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Selective-area fabrication of bulk metallic glass nanowires on silicon

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ABSTRACT

We report a facile technique to fabricate metallic nanowires on selective areas on silicon. Nanowires are fabricated by thermoplastic drawing of bulk metallic glass from microscale cavities etched in silicon. The metallic nanowires are formed only on selective areas by using aluminum foil masks. The mask restricts the flow of bulk metallic glass to predefined openings during thermoplastic processing and enables the formation of nanowires on selective areas on silicon. We show that nanowires with different aspect-ratios can be formed by tailoring the drawing conditions without changing the silicon. Inexpensive aluminum masks can produce a wide range of nanopatterned areas in the size range of 200 μm and larger.

1. Introduction

Nanowires have attracted significant attention due to their novel properties and large surface-to-volume ratio [1]. These unique attributes of nanowires are desirable for applications in electronics, sensors, energy conversion, and biological filtration [2–5]. Nanowires from a broad range of materials have been studied for specific applications [6–8]. Top-down and bottom-up manufacturing techniques have been advanced to synthesize nanowires with controllable shapes and properties. Although significant advancement has been made in the manufacturing of nanostructures, their selective positioning on substrates still requires complex lithography and nanomanipulation techniques [9–11]. It is necessary to controllably attach the nanostructures on specific locations on substrates to make nanoscale devices.

Selective-area growth of semiconductor nanowires has been demonstrated by lithographically patterning the substrates [12,13]. The substrate is pre-patterned with a metal or an oxide layer to enable the subsequent growth of nanowires in selective areas [12]. Selective-area nanopatterning research has been predominantly focused on semiconductors whereas metal nanostructures have received far less attention [14]. Metal nanostructures are usually prepared by solution-based methods and their manipulation is difficult due to high surface energy and poor dispersion [1]. We have previously shown that bulk metallic glass (BMG) nanowires can be formed by thermoplastic drawing from cavities etched in silicon (Si) [15,16]. Here, we show that the BMG nanowires can be selectively patterned on Si by using aluminum (Al) mask during thermoplastic drawing.

2. Materials and methods

The fabrication scheme for BMG nanowires on selective areas is illustrated in Fig. 1. The CAD model of a desired pattern area (e.g. plus sign) was fed into P20 PrismCut vinyl cutter which carved out the pattern in Al foil. The Al foil was aligned on Si mold containing 10 μm diameter holes. $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ (Pt-BMG) was thermoplastically pressed and pulled against the Si mold covered with Al mask. The forming experiments were performed at 270 °C using heating plates attached to a mechanical tester. It has been shown that the pressing-and-pulling of Pt-BMG against a mold can create BMG nanowires [15]. The Al mask blocks some areas of Si mold and results in formation of BMG nanowires only on the areas exposed by the mask (Fig. 1). Rapidly prototyped Al masks can produce different arrays of BMG nanowires without changing the Si mold.

3. Results and discussion

Fig. 2a-c show the scanning electron microscopy (SEM) images of different assemblies of Pt-BMG nanowires prepared by thermoplastic forming through Al masks using the same Si mold. The BMG nanowires are selectively assembled on Si in areas shaped as, plus sign (Fig. 2a), multiple rectangles (Fig. 2b), and UTD sign (Fig. 2c). The smallest dimension of the patterned area is about 200 μm which is limited by the resolution of our vinyl cutter. A slight misalignment of Al mask with the underlying Si cavities can create distortion in the pattern boundary as manifested in the UTD sign. However, the results clearly show that even a low-grade Al mask with visual alignment can enable the selective-area

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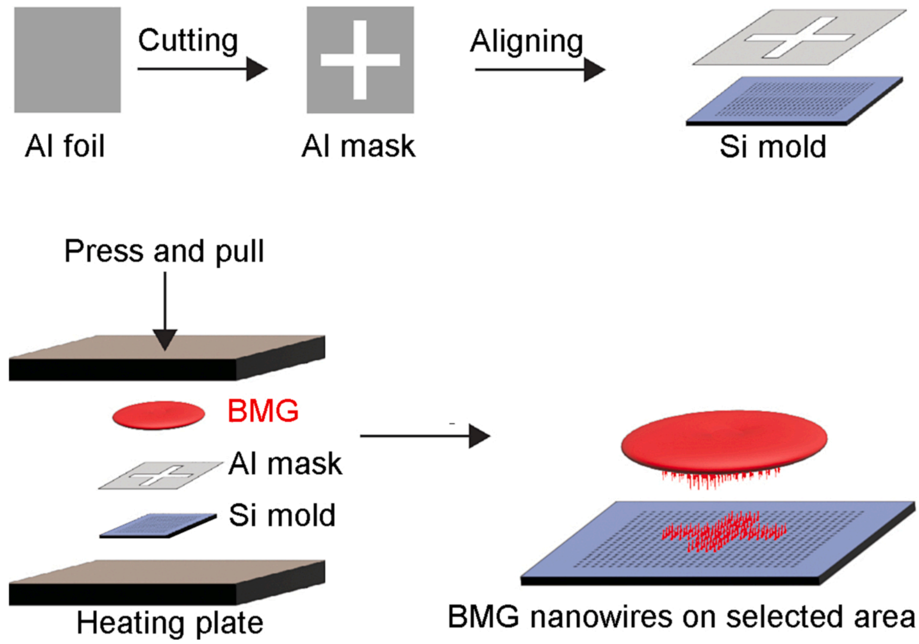

Fig. 1. Schematic illustration of selective area fabrication of BMG nanowires on Si. A mask is made by cutting an opening in Al foil. The BMG is thermoplastically pressed and pulled against a Si mold covered with Al mask. BMG nanowires are formed on Si areas exposed by the Al mask.

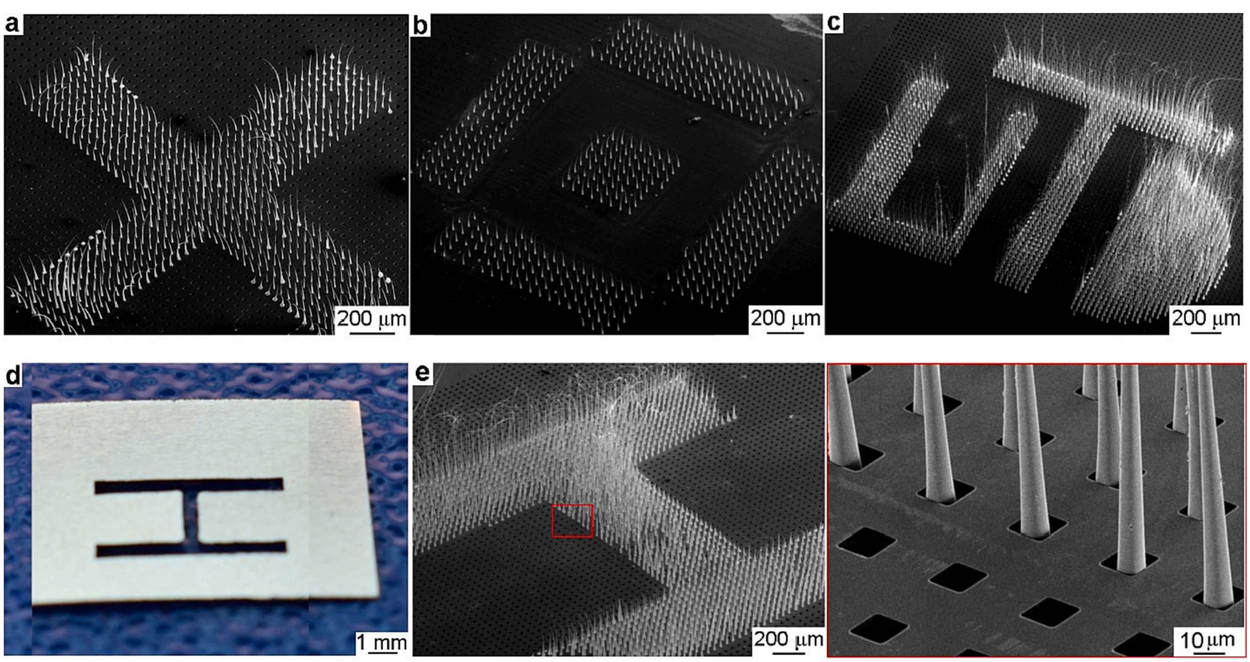

Fig. 2. (a–c) SEM images of BMG nanowires formed on different areas on Si using Al masks. (d) Laser-cut stencil mask of letter H in steel foil. (e) BMG nanowires on Si made by using laser-cut stencil. High magnification image of BMG nanowires on Si.

fabrication of metallic nanowires on substrates.

The resolution and the accuracy of BMG selective-area pattering is improved by using laser cut stencils. Fig. 2d shows an image of laser-cut steel foil stencil for letter *H* and the resulting BMG nanowires in *H* shaped area on Si (Fig. 2e). The magnified view shows distinct boundary between the patterned and the un-patterned areas on Si.

It has been shown that the BMG nanowires of different diameters and lengths can be thermoplastically drawn from the same mold by changing the drawing temperature or velocity [15]. Fig. 3 shows the SEM images of selectively patterned Pt-BMG nanowires with different lengths made by varying the drawing velocity using an Al mask with rectangular opening. Lower drawing velocity (5 mm/min) results in formation of short (~50 µm) nanowires whereas higher drawing velocity (15 mm/min) yields longer nanowires (~200 µm). The effects of drawing velocity and temperature on the morphology of BMG nanowires have been discussed in detail in our previous studies [15,16]. In brief, the slower drawing results in early fracture due to capillary stress but faster drawing increases the BMG flow stress and delays the fracture.

Similar ease in tunability of nanostructures in other selective-area nanopatterning techniques is not achievable. Site-specific attachment of BMG nanowires on Si can also be achieved by directly controlling the location of etching features in Si. Fig. 4a shows one such example where

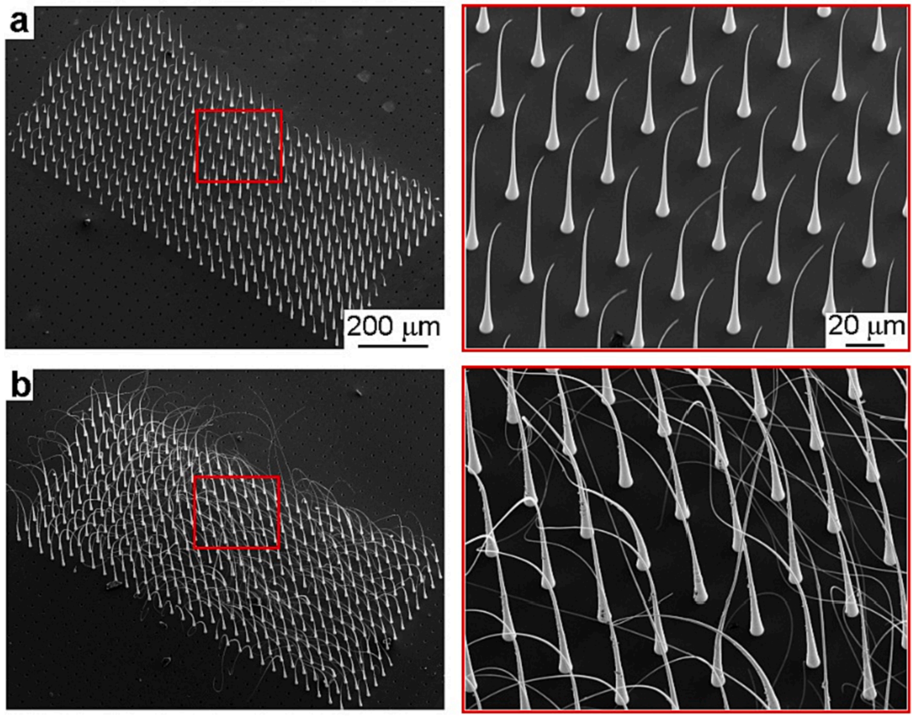

Fig. 3. SEM images of BMG nanowires with different lengths formed on a rectangular area of 400 × 1000 μm on Si. (a) Short and (b) long BMG nanowires. The scalebar is same in (a) and (b).

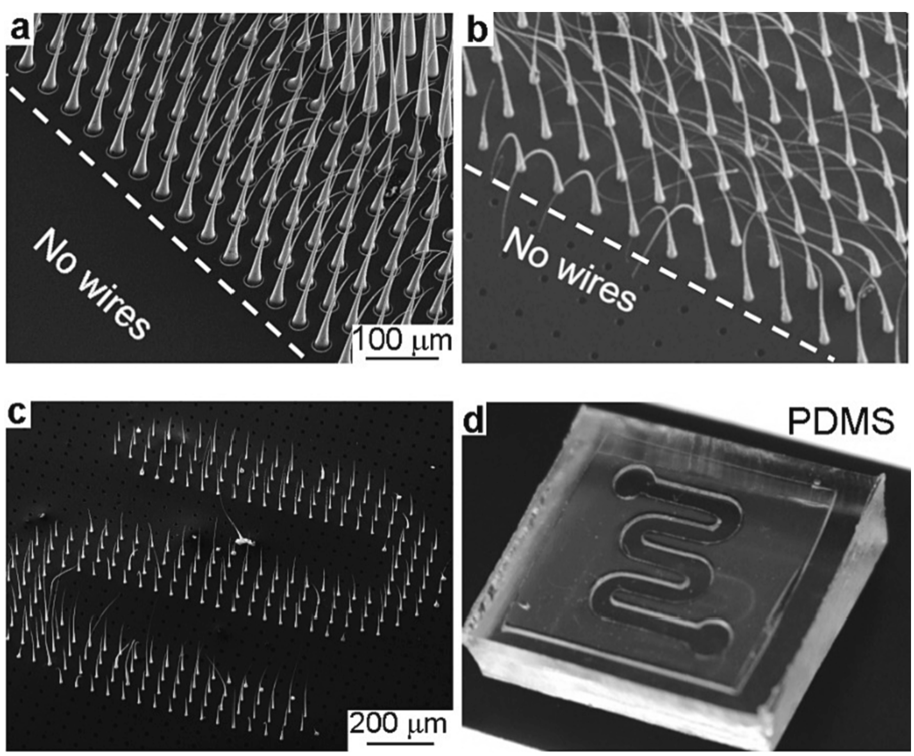

Fig. 4. (a) BMG nanowires prepared by using selectively patterned Si. (b) BMG nanowires prepared by selectively exposing the Si completely covered with microscale cavities. (c) BMG nanowires on Si in serpentine shaped area using a suitable Al mask. (d) An example of channel in PDMS.

a selectively patterned Si mold was used for BMG thermoplastic drawing. A distinct transition from the nanowire to "no nanowire" area on Si is observed because the BMG nanowires formed only on the etched sites. However, this approach requires new photomask and etching steps to change the arrangement of BMG nanowires. In contrast, the use of low-cost Al foil mask can allow fabrication of different nanowire areas using the same Si mold. Fig. 4a and b compare the selective area patterns obtained using selective Si pattering and Al mask, respectively. The SEM images indicate that the quality of selective-area patterning with Al masks is comparable with the directly patterned Si mold. Therefore, an inexpensive Al foil mask is a good alternative for selective-area patterning of BMGs when the required accuracy is not very high.

Ability to controllably attach the metallic nanostructures on substrates can enable new applications in the field of microdevices. One of such applications is incorporation of nanowires in microfluidic devices for analysis of biological samples [17,18]. The progress in this direction is hindered by manufacturing challenges to integrate nanowires in microfluidic channels [18]. The selective-area patterning scheme using BMGs and Al masks can allow fabrication of nanowire anchored microfluidic devices as illustrated in Fig. 4c and Fig. 4d. The BMG nanowires can be selectively formed in serpentine channel areas on Si using a suitable Al mask (Fig. 4c). A replica of the channel can be separately fabricated in PDMS using well established soft lithography techniques (Fig. 4d). Subsequently, the plasma bonding of PDMS and selectively patterned Si with nanowires will create a microfluidic channel with embedded BMG nanowires. The proposed methodology can significantly reduce the complexity and cost of nanowire embedded microfluidic devices.

4. Conclusions

In summary, we have demonstrated the selective-area patterning of metallic nanowires on silicon using thermoplastic forming of bulk metallic glasses. By utilizing custom-made aluminum foil masks to partially expose the silicon mold, we fabricated a broad range of bulk metallic glass nanowire areas. The low-cost aluminum mask results in excellent area selectivity which is comparable to the outcome from the directly patterned silicon template. The approach has great potential for improvement in resolution by using laser cut metal stencils. We also showed that the ability to place nanostructures in desired arrangement can enable unique applications such as microfluid devices with embedded nanowires.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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