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Formation mechanism of ordered stress-relief patterns in a free sustained Cu film system*

Chen Miao-Gen(陈苗根), Xie Jian-Ping(谢建平), Jin Jin-Sheng(金进生), Xia A-Gen(夏阿根), and Ye Gao-Xiang(叶高翔)†

Department of Physics, Zhejiang University, Hangzhou 310027, *China*

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A nearly free sustained copper (Cu) film system has been successfully fabricated by thermal evaporation deposition of Cu atoms on silicone oil surfaces, and a characteristic ordered pattern has been systematically studied. The ordered pattern, namely, band, is composed of a large number of parallel key-formed domains with different width w but nearly uniform length L; its characteristic values of w and L are very susceptible to the growth period, deposition rate and nominal film thickness. The formation mechanism of the ordered patterns is well explained in terms of the relaxation of the internal stress in the films, which is related to the nearly zero adhesion of the solid-liquid interface. By using a two-time deposition method, it is confirmed that the ordered patterns really form in the vacuum chamber.

Keywords: ordered pattern, thin film, internal stress
PACC: 6800, 6890, 7360D, 8115G

1. Introduction

Films and coatings fabricated by vapour deposition, sputtering, etc., often develop residual internal stresses during and after the deposition processes.[1,2] Large stresses can bend substrates, cause film fracture or de-adherence,[3] lead to hillock formation,[4] or result in fascinating structures or beautiful surface patterns.[5−7] Furthermore, the presence of internal stresses in the films is a key problem in some important fields of thin film applications. Therefore, the origin of the intrinsic stresses has been the subject of extensive research activities during the last few decades.[8−10]

In recent years, based on the fact that liquid surfaces can be used as thin film substrates, vapour phase deposition of metals on liquid substrates has been studied in a number of recent investigations.[11−16] The studies showed that atoms, atomic compact clusters and branched islands on liquid substrates have large mobility, and they can diffuse, rotate and aggregate on the liquid surfaces freely.[11] Moreover, various characteristic patterns may appear apparently in these nearly free sustained films,[12−16] which originate mainly from the relaxation of the internal stress in the films during or after deposition.

In this paper, we report the formation mechanism of the large spatial ordered patterns existing in a Cu film deposited on silicone oil surface. The ordered pattern, namely band, is composed of a large number of parallel key-formed domains and the characteristic maximum length and width of the domains observed in our experiment are $L_{\rm m} \approx 3.4 \times 10^2 \mu$m and $w_{\rm m} \approx 1.0 \times 10^3 \mu$m, respectively. The formation mechanism of the ordered pattern can be understood with the aid of a series of experiments for comparing different conditions. A two-time deposition method is introduced and it gives an experimental evidence that the ordered patterns really have formed under the vacuum condition, i.e., before the chamber was filled with air in our experiment.

2. Experiment

The samples were prepared by thermal evaporation of 99.999% pure Cu in a vacuum of 6×10^{-4}Pa. Commercial silicone oil (Dow Corning 705 Diffusion Pump Fluid) with a vapour pressure below 10^{-8}Pa was painted onto a frosted glass surface. The resulting oil layer with an area about 12×20mm^2 exhibited a uniform thickness of ≈ 0.5mm and was fixed 130mm below the evaporating filament (tungsten). The depo-

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†Corresponding author. E-mail: gxye@mail.hz.zj.cn

sition rate f and the nominal film thickness d were determined by a quartz-crystal balance, which was calibrated by a profilometer (α step-200 profilometer, TENCOR). After deposition, the sample was kept in the vacuum chamber (in vacuum condition) for a time interval Δt. Then the chamber was filled with air slowly, and finally the sample was removed from the chamber. All images of the surface morphologies of the samples were taken immediately with an optical microscope (Leica DMLM), equipped with a CCD camera (Leica DC 300) and interfaced to a computer for data storage and data processing.

3. Results and discussion

3.1. Structure and formation process of the ordered patterns

The typical ordered stress pattern in the Cu films deposited on the silicone oil surface is shown in Fig.1, where it can be seen that the band-shaped structure, namely band, is composed of a large number of parallel key-formed domains. Generally, the neighbouring domains possess nearly uniform length L but different width w (see Fig.1). The characteristic maximum length and width of the domains observed in our experiment are $L_{\rm m} \approx 3.4 \times 10^2 \mu$m and $w_{\rm m} \approx 1.0 \times 10^3 \mu$m, respectively. Figure 1(b) shows the corresponding micrograph (transmission mode) of the sample in Fig.1(a). It is noticed that some of the domains are broken in the band.

Based on the previous studies,[14−16] strong and detectable residual internal stress always exists in metallic films deposited on liquid substrates, and characteristic stress-relief surface morphologies can be observed in these nearly free sustained films. Here, we propose that the internal stress patterns in the films should be responsible for the band morphology. In our experiment, the Cu films and the silicone oil substrates both expand during deposition due to the heat radiation from the filament. In the subsequent cooling process, the contraction behaviours of the films and the substrates result in the detectable residual internal stress, which may be relieved by the spontaneous formation of the bands. Because the adhesion of the solid–liquid interface is very weak,[11] the Cu film may buckle under the compressive stress. When the local internal stress is beyond a critical value, the brittle film break in some regions and then the broken points will propagate through the film. During this period, the broken pieces of the film move freely on the silicone oil surface to relieve the compressive stress. As a result, the neighbouring pieces of the film will collide, crush and overlap with each other and domains will form one by one. In other words, if a domain in one film piece (for example, domain A in Fig.1(a)) moves onto the other film piece, the next domain (domain B in Fig.1(a)) should move under it, and so on. Finally, the domains, which in fact contain two layers, appear. In addition, due to the difference of expansions of the film and substrate and the mobile nature of the silicone oil substrate, the domains may separate each other and sometimes rupture in our experiment (see Fig.1).

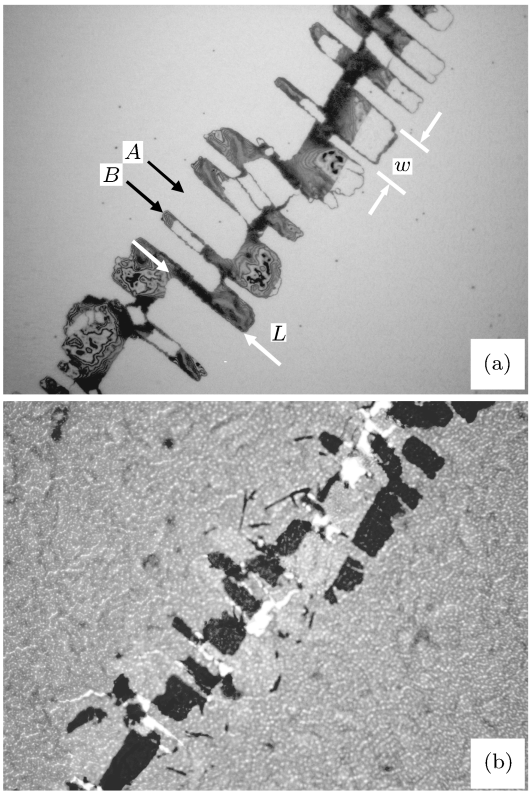


Fig.1. Typical morphology of a band existing in a Cu film sample, for f=0.05nm/s, Δt=1h, d=120nm. Each image has a size of $291 \times 216 \mu$m^2. (a) Determined by reflection mode; (b) determined by transmission mode.

A series of experiments were performed for further understanding the formation mechanism of the bands. Figure 2 shows the evolution of the bands in the Cu films with different nominal film thicknesses d but identical deposition rate f=0.08nm/s. As d increases, the ramified Cu atomic aggregates grow and connect with each other,[17] and then a continuous film forms gradually (see Fig.2(a)); for d >80.0nm, the bands, shown in Fig.2(b), start to grow and irregular

domains appear; when the film thickness $d \approx 100.0$nm, the bands with parallel rectangle domains form obviously, i.e., the domains grow regularly in the films; for $d > 180.0$nm, most of the domains appear irregularly but do not disappear. The results in our experiment are close to that of Xia and Yang,[15] in which Au films are deposited onto the silicone oil surfaces and the Au domains appear when $20.0\text{nm} \leq d \leq 80.0\text{nm}$. Therefore, we consider the evolution behaviours of the internal stress patterns are dependent on the material characteristics of the films.

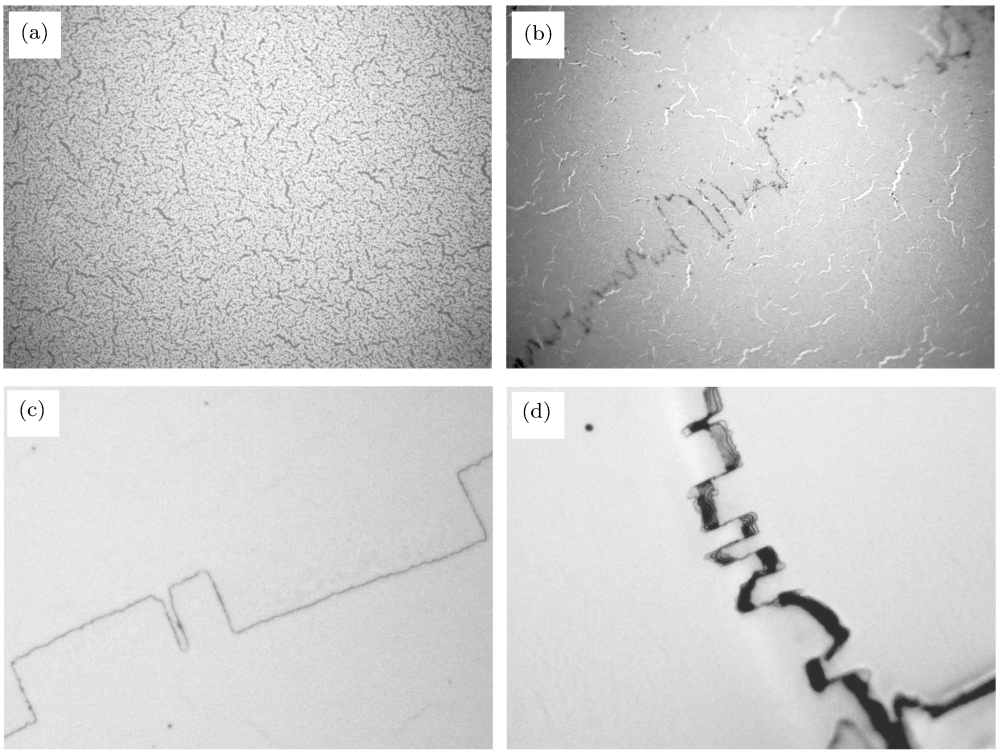


Fig.2. Evolution of the bands with the nominal film thickness d, for f=0.08nm/s, Δt=1h. Each reflection optical micrograph has a size of $291\times216\mu\text{m}^2$. (a) d=10nm; (b) d=90nm; (c) d=160nm; (d) d=200nm.

It can also be seen from Fig.2 that the domain length changes clearly when d increases. The dependence of the maximum length L_m of the domains on the film nominal thickness d has been systematically measured in our experiment and the corresponding result is shown in Fig.3. We find that, as d increases, L_m first increases and then drops monotonically. Based on the above experimental results, we suggest that the internal stress in the Cu films, which should be responsible for the band morphology, first increases with d and then decreases in the higher film thickness region.

In our experiment, if we increase the deposition time τ (i.e., increase the nominal film thickness when the deposition rate f is fixed), a larger amount of heat energy will reach the sample surface, which will result in the increase of the sample surface temperature.[12] In this case, the thermal expansion and the mobility of both the film and the oil substrate will go up obviously, which finally result in the positive slope of L_m-d curve (see Fig.3). On the other hand, if we further increase time τ , then the film becomes thick enough, i.e., $d > 140.0$nm in Fig.3, so that the thick Cu film on

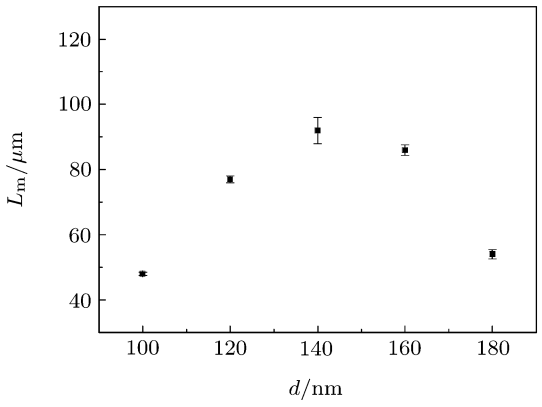


Fig.3. Dependence of the maximum domain length L_m on the nominal film thickness d.

the oil surface may shield the liquid substrate from the heat radiation of the filament and the bombardment of the subsequent deposited atoms. This shielding effect would weaken the thermal expansion of the liquid substrate, therefore the internal stress in the film decreases with the film thickness, which results in the negative slope of L_m-d curve shown in Fig.3.

Figure 4 shows the dependence of the ratio β ($\beta = \sum w_a / \sum w_b$) on the film thickness d, where $\sum w_a$ and $\sum w_b$ represent the corresponding total domain widths on the two sides of the band, respectively. It is noted that the values of β are around unity in our experiment, indicating that each band in the film is nearly axial symmetrical though the widths of each pair of vicinal domains in the band are generally different. The symmetric structures of the bands in Fig.4 are quite reasonable, since the symmetric and parallel structure of the domains in each band may balance the space deformation and then relieve the total free energy of the films.[5]

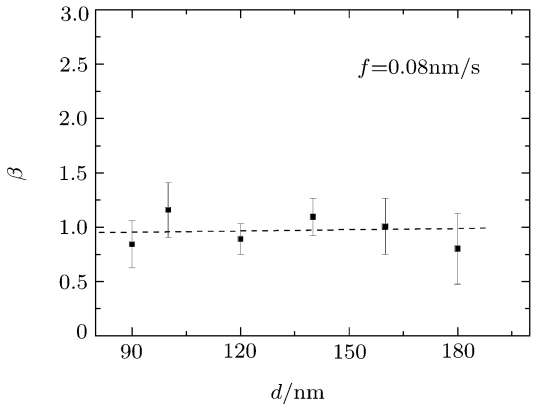


Fig.4. The ratio β as a function of the nominal film thickness d. The dashed line is a linear fit to the experimental data.

3.2. Two-time deposition method

Recently many, research efforts have been directed towards the formation mechanism of the ordered patterns in the film system on the liquid substrates.[14,15] Unfortunately, the exact time period, in which the ordered patterns form during or after the deposition, still remains unknown. In order to investigate the time period, a two-time deposition method has been introduced as follows:

(1) The evaporating material Cu was deposited on the silicone oil substrate with proper deposition rate f_1 and film thickness d_1.

(2) Then the sample was kept in the vacuum chamber for time period Δt_1. After that, Cu atoms were deposited on the substrate once again with suitable deposition rate f_2 and film thickness d_2.

(3) After another time interval Δt_2, the sample was removed from the vacuum chamber and all images of the surface morphology of the sample were taken immediately with an optical microscope.

In order to reduce the heat radiation effect on the film surface morphology formed before the second deposition, we assume that $d_2 << d_1$ in our experiment, then compared with the first deposition time τ_1, the second deposition time τ_2 is quite small (for example, in Fig.5, τ_1=2200s, τ_2=600s). Therefore, the heat radiation effect on the film surface morphology during τ_2 can be ignored.

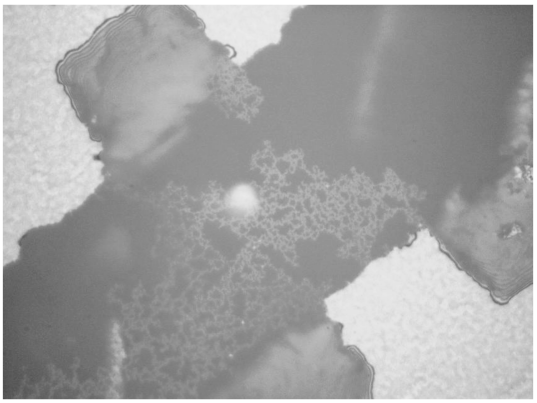


Fig.5. The morphology of a Cu film sample prepared by the two-time deposition method, for f_1=0.05nm/s, d_1=110 nm, Δt_1=12h; f_2=0.5nm/s, d_2=30nm, Δt_2=1h. The reflection optical micrograph has a size of $146\times108\mu m^2$.

Figure 5 shows the typical morphology of a Cu film sample prepared by the two-time deposition method. It is noticed that, in the crack of the band, ramified Cu atomic aggregates appear obviously. We propose that the phenomenon shown in Fig.5 can be traced to two stages: (1) First, during τ_1 and Δt_1, the continuous Cu film forms gradually and the band-shaped structures with the characteristic domains appear. Then the temperature of the films drops and the domains in the band may separate from each other during the later stage of Δt_1, which results in the crack in the film. (2) During τ_2 and Δt_2, Cu atoms are deposited on the oil surface in the cracked aggregate and form branched islands,[17] which leads to the existence of the branched aggregates and the domains simultaneously, as shown in Fig.5. Therefore, Fig.5 suggests that the ordered patterns have already formed

in the continuous Cu films before the second deposition. Comparing the experiments shown in Figs.1, 2 and 5, we can conclude that the ordered patterns really form in the vacuum chamber before it is filled with air.

Several works have attempted to theoretically understand the evolution of the stress-relief patterns in thin films.[14,16,18] It has been shown that various sinusoidal stress-relief patterns may exist simultaneously in the films on liquid surfaces. According to the Fourier transform principle, each characteristic appearance of the bands shows a corresponding spatial frequency spectrum. The experimental results shown in Figs.1, 2 and 5 indicate that the frequency spectra of the internal stress patterns in the nearly freely sustained Cu films are quite plentiful. Then the composition of the various sinusoidal stress patterns with different periods, phases and amplitudes results in the formation of the domains and then the band morphologies in the films. Therefore, the phenomenon shown in Fig.5 gives an evidence that strong internal stresses and stress-relief patterns with plentiful frequency spectra really exist in the Cu films before the second deposition.

4. Conclusion

In summary, we have described the formation mechanism of the large ordered stress-relief patterns in the Cu films deposited on silicone oil surfaces. The ordered patterns are composed of a large number of parallel domains. The sizes as well as the morphology of the domains depend on both the film thickness and the deposition rate. With the increase of the film nominal thickness, the evolution of the domain shapes is observed apparently: (1) Firstly, around d=80.0nm, the irregular domains start to appear. (2) Subsequently, for 100.0nm< d <180.0nm, the bands with rectangular domains form apparently in the films. (3) Finally, when d >180.0nm, the domains become irregular again. The experimental result obtained by the two-time deposition method confirms that the ordered patterns really form in the vacuum chamber before the chamber is filled with air.

The two-time deposition method provides us the direction to further study the formation process of the ordered patterns precisely. It is expected that the films deposited on liquid substrates by the two-time deposition method with different d_1, f_1, Δt_1, d_2, f_2 and Δt_2 may possess distinctive internal stresses, microstructures and other physical properties.

Recently, researchers have been much interested in both the theoretical understanding of the origin of the internal residual stress[19] and the experimental study on the formation and microstructure of corrugated films.[20] As is known, the internal stress and other physical properties of the films deposited on solid, liquid or polymer surfaces are strongly related to the characteristic microstructures of the films. Consequently, both experiments and calculations aimed at determining the microstructure of the films deposited on liquid substrates are now in progress. We believe that the mechanical property, including the evolution of internal stress relief, electrical behaviour and magnetic characteristics of the films on liquid substrates can be well understood with the further study on its microstructures.

References

[1] Shintani A, Sugaki S and Nakashima H 1982 *J. Appl. Phys.* **51** 165
[2] Pan A and Green J E 1981 *Thin Solid Films* **78** 25
[3] Bagchi A and Evans A G 1996 *Interface Sci.* **3** 169
[4] Murakami M, Kuan T S and Blech I A 1982 *Treatise on Materials Science and Technology* (New York: Academic) Vol.24
[5] Abdallah A A, Kozodaev D, Bouten P C P, den Toonder J M J, Schubert U S, and de With G 2006 *Thin Solid Films* **503** 167
[6] Ohzono T and Shimomura M 2004 *Phys. Rev.* B **69** 132202
[7] Brune H, Giovannini M, Bromann K and Kern K 1998 *Nature* **394** 451
[8] Shull A L and Spaepen F 1996 *J. Appl. Phys.* **80** 6243
[9] Koch R 1994 *J. Phys.: Condens. Matter.* **6** 9519
[10] Hoffman R W 1966 *Phys. Thin Films* **3** 211
[11] Ye G X, Michely Th, Weidenhof V, Friedrich I and Wuttig M 1998 *Phys. Rev. Lett.* **81** 622
[12] Ye G X, Zhang Q R, Feng C M, Ge H L and Jiao Z K 1996 *Phys. Rev.* B **54** 14754
[13] Jin J S, Xia A G and Ye G X 2002 *Acta Phys. Sin.* **51** 2144 (in Chinese)
[14] Yu S J, Zhang Y J, Ye Q L, Cai P G, Tang X W and Ye G X 2003 *Phys. Rev.* B **68** 193403
[15] Xia A G, Yang B, Jin J S, Zhang Y W, Tang F and Ye G X 2005 *Acta Phys. Sin.* **54** 302 (in Chinese)
[16] Cai P G, Yu S J, Ye Q L, Jin J S and Ye G X 2003 *Phys. Lett.* A **312** 119
[17] Chen M G, Xie J P and Ye G X 2006 *Phys. Lett.* A **360** 323
[18] Nir D 1984 *Thin Solid Films* **112** 41
[19] Chason E, Sheldon B W and Freund L B 2002 *Phys. Rev. Lett.* **88** 156103
[20] Bertel St and Abermann R 2005 *Thin Solid Films* **473** 1