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Tension behavior of interfaces between ZrCu metallic glass and Si or Zr

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ABSTRACT

In this study, an amorphous ZrCu layer was coated on different materials such as Si and Zr by sputter deposition and then fabricated into free-standing pull-off samples by focused ion beam (FIB). These samples were tested in tension in order to investigate the tension behavior of ZrCu/Si (ZCS) and ZrCu/Zr (ZCZ) interfaces. By examining the fracture modes and load–displacement curves, we estimated the interface strength of ZCS to be $\sim 0.6 \pm 0.1$ GPa, with fracture occurring exactly along the ZCS interface. In contrast, the ZCZ samples failed within the ZrCu layer with shear band penetrating though interface. The ZCZ interface strength appeared to be higher than that of ZrCu (which is $\sim 1.7 \pm 0.1$ GPa). This stress of tension results matched well with the micro-pillar compression results; the ZCS interface strength was consistently much lower than the ZCZ interface strength. It could be explained by modulus mismatch and different bonding states between ZrCu/Si and ZrCu/Zr interfaces.

1. Introduction

For improving the mechanical properties of amorphous alloys, bulk metallic glass matrix composites (BMGMCs) [1,2] and thin film metallic glasses (TFMGs) coated on various substrates have been investigated for many years [3–6]. TFMGs have been proposed to be applied in many areas, such as micro-electro-mechanical systems (MEMS), biomedical, and optic applications. As one kind of composite materials, the adhesion between the film and substrate imposes great impact on the performance during service. Several groups have reported the interface properties in metal–metal, polymer–polymer, metal–polymer and metal–ceramic systems [7–14], but the interface characteristics of TFMGs with various metal, ceramic or polymer layers or substrates have received much less attention.

Our group has reported the interface properties of ZrCu/Zr inclined pillars, using special sample designs prepared by the dual focus ion beam system (FIB) [15]. But the interface strength would be affected by the friction between two layers, it is easier to measure interface strength under tension than under compression. Some other methods measuring the interface strength have also been developed, including peel test, blister test, shear lag test, and direct pull-off test, etc. [16,17]. But the pure shear or tensile stress is sometimes difficult to be extracted from peel and blister tests without complicated analysis. The shear lag test and direct pull-off test for thin films specimens with multiple layers also have some restrictions for strong interfaces. For measuring the interface strength directly, we tried a new way in accordance with ASTM D4541 (direct pull-off testing) to demonstrate the measurement of interface properties.

2. Experimental procedures

There were two samples prepared in this experiment, the first one was the ZrCu thin film metallic glass (TFMG) directly coated on the (1 0 0) Si substrate, termed as ZCS for the characterization of the interface between TFMG and ceramic Si wafer. The second one was the Zr/ZrCu bilayer film deposited on the Si substrate, with Zr in between Si and ZrCu. This sample is termed as ZCZ, for the characterization of the interface between TFMG and metal Zr. Before magnetron sputtering, the Si substrates were cleaned by acetone, ethanol and DI water. The layer thicknesses of ZrCu and Zr layers were both 1 μm. The base pressure during sputtering was firstly pumped down to below 9×10^{-6} Torr, and then Ar gas was entered at a fixed 30 standard cubic centimeters per minute (sccm). A ZrCu (nominally $Zr_{50}Cu_{50}$ in at%) alloy target and a Zr target were used for depositing ZrCu and Zr films, using the DC gun power of 100 W and a working pressure of 4 mTorr. To produce uniform film thickness, the samples were rotated at an average speed of 10 rpm.

To examine the atomic structure, the as-deposited ZrCu or Zr thin films on the Si substrates were characterized by Bruker D8 Advance X-ray diffraction (XRD). To extract the interface

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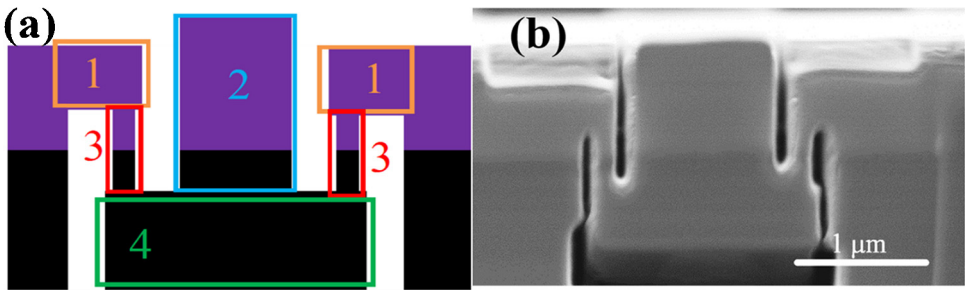

Fig. 1. (a) Schematic drawing of the freestanding pull-off sample, (b) SEM micrograph of the as-FIB-fabricated sample before loading.

mechanical properties, free standing pull-off samples for nano-tension tests were fabricated by using the SEIKO SMI3050 dual focus ion beam system (FIB), as shown by the schematic drawing in Fig. 1(a). First step is making a crater on the edge of sample which is larger than indenter tip for making sure that the tip would not contact other places during tension test. Then cut apart the sample from edge and keep a flake for final step. The final step needed to turn the whole sample vertically and cut the flake into free standing pull-off sample. For the discussion below, we have assigned four parts in this sample, as indicated in the drawing. Fig. 1(b) is an example of sample image taken by scanning electron microscopy (SEM). The two tensile sections, as indicated by arrows, are under tension when the flat-end tip compresses the central pillar. For the ZCS samples, the gauge section measured about 370 ± 20 nm in length, 250 ± 10 nm in width, and 120 ± 5 nm in thickness. For the ZCZ specimens, the gauge section measured 400 ± 20 nm in length, 110 ± 5 nm in width and 100 ± 5 nm in thickness. Such nano-tension samples were loaded by the MTS nanoindenter XP equipped with a flat-end Berkovich tip with a triangle cross-section measuring 13.5 μm in side length, under the loading rate control mode at 0.01 mN s^{-1}. The peak load of nano-tension was set to a high level of 0.06 mN, to ensure that the tension gage would be well over the elastic regime and eventually completely failed. The converted strain rates are ~0.01 s^{-1}. The downward loading from the flat-end Berkovich tip would result in the tension pulling for the two gage section on both sides. Micro-compression tests on micro-pillars (1 μm in diameter and 2 μm in height, as shown in Fig. 1(b)) were also conducted. All these tests were performed in the load controlled mode.

3. Results and discussion

3.1. Structure characterization

To identify the structure of ZrCu/Si and ZrCu/Zr/Si composite materials, the XRD patterns are shown in Fig. 2(a). There are a broad hump at 30–45°, it shows the ZrCu thin film is fully amorphous structure. The strongest three peaks of Zr are (1 0 1 0), (0 0 0 2) and (1 0 1 1) which are at 32°, 34.8° and 36.5°. Thus, the peak of ZrCu/Zr between 33 and 37° is sharper than pure amorphous hump. The peak of (1 0 0) silicon wafer is shown in Fig. 2(b) which is a very strong peak at 69.

3.2. Ga^+ damage caused by FIB

Before extracting the interface strength properties from these FIB prepared specimens, it is always necessary to evaluate the influence from Ga^+ damage. In this study, the fabrication steps of current nano-tension specimens were classified into two parts. FIB was firstly applied to cut one flake from the top, with the beam voltage of 30 keV and beam current of 7–12 nA. The following step adopted a very low beam current from 0.7 down to 0.09 nA to fabricate the fine structure, to prevent from the serious Ga^+ damage. It has been demonstrated [18] that the Ga^+ damage to single crystal Cu can be considered to be fully vanished at the depth of 400 nm from the surface if the beam current is 5 nA. Kiener et al. [19] found that the Ga^+ penetration depth can be 40 nm when the beam current is 10 nA. Sigle at al. [20] use TEM to trace the Ga^+ ion penetration in Al along the grain boundaries, when the FIB beam current is 0.01 nA for a long implantation time of 9 min. With decreasing beam current and short exposure time period, the damage depth will be significantly reduced. In our own previous work [21], with the low beam current about 0.1 nA, the Ga^+ penetrating depth as measured by Auger electron spectroscopy can only be 4 nm. Moreover, the time for fabricating the gauge section is less than 10 s. The accumulated Ga^+ ion concentration is considered to be rather low, and will not induce pronounced crystal structure of these pure metals. Although there might be a certain low percentage for the measured data, it is postulated that the Ga^+ damage would not cause major impact on the deformation mechanisms.

3.3. Interfaces strength analyses

The nano-tension specimens were prepared with the interface under consideration lying horizontally within the two gage sections, thus the tensile interface strength could be obtained when the fracture occurs along the interface. For the ZCS specimen, multiple tests were conducted, and the failure always proceeded exactly along the interface. One example of the recorded load–displacement is presented in Fig. 3(a). The load at failure (with a sudden increase of large displacement) is around 0.036 mN, and the failure displacement is only ~45 nm. The ZrCu/Si interface cross-sectional areas of two tensile gage sections, deformed concurrently in tension, are $30{,}000 \pm 1{,}000$ nm^2 (measured by SEM), denoted as A_1 and A_2. The same gage section before and after fracture is shown in Fig. 3(b). It is apparent that fracture occurs at the interface and the crack is basically perpendicular to the loading direction. The interface strength between the metallic glass ZrCu and Si layer can be calculated as:

$$\sigma_{ZCS} = \frac{F}{A_1 + A_2} = 0.6 \pm 0.1 \ GPa \quad (1)$$

In parallel, the ZCZ samples follow the same loading. Multiple tests were conducted, and the failure always occurred within the ZrCu layer. The recorded load–displacement is presented in Fig. 4(a), and gage section before and after fracture is shown in Fig. 4(b). It can be seen that fracture within the ZrCu metallic glass layer propagated along 45° shear band, leaving the ZrCu/Zr interface intact.

It has been reported that the plastic flow stress curves sometimes exhibit serration for larger metallic glass samples [22,23]. Jang and Greer [24] mentioned that nano-scaled samples could deform like ductile metals but fail like metallic glasses. Tian et al. [25] proved that the ductile behavior of MGs would be affected by sample size and strain rate. However, we need to emphasize that