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Amorphous phase formation of Zr–Cu thin films fabricated by magnetron co-sputtering

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Zr_xCu_{1-x} amorphous films were prepared on Si(111) substrates by magnetron co-sputtering of pure Zr and Cu targets. It was found that the amorphous forming ability of the films increased with x when x was smaller than 65. It was therefore different from their bulk counterparts, which only for $x = 35$ and 50 were reported to have high glass forming ability during casting. The structures of the films were sensitive to the substrate temperature and the sputtering pressure of argon. X-ray diffraction and atomic force microscopic analyses of the $Zr_{65}Cu_{35}$ amorphous films annealed at various temperatures confirmed that the crystallization temperature was approximately 573 K.

Key words: *Zr–Cu thin film; magnetron sputtering; amorphous film; crystallization*

1. Introduction

Amorphous alloys have been researched intensively since the 1960s [1, 2] due to their special properties, which result from the long-range disorder arrangement of atoms. Two main ways to obtain new amorphous alloy systems are: (i) enhancing the cooling rate during casting, and; (ii) finding appropriate chemical composition for a given alloy. A high cooling rate could be obtained easily during film preparation. In 1929, Kramer fabricated for the first time an amorphous alloy by electrodepositing Au–Si films [3]. In recent decades, amorphous alloy films have been the subject to intense research, due to the progress of preparation technology (deposited by sputtering or evaporation, solid-state reactions, ion beam mixing, etc.), and its excellent potential for direct or indirect exploitation in applications such as superconducting [4], ultra-high density magnetic recording [5], shape memory [6], etc. Although much progress has been achieved in research on bulk metallic glasses (BMGs), most of them developed so far have been complex multi-component alloys. Consequently, it is difficult to examine glass forming ability (GFA) with these alloy systems. As amorphous

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films can be prepared with relative simple alloy systems, they are, therefore, best candidates to understand GFA of alloys.

Zr–Cu alloy is an important amorphous alloy [7–10]. Several studies on the structure, mechanical properties [11–14] and superconductivity [15] of Zr–Cu amorphous alloy films have been reported in recent years. Dudonis et al. [16] fabricated Zr_xCu_{1-x} amorphous films in a wide composition range of ($5 \le x \le 95$) by using high working power (490–1380 W) in a relatively high vacuum ($p \le 3\times10^{-2}$ Pa) during magnetron sputtering deposition. As the structure of the deposited films depends on the deposition parameters, the aim of this study was to acquire detailed understanding of how conditions of film deposition influence the formation of amorphous Zr-Cu films.

2. Experimental

Zr_xCu_{1-x} alloy films were prepared by magnetron sputtering deposition in an argon atmosphere. Two targets, pure Cu (purity, 99.999%) and pure Zr (purity, 99.999%), were used for co-deposition of the alloy films. Through altering the sputtering power for the two targets, films with various compositions were obtained. In the present experiments, the power used for the Zr target was 40–85 W, and the power for the Cu target was 80–130 W. The target–substrate distance was 130 mm. The target dimension was ∅80 mm. Single crystal Si(111) substrates, ultrasonically cleaned before deposition, were placed on a rotating holder which could be electrically heated. Before deposition, the targets were sputtered for 20 min in order to remove contaminants and oxides on the surfaces. Samples of the prepared films were annealed at various temperatures for 30 min in a furnace having the base vacuum of 5×10^{-4} Pa.

The compositions of the alloy films were measured by the Kevex-Sigma level4 energy dispersive spectroscopy (EDS) and the percentage error of measurements was lower than ±1%. Small angle X-ray diffraction was used to investigate the structures of the films. To observe the surface morphology of the samples, a Solver P47 atomic force microscope was employed.

3. Results and discussion

3.1. Influence of chemical composition on the amorphous film formation

In order to investigate the influence of composition on the amorphous formation ability, the Zr_xCu_{1-x} films were deposited under the same processing parameters except the sputtering power. A series of film samples with various compositions were prepared at room temperature (substrates), under the argon pressure of 0.5 Pa; the voltage bias was –30 V, and the sputtering lasted 15 min. Results of the small angle X-ray diffraction experiments of the films are shown in Fig. 1. The $Zr_{35}Cu_{65}$ film sample clearly displays a crystalline characteristics of separated Cu- and Zr-based solid solution phases rather than a single solid solution phase or any Zr–Cu compound.

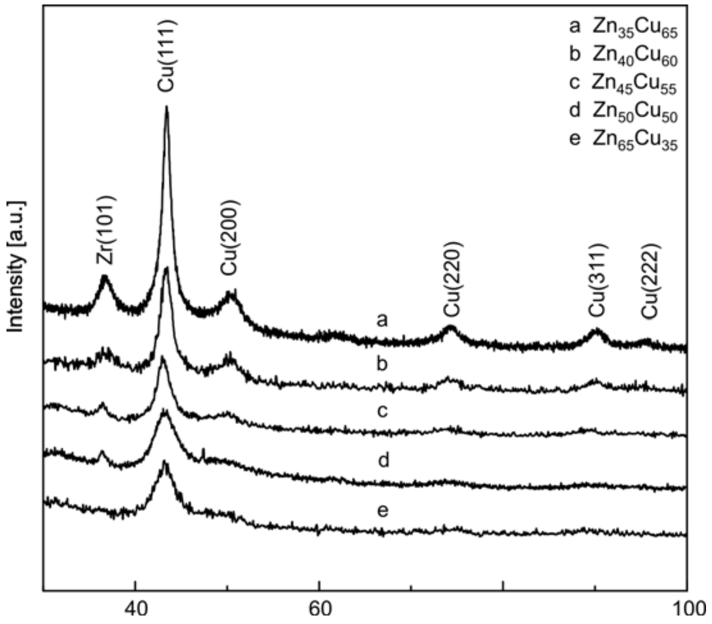

Fig. 1. XRD patterns of Zr_xCu_{1-x} films of several compositions

As the content of Zr in the composition increases in the $35 \leq x \leq 65$ range, both the phase separation tendency and the crystalline characteristics weaken. When $x = 65$, just one broad, diffuse peak was left, indicating a fully amorphous structure had been obtained. Beyond this composition range, the amorphous formation ability was decreased. Thus it can be concluded that the amorphous forming ability of Zr_xCu_{1-x} films increases continuously with the increase of Zr content. This result is apparently different from the bulk counterparts which have been reported that only with particular compositions did the amorphous structure form easily [7, 8, 11]. During casting, $Zr_{35}Cu_{65}$ alloy was proved to be a good glass former because it was around the eutectic composition and the liquid had a high stability which was beneficial for glass formation [17–20]. During the film deposition, this composition exhibited, however, rather low amorphous formation ability. In sputtering, the atoms or clusters were continuously deposited onto the surface of the substrates. Typically, deposited atoms had higher diffusion ability than the atoms in the liquid being quenched during casting. As reported [21, 22], the diffusivity was approximately by one order of magnitude higher during deposition. This was possibly why separated Zr- and Cu-based crystal phases were formed during deposition as only a limited solubility range was found in Zr-Cu alloy system from the phase diagram. Diffusion ability of the atoms, therefore, determines to some extent the formation ability of the amorphous film. As to the higher amorphous formation ability with increasing Zr content from 35 to 65 at. %, the most possible reason was also the atomic diffusion. Typically, atoms with smaller atomic diameters exhibit higher diffusion ability. Because the atom diameters of Cu and Zr are 0.256 nm and 0.320 nm, respectively, it is reasonable to conclude that Cu atoms have higher diffusion ability compared with that of Zr atoms. Therefore higher Cu content is not conducive for preparing amorphous film in Zr-Cu system.

3.2. Influence of the substrate temperature on the amorphous film formation

Substrate temperature is an important parameter influencing the structure of the alloy films. $Zr_{65}Cu_{35}$ films were sputtered at room temperature, 373 K and 573 K. According to the XRD patterns shown in Fig. 2, the film deposited at room temperature was fully amorphous. When the substrate temperature was, however, elevated to 373 K, the film showed crystalline characteristics. And when the temperature was further increased to 573 K, the crystalline peaks of Zr- and Cu-based phases were rather sharp.

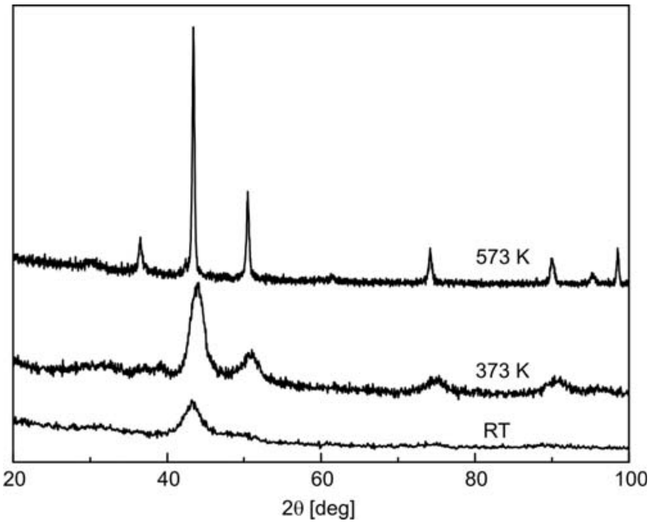

Fig. 2. XRD patterns of $Zr_{65}Cu_{35}$ films sputtered at various substrate temperatures

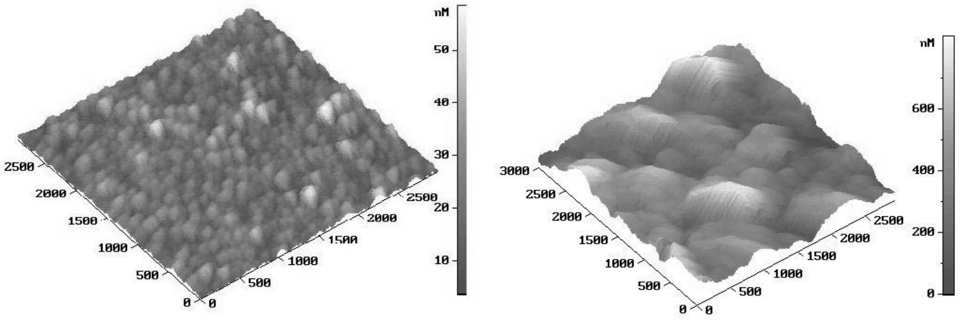

Fig. 3. AFM images of surfaces of $Zr_{65}Cu_{35}$ films sputtered at various temperatures of the substrate: 373 K (left) and 573 K (right)

AFM images of the morphologies formed at various substrate temperatures, as shown in Fig. 3, reveal that the higher substrate temperature was conducive to the crystalline formation. At a higher substrate temperature the atoms reaching the substrate had higher mobility and diffused more easily. Consequently higher substrate temperature was not conducive to the formation of the amorphous structure as pointed out above.

3.3. Influence of argon pressure on the formation of amorphous films

Appropriate argon pressure is necessary to deposit amorphous films. A relatively high pressure (≥ 2 Pa) decreases the quality of the films. On the other hand, if an ultra low argon pressure is employed, the plasma cannot be inducted, thus the deposition cannot take place. A pressure scale of 0.1–0.5 Pa was imposed in order to investigate the effect of working pressure on the amorphous formation of the films. For the composition of $Zr_{65}Cu_{35}$, obvious crystalline structure formed at the argon pressure of 0.5 Pa, as shown in Fig. 4.

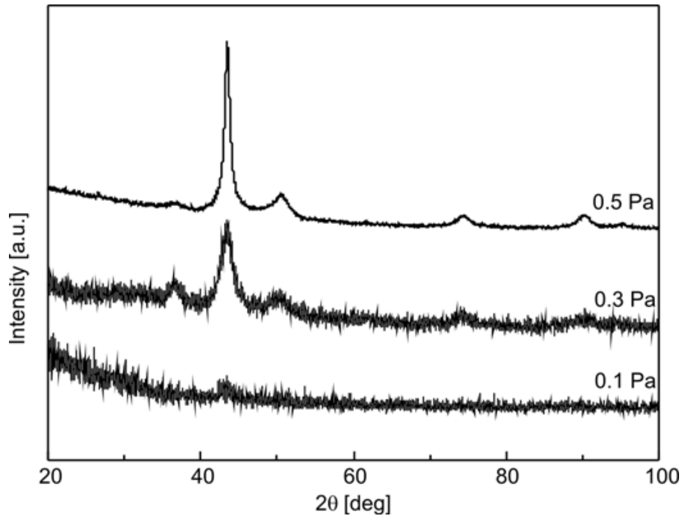

Fig. 4. XRD patterns of $Zr_{65}Cu_{35}$ films sputtered at various argon pressures

By decreasing the argon pressure, the amorphous formation ability was increased, and the pressure of 0.1 Pa was the optimum pressure for the formation of amorphous structure, assuming that the method of deposition satisfies all the conditions described earlier. When the pressure was smaller than 0.1 Pa, the deposition was too slow. The mechanism of the influence of pressure on the formation of amorphous films is hard to be explained. When the argon pressure was high, the atoms and the clusters sputtered from the Zr and Cu targets had higher energy and, and this consequently led to a higher diffusivity on the substrates. As pointed out above, separate Zr- and Cu-based crystalline phases formed more easily.

3.4. Annealing and crystallization of the $Zr_{65}Cu_{35}$ amorphous films

$Zr_{65}Cu_{35}$ amorphous film samples were annealed for 30 min at 373, 473, 573, 623, 673, and 773 K, respectively. The XRD results of the annealed samples as well as of the as-sputtered one are shown in Fig. 5.

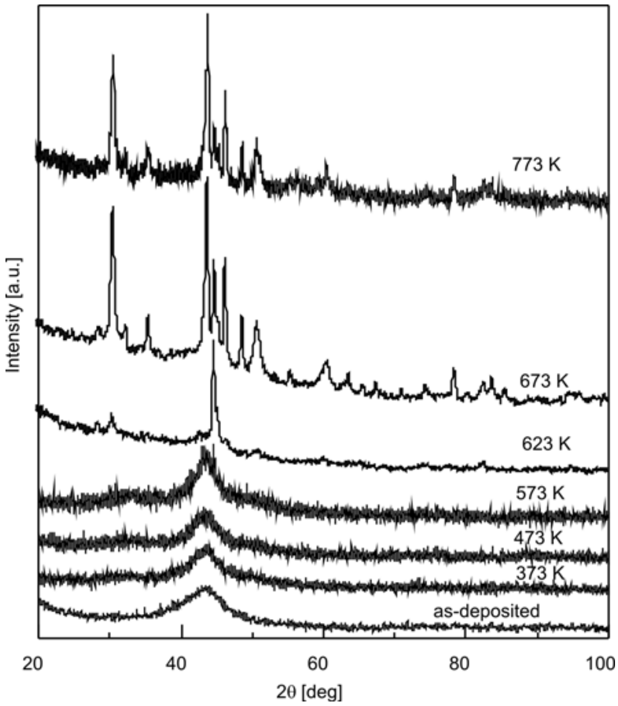

Fig. 5. XRD patterns of as-sputtered and annealed $Zr_{65}Cu_{35}$ films

It can be seen that the crystallization of the films did not occur when the temperature was lower than 473 K. However, some small crystal peaks can be seen in the XRD pattern of the sample annealed at 573 K. When the annealing temperature increased to 623 K, obvious crystalline peaks could be found in the XRD pattern. The film crystallized even further when annealed at 673 K. Thus, the onset temperature (T_x) of crystallization was at about 573 K.

4. Conclusions

In the range $35 \leq x \leq 65$, the amorphous forming ability of Zr_xCu_{1-x} films increased continuously with x. The amorphous formation ability was sensitive to the deposition parameters. If the argon pressure ranged between 0.1~0.5 Pa, a lower pressure was conducive to the formation of amorphous film. A high substrate temperature was unfavorable to the formation of the amorphous structure. The effect of the parameters investigated in this paper on the formation of the amorphous phase is probably due to their influence on the diffusivity of atoms or clusters deposited on the substrates.

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