Thin Solid Films 651 (2018) 131–137

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Ring-shaped buckles in metal films induced by evaporation of micro-scaled silicone oil droplets

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ARTICLE INFO

Keywords:
Thin film
Buckling
Delamination
Internal stress
Ring-shaped pattern

ABSTRACT

We report on the spontaneous formation of ring-shaped buckles in cobalt films induced by evaporation of micro-scaled silicone oil droplets. Many small silicone oil droplets were generated on the glass substrate near a silicone oil reservoir during deposition. Due to the coffee ring effect, the silicone oil residue tends to gather at the droplet edges when the silicone oil evaporates, which results in the interfacial weakening and formation of ring-shaped buckles. The structural characteristics of the ring-shaped buckles have been investigated by atomic force microscopy, focused ion beam milling, numerical simulation and theoretic analysis. The maximum buckle height is found to increase approximately linearly with increasing the buckle width, but it is insensitive to the ring size. The structure characteristics of the ring-shaped buckles for small ratio of ring diameter to buckle width are also investigated by numerical simulation.

1. Introduction

High compressive stresses are very common in elastic films deposited on rigid substrates due to intrinsic (non-equilibrium growth, lattice mismatch, etc.) and extrinsic (thermal mismatch, external loading, etc.) factors. When the residual stress is beyond a critical value, namely buckling threshold, the films are susceptible to delaminating from the substrates, resulting in many fascinating buckling patterns such as circular blisters, finger branches, straight-sided buckles, streams of bubbles and telephone cord structures. Both the theoretical studies and experimental observations showed that the straight-sided buckles (Euler mode) are first appeared when the residual compression is slightly larger than the buckling threshold [1–3]. They tend to change into other buckle-delamination morphologies (mainly the telephone cord structures [4–7]) as the residual stress increases to trigger a secondary buckling instability. The stability diagram theory further predicted that the straight-sided buckles and streams of bubbles are associated with high anisotropy of stresses, whereas the telephone cord structures are more stable under high isotropic stresses [8,9]. The straight-sided buckles are favorable for higher transversal stress and the streams of bubbles are favorable for higher longitudinal stress. This theoretical prediction has been confirmed by many experimental observations by tuning the stress anisotropy using mechanical loading/unloading. For examples, the straight-sided buckling mode is favorable under uniaxial external loading [10,11]. As the uniaxial compression is released, the straight-sided buckles may evolve into streams of bubbles or telephone cord structures [12,13]. Our previous studies showed that the straight-sided and telephone cord buckles with smaller delamination widths can change into bubbles after ridge cracking due to the stress anisotropy near the cracks [14,15]. Many previous studies also showed that the circular blisters can spontaneously form due to film impurities [16] or be triggered by indentation [17] in homogeneous films. If the sizes are very small, the circular blisters can be stable. When they grow, however, the edges destabilize gradually to form finger branches and telephone cord buckles [16–18].

The circular blisters, finger branches, straight-sided buckles, streams of bubbles and telephone cord structures have been extensively investigated in experiments and based on continuum elastic theory (Föppl–von Karman equations). Recently, an elegant study showed that a ring-like blister could be formed due to the combined interaction of film plasticity and atmosphere pressure [19]. It seems that the ring-shaped buckles possess harsh formation condition and they are very rare in experiments. In this paper, we report on the spontaneous formation of ring-shaped buckles in cobalt films by generating micro-scaled silicone oil droplets on the glass substrate during deposition. The silicone oil residue tends to gather at the droplet edges due to the coffee ring effect when the silicone oil evaporates [20,21]. We believe that formation of the observed ring-shaped blister may be due to the

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https://doi.org/10.1016/j.tsf.2018.02.029
Received 14 September 2017; Received in revised form 11 February 2018; Accepted 17 February 2018

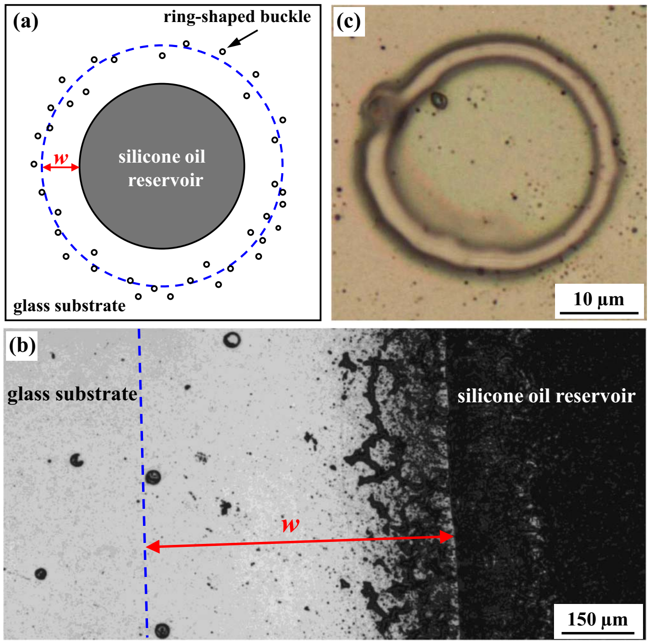

Fig. 1. (a) Schematic drawing of the formation of ring-shaped buckles near a silicone oil reservoir. (b) Typical surface morphology of the cobalt film near the silicone oil reservoir taken by the optical microscopy. (c) The ring-shaped buckle shown at a higher magnification. The letter *w* represents the average distance from ring-shaped buckles to silicone oil edge.

propagation of the buckle-delamination templated by the ring-like low adherence area. The structure characteristics of the ring-shaped buckles are investigated by using optical microscopy, atomic force microscopy and focused ion beam milling. The ring-shaped buckles with varied sizes are recovered and elucidated by numerical simulation and theoretic analysis based on Föppl-von Kármán plate theory, in good agreement with the experimental observations.

2. Experimental details

The samples were prepared by direct current magnetron sputtering technique at room temperature. Before deposition, a large silicone oil drop with ~4 mm diameter (DOW CORNING 705 Diffusion Pump Fluid) was dripped onto a clean glass surface, serving as a silicone oil reservoir, as sketched in Fig. 1(a). The glass is simple microscope slides with 1.2 mm thickness, purchased from Citotest Labware Manufacturing Company in China. The glass surface is partially wetted with the silicone oil and the equilibrium contact angle is about 50°. Then the glass substrate was placed into the vacuum chamber for film deposition. The sputtering target was a cobalt disk (purity 99.9%) with the diameter of 60 mm. The target-substrate distance was about 80 mm. The sputtering power was fixed to be 100 W and the deposition time was 20 min. The film thickness, measured by a focused ion beam (FIB 200), was ~600 nm. The surface morphologies of the sample were taken with an optical microscope (Leica DMLM), equipped with a charge coupled device camera (Leica DC 300). The structural details and cross sections of buckling patterns were determined by the focused ion beam and an atomic force microscopy (Dimension 3100, Veeco) operated in tapping mode.

3. Results and discussion

3.1. Morphologies of ring-shaped buckle

The typical surface morphology of the cobalt film near the silicone oil reservoir is shown in Fig. 1(b). On the silicone oil surface, the cobalt film tends to form wrinkling patterns, where the film remains well attached to the substrate [22]. On the glass substrate that is very close to the silicone oil reservoir, disordered delaminating or wrinkling patterns can be observed. As the distance from the oil edge increases, the disordered delaminating or wrinkling patterns disappear gradually and finally a comparatively smooth cobalt film forms. Unexpectedly, some ring-shaped buckles can be observed in this film region, as shown in Fig. 1(b). The ring-shaped buckles only appear near the silicone oil reservoir. The average distance from the ring-shaped pattern to the oil edge, namely *w*, is about 600 μm. A ring-shaped buckle is enlarged as shown in Fig. 1(c). Since the ring-shaped buckles are only appeared near the silicone oil reservoir, the formation of this pattern should be closely related to the silicone oil.

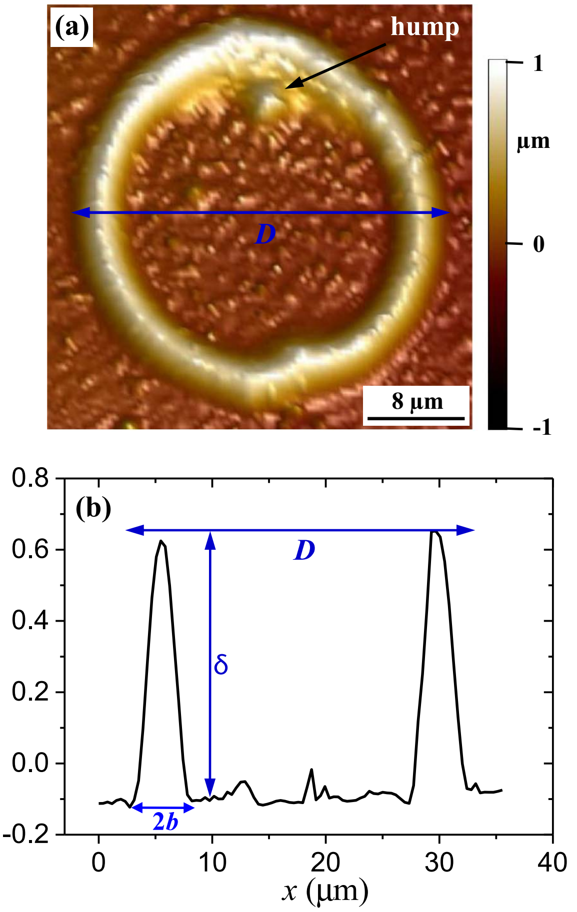

Fig. 2. Typical atomic force microscopy (AFM) image (a) and corresponding profile (b) of the ring-shaped buckle. The ring diameter, half buckle width and maximum buckle height are denoted as *D*, *b* and *δ*, respectively. The black arrow denotes the circular hump.

In order to detect more structural details of the ring-shaped pattern, it has been taken by the AFM and FIB, as shown in Figs. 2 and 3, respectively. We find that the film regions inner and outside of the ring are located at the same level, suggesting that the film inner the ring remains well attached to the glass substrate. The diameter of the ring buckle is defined as the distance between the outer buckle minimums, namely *D*. The half width and maximum height of the buckle are defined as *b* and *δ*, respectively, as shown in Fig. 2(b). In our experiment, the observed smallest ring is about 19 μm, whereas the largest ring can be beyond 34 μm. The morphologies of the ring-shaped buckles with varied sizes are shown in Fig. 4(a)–(d). In order to further understand the mechanical mechanism of the ring-shaped buckles, we measured the dependence of the buckle height *δ* on the half width *b* for different ring sizes, and the result is shown in Fig. 4(e). These values were obtained by measuring more than 30 ring (or half ring) buckles in the