Compositional dependence of Young’s moduli for amorphous Cu–Zr films measured using combinatorial deposition on microscale cantilever arrays

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Young’s moduli of amorphous Cu–Zr thin films have been determined with unprecedented compositional resolution, via combinatorial film deposition and force–deflection measurements of microscale cantilevers. This elastic property increased monotonically with increasing Cu content. Such cantilever-based surveys of compositional libraries are considerably more rapid than that required of bulk samples. Additionally, interpretation of the film elastic modulus \(E_f\) via this approach is advantageous over indentation-based methods, particularly in terms of straightforward calculation that does not require knowledge of the glass’s Poisson’s ratio.

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Bulk metallic glasses have attracted significant interest and have been produced in various alloy systems, owing to the distinct functional properties of these amorphous metals as compared to their crystalline counterparts [1–4]. In our recent studies, we developed a novel experimental method for measurement of the density change upon crystallization of amorphous metallic thin films using microscale cantilevers and a combinatorial deposition technique [5,6], and compared the results with the corresponding glass-forming abilities of the alloys. In the Cu–Zr [5] and Zr–Cu–Al [6] systems, we found a clear correlation between small density changes and high glass-forming abilities. This method may help in the search for new glass-forming alloys, as well as in more precisely defining optimum compositions with the highest glass-forming ability in a given alloy system.

In the present study, we have extended this method to investigate the compositional dependence of Young’s elastic moduli for amorphous Cu–Zr thin films coated on SiN microcantilevers, by measuring the deflection when a point force is applied to the top of a cantilever [7,8]. It has been proposed that the elastic moduli of metallic glasses correlate with their thermal and mechanical properties, such as the glass-transition temperature \(T_g\) [9–11], the strong/fragile characteristics of the undercooled liquid [1,12] and the toughness/brittleness of the glass [11–13]. To study the correlation between amorphous alloy compositions and elastic properties, conventional measurements using bulk glass samples suffer from a lack of compositional resolution, due to tedious and labor-intensive preparation of bulk samples. The highest compositional resolution previously achieved in binary glasses is only 1–2 at.% variation between samples [14,15]. The compositional resolution achieved in systems with three or more components is even poorer [16], and is limited to quite narrow composition ranges. This limited compositional resolution is an obstacle to the development of such materials, as it has been reported that a compositional
change of less than 1 at.% can lead to a substantial difference in the packing efficiencies, mechanical properties and/or glass-forming abilities for a multi-component glass [5,6,14,16]. Therefore, more detailed measurements over large composition ranges are desired.

Owing to the small size and close spacing of the microcantilevers, the combinatorial deposition of amorphous metallic thin films can meet both the requirements for large composition coverage and excellent compositional resolution. Figure 1 shows designs of an entire sample and a single set of cantilevers used in this work. The long strip-shaped sample (Fig. 1a) contains 116 × 20 = 2320 sets of cantilevers, with each set including 17 cantilevers (Fig. 1b). Free-standing SiN microcantilevers of 228 ± 1 nm thickness and low residual stress were manufactured based on the designs illustrated in Figure 1, using standard microfabrication techniques [17]. Subsequently, Cu–Zr films with thicknesses of 161 ± 5 nm were sputter-deposited on the cantilevers by means of separate elemental sources [5]. Because the position of the cantilevers varied relative to the Cu and Zr targets, a composition gradient was created along the sample surface in the direction indicated in Figure 1a, varying from approximately 42 to 68 at.% Cu, as determined using energy-dispersive X-ray spectroscopy (EDX). The error of the EDX composition measurements was estimated to be within 1.0 at.% X-ray diffraction analysis was carried out at different locations along the direction of the composition gradient, and the structure of the as-deposited film was confirmed to be fully amorphous on all cantilevers.

We used an atomic force microscope (AFM; MFP 3D, Asylum Research) instrumented with an AFM cantilever (ATEC-FMAu, Nanosensors) to determine the elastic properties of the amorphous Cu–Zr films. Here, the piezoactuated AFM cantilever is employed as a calibrated force–displacement sensor to deflect the sample cantilever of a uniform width \(w = 10 \mu m\) and effective lengths \(L\) along the sample cantilever length (Fig. 2a).

By knowing the spring constant \(k_{AFM}\) of the AFM cantilever and the dimensions of the sample cantilever, the spring constant of the sample cantilever \(k_b\) can be calculated from the linear loading/unloading force–displacement responses [18,19]. Here, \(k_b\) is related to the cross-sectional stiffness \(S\) of the Cu–Zr/SiN bilayer cantilever by [20]:

\[
k_b = \frac{3S}{L}
\]

where \(S\) is a function of the Young’s elastic moduli of the film \((E_f)\) and substrate \((E_s)\), the thicknesses of the film \((h_f)\) and substrate \((h_s)\), and the width of the sample cantilever \((w)\) [20]:

\[
S = \frac{E_s w h^3}{12} \left\{ 1 + \frac{E_f}{E_s} \frac{h_f}{h_s} \left[ 3 \left( 1 + \frac{h_f}{h_s} \right)^2 + \frac{h_f}{h_s} \right] \right\}
\]

Therefore, once \(k_b\) is obtained from measurements for a given effective cantilever length \(L\), \(S\) can be calculated directly. The Young’s modulus of the film \(E_f\) can then be extracted provided the Young’s modulus of the substrate and the layer thicknesses are known.

To minimize the error caused by uncertainties in determining the effective length \(L\), which is related to \(k_b\) by its cube (Eq. (1)), three sets of measurements were performed on each cantilever, at nominal distances from the support of \(L_0\). \(L_1 = L_0 + d\), \(L_2 = L_0 + 2d\). This is shown schematically in Figure 2b. In practise, \(L_0\) was estimated via the integrated optical microscope for this AFM (IX71, Olympus), and the relative displacements \(d\) between each loading position were determined with nanometer accuracy via piezoactuation of the AFM.

![Figure 2a](image-url) **Figure 2a.** Schematic illustration of measurement of Young’s modulus using an AFM. \(k_b\) is the spring constant of the sample cantilever (unknown), \(k_{AFM}\) (known) is the spring constant of the AFM probe. \(L\) is the effective length of the sample cantilever being deflected, \(z\) is the displacement of the AFM cantilever fixed end and \(\delta\) is the deflection of the AFM cantilever free end. \(z\) and \(\delta\) were used in the calculation of \(k_b\) [18,19].

![Figure 2b](image-url) **Figure 2b.** Top view of a cantilever, showing three measurement locations. \(L\) is the length of the sample cantilever, \(w\) is the width of the cantilever, \(L_0\) is the effective length of the first AFM measurement and \(d\) is the relative displacement between the three sets of measurements.

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**Figure 1.** Layout of the cantilever arrays used in this study. (a) Sketch of a sample in plan view. Each 16 mm × 64 mm strip-shaped sample comprised 2320 “pits”, over which 17 cantilevers were fabricated. (b) Layout of a “pit” with a set of cantilever-shaped patterns extending from the sides of a 250 μm × 250 μm square. Starting from the bottom side of the square and moving clockwise, the dimensions of the cantilevers are 10 μm × 50 μm, 10 μm × 40 μm, 10 μm × 40 μm and 10 μm × 50 μm, respectively.
sample stage. Therefore, although the absolute values of $L_0$, $L_1$ and $L_2$ may not be precise, the relative displacements of the test locations $d$ are known accurately. The corresponding spring constants obtained from those three serial tests are:

$$k_1 = \frac{3S}{L_0^3}$$  

(3a)

$$k_2 = \frac{3S}{(L_0 + d)^3}$$  

(3b)

and

$$k_3 = \frac{3S}{(L_0 + 2d)^3}$$  

(3c)

A best-fit linear regression to these three data points, $k^{-1}$ ($k = k_1$, $k_2$ and $k_3$) vs. $L$ ($L = L_0$, $L_0 + d$ and $L_0 + 2d$), allows determination of $S$ from the slope ($3S^{-1}$) of the fitted line, independently of the absolute value of $L_0$. In actual measurements and data analysis, $L_0$ was estimated to be 20 $\mu$m and $d$ was set to be 5 $\mu$m, so that the effective cantilever dimensions for the three measurements were 10 $\mu$m $\times$ 20 $\mu$m, 10 $\mu$m $\times$ 25 $\mu$m and 10 $\mu$m $\times$ 30 $\mu$m. The spring constant of the AFM cantilever, $k_{AFM}$, was calibrated via the thermal noise method to be 1.90 nN $\text{nm}^{-1}$ [21], and the Young’s modulus of SiN was assumed to be 195 $\pm$ 7 GPa [22].

These AFM deflection measurements were conducted for different cantilevers along the composition gradient (Fig. 1a) at a compositional resolution of about 0.3 at.%. Figure 3 shows the measured Young’s modulus of the amorphous Cu–Zr films as a function of Cu at.%, as well as a few reported modulus data points measured from bulk Cu–Zr metallic glass samples [14]. The error bars indicate the standard deviation for approximately 10 individual measurements for each cantilever sample. Variation in the error range can be attributed to minor variations in probe placement on each cantilever sample. It is clearly seen that there is a general trend of increasing Young’s modulus (roughly from 40 to 80 GPa) with increasing Cu content. There are no special features or deviations from this monotonic increase at specific compositions. This trend is thus in contrast with our earlier measurements of the density change on crystallization, where density change minima were observed at approximately Cu$_{50}$Zr$_{50}$, Cu$_{56}$Zr$_{44}$ and Cu$_{62}$Zr$_{38}$ [5].

Among the elastic constants of metallic glasses, the shear modulus $G$ and the Poisson’s ratio $v$ (or, equivalently, the bulk/shear modulus ratio, $B/G$) have attracted the most research interest, since it has been proposed that they closely correlate with the alloy’s fracture energy [13,23], failure strain [24,25], fragility in the undercooled liquid regime [12,23] and glass-forming ability [12,23]. Young’s modulus $E$ has been found to scale with the glass-transition temperature $T_g$ [9–12] and the tensile fracture strength $\sigma_f$ [11,12] of metallic glasses. This is not unexpected, in that all three properties are related to the atomic bond stretching resistance among the constituents [9,11,12]. Therefore, the results shown in Figure 3 suggest that the ratio of atomic bond stiffness to bond length increases monotonically with increasing Cu content. Such a trend is consistent with available elastic modulus data from the literature, for both computational simulations and experimental measurements from bulk Cu–Zr glasses [14,26]. In addition, the $T_g$ of Cu–Zr glasses has also been reported to increase monotonically with increasing Cu content [14,27], confirming the correlation between $T_g$ and $E$ in the Cu–Zr system.

Figure 3 also illustrates that, while the measured compositional trend in the thin film elastic moduli is similar to that measured in bulk materials, the magnitudes of film elastic moduli are significantly lower. This may be explained in terms of the high effective cooling rate of sputter deposition and the resulting higher quenched-in free volume content in the amorphous film. It has been extensively reported that, in various alloy systems, the relaxation of metallic glasses at or below $T_g$ would result in an increase in Young’s modulus, attributed ostensibly to the annihilation of free volume and the subsequently shorter average interatomic distance [28–31]. Since the sputter-deposited films may have systematically lower density (i.e. greater free volume) compared to glasses formed by liquid quenching [5], it is not unexpected that the amorphous Cu–Zr films have substantially lower Young’s moduli. Indeed, in previous studies, sputter-deposited Pd-based amorphous films were found to exhibit Young’s modulus approximately 25% lower than that of bulk amorphous samples of the same alloy compositions [32,33]. This 25% relative difference agrees reasonably well with the relative decrease observed in this work for Cu–Zr (approximately 20–30%, as shown in Fig. 3).

Chou et al. [34] have previously conducted nanoindentation measurements on amorphous Cu–Zr films with uniform compositions sputter-deposited on Si wafers, and reported that the Young’s moduli of the Cu–Zr films ranged from 80 to 100 GPa for 30–50 at.% Cu. Those elastic moduli are substantially higher than the range observed in the present work (40–80 GPa for 42–68 at.% Cu). Those values obtained via nanoindentation for 50 at.% Cu also exceed that measured for Cu$_{50}$Zr$_{50}$ bulk metallic glass (70 GPa [14]). This apparent overestimation of film elastic moduli via indentation can be attributed to several well-established challenges in the accurate inference of thin film elastic properties, including contributions of the underlying, stiffer substrate [35–37] and uncertainties of the indenter contact area [38–40]. Although the determination of Young’s modulus from cantilever deflection also requires some modeling to reduce experimental errors and uncertainties [41,42], the
data obtained in this work (Fig. 3) are a more direct inference of the elastic moduli. Uncertainties associated with the modeling are reduced by acquiring measurements at different effective cantilever lengths (Fig. 2b). Further, the general accuracy of this approach is supported by agreement with the literature for other (Pd-based) metallic glasses, in terms of the relative difference between the moduli of bulk glass samples and the corresponding thin films [32,33]. Moreover, even if the absolute values of $E_t$ obtained from cantilever measurements are inaccurate, the high compositional resolution afforded by the cantilever approach renders the comparison between relative values useful in the identification of unique compositions or trends (see Fig. 3).

Additionally, an important advantage of the cantilever approach is that the calculation of $E_t$ via this method does not require knowledge of the Poisson’s ratio $v$ of the sample [20]. In contrast, indentation requires this second elastic constant to determine the $E$ value of the sample [35], this value typically being assumed rather than measured directly. In a few metallic glass systems, the compositional dependence of $v$ has been reported to be complex and non-monotonic [9,16,25], and it has been argued that this is related to the non-monotonic compositional dependence of ductility. Consequently, the assumptions made about $v$ may not be correct in the calculation of $E_t$ from indentation measurements. Further, as mentioned earlier, it has been postulated that glass formation ability (GFA) correlates with $v$ [12,23]. Given our recent finding of a strong compositional dependence of GFA [5], one would therefore expect a strong compositional dependence for $v$. Our finding that $E_t$ does not correlate in the same way with GFA indicates that other techniques that measure moduli dependent on both $E_t$ and $v$ can be used to search for correlations between $v$ and GFA.

In summary, the combinatorial deposition of amorphous Cu–Zr films on microscale cantilever arrays enabled facile determination of correlations between the compositions and Young’s moduli of these films. AFM-based deflection of the cantilevers demonstrated a monotonic increase in Young’s modulus with increasing at.% Cu, with no significant outliers. Further, we found that these elastic moduli are approximately 25% lower than that reported for bulk Cu–Zr glasses over the same compositional range. We attribute this difference to the higher effective cooling rate during sputter deposition compared to bulk metallic glass synthesis. Such cantilever-based surveys of correlations between composition and mechanical properties can be obtained more quickly and with higher compositional resolution than measurements on bulk or conventional thin film samples of fixed composition. In addition, the use of cantilever deflection instead of indentation simplifies the calculation of film elastic moduli and, importantly, does not require the measurement or assumption of values for Poisson’s ratio in amorphous metallic alloys.

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