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Nanolaminate of metallic glass and graphene with enhanced elastic modulus, strength, and ductility in tension

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ABSTRACT

We fabricate a nanolaminate by repeated co-sputter deposition of a 60 nm-thick $Cu_{50}Zr_{50}$ metallic glass layer alternating with transfer of graphene. In situ micro-tensile tests reveal that the addition of a very small fraction (0.46 vol%) of graphene in the nanolaminate improve the elastic modulus and yield strength of the nanolaminate by 9.6% and 14%, respectively, comparing with those of the 360 nm-thick monolithic $Cu_{50}Zr_{50}$ metallic glass. The nanolaminate also show enhanced tensile ductility: an ultimate tensile strength of 2.23 GPa and fracture strain of 5.39% were attained by strain-hardening after yielding at 1.98 GPa stress and 3.69% strain.

Metallic glasses exhibit superior strength and high elastic limits, but they generally have a lack of tensile ductility that results in sudden and catastrophic failure [1,2]. Considerable work has been aimed at improving the tensile ductility of metallic glasses [3,4], and the development of glass-matrix composites with high toughness and tensile ductility is being explored [5]. Two basic techniques are employed to attain high tensile ductility: introducing a softer secondary phase in the metallic glass matrix to induce generation of local shear banding around the secondary phase and reducing its external dimensions to suppress a propagation of shear bands or occur homogeneous flow instead, leading to enhanced strength and ductility [6–9]. Since there are limited structural applications for monolithic metallic glass with dimensions of the order of 100 nm, nanolaminates with alternating layers of metallic glass (with dimensions of 100 nm or less) and another material have been suggested as a more practical material [10,11]. Metallic glass-based nanolaminates with proper interfacial material and optimum layer thickness exhibit improved strength and ductility by utilizing size-dependent homogeneous flow of metallic glass [12,13]. Graphene is known to have an intrinsic breaking strength of 130 GPa at 25% [14] strain, which is promising for application as a corrosion barrier, lubricant material, or interfacial material in nanolaminates [15,16]. While the role of graphene as a reinforcing constituent material in metal-based nanolaminates has been investigated, the strengthening effect of graphene interfacial layers with metallic glass has not been studied.

We investigate a nanolaminate with alternating layers of $Cu_{50}Zr_{50}$ metallic glass and CVD-grown graphene with enhanced tensile strength and ductility. We fabricate monolithic 360 nm-thick $Cu_{50}Zr_{50}$ metallic glass and a nanolaminate consisting of 60 nm-thick $Cu_{50}Zr_{50}$ metallic glass and graphene, and conduct in situ micro-tensile testing. Compared with the 360 nm-thick monolithic metallic glass, which shows typical brittle fracture behavior, i.e., linear elastic deformation followed by catastrophic failure, the nanolaminate shows 14% higher yield strength and enhanced plasticity. Through interrupted micro-tensile testing, we investigate the strain-hardening behavior of the nanolaminate by suppressing shear-band propagation in the 60 nm-thick metallic glass layer.

Fig. 1 illustrates the process used to prepare a nanolaminate with alternating layers of 60 nm-thick $Cu_{50}Zr_{50}$ metallic glass; the nanolaminate consisted of a total of five layers of graphene interleaving between a total of six layers of $Cu_{50}Zr_{50}$ metallic glass. The $Cu_{50}Zr_{50}$ metallic glass was deposited on a Si(100) substrate by co-sputtering using two separated pure Cu and Zr targets. The chemical composition of the $Cu_{50}Zr_{50}$ metallic glass was measured by energy-dispersive X-ray spectroscopy (EDS), and the existence of $Cu_{50}Zr_{50}$ in the amorphous phase was confirmed by transition electron microscopy (TEM). Graphene was synthesized on a 25 μm-thick Cu foil by CVD and transferred on $Cu_{50}Zr_{50}$ metallic glass thin film by PMMA-assisted method [17]. We measured the ratio of the intensities of the 2D and G peaks (I_{2D}/I_G) for transferred graphene on the $Cu_{50}Zr_{50}$ layer using Raman spectroscopy,

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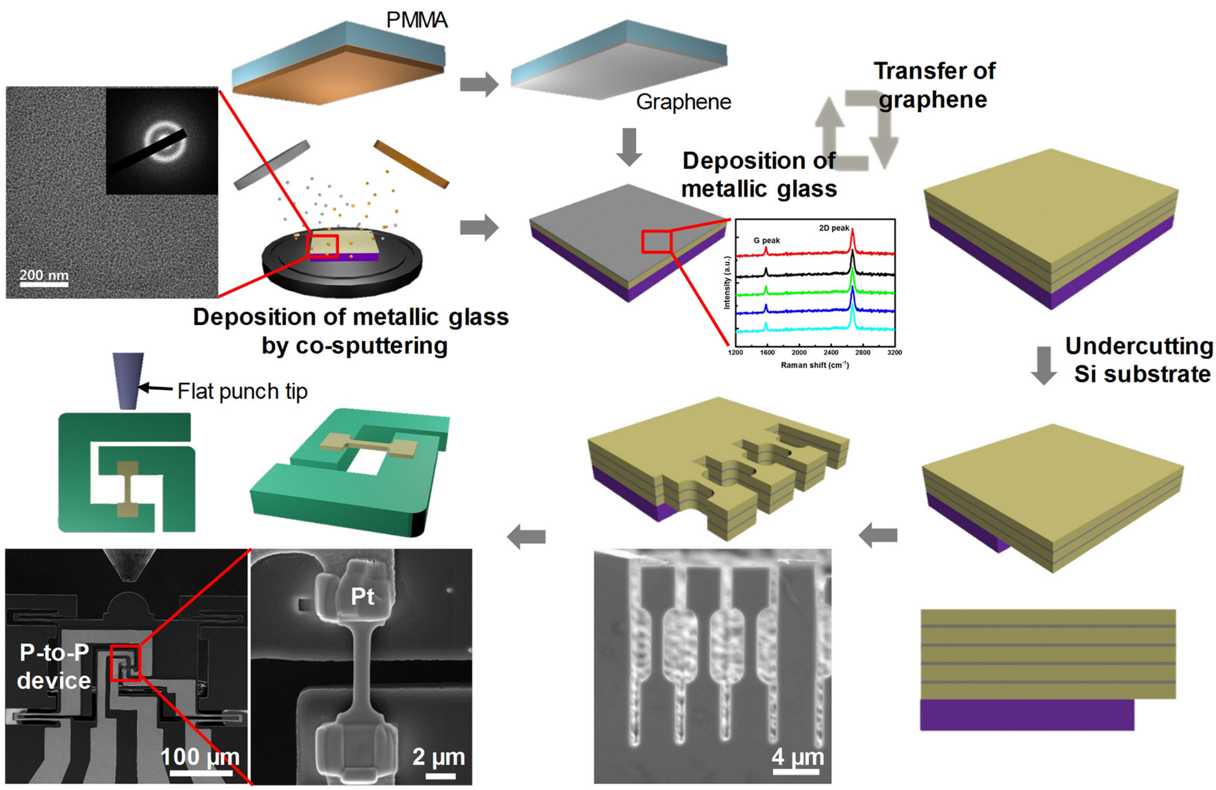

Fig. 1. Fabrication of nanolaminate with alternating layers of $Cu_{50}Zr_{50}$ metallic glass and graphene, and sample preparation for in-situ SEM micro-tensile testing.

which confirmed most transferred area was monolayer graphene as shown in inset of Fig. 1.

Freestanding film samples of the monolithic metallic glass and nanolaminate were prepared by undercutting the Si substrate by isotropic dry-etch with XeF_2 gas. Dog-bone-shaped specimens with dimensions of 1 μm (gauge width) × 4 μm (gauge length) were prepared by FIB (Quanta 3D, FEI, USA) milling and then transferred onto push-to-pull (P-to-P) devices (Hysitron, USA) using a micromanipulator for in situ SEM micro-tensile testing. In situ SEM uniaxial micro-tensile tests were performed using a picoindenter (PI-87, Hysitron, USA). The micro-tensile tests were carried out at a constant strain rate of 1×10^{-3} s^{-1}, and real-time movies were recorded with a field-emission SEM (FE-SEM; Quanta200, FEI, USA). The actual force exerted on each dog-gone-shaped specimen was computed by subtracting the estimated force using the stiffness of the push-to-pull devices. The initial geometry of the specimen was measured using SEM images, and the change in gauge length was measured using still images extracted from the movie, from which the true stress and strain were calculated.

Fig. 2 shows typical stress–strain curves of the specimens. The monolithic metallic glass showed typical brittle fracture behavior: linear elastic deformation followed by sudden and catastrophic failure directly after yielding at a yield strength of 1.74 ± 0.03 GPa, which were measured by the 0.2%-offset method. Compared to the monolithic metallic glass, the nanolaminate of metallic glass and graphene showed a higher yield strength of 1.98 ± 0.04 GPa and enhanced ductility after yielding, leading to an ultimate tensile strength of 2.23 ± 0.06 GPa and strain of 1.7% from yielding to failure. The elastic modulus, fracture strength, and strain of graphene via computational simulation have approximate values of 1 TPa, 100 GPa, and 20% [18], respectively, even though they deviate slightly depending on the loading direction and methodology. An elastic modulus of 1 TPa and intrinsic breaking strength of 130 GPa at strain of 25% were measured through hole-nanoindentations in single-crystalline graphene [14]. More recently, a fracture strength of 98.5 GPa and elastic modulus of 979 GPa were measured for CVD-grown graphene with grain sizes of 1–5 μm, and a fracture strength of 118 GPa and elastic modulus of 1011 GPa were measured for CVD-grown graphene with grain sizes of 50–200 μm [19]. These values are in good agreement with those predicted by computational simulations of single-crystalline graphene. The CVD-grown graphene used in this study is likely to have a grain size about 10 μm [20]. It is likely that few grain boundaries were included in the five graphene layers in the nanolaminate gauge section measuring 1 μm × 4 μm. The nanolaminate specimens were under iso-strain and their fracture strain was 5.39% ± 0.32%, which is much lower than the fracture strain of graphene. Regardless of the graphene grain size, it seems reasonable to assume that as a nanolaminate constituent, graphene showed elastic behavior with an elastic modulus of 1 TPa until nanolaminate failure occurred.

The elastic modulus was measured from the slope of the stress–strain curve in the linear elastic region; it had a value of 51.0 ± 2.14 GPa for monolithic metallic glass and 55.9 ± 1.68 GPa for the nanolaminate. The elastic modulus in laminated materials is generally calculated by a simple rule-of-mixture when tensile force is applied along the in-plane direction. The rule-of-mixture was applied to the six layers of 60 nm-thick metallic glass with elastic modulus 51 GPa and five layers of 0.335 nm-thick graphene with elastic modulus of 1 TPa [14], which predicted an elastic modulus of 56 GPa for the resulting nanolaminate, which is similar to the value obtained in our measurements. Despite the very low volume graphene fraction in the nanolaminate, 0.46%, the graphene layers enhanced the elastic modulus of the nanolaminate by 9.6% because of graphene's ultra-high elastic modulus.

The yield strength of the nanolaminate was 14% above that of monolithic metallic glass. As with the elastic modulus, the stress applied to constituents in laminated materials can also be calculated by a simple rule-of-mixture when tensile force is applied along the in-plane direction: $\sigma_{nanolaminate} = \sigma_{MG}V_{MG} + \sigma_{graphene}V_{graphene}$ where σ is the stress, V is the volume fraction, and subscript MG indicates metallic glass. Using the measured yield strength of 1.98 GPa for the nanolaminate, the stress applied on graphene, obtained at a yield strain of 3.69% for the nanolaminate, was calculated from an elastic modulus of 1 TPa