Material Property Analysis of Amorphous Metallic Thin Films as Diffusion Barrier Layer

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Abstract. Amorphous metallic films have been considered to be the most effective barriers layer for Cu metallization due to the absence of grain boundaries and immiscibility with copper. The time and cost required for nano-scale experiment may be exceedingly large, and for this reason molecular dynamics have been used to analyze the material properties of CuAg amorphous metal films in this study, including the glass transition process of amorphous metal films, the effect of composition ratio and quenching rate on the internal microstructure of amorphous metal films, diffusion properties and the strength of the interface between polycrystalline and amorphous thin film. The results show that for CuAg alloys, Cu\textsubscript{20}Ag\textsubscript{80} present 50% amorphous at quenching rate of 25 K/ps, but Cu\textsubscript{40}Ag\textsubscript{60} and Cu\textsubscript{60}Ag\textsubscript{40} present more than 95% of the amorphous at quenching rate between 0.25 K/ps and 25 K/ps, which indicates that it has a good glass forming ability. For the diffusion side, the better barrier performance will be with the higher of the amorphous ratio.

Introduction

Amorphous metals (also known as metallic glass or glassy metal) have been developed for long time, exhibiting unique characteristics, such as good corrosion resistance, larger elastic energy storage and high strength [1]. Amorphous metal is a solid metallic material, usually an alloy, with a random or disordered atomic structure. Compared with crystalline alloys which have a highly ordered or long range ordered arrangement of atoms, amorphous alloys are disorder arrangement and non-crystalline. The lack of crystalline structure means no crystal defects, such as dislocations and grain boundaries. Due to no crystal defect, amorphous alloys can exhibit special mechanical, thermal, magnetic and chemical properties. Most metals and alloy are crystalline in their solid state, which means they have a highly ordered arrangement of atoms. Amorphous metals are non-crystalline, and have a liquid or glassy structure. Different from common glasses, amorphous metals have good electrical conductivity. There are several ways in which amorphous metals can be produced, including extremely rapid cooling, physical vapor deposition, ion irradiation, and mechanical alloying.

Thin film metallic glasses (TFMGs) have been studied and found to be excellent diffusion barriers in integrated circuits applications [2]. These kinds of barriers block the interaction between the interconnect materials and the silicon. In particular, refractory metal nitrides, deposited by reactive sputtering have been shown to be promising diffusion barriers. Based on these studies, it is suggested that amorphous thin films are potentially useful as the diffusion barrier in other systems, in addition to those between the interconnect materials and the silicon [3-4].

Numerical Simulation

The amorphous structure of Cu-Ag at a temperature of 300K was obtained by performing simulations with the following parameter settings and heat treatments. First, a crystal Cu-Ag alloy was created with a face-centered cubic copper lattice of 184,950 atoms and replaced enough copper atoms with silver to give the system the desired composition. Subsequently, a series of simulations of heat treatment was conducted within the isothermal isobaric ensemble with an external pressure of zero. Three-dimensional periodic boundary conditions were applied. The most at atom velocities were
adjusted in order to maintain them in an isothermal state with a specific temperature, obeying Newton’s second law. The model was initially relaxed under periodic boundary conditions at 300 K for 200 ps within an NPT (constant pressure and constant temperature) ensemble. The system was heated from 300K to 2200K at a constant heating rate of $5 \times 10^{11}$ K/s to $5 \times 10^{13}$ K/s, which produced an amorphous structure. To make the state of the system as natural as possible, the liquid system was relaxed for 20 ps at 2200 K. Finally, the system was quenched from 2200K to 300K at a quenching rate of $5 \times 10^{13}$ K/s, followed by relaxation for 20 ps at 300 K. The amorphous alloy model was prepared by simulating melting and quenching. The temperature history stages include (a) heating state, (b) holding state and (c) quenching state.

To obtain Cu (polycrystalline)/Cu-Ag (after quenching) interface model of size 30 nm width (x-axis) × 30 nm height (z-axis) × 5 nm thick (y-axis), we start with constructing Cu/Cu-Ag crystalline model. The bottom layer is filled with Cu atoms (15 nm height) and above it, the simulation box is filled with Cu-Ag atoms. Initially, both Cu and Cu-Ag are kept in contact along the interface in the x–y plane with a separation distance of 3.5 Å. The interface separation distance is chosen based on the equilibrium bond lengths. It is shown that as long as the interface separation distance is not too small or not too large, it does not affect the results [5]. Atomic snapshots of Cu-Ag model for diffusion process and deformation process are as shown in Fig.1.

![Atomic snapshots of Cu-Ag model](image)

Figure 1. Atomic snapshots of Cu-Ag model for (a) diffusion process and (b) deformation process.

Figure 2 indicates that the glass forming ability (GFA) of binary Cu–Ag system with different quenching rate as 20 to 80 at% Cu. The GFA of more compositions were created through interpolation for visual appeal. From this figure, the predicted GFA of the Cu-Ag system indicated the glass formation composition range of the Cu-Ag system as 35–70 at% Cu with quenching rate of 2.8 K/ps. However, once the quenching rate reach of 28 K/ps, all of the composition range of 20 to 80 at% Cu can form amorphous. In addition, when the ratio of Cu and Ag atoms nearly 1 : 1 has better GFA. Figure 3 shows the Common Neighbor Analysis (CNA) of binary Cu$_{20}$–Ag$_{80}$ system with different quenching rates. The white, green, yellow, red, and blue balls represent amorphous, FCC, HCP, BCC and ICO structure, respectively.

The MSD profiles at temperatures ranging from 300 K to 900 K points of Cu and Cu-Ag were used to investigate their dynamical properties. Figure 4(a) shows the MSD of Cu and Cu-Ag as a function of time at various temperatures obtained in the present work. It is clear that the slopes of MSD profile are generally larger at a higher temperature and the MSD values of Cu-Ag alloy made from slow quenching rate are larger, indicating the mobility of atoms in Cu-Ag alloy made from slow quenching rate is higher than those made from high quenching rate. According to the MSD profiles of different temperatures and the Einstein equation, the total diffusion coefficients near the Cu/Cu-Ag interface at different temperatures can be obtained and shown in Figure 4(b). It can be inferred that the diffusion coefficients of both Cu and Cu-Ag significantly increase with the increasing temperature when the system temperature exceeds the glass transition temperature. The values of these diffusion coefficients range between $10^{-10}$ and $10^{-12}$ m$^2$/s, which has the same order than those found in the experimental measurement for the bulk inter-diffusion region. It is worth noting that the MSD
calculated by the MD may be slightly lower than the experimental value. This is due to the MD is relatively unable to consider the satiation of bulk materials, such as defects and so on.

Figure 2. The relationship between glass forming ability, quenching rate and elemental composition.

Figure 3. CNA distribution of Cu$_{20}$Ag$_{80}$ alloy with quenching rates of (a) 25 K/ps, (b) 2.5 K/ps and (c) 0.25 K/ps.

Figure 4. (a) The MSD and (b) diffusion coefficient of Cu and Cu$_{20}$Ag$_{80}$ as a function of time at various temperatures and quenching rates.

In order to understand the mechanical behavior dependence of the properties of amorphous state and crystalline state, bilayer structural material (Cu/Cu-Ag) with two different amorphous ratios made by different quenching rate of Cu-Ag alloy under tensile deformation are compared as Fig. 5. Figure 5(a) representative the stress–strain response of the Cu/Cu-Ag under mode-I loading of the perfect interface model, simulated at a temperature of 100 K and strain rate of $1 \times 10^{10}$ s$^{-1}$. Stress strain curves for the shortest and longest quenching times at the lowest strain rate for each of the two systems, from its initial state to fracture. The inset images show the stress–strain curves for Cu/Cu$_{20}$Ag$_{80}$. For Cu$_{20}$Ag$_{80}$ produced at slower quenching rate (0.25K/ps), the stress reaches a higher maximum and then suddenly drops. This is followed by a more steady flow regime during which some serrations are evident. The sudden drops are caused by the formation of a void arises from the Cu/Cu$_{20}$Ag$_{80}$ interface. However, for samples produced with short quenching time, the stress strain
curves are smoother and the behavior is close to the ideal elastic–perfectly plastic response. This phenomenon of sudden drop in stress is different with single crystal metallic of dislocations undergoing slippage along the slip plane [5-6]. The void nucleation is attributed to the fact that there exist more defects in this local region, and they are generally formed by the coalescences of the free volume present in the metallic glass system [7], which becomes the weakness during the tensile deformation. Figure 5(b) shows the atomic position snapshots of the interface model captured at different strains till fracture. The extension of the model begins with an elastic deformation from its initial state to the first yield state. When comparing Figure 5(b) with Figure 5(c), as the Cu$_{20}$Ag$_{80}$ alloy at faster quenching rate(25K/ps) gets closer to the amorphous state, the initial position of the void will move from the Cu/Cu-Ag interface to the middle of the Cu-Ag, which indicates that the Cu/Cu-Ag interface is stronger than Cu-Ag alloy. In addition, it is observed that larger voids are created in Cu$_{20}$Ag$_{80}$ with quenching rate of 25K/ps than Cu$_{20}$Ag$_{80}$ with quenching rate of 0.25K/ps specimen at 13\% strain. On the other hand, the specimens with Ag content between 40 ~60 at.\% show occurrence of voids at higher (15\% strain) strain values. This indicates that with Ag content between 40 ~60 at.\% in the metallic glass specimen increases its plasticity. From the microstructure side, by quenching the model at different quenching rates, different degree of structural ordering of the ordered clusters can be produced. These samples also exhibit different mechanical properties. It is found that the fraction of icosahedra in the as-quenched Cu–Zr MG sample increases considerably with decreasing quenching rate. The increasing number of icosahedral clusters form a more extended and stronger elastic backbone, leading to the higher stiffness (Young's modulus) and yield strength. The above observations and conclusions are in good agreement with prior simulations conducted [8-10].

Figure 5. (a) Stress-strain plot of the Cu/Cu$_{20}$Ag$_{80}$ interface model under mode-I loading; (b) Atomic position snapshots (I), CNA snapshots (II) and atomic strain snapshots (III) of the interface captured with C$_{20}$Ag$_{80}$ under quenching of 0.25K/ps at different strains; (c) Atomic position snapshots (I), CNA snapshots (II) and atomic strain snapshots (III) of the interface captured with C$_{20}$Ag$_{80}$ under quenching of 25K/ps at different strains.

**Summary**

In summary, the local atomic pairing arrangement of Cu-Ag system with different composition ratio and quenching rate is simulated by MD simulation method. It can be concluded that Cu$_{20}$Ag$_{80}$ present
50% amorphous at quenching rate of 25 K/ps, whereas Cu$_{40}$Ag$_{60}$ and Cu$_{60}$Ag$_{40}$ present more than 95% of the amorphous at quenching rate between 0.25 K/ps and 25 K/ps. Moreover, more amorphous microstructures can be achieved when quenching rate reach higher, and no significant diffusion behavior was observed between the Cu and Cu$_{20}$Ag$_{80}$ interface.

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