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On the amorphous nature of sputtered thin film alloys

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ABSTRACT

The power-law scaling behavior between the average interatomic distance and the atomic volume of sputter deposited Zr–Cu thin films has been compared with published data on Zr–Cu bulk metallic glasses. Despite the strong differences in the quench rate of the synthesis methods, the same scaling behavior is found which implies that the driving force for the alloy internal structure is the composition, not the magnitude of the quench rate. The validity of this statement was further tested for other nearly-equimolar multi-element alloy thin films deposited by magnetron sputter deposition. Binary, ternary, quaternary, and quinary alloys have been synthesized out of 5 base elements: Al, Cr, Cu, Ta, and Ti. Twenty-two (out of 26) thin films are XRD-amorphous. Based on the packing fraction of these alloys a subdivision can be made. Alloys with a high packing fraction follow the power-law scaling behavior for metallic glasses, whereas no clear correlation can be found for low packing fraction alloys. The thin film intrinsic stress for this latter group was substantially higher which shows that in the case of thin film deposition both composition and deposition conditions influence the internal structure of the amorphous alloys.

1. Introduction

Amorphous metallic alloys such as metallic glasses (MGs) are non-equilibrium solids which can be produced by various non-equilibrium techniques. Rapid solidification of the melt is required to bypass crystallization and to retain the glassy state [1–3]. Over the years, compositions with a good glass-forming ability (GFA) have been found which makes rapid solidification unnecessary, hence these bulk metallic glasses (BMGs) can be produced with conventional casting methods [4]. Still, a high quench rate is a prerequisite to synthesize metallic glasses with a lower glass-forming ability. Vapor deposition inherently presents high quench rates, so the synthesis of thin film metallic glasses (TFMGs) occurs even farther from equilibrium. Therefore, the composition range for amorphization of TFMGs is wider than for BMGs [5]. A comparison between TFMGs and BMGs regarding their properties and GFAs has to be done cautiously since not only the quench rate during vapor deposition is orders of magnitude higher but mainly the synthesis processes are fundamentally different. In the bulk case, a liquid-to-solid transition is made and when the supercooled liquid approaches the glass transition temperature, polytetrahedral clusters such as the icosahedron become prominent and the backbone of the amorphous phase is formed [6–10]. For TFMGs there is, in contrast to the bulk case, a transition from vapor-to-solid. Vapor quenching methods are non-equilibrium, atomistic processes whereby the film growth is governed by a competition between thermodynamics and kinetics. Early research was primarily focused on the synthesis of binary amorphous alloys by evaporation [11–15] and sputtering [16–20]. However, it is important to emphasize the differences between the two deposition techniques. The average energy of the sputtered atoms is at least two orders of magnitude higher than the average energy of the arriving atoms during thermal evaporation. Furthermore, the energy distribution of the sputtered atoms contains a non-negligible fraction of energetic atoms (10–100 eV). During thin film growth the migration of adatoms is the most fundamental process which can be defined by the mean free path of diffusing adatoms before they create a new nucleus or become captured by existing islands [21,22]. This characteristic diffusion length scales with the available energy per arriving atom which implies that the effective quench rate during sputter deposition is lower than during thermal evaporation [23].

A very important aspect that is sometimes overlooked during the deposition of TFMGs is the kinetic aspect of magnetron sputtering. Momentum-driven processes can significantly alter the growth and the resulting properties of the films. Essentially, there are two sources of momentum. Firstly, heavy sputtered atoms are

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less prone to scattering and maintain their initial momentum through the gas phase [24]. Secondly, heavy target atoms serve as reflection centers for the inert gas ions whereby the backscattered gas atoms bombard the growing film and deliver an extra source of momentum. Depending on the deposition conditions such as the target–substrate distance, pressure and mass ratio of the target material and the inert gas, the kinetic effects can outweigh the diffusion-related processes. In many cases, these kinetic effects are desired since they densify and harden the thin film. On the other hand, the atomic bombardment introduces intrinsic stresses and can destroy the expected film structure based on the energy per arriving atom concept [25]. This makes the interpretation of the obtained film properties more complex.

This paper tries to tackle three issues: (1) are the atomic structures of well-known metallic glasses prepared by liquid-to-solid and vapor-to-solid methods similar? To do this, the power-law scaling behavior of the average interatomic distance and the atomic volume of Zr–Cu TFMGs will be compared with Zr–Cu BMGs. (2) Can magnetron sputter deposition be used to investigate a wider range of new, complex alloys? (3) Does the atomic structure of these new complex alloys follow the same scaling law as determined for BMGs? Out of 5 base elements (Al, Cr, Cu, Ta and Ti), nearly-equimolar binary, ternary, quaternary and quinary alloy thin films have been deposited and their phases have been determined. After a careful examination of their composition, intrinsic stress state and packing fraction, the amorphous films can be categorized.

2. Experimental

The thin films were deposited in a stainless steel vacuum chamber with a base pressure lower than 3×10^{-4} Pa. The magnetron was a homemade 2 inch planar magnetron powered by a Hüttinger 1500 DC power supply. Sputter deposition was performed at a constant current of 0.17 A. The working pressure was 0.4 Pa by applying 99.9% pure argon gas at a flow rate of 30 sccm. The target–substrate distance was fixed at 7 cm. The substrate holder was grounded and films were deposited on silicon wafers covered with a native oxide. The 0.55 mm thick (111)-oriented Si wafers were cleaned in a Piranha solution prior to deposition. The sample thickness was measured by contact profilometry (Taylor-Hobson Talystep). The chemical composition of the films was obtained with SEM/EDX (FEI Quanta 200F) with a beam current of 208 μA and a voltage of 20 kV. Conventional XRD measurements were carried out on a Brüker D8 Discover equipped with a LynxEye silicon strip detector and Cu Kα radiation was used. An offset angle of 5° between the X-ray source and the detector was set to minimize the contribution of the Si substrate. The samples were scanned from 20° to 100° with a resolution of 0.02° per step and a step time of 5 s. The film density was measured with X-ray reflectometry (XRR). For this purpose a Brüker D8 Advance was equipped with a scintillation detector and Cu Kα radiation was used. The samples were scanned from 0.3° to 6° with a step size of 0.01°. The amorphous nature of a selected sample was verified with transmission electron microscopy (FEI Tecnai G2 operated at 200 kV) of an ion-milled cross-section of the deposited material.

2.1. Zr–Cu thin films

The Zr–Cu thin films were deposited by sputtering solid Zr targets whereby the erosion groove was equipped with Cu inserts. A similar approach was used before for the deposition of Al-doped TiO_x thin films [26]. The copper concentration was altered by adjusting the number of Cu inserts. The targets were pre-sputtered for 10 min to remove surface contaminants. After calibration of the deposition rates, the deposition times were adapted to obtain 1000 nm films.

2.2. Al–Cr–Cu–Ta–Ti thin films

Five base elements (Al, Cr, Cu, Ta, Ti) were chosen based on their price and distinctive properties. The combination of the selected base elements resulted in the deposition of 10 binary, 10 ternary, 5 quaternary and 1 quinary quasi-equimolar alloys. To deposit this large number of alloys, cold-pressed powder targets were used. More details on the production and the use of powder targets can be found in previous work [27–29]. All powders were 99.9% pure, −325 mesh filtered metals. The powders were uniaxially cold-pressed (90 MPa) into 2 inch targets of thickness 2 mm. The powder targets were pre-sputtered for 25 min to obtain the required steady-state composition. After calibration of the deposition rates, the deposition times were adapted to obtain 500 nm films.

3. Results

3.1. Zr–Cu thin films

3.1.1. X-ray analysis

The atomic-level stress theory of Egami can be used to predict the required solute concentration to promote amorphization of ZrCu alloys [30]. Based on this theory, the critical threshold concentration for amorphization is 25 at% Cu. Therefore, thin films with a composition higher than 25 at% Cu were deposited. In agreement with the theory of Egami, only a broad hump is noticed in the XRD patterns (see Fig. 1), owing to the amorphous nature of the films.

3.1.2. Scaling behavior

A study by Ma et al. [31] suggested that the medium-range order (MRO) of bulk metallic glasses may be characterized by a self-similar, fractal packing of atomic clusters. They noticed that the position of the first sharp diffraction peak (FSDP) and the average atomic volume (V_a) of metallic glasses are closely related by a universal scaling law:

$$q = 9.3\left(\frac{1}{V_a}\right)^{0.433} \quad (1)$$

with $q = \frac{4\pi}{\lambda}\sin\theta$ and with a power coefficient n = 0.433

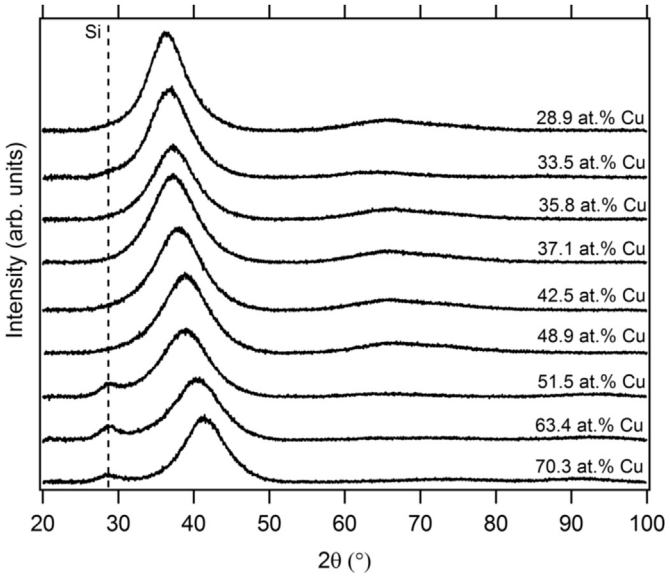

Fig. 1. XRD patterns of the Zr–Cu thin films deposited by magnetron sputtering.