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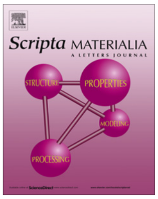

Patterning of metallic glasses using polymer templates

Z. Hu, S. Gorumlu, B. Aksak, G. Kumar *

Department of Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States

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ABSTRACT

We demonstrate patterning of metallic glasses using flexible and reusable polymer templates. The elastic deformation of polymer templates is utilized to pattern features of varying dimensions and oblique angles on planar and non-planar surfaces. This is enabled by low thermoplastic processing temperatures of certain metallic glasses and the stability of thermosetting polymers used as the mold making material. The polymer templates are fabricated by standard replica molding of silicon master templates. This provides a scalable method for patterning of metallic glasses which otherwise requires expensive disposable silicon templates.

Patterning of materials is an integral component of fabrication process in microelectronics [1], optical devices [2], and surface engineering [3]. There is an overwhelmingly growing demand for patterning smaller features on novel materials along with reduction in cost of scalability. As a result, tremendous progress has been made in advancement of patterning techniques such as lithography [4], nano-imprinting [5,6], embossing [3,7], self-assembly [8,9], LIGA [10,11], and laser processing [12]. Despite these efforts, patterning of metallic materials is far less advanced compared to polymers and semiconductors. This deficit is related to inherent challenges in metal processing such as high surface energy, oxidation, rapid grain growth, and incompatibility with mechanical embossing. Recent work on thermoplastic molding of metallic glasses (MGs) appears to bridge this processing capability gap between metals and polymers [13–17]. Pattern features in the range of sub-100 nm have been demonstrated by thermoplastic embossing of MGs [16,18–20]. After embossing, the MGs can be crystallized by thermal annealing if patterns in crystalline metals are desired [21]. Though thermoplastic shaping of MGs exhibits a great potential for scientific studies [19,22–25], the template cost poses a major hurdle for large-scale implementation. Typically, silicon templates prepared by lithography are used because of their precision and rigidity [15,17]. MGs cannot be released from silicon templates without etching because of their thermal expansion mismatch and scalloping roughness of silicon templates. This limits the template usage to a single molding operation even for low-aspect-ratio features without undercuts. Additionally, the employment of rigid templates limits the patterning application to planar surfaces. To overcome these issues, we explore the application of polymer templates for patterning of MGs with low glass transition temperatures. The polymer templates offer several advantages such as: inexpensive fabrication by replica molding of the master template, ease in demolding, reusability, and conformation to non-planar shapes [26–28]. Furthermore, elastic deformation (stretching, compression or bending) of polymer templates can be used to vary the size and orientation of features without the need of a new template [29]. The key requirement for using polymer templates is their stability at thermoplastic molding temperatures (~150–450 °C) of MGs. There is a wide range of thermosetting polymers which are stable up to 300 °C. In the present study, we used PDMS (Polydimethylsiloxane) as a template for Pt-based ($Pt_{57.3}Cu_{14.6}Ni_{5.3}P_{22.8}$) MG, which has a glass transition temperature (T_g) of 230 °C [30]. The technique described here can be applied to other combinations of thermosetting polymers and low T_g MGs such as Ce-based [31], Mg-based [32], and Au-based [33]. PDMS (Sylgard 184, Dow Corning) base and curing agent were mixed in 5:1 ratio followed by degasing in a vacuum chamber for 5 min. The degassed PDMS mixture was poured onto the master template and was cured at 70 °C for 24 h. The thermoplastic embossing experiments were conducted at 270 °C using a custom-built set-up described elsewhere [21,34].

Fabrication of polymer templates and their use in patterning of MGs are illustrated in Fig. 1. A lithographically patterned silicon or a thermoplastically patterned MG can be used as the master template. The features of master templates are replicated in a cross-linking polymer by a standard replica molding process (casting and curing). Once cured, the polymer serves as an inexpensive template for the subsequent patterning of multiple MGs. An

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* Corresponding author.
E-mail address: golden.kumar@ttu.edu (G. Kumar).

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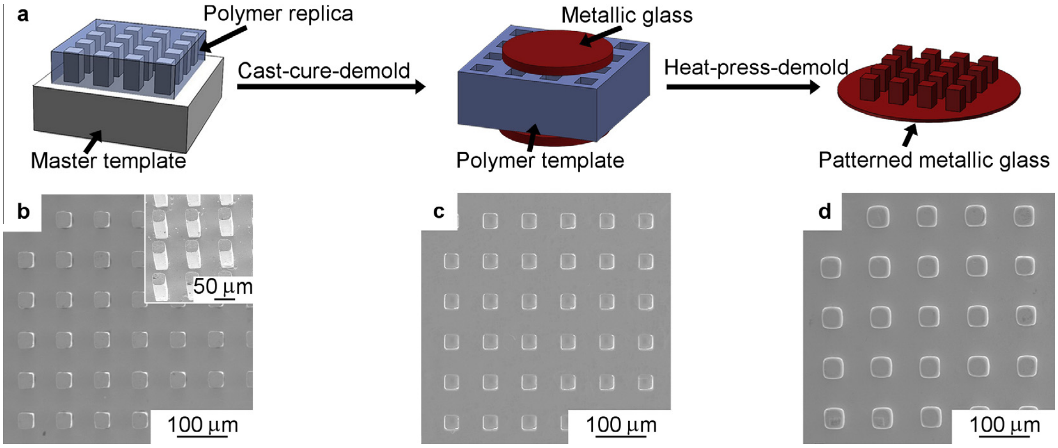

Fig. 1. Fabrication of textured polymer and their use as templates for thermoplastic patterning of MGs. Schematic illustration of the processing scheme (a), an example of silicon master template with micro-pillars (b) and its tilted view (inset), a PDMS template with micro-holes prepared by replica molding (c), and a Pt-based MG surface patterned by using the PDMS as a template (d). Two MG disks, one on each side, are pressed to establish similar boundary conditions on the top and the bottom surfaces of the PDMS template.

additional MG disk was placed at the unpatterned side of the polymer template to create similar boundary conditions on both sides of the template. The SEM (Scanning Electron Microscopy) images of the silicon master template (Fig. 1b), the polymer replica (Fig. 1c), and the subsequently patterned MG (Fig. 1d) demonstrate the feasibility of the proposed fabrication approach. The master template consists of square shaped micro-pillars (25 × 25 μm) with aspect ratios of three fabricated by photolithography and DRIE (Deep-Reactive-Ion-Etching). The PDMS precisely replicated the features of the silicon master template, resulting in the formation of square shaped holes. The textured PDMS could be used multiple times to pattern MG samples because of nondestructive demolding facilitated by the flexibility of the template. As shown in Fig. 1d, the size, the shape, and the spacing of features are highly uniform in Pt-based MG patterned using the PDMS template. There is a clear increase in the size of the pattern features in the MG compared to the master (and the polymer) template because of the elastic deformation of the polymer template during compression molding. This dimensional change in pattern features can be predicted by using finite element modeling based on the loading response of the polymer [26]. The master template can be designed to account for the elastic deformation of polymers for a desirable final pattern in MGs. Alternatively, polymer templates with higher stiffness can be used to minimize the variation in pattern dimensions. Besides PDMS, many other thermosetting polymers exhibit suitable properties for applications as templates for patterning of MGs. The properties of template materials that affect the outcome of MG patterning are: thermal stability, Young's modulus, compressive yield strength, and strain limit. These properties for few common thermosetting polymers and their applications as templates are listed in Table 1. It should be noted that the mechanical property data are from room temperature measurements and should be used only for a comparison. For quantitative modeling of template deformation during embossing the mechanical response of polymers at the embossing temperature should be measured. The maximum service temperature of common thermosetting polymers suggests their applicability to a range of MGs such as Ce-based, Au-based, Mg-based, La-based, and Pt-based. Further increase in thermal stability of polymers through composite approach may extend their use for other MGs with higher glass transition temperature.

Thermoplastic patterning of MGs using rigid templates is well parameterized in terms of embossing temperature and pressure [35–37]. However, the lateral dimensions (diameter and spacing) of features are fixed by the rigid template and cannot be varied by processing conditions. The use of flexible templates, however, introduces an additional variable – template deformation – that can be utilized to control the patterning outcome without changing the template. One way to affect the template deformation, and hence the pattern dimensions, is by varying the embossing pressure. Fig. 2 shows the SEM images of Pt-based MG pressed on the same PDMS template under 150 N (Fig. 2a), 200 N (Fig. 2b), and 300 N (Fig. 2c). Microstructural characterization of these samples reveals a systematic variation in size and spacing of pattern features with applied load. Individual pillar size (d1) increased from 36.3 μm (@150 N) to 42.6 μm (@200 N), and ultimately to 48.7 μm (@300 N). The edge-to-edge spacing (d2) decreased from 64.3 μm (@150 N) to 63.6 μm (@200 N), and finally to 61.8 μm (@300 N).

The load-dependent dimensional change in MG features stems from the template's incompressible nature which inversely converts the large vertical strain caused by compressive stress into lateral expansion. This enables patterning of MGs with features of different sizes and spacings using a single template, which significantly lowers the processing cost compared to the conventional approach that relies on customized silicon templates. In addition, the MG features molded using polymer templates displayed a smooth surface whereas silicon templates often transfer scalloping roughness to the MG surface [38].

Besides the variation in feature size under uniform deformation, the flexible templates can also be subjected to non-uniform

Table 1
Maximum service temperature and mechanical properties of some common thermosetting polymers for template applications.

Template	Maximum service temperature (°C)	Young's modulus (MPa)	Compressive yield strength (MPa)	Elongation limit (%)	Applications as a template material
Silicone rubber	<250	∼1	<20	90–1000	Feature size variation and non-planar patterning
PDMS	<280	5–10	30–50 (ultimate strength)	160	Feature size variation and non-planar patterning
Polyurethane	<250	70–1000	30–100	∼800	Medium-aspect-ratio features
SU-8	<250	2000–4000	50–75	4–6	Precise and high-aspect-ratio features
Epoxy resin	<300	>2000	∼80	5–10	Precise and high-aspect-ratio features

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