

**Spontaneous formation of ordered patterns in Al films deposited on silicone oil surfaces**Sen-Jiang Yu,<sup>1</sup> Yong-Ju Zhang,<sup>1,2</sup> Quan-Lin Ye,<sup>1</sup> Ping-Gen Cai,<sup>1</sup> Xiao-Wei Tang,<sup>1</sup> and Gao-Xiang Ye<sup>1,\*</sup><sup>1</sup>*Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China*<sup>2</sup>*Department of Physics, Taizhou University, Linhai 317000, People's Republic of China*

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We report the spontaneous formation of large spatial ordered patterns in a continuous aluminum (Al) film system deposited on silicone oil surfaces by a thermal evaporation method. The growth mechanism of the ordered patterns can be traced to a three-stage process, the first of which involves nucleation and growth of strips with a characteristic domain structure in the films. In the subsequent stage, triangle-shaped domains with different sizes appear in the strips. Then the domains grow and finally form the ordered and band-shaped patterns. The experiment shows that the ordered patterns result from the spontaneous ordered organization of the Al atoms and atomic clusters driven by the internal stress in this nearly free sustained film system.

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Spontaneous generation of complex order in apparently simple systems is of long-standing and continuing interest not only for its aesthetic appeal, but also for its fundamental and technological relevance.<sup>1-9</sup> In natural systems there are large varieties of self-organized phenomena that potentially span a wide range of scales, from macroscopic ground surface morphologies<sup>1</sup> and granular materials<sup>2</sup> to nanometer-scale structures such as microporous materials,<sup>3</sup> nanocrystals (including nanoclusters, nanowires, nanotubes, etc.) in semiconductors,<sup>4</sup> nanostructure arrays on strained crystal surfaces,<sup>5</sup> and complex biological and nonbiological structures organized with supramolecules (or molecules).<sup>6,7</sup> Some previous studies demonstrated that the ordered patterns existing in thin films deposited both on solid substrates<sup>5,10,11</sup> and on soft polymer substrates<sup>8,9</sup> are induced by the buckling of the films owing to the relief of the internal stress.

Vapor phase deposition of metals on liquid substrates was studied in a number of recent investigations.<sup>12-15</sup> It is observed that atoms, atomic compact clusters, and branched islands on liquid substrates possess large mobility and they can diffuse, rotate, and aggregate on the liquid surfaces freely. In principle, the phenomena resulted from the internal stress in continuous thin films deposited on liquid surfaces can emerge obviously because of the weak interaction between the films and the liquid substrates. Therefore it is expected that various characteristic patterns caused by the internal stress relief may appear apparently in these nearly free sustained films.<sup>12</sup> Here we report the spontaneous formation of large spatial ordered stress relief patterns existing in continuous aluminum (Al) films deposited on silicone oil surfaces. We anticipate that this nearly free sustained metallic film system subjected to the distinctive effect of the underlying liquid layers will provide a test bed not only for the fundamental research on the internal stress in the films, but also for the technological application of various free sustained films on liquid substrates.

The samples were prepared by thermal evaporation of 99.999% pure Al in a vacuum of  $6 \times 10^{-4}$  Pa at room temperature. Commercial silicone oil (Dow Corning 705 Diffusion Pump Fluid) with a vapor pressure below  $10^{-8}$  Pa was painted onto a frosted glass surface, which was fixed 120 mm below the filament (tungsten). The resulting oil substrate

with an area about  $10 \times 10$  mm<sup>2</sup> had a uniform thickness of  $\approx 0.5$  mm. In fact, in the oil thickness range of 0.2–0.8 mm, no obvious change of the surface morphologies of the Al films can be observed in our experiment. The deposition rate  $f$  and the nominal film thickness  $d$  were determined by a quartz-crystal balance, which was calibrated by a profilometer ( $\alpha$ -step 200 profilometer, TENCOR). After deposition, the sample was kept in the vacuum chamber (in vacuum condition) for time  $\Delta t$  and then removed from the chamber. All images for the surface morphologies of the samples were taken with an optical microscope (Leica DMLM), equipped with a charge-coupled device camera (Leica DC 300) which was interfaced to a computer for data storage and data processing.

The typical ordered patterns in the Al films are shown in Fig. 1, where it can be seen that the band-shaped patterns, namely bands, are composed of a large number of parallel key-shaped domains, namely keys. Generally, the neighboring keys possess different width  $w$  but nearly uniform length  $L$  (see Fig. 1). The experiment indicates that the bands grow from the outer edge of the sample and then extend towards its central region. The average key length near the sample edge is generally longer than that in the central region of the sample. According to the growth direction of the bands, we can identify that in many cases two bands may coalesce or one band may bifurcate harmoniously [Fig. 1(b)]. An interesting phenomenon is that approximately the key length before bifurcation (or after coalescence), i.e.,  $L_1$ , equals the sum of the key lengths in the two branched bands, i.e.,  $L_2$  and  $L_3$ , and all the keys before and after bifurcation (or coalescence) are nearly parallel [Fig. 1(b)].

The experimental results show that the appearance of the bands depends on the time  $\Delta t$ , deposition rate  $f$ , and nominal film thickness  $d$ . We find that if  $\Delta t = 0.5$  h, in the ranges of  $f = 0.05$ – $0.50$  nm/s and  $d = 10$ – $120$  nm, various bands with different  $L$  and  $w$ , as shown in Fig. 1, can be observed in the films. The maximum value of the key length observed in our experiment is  $L \approx 110$   $\mu$ m and the total length of one band can be more than 10 mm. In addition, it should be emphasized that the bands can also be observed in the samples with  $d < 10$  nm if we greatly increase the time  $\Delta t$ . For instance, if

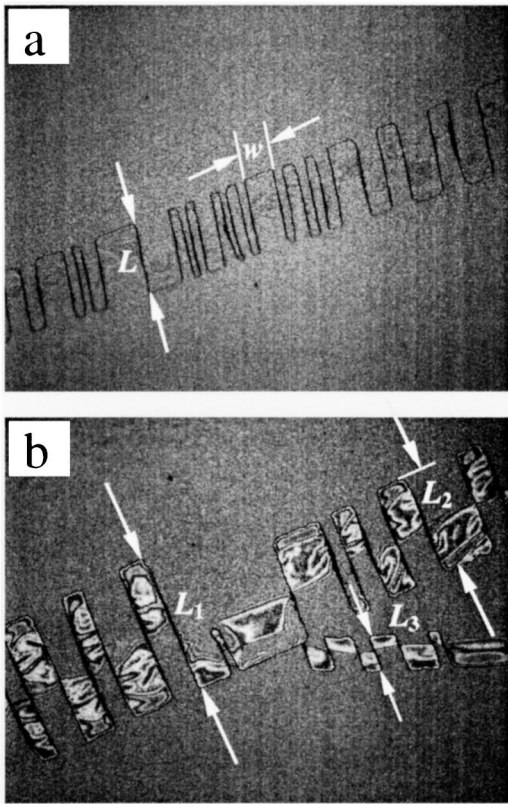


FIG. 1. Reflection optical micrographs for the bands in the Al films deposited on silicone oil surfaces.  $f=0.10$  nm/s,  $\Delta t=0.5$  h. (a)  $d=50$  nm, image size is  $260 \times 200 \mu\text{m}^2$ ; (b)  $d=25$  nm, image size is  $130 \times 100 \mu\text{m}^2$ .

$\Delta t \geq 10$  h, complete bands also appear in the samples with  $d=8$  nm. Our experiment indicates that the ordered patterns grow successively in vacuum condition and, once the samples are removed from the vacuum chamber, the growth process stops immediately.

In order to investigate the growth mechanism of the bands, a series of experiments was performed in which the time  $\Delta t$  was varied between  $\Delta t=0.5$  and 12 h. Examples of the band growth in vacuum condition as a function of  $\Delta t$  are shown in Figs. 2(a)–(d). After deposition, with the increase of  $\Delta t$ , strips with a characteristic domain structure appear in the Al films first. Then, around  $\Delta t \approx 0.5$  h, depending on the nominal film thickness  $d$  and the location of the strips, triangle-shaped domains with different sizes start to appear in the strip [Fig. 2(a)]. Approximately, almost all the domains are isosceles triangles and their bottom sides locate on the same edge of the strip. Then as  $\Delta t$  further increases, the triangle-shaped domains grow gradually until they connect each other [Fig. 2(b)]. In the subsequent period, the domains grow steadily in the directions perpendicular to the strip [Figs. 2(b) and (c)], which finally results in the formation of the band with a quasiperiodic structure, as shown in Figs. 1 and 2(d).

It can be seen from Fig. 2 that the key length  $L$  increases obviously with the time  $\Delta t$ . In order to further understand the growth process of the bands in vacuum condition, we measured the dependence of the maximum key length  $L_m$  in

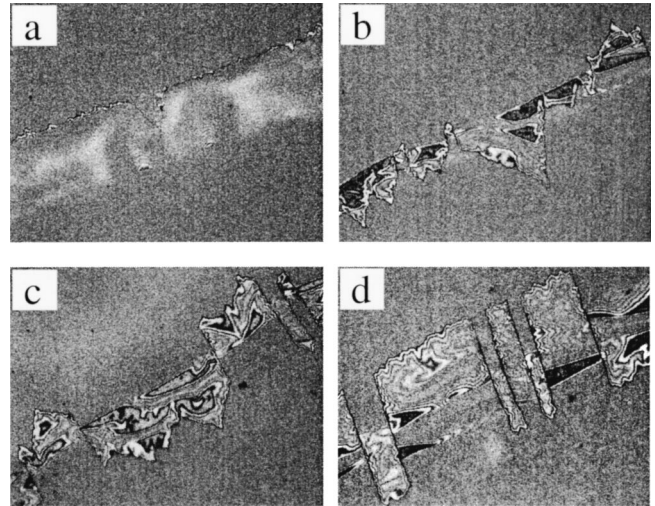


FIG. 2. Growth of the band with the time  $\Delta t$ .  $f=0.10$  nm/s,  $d=8$  nm. Each reflection optical micrograph has a size of  $65 \times 50 \mu\text{m}^2$ . (a)  $\Delta t=1$  h; (b)  $\Delta t=2.5$  h; (c)  $\Delta t=4$  h; (d)  $\Delta t=12$  h.

each sample on the time  $\Delta t$  and the result is shown in Fig. 3. One finds that  $L_m$  increases rapidly with  $\Delta t$  first, then its growth speed slows down, and finally  $L_m$  approaches a saturated value  $L_0$ . Furthermore, the experimental data (black dots) in Fig. 3 can be well fitted with a formula

$$L_m = L_0 \left[ 1 - \exp\left(-\frac{\Delta t}{\tau}\right) \right], \quad (1)$$

where  $\tau$  is the relaxation time. For the samples in Fig. 3, for instance,  $L_0$  and  $\tau$  are found to be  $51 \mu\text{m}$  and 1.7 h, respectively. Generally, neither  $L_0$  nor  $\tau$  is a constant and for the samples with  $f=0.10$  nm/s, for example,  $L_0$  increases and  $\tau$  decreases with the nominal film thickness  $d$ . According to the previous studies,<sup>5,8–11,16,17</sup> strong and detectable residual internal stress frequently exists in films after deposition and it relaxes gradually with time. We suggest that the phenomenon shown in Fig. 3 can be considered as the stress relief

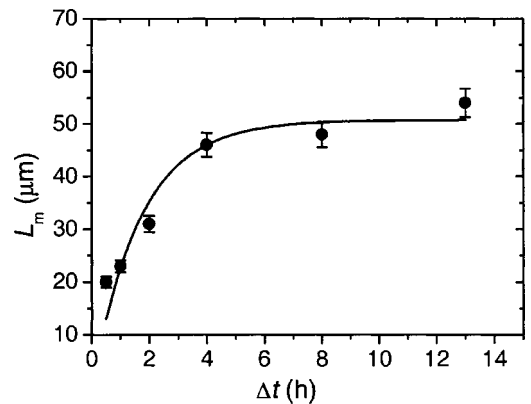


FIG. 3. The maximum key length  $L_m$  in each sample as a function of the time  $\Delta t$ .  $f=0.10$  nm/s,  $d=20$  nm. The solid line is a fit to the experimental data (black dots). We find  $L_m = L_0 [1 - \exp(-\Delta t/\tau)]$ , with  $L_0 \approx 51 \mu\text{m}$  and  $\tau \approx 1.7$  h.

process and the characteristic relaxation time of the internal stress relief in this Al film system is of the order of  $\tau \approx 2$  h. For  $\Delta t > 10$  h, the band reaches its stable state and the free energy approaches minimum.

Many previous works have reported that during stress relief the film materials always orderly organize in some regions driven by the internal stress and form characteristic buckling patterns such as sinusoidal shapes.<sup>8-11</sup> We propose here that the ordered patterns shown in Figs. 1 and 2 also originate from spontaneous material organization owing to the stress relief. This proposal is based on the following two facts. First, stress relief patterns can exhibit obviously in the film system with a weak interaction between the films and substrates since the formation of the patterns depends strongly on the adhesion energy of film-substrate interfaces.<sup>10,18</sup> Therefore the characteristic structure of the bands shown in Figs. 1 and 2 should not be a surprise in view of the nearly zero adhesion of the solid-liquid interface. Second, it has been proved that the diffusion coefficient of metallic atoms and atomic clusters on liquid surfaces is much larger than that on solid substrates.<sup>13,14</sup> Therefore the Al atoms and clusters can diffuse easily and organize spontaneously in some regions of the film so that the total stress energy approaches minimum.

If the description above is correct, the difference between the film densities or microstructures in and out of the keys should be detectable. In order to take transmission optical micrographs<sup>19</sup> for the Al films and meanwhile avoid the influence of the underlying oil layers on the transmission micrographs, two Al films were separated from the oil substrates and adhered directly to glass surfaces. After being washed with acetone, the transmission optical micrographs of the films were taken with the optical microscope and the results are shown in Fig. 4. One finds from Fig. 4 that the color of the areas in the keys are obviously darker than that of the other regions, providing evidence that the densities or structures in and out of the keys are different and therefore the bands really result from the spontaneous ordered organization of the film materials.

A characteristic stress relief pattern generally represents an internal stress distribution since its propagation perpendicular to the axis of highest stress enables greatest stress energy release,<sup>8-11</sup> providing an effective method that one can use to calculate the stress distribution to theoretically understand these patterns in thin films. Several works have previously applied a general theory of buckling of shells to analyze the stress relief patterns and the buckling equation as<sup>10,11</sup>

$$D \left( \frac{\partial^4 W}{\partial x^4} + 2 \frac{\partial^4 W}{\partial x^2 \partial y^2} + \frac{\partial^4 W}{\partial y^4} \right) + \sigma_x d \frac{\partial^2 W}{\partial x^2} + \sigma_y d \frac{\partial^2 W}{\partial y^2} + 2 \tau_{xy} d \frac{\partial^2 W}{\partial x \partial y} + F = 0, \quad (2)$$

where  $D$  is the moment of inertia of the film,  $d$  is the film thickness,  $x$  and  $y$  are the coordinates relative to the substrate,  $W$  is the film coordinate as defined in the elastic theory,  $\sigma_x$  and  $\sigma_y$  are the internal compressive stresses,  $\tau_{xy}$  is

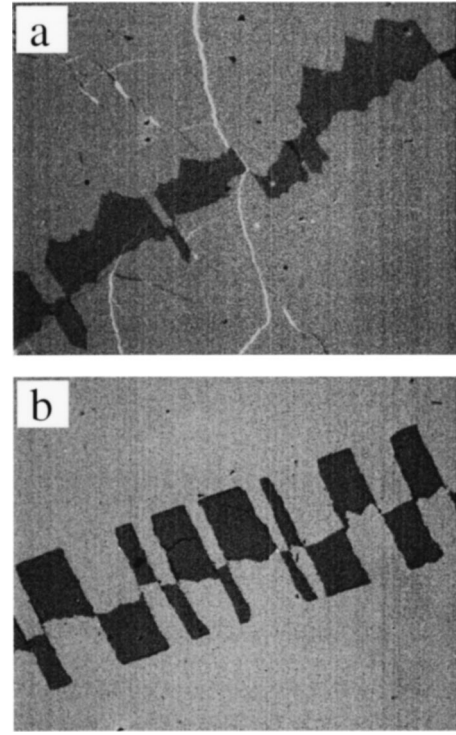


FIG. 4. Transmission optical micrographs for the bands in two Al films, which were separated from the oil substrates and adhered directly to glass surfaces. Each image has a size of  $100 \times 80 \mu\text{m}^2$ . (a)  $f=0.10$  nm/s,  $d=8$  nm,  $\Delta t=4$  h; (b)  $f=0.10$  nm/s,  $d=25$  nm,  $\Delta t=0.5$  h.

the shear stress, and  $F$  is the external force. One type of solution of Eq. (2) which is physically acceptable is<sup>10</sup>

$$W = 1 + \cos(kx + qy). \quad (3)$$

This solution implies that the film buckling perpendicular to the direction of the highest stress is along a straight line given by

$$kx + qy = 2n\pi, \quad n = 0, \pm 1, \pm 2, \dots \quad (4)$$

Introducing Eq. (3) into Eq. (2) shows that for each  $k$  value there are two permissible values of  $q$ , and therefore the solution of Eq. (4) consists of two classes of parallel line families with slopes of  $\pm |k/q|$ , which cross each other.<sup>10</sup> Many stress relief patterns can be well explained by making use of this model. For example, if a propagating buckling reaches a point where two lines cross each other, it jumps from one line to the other with different slope and this process may result in the sinusoidal pattern.<sup>10,11</sup>

It is clear that a pair of values of  $k$  and  $q$  corresponds to a kind of distribution of the internal stress. In fact, the values of  $k$  and  $q$  are not unique and Eq. (2) can be satisfied by many different real values of  $k$  and  $q$  [see Eqs. (3) and (4)], which means that many kinds of sinusoidal stress relief patterns can exist simultaneously in each film. Our experimental results indicate that the Al films shown in Figs. 1, 2, and 4 may contain various sinusoidal (or cosine) stress relief patterns with different periods, phases, and amplitudes. Therefore the oscillatory spectrums of the stress relief patterns in

the films are quite plentiful and evolve with the time  $\Delta t$  (see Fig. 2). Finally the composition of these sinusoidal stress relief patterns results in the formation of the keys and then the bands shown in Figs. 1, 2, and 4. We believe that the plentiful spectrums of the stress relief patterns in the Al films strongly relate to the characteristic interaction between the Al films and the liquid substrates.

The spontaneous formation of the characteristic ordered patterns shown in Figs. 1, 2, and 4 presents us with an example that the films deposited on liquid substrates may possess distinctive internal stresses, characteristic microstructures, and subsequently anomalous physical properties, which we believe may lead to a new field of thin-film studies. Up to now, the details of the interactions among the Al atoms (or clusters) and between the films and the liquid sub-

strates, which should be responsible for the film microstructures and the ordered patterns with quasiperiodic structure, still remain poorly understood. Therefore many new avenues of investigation are still open to us. Further studies include the theoretical explanation for the formation mechanism of the large scale ordered patterns, the investigation for the distribution and evolution of the internal stress in these nearly free sustained films, and the research for various physical properties to reveal the potential application prospect of these films.

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