Expansion effect of liquid substrates on the ordered structures in the Al films

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Abstract

An aluminum (Al) film system deposited on silicone oil drop surfaces by thermal evaporation method has been fabricated. A characteristic ordered pattern, namely, band, is observed in the continuous Al film system. Each band is composed of a large number of parallel key-shaped domains, which formed naturally during the deposition. It is found that these bands develop along the circumference of the silicone oil substrates and the length of the key-shaped domains show a marked dependence on the liquid expanding speed and other deposition conditions.

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1. Introduction

Most recent research effort has been directed towards the first stage of the mechanical failure of thin films. Stress distribution, stress origin, edge effects, grain boundaries, plastic flow and phase changes under stress are some of the topics treated in the recent literatures [1,2]. Films and coatings fabricated by vapor deposition, sputtering, etc., often develop residual compressive stresses during the deposition process itself [3,4]. Additional residual stresses may be induced during cooling when a thermal expansion mismatch exists between the films and the substrates [5,6]. Thin films containing such large residual compressive stress are susceptible to delamination and spalling or, when exposed to atmospheric conditions [7,8], deformation, which may result in very interesting topographical patterns [9–12]. Recently, it is reported that some characteristic microstructures may exist in the metallic film systems owing to the expansive and mobile nature of the silicone oil substrates [13–15]. Therefore, it is naturally speculated that various characteristic patterns, mirroring the internal stress distribution and evolution in the films, may occur apparently in these nearly free sustained films [16].

In this Letter, we report a large scale ordered pattern existing in a continuous aluminum (Al) film system deposited on silicone oil drop surfaces. The most interesting phenomenon is that the ordered pattern, namely band, develops along the circumferences of the silicone oil drops. The formation mechanism of the ordered pattern can be understood with the aid of experiments comparing different film thickness, deposition rates, and the expansion speed of the oil drops.

2. Experiment

The samples were fabricated by thermal evaporation of 99.99% pure Al in a vacuum chamber of $6 \times 10^{-4} \text{ Pa}$ at room temperature. A drop of pure commercial silicone oil (Dow Corning 705 Diffusion Pump Fluid, saturated vapor pressure $<10^{-8} \text{ Pa}$) with a diameter $\phi = 2–4 \text{ mm}$ was dripped on a piece of glass surface, which was fixed 190 mm above the evaporating filament (tungsten). The deposition rate $f$ and the nominal film thickness $d$ were determined by a quartz-crystal thickness monitor (a step-200 profilometer, TENCOR), which was located just beside the substrate. After the samples were removed from the vacuum system, all images for the surface morphologies of the

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3. Results and discussion

The schematic view of the Al film deposited on the oil drop surface is shown in Fig. 1. An important phenomenon in the experiment is that the radius of the oil drop expanded steadily during deposition mainly due to the heat radiation from the filament and the bombardment of the deposition atoms [13,14], which is the key property of the liquid drops used in our experiment. For each sample, there is a ring-shaped Al film on the glass surface, as shown in Fig. 1(b). The film thickness in the ring-shaped film increases linearly from the inner radius \( r_1 \) to the outer radius \( r_2 \) approximately, indicating that the oil drop expands and its radius \( r \) (or its radius increment \( \Delta r = r_2 - r_1 \)) increases uniformly during the deposition [14].

The typical ordered patterns, i.e., the bands, in the Al films deposited on the silicone oil drop surfaces are shown in Fig. 2. The bands are consisted of a large number of parallel key-shaped domains, namely keys, and generally the neighboring keys possess different width \( w \) but nearly uniform length \( L \) (see Fig. 2). The most interesting observation is that the bands almost develop along the circumferences of the silicon oil drops. In Fig. 2(b) we can see that two bands exist together along the film edge, which is approximately perpendicular to the expansion direction of the oil drop. In the experiment, we find that the average length of the keys in the bands, i.e., the average length of the bands, near the oil drop edges are usually larger than that of the bands which are located far away from the substrate edges (see Fig. 2(b)). The total length of each band in our experiment may be more than 10 mm. When the bands extend, they may undergo a gradual and slight change in their propagation directions. Depending on the nominal film thickness \( d \), deposition rate \( f \) and the locations, the size of the keys varies widely from a few micrometers to several hundred micrometers. The maximum length and width of the keys observed in our experiment are \( L_m \approx 180 \, \mu \text{m} \) and \( w_m \approx 400 \, \mu \text{m} \), respectively.

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 bucking patterns such as sinusoidal shapes [17,18]. We propose here that the ordered patterns shown in Fig. 2 also originate from spontaneous material organization owing to the stress relief. According to the previous studies [19–21], strong and detectable residual internal stress always exists in metallic films deposited on liquid substrates and characteristic stress-induced surface morphologies can be observed in these nearly free sustained films. We believe that the Al films and the silicon oil substrates both expand during deposition owing to the heat radiation from the
In the subsequent cooling process, the contraction behaviors of the films and the substrates result in the detectable residual internal stress, which may be relieved by the spontaneous formation of the bands. On the other hand, we suggested that the formation of the bands should be related to the expansion effect of the oil drops since the bands extend along the edges of the oil drops.

During deposition, when the oil drop was covered with several layers of Al atoms, the volume of oil drop increased and its surface tension decreased due to the local temperature rise, which would result in the increase of the radius $r$. This process continued through all the deposition period and finally a metallic film with a characteristic inhomogeneous edge formed on the edge of the oil drop surface, as shown in Figs. 1 and 2 [13]. In viewing of this, we propose that the occurrence of the ordered pattern illustrated in Fig. 2 are dependent on the instability growth of the inhomogeneous film edge since poorly bonded areas or heterogeneities in the layer may cause buckles, ripples or cracks [22]. If the qualitative growth model described above is correct, the compressive stress distribution in samples should be quite different from those of the other films [22].

A series of experiments and measurements were performed for further understanding the formation mechanism of the bands. Fig. 3 shows the dependence between the maximum length $L_m$ of the keys and the film thickness $d$. It can be seen in Fig. 3 that, as the thickness $d$ increases, the length $L_m$ increases first and then drops monotonically. In fact, in our experiment, the ordered patterns can be observed only in the films with 40.0 nm < $d$ < 120.0 nm, indicating the evolution behavior of the internal stress pattern in the Al films with the film thickness.

For thinner films, i.e., $d$ < 70 nm in Fig. 3, as the film thickness increases, more and more heat radiation reaches the sample surface and the relative motion between the film and the oil increases due to the thermal expansion of the oil and the thermal motion of the thin Al atomic layer. Therefore, the internal stress in the Al film increases, which may result in the increase behavior of $L_m$ when $d$ < 70 nm in Fig. 3. On the other hand, for thicker films, i.e., $d$ > 70 nm in Fig. 3, as the film thickness increases, the Al film on the silicone oil surface would shield the liquid substrate from the heating radiation of the filament and the bombardment of the subsequent deposited atoms directly. This shielding effect would weaken the thermal expansion of the liquid substrate and therefore the internal stress in the film decreases with the film thickness, which may result in the decrease behavior of $L_m$ when $d$ > 70 nm in Fig. 3.

Most probably, the large inertia property and the strength of the thicker films also contribute to the decrease behavior of $L_m$ when $d$ > 70 nm.

Figs. 4 and 5 show the dependence between the average key length $L_a$ and the deposition rate $f$. It can be seen from Fig. 5 that $L_a$ drops quickly with the rate $f$. If $f$ goes beyond a critical rate $f_c$, the stress relief patterns disappear. Our experiments show that the value of $f_c$ depends on the film thickness $d$ and it generally goes up when $d$ increases. For the sample with $d$ = 70 nm, for instance, $f_c$ ≈ 0.40 nm/s.

According to the previous experimental studies [13], the total radius increment $\Delta r = r_2 - r_1$ (see Fig. 1) resulted from the thermal expansion effect is mainly controlled by the deposition period or by the deposition rate $f$. For the films with a fixed thickness, the larger the rate $f$ is, the smaller the radius increment $\Delta r$ will be. Therefore, the phenomenon in Fig. 5 indicates that the average key length $L_a$ increases with the radius incre-
Fig. 5. The average key length $L_a$ of the samples as a function of the deposition rate $f$. $d = 70.0$ nm/s.

Fig. 6. The average key length $L_a$ vs expansion speed $v$ of the oil drops. $d = 50.0$ nm, $f = 0.10$ nm/s. The dash line is a fit to the experimental data (black dots).

4. Conclusion

In summary, we have described the experimental observations of the large ordered structures in the Al films deposited on silicone oil drop surfaces. The ordered structures, or bands, are composed of a large number of parallel keys with different width but nearly uniform length, which are normally develop along the circumferences of the silicon oil drops. The average length of the key-shaped domains in each band displays a marked dependence on the expansion speed of the liquid substrate, deposition rate, film thickness and other deposition conditions.

The phenomena presented in this Letter provide us with an example that, due to the expansion and flowing behaviors of the liquid substrates, the films deposited on the substrates may possess distinctive internal stresses, characteristic microstructures and subsequently anomalous physical properties. Up to now, the details of the growth mechanism of the film microstructures, which should be mainly responsible for the exact patterns of the internal stress distribution in the films, still remain poorly understood. Therefore, further experimental and theoretical studies on these nearly free sustained metallic films are still needed.

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