AIP Journal of Applied Physics

Large size metallic glass gratings by embossing

J. Ma, J. Yi, D. Q. Zhao, M. X. Pan, and W. H. Wang

Citation: J. Appl. Phys. **112**, 064505 (2012); doi: 10.1063/1.4752399
View online: http://dx.doi.org/10.1063/1.4752399
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v112/i6
Published by the American Institute of Physics.

JOURNAL OF APPLIED PHYSICS 112, 064505 (2012)

Large size metallic glass gratings by embossing

J. Ma, J. Yi, D. Q. Zhao, M. X. Pan, and W. H. Wang[a)]
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

(Received 20 June 2012; accepted 9 August 2012; published online 18 September 2012)

Bulk metallic glasses have excellent thermoforming ability in their wide supercooled liquid region. We show that large-size metallic glass grating ($\sim 8 \times 8$ mm^2) with fine periodicity and ultra smooth surface feature can be readily fabricated by hot embossing. The method for fabrication of gratings is proved to be much cheaper, and requires low pressure and short time (less than 30 s). The metallic glass gratings exhibit comparable optical properties such as rainbow-like spectrum when shone by fluorescent lamp light. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4752399]

I. INTRODUCTION

Bulk metallic glasses (BMGs) have superior thermoforming ability in their supercooled liquid region (SLR), which is a wide temperature region between glass transition temperature T_g and crystallization temperature T_x.[1,2] The viscosity dramatically drops with the increase of temperature in the SLR, which drives the transition of metallic-like to plastic-like behavior, enables the convenient hot embossing of bulk metallic glasses.[3,4] Compared with the most thermoplastic materials, BMGs show unique features of high molding precision owing to their lack of crystallinity and shrinkage upon solidification,[5–10] recoverable splendid mechanical performance such as high strength, and good electric conductivity after thermoplastic treatment.[1] Previous work had revealed that various three-dimensional microscale structures can fabricated by hot embossing of BMGs.[8,10,11] However, very little work on the optical properties of the micro structured BMGs was conducted.

Gratings with excellent properties are urgently required with the rapid development of spectroscopic analysis and sensor technology. Currently available methods of manufacturing gratings such as mechanical ruling or replicating are either easy to bring in defects (e.g., target patterns) or too complicated of the structure and fragile for practical use. Furthermore, these methods are expensive.[12] Previous work showed that the BMGs were suitable for the fabrication of gratings.[13] However, the grating area (less than $600 \times 600\,\mu$m^2) was too small for practical use. In this paper, we report that the large-size gratings with an area of about 8×8 mm^2 and fine profile parameters can be conveniently fabricated by hot embossing of BMGs.

II. EXPERIMENTAL

To choose a proper BMG for hot embossing, some characteristics of the BMGs must be considered. The BMG should have uniform flow properties and should be hot stable in its SLR for the hot embossing. $Pd_{40}Cu_{30}P_{20}Ni_{10}$ (at. %) has a large fragility coefficient $m \sim 59$, which is a measure of the temperature dependence of the viscosity η around T_g, standing for a dramatic drop of η when heated into its SLR. A parameter $f = m\Delta T/T_x$ (where, $\Delta T = T_x - T_g$ is the width of the SLR) was proposed[15,17,18] to evaluate the thermoforming ability of BMGs. The value of f for $Pd_{40}Cu_{30}P_{20}Ni_{10}$ is 8.6 and larger than that of Zr-, Mg-, and Fe-based BMGs, indicating the good formability of the $Pd_{40}Cu_{30}P_{20}Ni_{10}$ BMG in its SLR. Grating-like microstructured Si master template, which was used as die for hot embossing, was fabricated by photoetching technology. The $Pd_{40}Cu_{30}P_{20}Ni_{10}$ BMG plate with a thickness of 1 mm and width of 8 mm was prepared by conventional water cooled copper mould casting. The amorphous nature of the samples was ascertained by x-ray diffraction (XRD) with Cu K_α radiation and differential scanning calorimetry (DSC). The surface feature of the structured BMG plate and Si die were examined by scanning electron microscopy (SEM). The SEM observations were performed in Philips XL30 SEM instrument.

The hot embossing was carried out on electromechanical INSTRON 3384 equipment equipped with a heating furnace. The furnace was heated to 620 K (high temperature side in SLR of the Pd-based BMG to obtain good viscous flow properties during hot embossing) and then the Si die and BMG plate (on the top of Si die) were placed on the hot plate of the furnace, a force of 20 MPa was applied for 25 s afterwards.

III. RESULTS AND DISCUSSION

The BMG plate was then cut into a length of about 8 mm with a diamond saw. The surface of the plate was first polished by hand with abrasive papers up to No. 1200 and then 1.5 μm diamond paste on the polishing machine. The whole embossing process conducted in the air lasted for less than half a minute. Figure 1(a) shows the XRD patterns of the as-prepared BMG and the BMG plate after hot embossing. It can be seen that the BMG plate remains glassy state after the mechanical polishing and hot embossing. Figure 1(b) is the DSC trace of the BMG, which confirms the glass nature of the BMG.

[a)]Author to whom correspondence should be addressed. Email: whw@iphy.ac.cn.

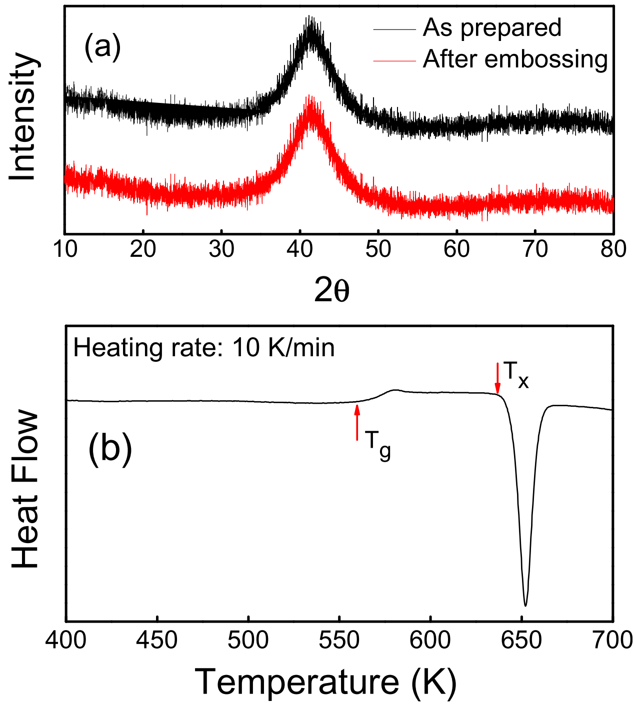

FIG. 1. (a) XRD patterns of the as prepared and embossed $Pd_{40}Cu_{30}P_{20}Ni_{10}$ metallic glass. (b) DSC scans (at a heating rate of 10 K/min) of the Pd-based BMG.

Figure 2 presents SEM images of the Si die and BMG plate after hot embossing. Figures 2(a) and 2(c) are the top view, and Fig. 2(e) is the side view of the Si die. The width of the grating ridges of the Si die is 4.2 μm, and the grating hollow is 3.8 μm with an etched depth of ~15 μm. Figures 2(b) and 2(d) show the top view, and Fig. 2(f) exhibits the side view of the formed structure of the BMG replica. The stained fracture surface in Fig. 2(f) is induced by snapping the BMG plate in order to characterize the filling depth by SEM. The width of the BMG grating ridges is 3.5 μm, and the grating hollow is 4.4 μm with a filling depth of 2.2 μm. The relationship between the filling depth of BMG replica and applied pressure is given by[7,8]

$$p = \frac{32\eta}{t}\left(\frac{l}{d}\right)^2, \quad (1)$$

where p is the applied pressure, η is the viscosity of softened BMG, t is the processing time for hot embossing, d is the characteristic dimension of the microstructure, and l is the filling length. By substituting $\eta = 5 \times 10^7$ Pa·s,[16] $d = 3.8\,\mu$m, and $p = 20$ MPa into Eq. (1), the calculated filling depth l is 2.1 μm, which is in agreement with the experimental result. Based on Eq. (1), the filling depth l could be tuned by adjusting hot embossing parameters (e.g., applied pressure or processing time). The grating constant shrink from 8 μm of Si die to 7.9 μm of the BMG replica, which is a slight shrinkage of ~1.25%. Figure 1 also shows the ultra smooth surface of BMG grating, which is perfectly identical with the Si die.

The atomic force microscopy (AFM) (SPA-400) was used to characterize the profile of the BMG grating surface. The scanning area is $20 \times 20\,\mu m^2$, owing to the large difference from peak to valley; some details in the hollow of the gratings are not revealed, which is limited by the maximum measuring range of AFM. Figure 3(a) and 3(b) show the AFM images of single grating ridge of the Si die and the surface structured BMG, respectively. The height fluctuation is less than 25 nm at a length of 20 μm parallel to the direction of grating ridges for the BMG, indicating the excellent surface quality after hot embossing. Figure 3(c) illustrates how the BMG is squeezed into the Si mould. The frictional force between BMG and the side wall of the microcavity of Si die slows the filling speed of the contact area (blue dashed line area in Fig. 3(c)) comparing with the free surface [green dashed line area in Fig. 3(c)] that has lower filling resistance. One can see that the free surface in the microcavity of Si die slightly extrudes and causes the sine shape grating, corresponding to the results of AFM measurement.

It is known that the gratings diffract light into certain angles obeying grating equation. When compound light (e.g., sunlight) shines upon grating, each individual light, which composes the compound light, is separated towards certain direction. Figure 4 shows the BMG plates, which were shone by fluorescent lamp light. The colorful rainbow-

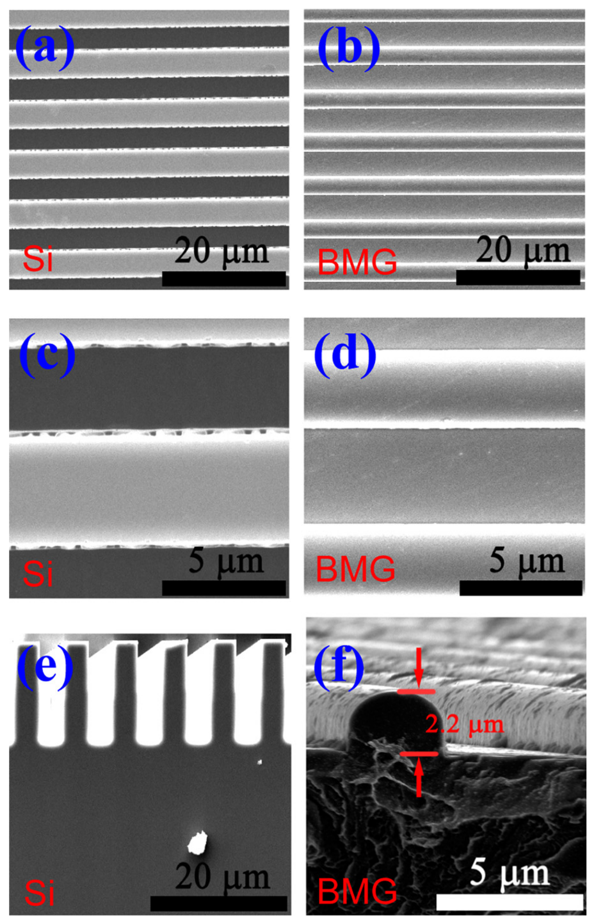

FIG. 2. SEM photographs of Si die and hot embossed BMG grating. (a) and (c) are the top views and (e) is the side view of the Si die. (b) and (d) are the top views of BMG grating and (f) is the side view. (c) and (d) are the close-up views of (a) and (b), respectively.

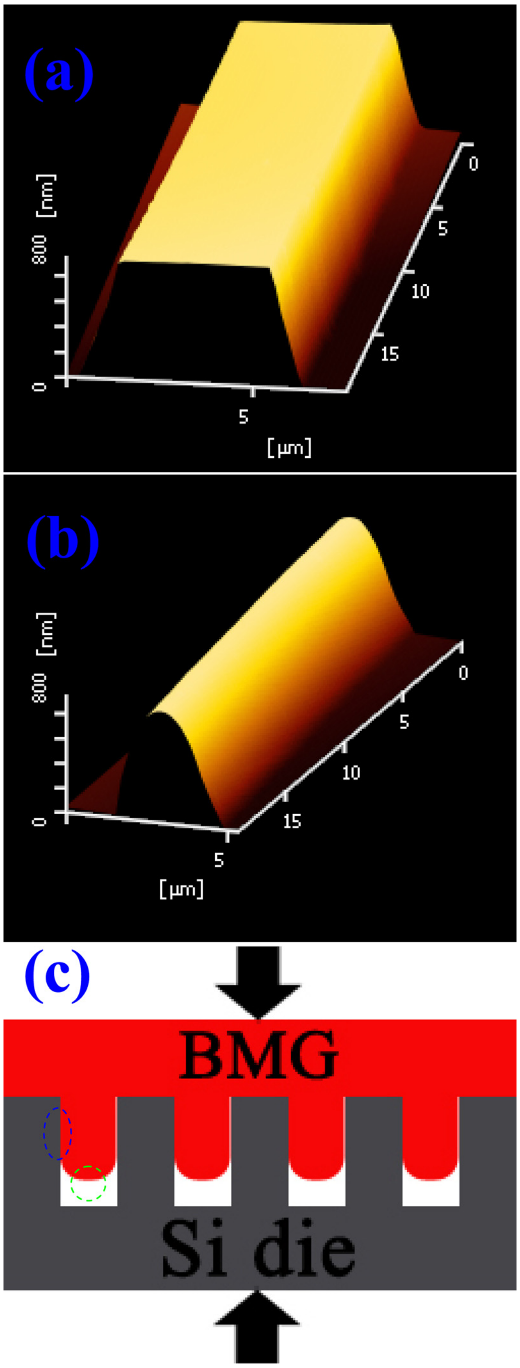

FIG. 3. AFM images of (a) single Si die, and (b) BMG grating ridges, (c) the schematic diagram of the hot embossing process.

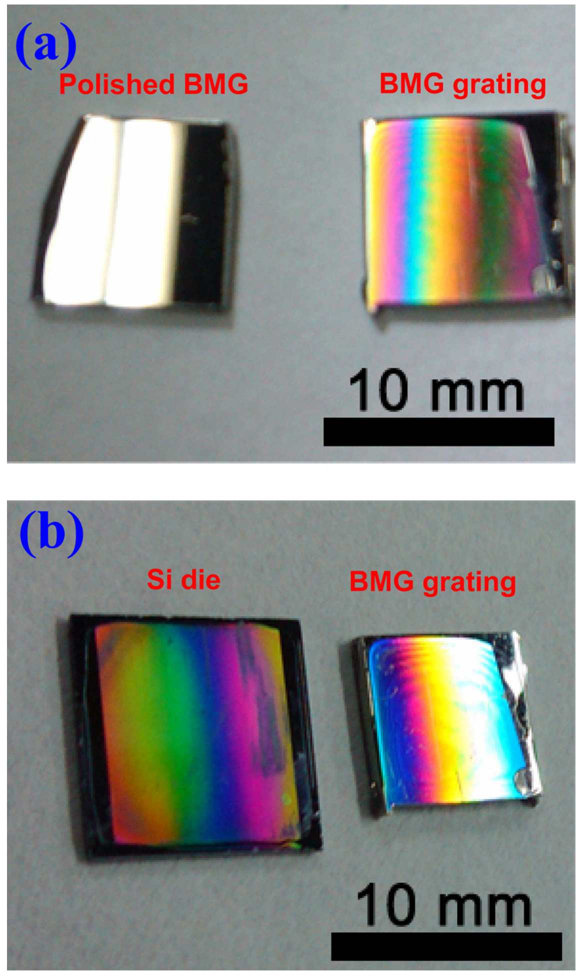

FIG. 4. (a) Photographs of polished BMG plate (left) and BMG grating (right) when fluorescent lamp light shines upon them. (b) Photographs of Si die (left) and BMG grating (right) under the shine of fluorescent lamp light.

like BMG plate with grating structure fabricated by hot embossing is in contrast with the polished one which only has metallic luster [See Fig. 4(a)]. In addition, due to the high reflectance (which is caused by the ultra smooth surface), the BMG replica is even more brilliance than Si die, indicating a better diffraction efficiency [Fig. 4(b)]. This may casts a new light on the fabrication of integrated optical components such as diffractive optical microstructured elements with the hot embossed BMG gratings. Furthermore, these replicated BMG gratings can also be used as molding dies to further create the second-generation replicas on thermoplastic polymers.[13,14]

IV. CONCLUSIONS

The desirable thermoforming ability and net-shape forming ability of BMGs make them be ideal candidate for fabricating optical gratings. The centimeter scale large-size metallic glass grating with fine profile and ultra smooth surface, excellent mechanical properties such as high strength and wear resistance can be fabricated by the convenient, precise, and economical hot embossing. The method provides a simple, controllable, cheaper, and time saving gratings fabrication method in contrast with conventional ones.

ACKNOWLEDGMENTS

The financial support of the MOST 973 of China (Grant Nos. 2010CB731603 and 2011CB012806) and NSF of China (Grant Nos. 50890171, 5092109,1 and 51171204), and experimental assistance from the Laboratory of Microfabrication, and Technology Department of Institute of Physics, CAS, are appreciated.

[1]A. Inoue, N. Nishiyama, and H. Kimura, Mater. Trans. JIM **38**, 179 (1997).
[2]W. H. Wang, Prog. Mater. Sci. **57**, 487 (2012).
[3]G. Kumar, H. X. Tang, and J. Schroers, Nature **457**, 868 (2009).

[4]W. H. Wang, Adv. Mater. **21**, 4524 (2009); B. Zhang, D. Q. Zhao, W. H. Wang, and A. L. Greer, Phys. Rev. Lett. **94**, 205502 (2005).
[5]B. Zhang and W. H. Wang, J. Non-Cryst. Solids **352**, 5687 (2006).
[6]B. Zhang, D. Q. Zhao, M. X. Pan, R. J. Wang, and W. H. Wang, Acta Mater. **54**, 3025 (2006).
[7]X. F. Liu, R. J. Wang, D. Q. Zhao, M. X. Pan, and W. H. Wang, Appl. Phys. Lett. **91**, 041901 (2007).
[8]J. Schroers, JOM **57**, 35 (2005); Adv. Mater. **22**, 1566 (2010).
[9]K. Zhao, X. X. Xia, H. Y. Bai, D. Q. Zhao, and W. H. Wang, Appl. Phys Lett. **98**, 141913 (2011).
[10]J. Yi, L. S. Huo, H. Y. Bai, and W. H. Wang, Sci. Chin. G **54**, 609 (2012).
[11]G. P. Zhang, Y. Liu, and B. Zhang, Adv. Eng. Mater. **7**, 606 (2005).
[12]C. Palmer, *Diffraction Grating Handbook*, 6th ed. (Newport Corporation, New York, 2005), p. 220.
[13]J. P. Chu, H. Wijaya, C. W. Wu, T. R. Tsai, C. S. Wei, T. G. Nieh, and J. Wadsworth, Appl. Phys. Lett. **90**, 034101 (2009).
[14]J. Yi, X. X. Xia, D. Q. Zhao, M. X. Pan, H. Y. Bai, W. H. Wang, Adv. Eng. Mater. **12**, 1117 (2010).
[15]J. Yi, H. Y. Bai, D. Q. Zhao, M. X. Pan, and W. H. Wang, Appl. Phys. Lett. **98**, 241917 (2011).
[16]R. Busch, J. Schroers, and W. H. Wang, MRS Bull. **32**, 620 (2007).
[17]J. Ma and W. H. Wang, J. Appl. Phys. **112**, 024506 (2012).
[18]N. Zhang, C. J. Byrne, D. J. Browne, and Mi. D. Gilchrist, Mater. Today **15**, 216 (2012).