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# Hillock growth in CuZr metallic glass



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## ABSTRACT

While hillock has so far been only observed in crystalline metals, here we show that hillock appeared on the surface of CuZr metallic glass film after annealing treatment. Other than compressive stresses generated upon annealing, surface selective oxidation processes, i.e., preferential oxidation of zirconium arouses the formation of surface ZrO<sub>2</sub> layer and Cu-enriched area in the subsurface, were proposed to play a crucial role in hillock formation in metallic glasses. Cu atoms diffused faster than Zr from the Cu-enriched area towards the film surface, promoting the formation of Cu or Cu-enriched hillocks. Different from the diffusion mechanism in crystal films, the mechanism of atom diffusion to surface with vacancy to relieve compressive thermal stresses dominated the formation of hillocks in CuZr metallic glass films.

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## 1. Introduction

Hillock formed in crystalline metals have been investigated for decades, as a hillock could grow long enough to ridge neighboring conductors and create short circuits in electronic devices. For crystalline thin films, numerous diffusion mechanisms including surface diffusion [1], lateral diffusion [2], interfacial diffusion [3], and grain-boundary diffusion [4] have been proposed to interpret the physical formation process of hillocks; and it has been widely accepted that compressive stresses plays a key role in hillock formation [2,3,5–7]. However, only a few studies, if any, have concerned on hillocks formed in metallic glasses.

Unlike crystalline metals, the atomic structure of a metallic glass exhibits short (medium)-range ordering. Attributed to the specific “disordered” local structure, metallic glass exhibits unique mechanical properties superior to that of their crystalline counterparts, such as large elastic limit, high strength and strong wear resistance, etc. [8]. Then, metallic glasses emerged to be potential applications in the areas such as sport industry, aeronautical field, medical application, magnetic device and micro electro-mechanical systems, etc. [9]. Similar to the crystal materials, specifically, hillock formation may also reduce the lifetime of metallic glass devices. Therefore, the possibility and formation mechanisms of hillock formation in metallic glass need to be explored for the purpose of inhibiting hillock and improving the engineering application of metallic glasses.

For metallic glass with no crystal lattice structures inside, solid-state mass transport could only occur through free volume or shear transformation zone. In addition, as metallic glass is in an unstable state, structure relaxation is inevitable to change the atomic structure progressively towards more stable state. This process involves atomic diffusion and rearrangements of the atomic structure, which should be considered for the hillock formation in metallic glass. Therefore, the mechanisms related to dislocation and grain boundary previously proposed in crystal materials may not operate in the formation of hillocks in metallic glasses. New formation model should be built considering the unique structure in metallic glass.

In the present study we report the formation of hillocks in annealed CuZr metallic glass thin films. By comparing hillocks formed between capped and un-capped CuZr metallic glass films, a model for hillock formation controlled by surface selective oxidation and vacancy diffusion in metallic glasses was proposed.

## 2. Experiment

CuZr based metallic glass films (~800 nm) were deposited on single crystal Si substrate by magnetron co-sputtering on Cu (30 W with direct current) and Zr targets (120 W with radio frequency). With identical sputtering condition, two bi-layer films by adding a 50 nm cap layer of crystal Cu (or Zr) on CuZr film surface were prepared without breaking the vacuum, i.e., Cu/CuZr/Si and Zr/CuZr/Si referred to hereafter. Subsequently, all the films were annealed at 200 °C and 350 °C for 2 h, respectively.

Surface morphologies of the annealed films were observed with scanning electron microscopy (SEM, SU-6600). The components of

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hillock were conducted by energy dispersive spectroscopy (EDS). Meanwhile, X-ray photoelectron spectroscopy (XPS) was used to characterize the bond state of Cu and Zr.

### 3. Results and discussion

Fig. 1 presents the surface morphologies of CuZr/Si films. Clearly, no precipitated particles (i.e., hillock) were observed in the as-deposited CuZr film [Fig. 1(a)], while lots of hillocks appeared in the surface of the 200 °C annealed sample [Fig. 1(b)] and much more in the 350 °C annealed one [Fig. 1(c)].

Correspondingly, as shown in Fig. 2, EDS analysis indicated that the composition of hillocks at 200 °C annealing was only Cu element [Fig. 2(a)], while at 350 °C it was Cu-enriched, containing tiny zirconium and oxygen [Fig. 2(b)].

By adding a crystalline cap layer, the formation of hillock was effectively suppressed. Specifically, for Cu/CuZr/Si, hillock was completely suppressed when it was annealed at either 200 °C [Fig. 3(a)] or 350 °C [Fig. 3(b)]. For Zr/CuZr/Si, however, only very few hillocks appeared

upon 350 °C annealing [Fig. 3(d)], while no hillock was observed if it was annealed at 200 °C [Fig. 3(c)].

The fact that abundant hillocks appeared in CuZr/Si films but were nearly completely suppressed with cap layer indicated that free surface plays a crucial role in the formation of hillocks in CuZr/Si. By examining the chemical states of Cu and Zr in the surface of CuZr/Si via XPS test, significant influence of selective surface oxidation was revealed, as discussed below. Through the peak-fit processing (red and blue line in Fig. 4), we obtained the characteristic peaks of Cu, Zr and O, which were labeled in the pictures. The characteristic peak indicated that, in the surface of CuZr/Si annealed at 200 °C or 350 °C, Cu atoms are not in bonded states while Zr atoms are bonded with oxygen to be ZrO<sub>2</sub>. Due to greater affinity of oxygen, Zr is oxidized prior to Cu [10–12]. The depletion of Zr to form ZrO<sub>2</sub> could inevitably result in composition segregation. Therefore, as a result of the back diffusion of Cu atoms from the oxide layer [11], a Cu-enriched subsurface formed underneath the ZrO<sub>2</sub> layer.

At the boundary between segregated regions, viscosity mismatch generated excessive free volume and enhanced diffusion and crystallization in metallic glasses [13]. Thus, we speculated that hillocks formed in CuZr metallic glasses may stem from Cu-enriched subsurface via diffusion related mechanisms, consistent with subsurface precipitation in crystalline materials [14].

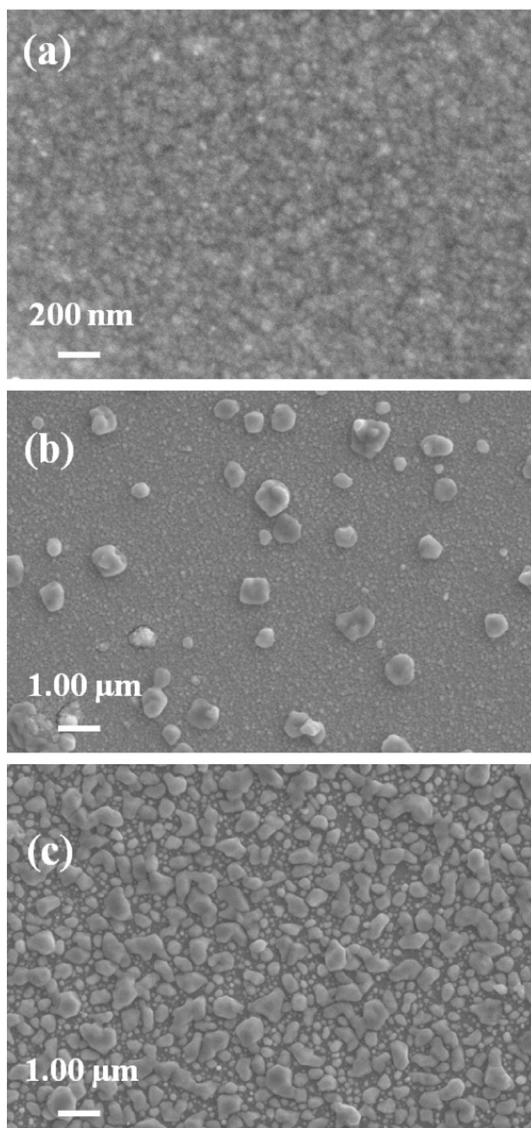


Fig. 1. Surface morphologies of (a) as-deposited, (b) 200 °C annealed and (c) 350 °C annealed CuZr/Si.

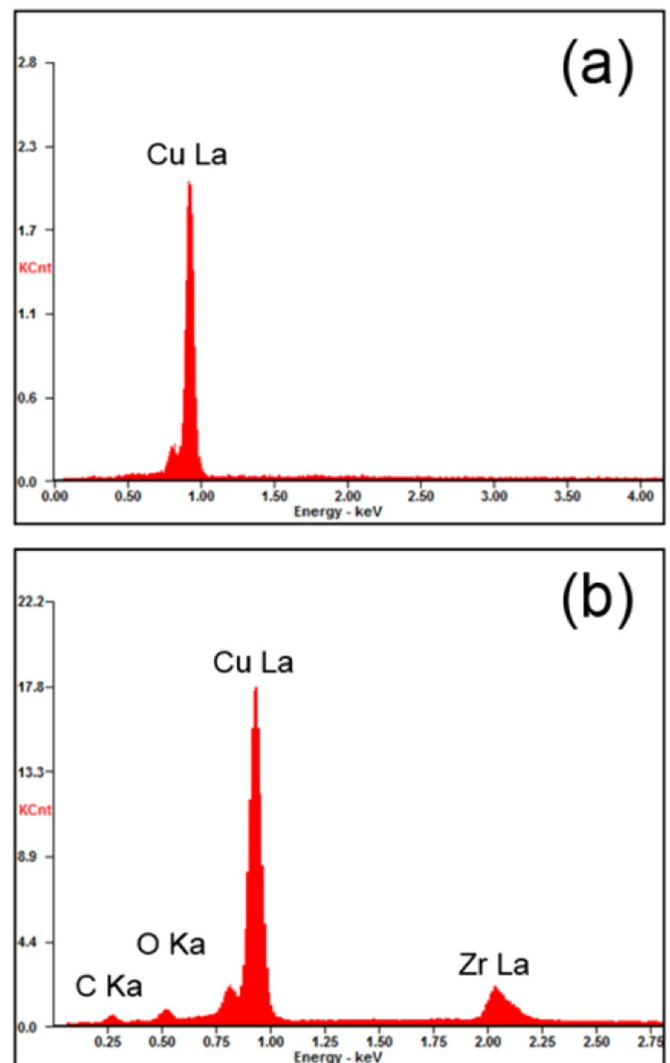


Fig. 2. EDS analysis of CuZr film annealed at (a) 200 °C and (b) 350 °C.

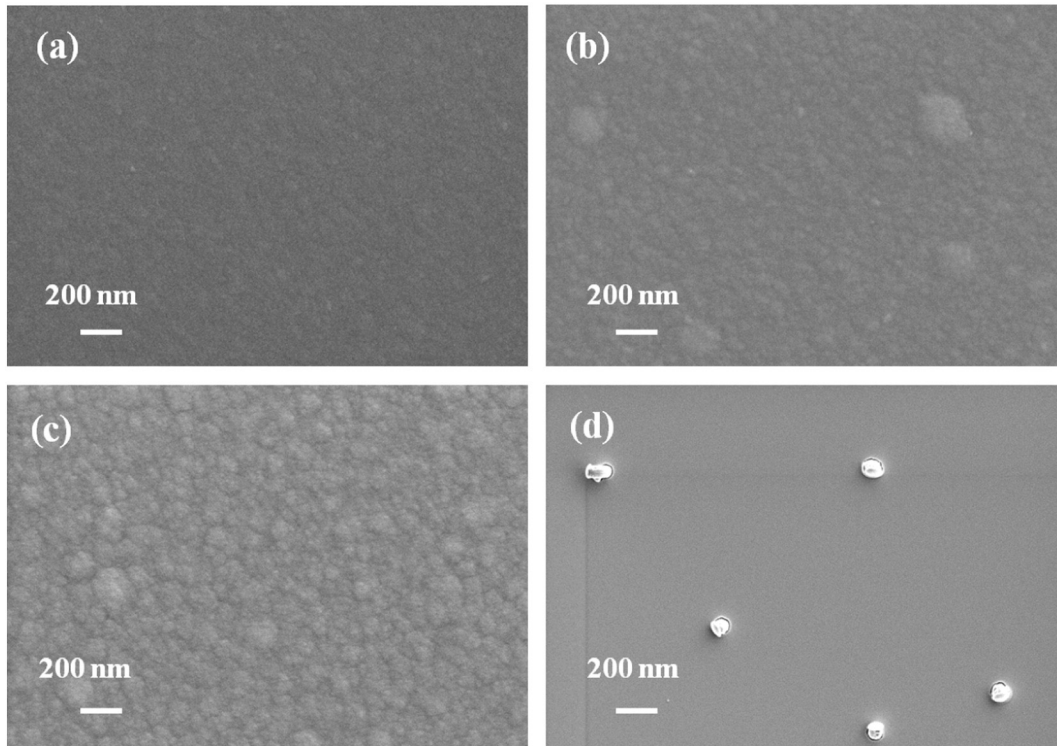


Fig. 3. Surface morphologies of Cu/CuZr/Si annealed at (a) 200 °C and (b) 350 °C and of Zr/CuZr/Si annealed at (c) 200 °C and (d) 350 °C.

Precipitating hillock was well known as a diffusion controlled process, and the diffusion rate could be described by the Stokes–Einstein relation:

$$D = \frac{k_B T}{6\pi r \eta} \quad (1)$$

where  $D$  was the diffusivity,  $T$  was the environmental temperature,  $r$  was the atomic radius,  $k_B$  was the Boltzmann constant, and  $\eta$  was the viscosity. Consequently, the diffusion rate of Cu should be faster than Zr as the atomic radius of Cu and Zr are 0.128 nm and 0.159 nm, respectively. As the effect of atomic radius on diffusion rate should not rely on whether the atomic structure is crystalline or amorphous, the diffusion controlled process previously proposed for the formation of hillock in crystalline metals could apply to metallic glasses as well.

Except for the model related to yield strength proposed by Hwang [15], compressive stress was required in nearly all the existing studies on hillocks formation in crystalline metals [2,3,5–7]. Upon annealing, the thermal stress in a film/substrate system could be calculated as:

$$\sigma_{th} = \left\{ \frac{E_f}{1-\nu_f} \right\} (\alpha_s - \alpha_f) (T_1 - T_0) \quad (2)$$

where  $E$ ,  $\nu$ ,  $\alpha$  and  $T$  were the Young's modulus, Poisson ratio, thermal expansion coefficient, and temperature, respectively; and subscript  $s$  and  $f$  represented separately the substrate and film. For the film/substrate system studied here:  $E_f = 120$  GPa,  $\nu_f = 0.3$ ,  $\alpha_f = 8.3 \text{ a}^{-6}/\text{K}$ ,  $\alpha_s = 2.6 \text{ a}^{-6}/\text{K}$ ,  $T_0 = 25$  °C and  $T_1 = 200$  °C (or 350 °C). Based on Eq. (2), the thermal stress in a CuZr film was compressive,  $-171$  MPa if annealed at 200 °C and  $-318$  MPa if annealed at 350 °C. In the presence of a larger compressive stress, more atoms diffused towards the surface, resulting in a larger density of hillocks; see Fig. 1(b) and (c).

However, the mechanism of grain boundary diffusion does not hold in the present CuZr metallic glass films, even though it was a plausible mechanism for hillock growth in crystalline films. As metallic glasses did not have periodic lattice structure, solid-state mass transport could only occur through free volume or shear transformation zone. As a stress relief process, free volume inside the metallic glass could be an important factor in hillock growth. Besides its influence on selective oxidation, free surface was a good source and sink of vacancy, enabling diffusion of atoms to surface due to more possibilities of atom/vacancy exchange. The contribution of free surface to hillock growth could be judged by examining the morphologies of Cu/CuZr/Si and Zr/CuZr/Si films shown in Fig. 3, for which the free surface was covered by cap layer. Further, it should be mentioned that very few hillocks were observed in Zr/CuZr/Si, and the mechanism underlying the formation of hillocks in capped metallic glass films will be explored in a future study.

Similar to hillock growth in crystalline films [3], compressive stresses in CuZr/Si films could not distribute uniformly. Stress gradient appeared in certain local areas, causing massive atom flow to relieve the stress. Moreover, a metallic glass was in metastable state in comparison with its crystalline counterpart. Upon annealing, structure relaxation would occur, but not in the same state everywhere. The diffusion coefficient was several orders higher in the un-relaxed area than that in the equilibrium state [16]. In the presence of compressive thermal stresses, Cu atoms were preferably pushed out from its base to nucleate a hillock in a specific location. Once a hillock was nucleated, the vacancies where the escaped Cu atoms occupied previously became the diffusion path, enabling the Cu atoms to flow successively to the hillock until the local stress gradient was effectively eliminated.

Fig. 5 displayed schematically the mechanism underlying hillock formation in annealed CuZr metallic glass thin films. With selective oxidation of Zr, a Cu-enriched subsurface layer formed due to element segregation. Cu atoms in the subsurface moved towards the surface, leaving abundant vacancies, and precipitated on the surface to relieve compressive stresses generated due to thermal expansion mismatch upon annealing.



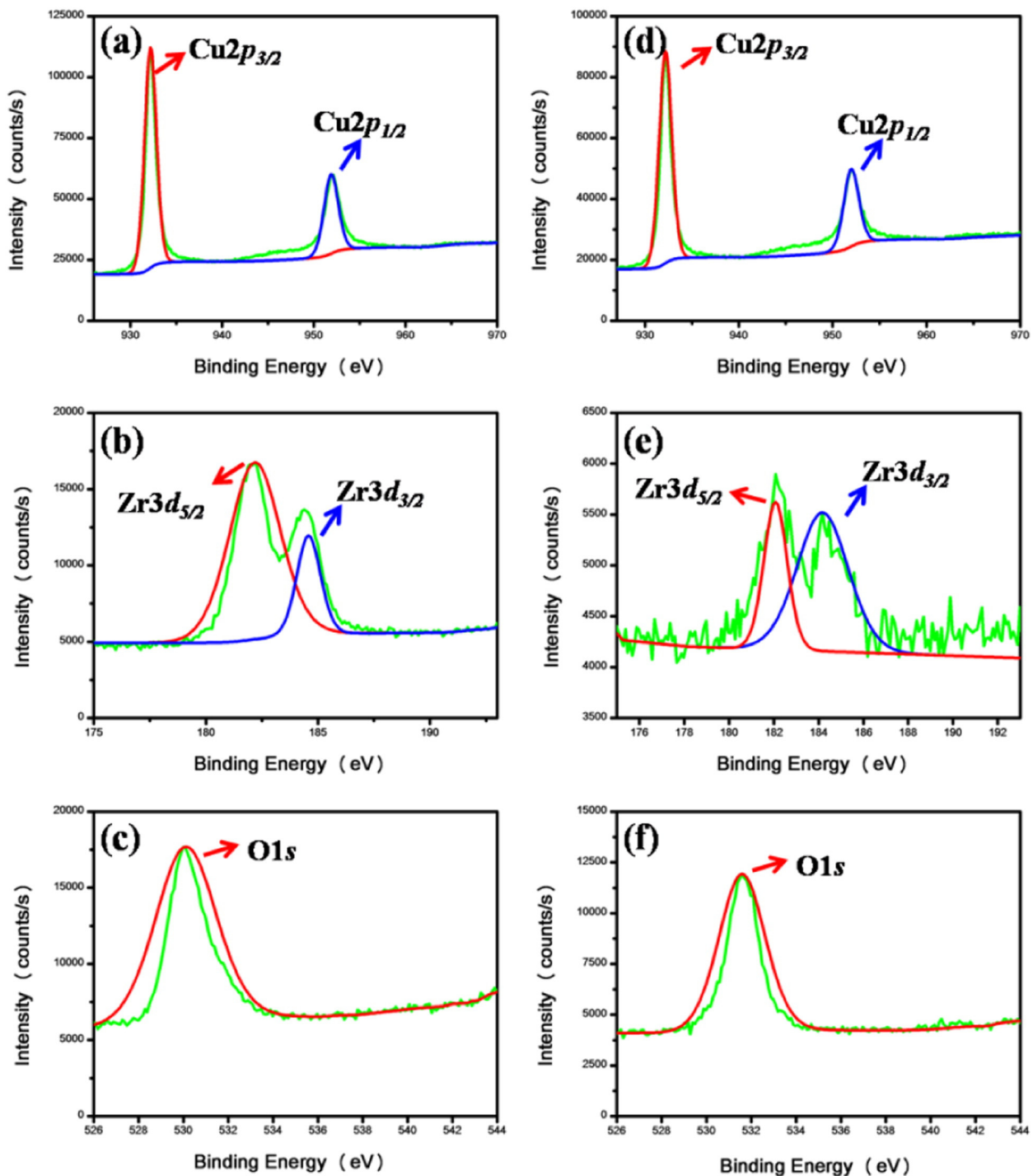


Fig. 4. XPS results of Cu (a), Zr (b), and O (c) spectra from annealed films at 200 °C; (d), (e) and (f) characterize element states of Cu, Zr and O at 350 °C. The green line is the original results of XPS test; the red and blue lines are obtained through the peak-fit processing. The characteristic peaks of Cu, Zr and O have been labeled in the pictures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

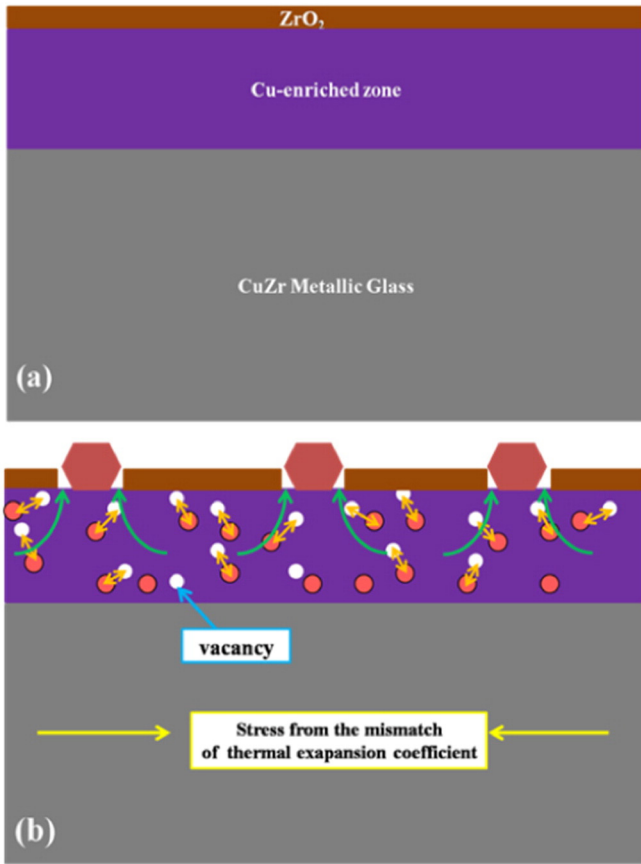
#### 4. Conclusion

Formation of hillocks was observed in CuZr metallic glass thin films. Pure Cu (or Cu-enriched) hillocks appeared in annealed CuZr/Si samples but not in as-deposited ones. The larger compressive stress generated upon annealing, the more hillocks formed. Introducing a crystalline cap layer on the top of CuZr/Si suppressed completely the formation of hillocks. It was proposed that both element segregation induced by elective surface oxidation of Zr and vacancy diffusion of Cu atoms driven

by compressive thermal stresses contributed to hillock growth in CuZr metallic glasses.

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**Fig. 5.** Schematic of hillock growth process in annealed CuZr metallic glass thin film: (a) selective oxidation of Zr led to the formation of  $ZrO_2$  and Cu-enriched layer; (b) atoms in Cu-enriched zone moved towards surface, leaving abundant vacancies, and precipitated on the surface to relieve compressive thermal stresses.

## References

- [1] H.L. Wei, L. Zhang, Z.L. Liu, H.C. Huang, X.X. Zhang, *J. Cryst. Growth* 297 (2006) 300.
- [2] E. Iwamura, T. Ohnishi, K. Yoshikawa, *Thin Solid Films* 270 (1995) 450.
- [3] P. Chaudhari, *J. Appl. Phys.* 45 (10) (1974) 4339.
- [4] K. Tsujimoto, S. Tsuji, H. Saka, *Philos. Mag. A* 81 (2) (2001) 287.
- [5] H.L. Sun, Z.X. Song, F. Ma, K.W. Xu, *Appl. Surf. Sci.* 255 (2009) 8972.
- [6] H.L. Sun, Z.X. Song, F. Ma, J.M. Zhan, K.W. Xu, *Scr. Mater.* 60 (2009) 305.
- [7] C. Kylner, L. Mattsson, *J. Mater. Res.* 14 (10) (1999) 4087.
- [8] C. Schuh, T. Hufnagel, U. Ramamurty, *Acta Mater.* 55 (12) (2007) 4067.
- [9] J.C. Qiao, J.M. Pelletier, *J. Mater. Sci. Technol.* 30 (6) (2014) 523.
- [10] W. Kai, W.S. Chena, Y.H. Wua, P.C. Lin, C.P. Chuang, P.K. Liaw, *J. Alloys Compd.* 5365 (2012) S103.
- [11] K.R. Lim, W.T. Kim, D.H. Kim, A. Gebert, J. Eckert, *J. Mater. Res.* 27 (8) (2011) 1178.
- [12] K.R. Lim, J.M. Park, S.S. Jee, S.Y. Kim, S.J. Kim, E.-S. Lee, W.T. Kim, A. Gebert, J. Eckert, D.H. Kim, *Corros. Sci.* 73 (2013) 1.
- [13] K.J. Laws, D.W. Saxey, W.R. McKenzie, R.K.W. Marceau, B. Gun, S.P. Ringer, M. Ferry, *Mater. Sci. Eng. A* 556 (2012) 558.
- [14] N.D. Rosen, *Surf. Interface Anal.* 24 (1996) 119.
- [15] S.-J. Hwang, W.D. Nix, Y.-C. Joo, *Acta Mater.* 55 (2007) 5297.
- [16] H.S. Chen, L.C. Kimerling, J.M. Poate, W.L. Brown, *Appl. Phys. Lett.* 32 (8) (1978) 461.