulation of the AKS equation (3) which governs the dynamics of the surface of an elemental material that is subject to dual-beam OIIB. (*d*)–(*f*): greyscale plots of u from a simulation of the coupled equations (1) and (2) which give the time evolution of the surface height and composition of a binary material subjected to dual-beam OIIB. For both simulations, the parameter values are $r_1 = 2$, $r_3 = 1$ and $\lambda = -0.3$, with the additional values $r_2 = 0.2$, $a = 0.8$, $c = 0.9$, $b = 0.95b_T = 8.92$, $\nu = 0$ and $\gamma = 10$ for the coupled equations. The times are $t = 100$ for (*a*) and (*d*); $t = 200$ for (*b*) and (*e*); and $t = 800$ for (*c*) and (*f*). In all plots, the spatial domain is $-40 \leqslant x, y \leqslant 40$ and the shading is light (dark) where u is large (small). The numerical integrations were performed on a 512×512 spatial grid with periodic boundary conditions using a Fourier spectral method. Insets: the magnitude of the Fourier transform of u, plotted on the domain $-12 \leqslant k_x, k_y \leqslant 12$. (*g*): plots of the locus of points given by $R(\boldsymbol{k}) = 0$ in the first quadrant for three values of b just below b_T. The values of the parameters a, c, r_1 and r_2 chosen are the same as in the simulation shown in panels (*d*)–(*f*). The growth rate $R(\boldsymbol{k})$ is positive for $\boldsymbol{k}$ between the curves and the k_x-axis, and $R(\boldsymbol{k})$ is symmetric with respect to reflections across both axes.

grow sharper with the passage of time. As for normal-incidence ion bombardment of a binary material [14–16], in the steady state the surface concentration of the preferentially sputtered species is higher at the peaks than in the depressions. We have verified that comparable results are obtained for a range of parameter values a, c, r_1 and r_2 in region $\mathcal{R}$.

For the sake of simplicity, we have considered dual-beam OIIB. If only a single beam is employed, the ripples will propagate over the surface, but otherwise our results do not change significantly [17]. We have also omitted the shot noise in the ion beam. In an experiment, shot noise is of course present and, as a consequence, we expect that some defects will remain even after a long period of ion bombardment.

The key finding of this Communication is that when a binary material is subjected to OIIB, the coupling of the surface height to the surface composition can lead to the emergence of highly ordered surface ripples. From a physical standpoint, this order is the result of momentum transfer from the incident ions to atoms near the surface of the solid. For parameter values that yield nearly defect-free ripples, momentum transfer produces a net flow of the species with the lower sputter yield from the crests of a small-k sinusoidal disturbance to the adjacent troughs. There is a tendency for the peaks of the sinusoidal disturbance to be eroded away as an excess of the species with the lower sputter yield accumulates in the troughs. If b/a is greater than r_1/r_2 and 1, this stabilizing effect prevails over the destabilizing effect of the curvature dependence of the sputter yields, and the amplitude of the small-k surface disturbance attenuates to zero. The small-k instability that is inherent to the BH theory for OIIB of elemental materials is therefore absent in the case of a binary material if b is sufficiently large.

There is some experimental support for our prediction that highly ordered surface ripples can be generated by OIIB of binary compounds: it has been shown that oblique-incidence bombardment of SiC produces completely defect-free ripples for a fortuitous choice of ion species, energy and angle of incidence [19].

Ideally, one would like to be able to specify the precise experimental conditions needed to produce nearly defect-free ripples on a particular binary compound. This is unfortunately not possible at the present time because the two parameters that characterize the atomic mass currents induced by momentum transfer [15] are not currently known for any binary material or ion species. These parameters are denoted by μ_A and μ_B in [15] and are defined precisely there. Once μ_A and μ_B have been measured experimentally or have been obtained from simulations, it will become possible to predict which ion energies and angles of incidence will induce the formation of highly ordered ripples for a given choice of ion species and target material.

There *is* an experimental procedure that will produce nearly defect-free ripples on the binary compound GaSb even though the values of μ_A and μ_B are currently unknown. To begin, a well-ordered array of nanodots is obtained by normal-incidence bombardment; the experimental conditions required to do this have been documented [2]. The angle of incidence θ is then changed to a nonzero but relatively small value (say 10°) and ion bombardment is continued. This will yield a pattern of ripples, but the pattern may be fairly disordered. The ion energy is then adjusted, the sample is bombarded, and the density of defects is measured. Continued adjustments are made until the number of defects in the ripples is optimally reduced. The value of θ can then be increased once more; after varying the ion energy a nearly defect-free ripple topography is again obtained. Clearly, this procedure can be continued to any desired angle of incidence.

It is illuminating to discuss what happens during this procedure from a theoretical vantage point. For $\theta = 0$, the value of b is just below the critical value b_T and a well-ordered pattern develops. When θ is increased, the values of b and b_T change, but by varying the ion energy, b can be restored to a value just below b_T, yielding a highly ordered pattern once more.

A theory akin to the BS theory applies if impurities are deposited during ion bombardment of an elemental material [20]. We therefore expect that OIIB of an elemental material with co-deposition of an impurity will produce nearly defect-free surface ripples provided that the elemental material as well as the species, energy and angle of incidence of the ions are appropriately chosen. In fact, surface ripples with an exceptionally low density of defects have already been generated by OIIB of silicon [21]. It is now known that impurities were inadvertently deposited on the sample surface during these experiments [22].

In summary, our analysis and simulations reveal that oblique-incidence ion bombardment of a binary compound will produce nearly defect-free surface ripples if the experimental conditions are chosen appropriately. These ripples have a much higher degree of order than ripples generated by bombardment of an elemental material. This is a consequence of the preferential sputtering of one of the two atomic species that make up the binary material, and of the resulting coupling between the surface height and composition.

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