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Molecular dynamic simulation of binary Zr_xCu_{100-x} metallic glass thin film growth

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ABSTRACT

In this work, we employed classical molecular dynamics simulations model to study Zr_xCu_{100-x} ($3 \le x \le 95$) metallic glass films deposited on a silicon (1 0 0) substrate. Input data were chosen to fit with the experimental operating conditions of a magnetron sputtering deposition system. The growth evolution is monitored with variable compositions of the incoming atom vapor. The Zr–Zr, Cu–Cu and Zr–Cu interactions are modeled with the Embedded Atom Method (EAM), the Si–Si interaction with Tersoff potential, the Zr–Si and Cu–Si interactions with Lennard-Jones (12-6) potential. Different film morphology and structure were detected and analyzed when the Zr to Cu ratio is varied. The results are compared with X-ray diffraction and scanning electron microscopy analyses of experimentally deposited thin films by magnetron sputter deposition process. Both simulation and experiment results show that the structure of the Zr_xCu_{100-x} film varies from crystalline to amorphous depending on the elemental composition.

1. Introduction

Recently, there has been a huge interest in the atomic-level structure and structure-property relationship in metallic glasses (MGs). These materials have been studied for 40 years because of their promising properties belonging to both metals (electron, heat conductivity, ductility, etc.) and glasses (hardness, etc.) [1,2]. To stabilize an amorphous phase in metallic alloys, atomic diffusion must be prevented. This could be achieved by playing with the chemical composition (mixing of elements with different atomic sizes) or by freezing a low ordered phase during the synthesis process [3]. It has been shown that deposition of thin films by condensation onto cold substrates allows stabilizing low ordered structure in metallic systems.

As an example, ZrCu alloys have attracted interest in recent years, due to its bulk metallic glass properties [4–8], and as amorphous alloy films for its mechanical [9–11] and superconductivity properties [12]. Dudonis et al. [13] prepared thin films with composition in the range of ($5 \le x \le 95$) by using high working power (490 W and 1380 W on Cu and Zr targets, respectively) during magnetron sputtering deposition.

Numerous theoretical studies have also been conducted on Zr–Cu systems. Sha et al. [14,15] employed atomistic methods for studying Zr–Cu MGs forming conditions. Almyras et al. investigated the microstructure of $Zr_{35}Cu_{65}$ and $Zr_{65}Cu_{35}$ MGs and found that these systems consist of small touching and/or interpenetrating icosahedral-like clusters which results in "supercluster" (SCs) satisfying the system composition [16]. They thus claimed that seeking the equilibrium configuration for interpenetrating ICO-like clusters allows the prediction of the MG microstructure.

While bulk amorphous structure is known to be formed under specific synthesis conditions, the ZrCu amorphous thin film growth has not been so much studied. A better understanding of thin film growth can be achieved via simulations and compared to available experimental data as X-ray diffraction patterns. Molecular dynamics (MD) has proven to be a very successful technique for a detailed understanding of growing processes of metal films, allowing us to explore film forming evolution at the atomic level.

In this work we report on results of molecular dynamics simulations and on a structural study of Zr_xCu100_{100-x} metal alloy thin films grown by magnetron plasma sputter deposition. The main goal is to investigate the relationship between the composition and the structure.

2. Experimental

The Zr_xCu_{100-x} alloy films were prepared by DC magnetron sputter deposition in argon atmosphere (0.25 Pa) and at room temperature. Two targets, pure Cu (purity, 99.999%) and pure Zr (purity, 99.999%), were used at the same time for co-deposition of the alloy films. The distance between the target and the substrate was set to 10 cm. By altering the sputtering power of both

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targets, Zr_xCu_{100-x} thin films with different compositions were synthesized on Si (1 0 0) wafers. Typical deposited thickness was 600 nm. In order to study the structure of the Zr_xCu_{100-x} metallic films X-ray diffraction analysis (Cu Kα radiation, λ = 0.15405 nm, Bregg–Brentano geometry) was performed. Microstructure of the deposits was observed on SEM images (Carl Zeiss-Supra40 – FEG-SEM)

3. Molecular dynamics simulation details

3.1. Potential functions

MD is a simulation technique for computing the equilibrium and transport properties of a classical many-body system. Giving an initial set of positions and velocities of a system of *N* atoms, each atom is treated as a point mass and the atomic motion is solved using Newton's equations [17].

The MD package LAMMPS [18] is used to simulate the deposition of atoms. A script driving the LAMMPS code was written for automating the deposition and the relaxation of the system. Implementing suitable interatomic potentials is certainly the most important issue in molecular dynamics simulation. For describing the interaction between Zr–Zr, Zr–Cu, Cu–Cu, we use the many-body EAM potential [19–21]. Such a potential is non-pairwise in the sense that it is based on concepts coming from density functional theory, which stipulates in general that the energy of a solid is a unique function of electron density. It is well adapted to simulate the interaction between such metal atoms.

The total energy E_{tot} of an atomic system can be expressed as:

$$E_{tot} = \sum_i V_i$$

$$V_i = \frac{1}{2}\sum_i \phi_{ij}(r_{ij}) + F(\rho_{ij})$$

$$\rho_i = \sum_{i \neq j} f_i(r_{ij})$$

V_i is the internal atom energy and ρ_i is the electron density associated with atom i due to the presence of other atoms in the system. $F(\rho_i)$ is the energy required to 'embed' the atom i in the electron density ρ_i. $\phi_{ij}(r_{ij})$ is a suitable pair potential.

Tersoff [20] Silicon empirical potential is used for describing the interaction between the Si atoms. This potential has been successfully used to investigate the structural, thermal vibration and surface properties of Si [20].

The Tersoff interatomic potential involves both two- and three-body terms:

$$E = \sum_i V_{ij}$$

where $V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})]$

Here *i* and *j* are labels for the interacting atoms. The term f_R represents a repulsive pair potential due to electron overlap, while f_A represents an attractive pair potential associated with bonding. The function f_C is merely a smooth cutoff function which limits the range of the potential. The coefficient b_{ij} (bond order) corresponds to a many-body interaction of the form:

$$b_{ij} = \chi_{ij}(1 + \beta_i^{n_i}\xi_{ij}^{n_i})^{-1/2n_i}$$

$$\xi_{ij}^{n_i} = \sum_{k \neq i,j} f_C(r_{ik})g(\theta_{ijk})$$

where

$$g(\theta_{ijk}) = 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos\ \theta_{ijk})^2}$$

And the constants χ_{ij}, β_i, n_i, c_i, d_i and h_i depend on the atomic species and θ_{ijk} is the angle between an *i*—*j* bond and an *i*—*k* bond. The EAM and Tersoff parameters are implemented in the LAMMPS software.

We use a Lennard-Jones potential for the interactions between deposit atoms and substrate [17]:

$$V_{ij}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

The parameters σ and ε of LJ potentials of Zr, Cu and Si are summarized in Table 1 [20,22]. σ is the distance canceling the LJ potential $V_{ij}(\sigma) = 0$ and $-\varepsilon$ is the well depth of the LJ potential.

Species	ε (eV)	σ (Å)
Zr	0.7382	2.9318
Cu	0.409	2.338
Si	0.0175	3.826

When pair potential parameters for compound materials are not directly available, mixing rules can be used to make approximations [17]. As example, the Lorentz–Berthelot mixing rule is suitable for Lennard-Jones potentials of species *i* and *j*, giving: $\varepsilon_{ij} = (\varepsilon_i\varepsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$.

3.2. Computational model and analysis methods

MD simulation was carried out in a three dimensional cell, which was periodic only along *x* and *y* directions. The deposition of each particle is simulated at the *NVE* ensemble (i.e. the number of particles *N*, the system volume *V* and the total energy *E* are kept constant). The dimensions of the Silicon (1 0 0) substrate are $(25 \times 25 \times 10)$ Å^3. The first two bottom layers of the substrate are fixed (red atoms in Fig. 1), while the other layers are temperature – controlled layers using a Berendsen thermostat [23].

When an atom is deposited, the system is in a non-equilibrium state. The high energy of the deposited Zr and Cu atoms can be dissipated with Berendsen thermostat in the course of simulation to keep the whole temperature around 300 K (room temperature) corresponding to the value in the experiment. The initial configuration of the deposition model is pictured in Fig. 1.

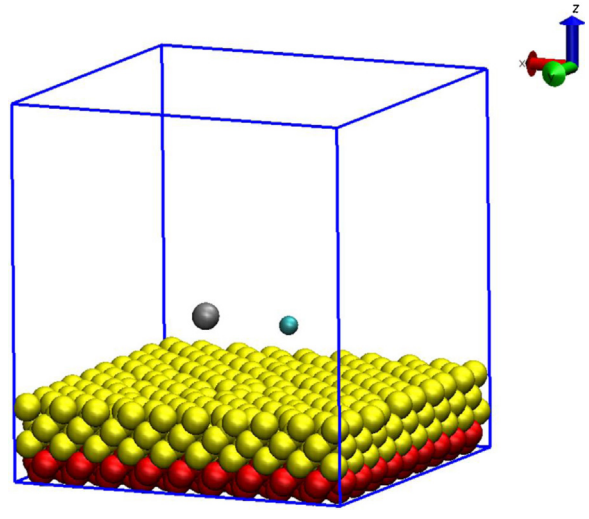

Fig. 1. Schematic picture of the deposition model. Gray atom is Zr, blue atom is Cu, yellow atoms are moving Si atoms, red atoms are Si fixed atoms.