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Rapid nanopatterning of a Zr-based metallic glass surface utilizing focused ion beam induced selective etching

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A simple and rapid method is proposed for nanoscale patterning on a metallic glass surface using focused ion beam irradiation followed by wet etching. It was found that the etch rate of a metallic glass surface irradiated with Ga^+ ions could be drastically changed, and rapid patterning was possible with this method. Cross-sectional transmission electron microscopy observation reveals that the metallic glass substrate maintains an amorphous phase following irradiation. Etching enhancement was not observed for irradiation with Ar^+ ions. The results indicate that enhancement of etching results from the presence of implanted Ga^+ ions rather than a change in crystallography. © 2006 American Institute of Physics. [DOI: 10.1063/1.2360181]

Metallic glass is an amorphous alloy that has unique mechanical, thermal, and magnetic properties¹⁻³ and is expected to have application in various industrial fields. This material is homogeneous and free from defects, e.g., lattice defects and grain boundary, and is therefore, considered to be a suitable material for microscale/nanoscale structures. Therefore, development of microfabrication/nanofabrication technology for metallic glass is required.

Several attempts to fabricate microstructures/nanostructures on a metallic glass have been demonstrated in recent years.^{4,5} In particular, the focused ion beam (FIB) direct milling technique has been effective, and a structure with a minimum linewidth of 12 nm can be fabricated.⁵ However, in the case of fabrication of a deeper and wider structure, a more productive method is necessary because the direct milling approach requires a time consuming step.

A simple and rapid method is proposed for nanoscale patterning on a metallic glass surface using FIB irradiation followed by wet chemical etching. It was found that a metallic glass surface irradiated with Ga^+ ions is rapidly dissolved in HN solution, which consists of hydrofluoric acid (HF), nitric acid (HNO_3), and water (H_2O), and consequently a concave structure with a depth of several tens to hundreds of nanometers could be fabricated on the irradiated area. To investigate the mechanism, a transmission electron

microscopy (TEM) analysis was performed. In addition, shape dependence on ion irradiation parameters was investigated. From these results, a rapid nanopatterning method for a metallic glass surface was proposed using FIB irradiation and wet chemical etching.

A bulk metallic glass of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ (at. %) prepared by a casting method was used in this study. The sample was covered with a native oxide layer approximately 8 nm thick. FIB irradiation experiments were conducted by employing a Hitachi FB-2000A FIB facility with a gallium liquid metal ion source. The Ar^+ ion irradiation experiment was conducted using the ion irradiation facility at Kochi University of Technology.⁶

Ga^+ ions with ion energy of 30 keV and a 24 pA beam current were irradiated on the metallic glass surface at room temperature. After irradiation, the sample was etched in HN solution at 24 °C. The concentration of the HN solution was $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}=1:657:387$ by weight. All measurements were conducted using an atomic force microscope (AFM) (Shimadzu SPM-9500J2).

Figure 1 shows AFM topography images of structures fabricated using the FIB irradiation and wet chemical etching method proposed in this study. Structures with a minimum linewidth of 100 nm and with depths of several tens to hundreds of nanometers were fabricated on the irradiated areas. The nonirradiated metallic glass surface withstands etching in HN solution, due to the native oxide layer. Therefore, the

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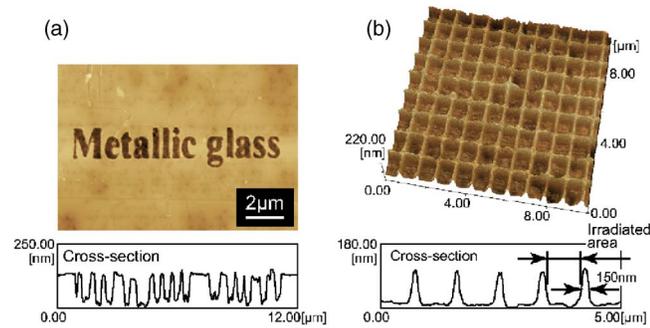


FIG. 1. (Color online) AFM topography image of a structure fabricated using FIB irradiation and wet chemical etching. Character strings of (a) “Metallic glass,” and (b) lattice pattern. The structures are fabricated using FIB irradiation at a dose of $84 \mu\text{C}/\text{cm}^2$, and subsequent wet chemical etching in HN solution for 3 s.

structure was fabricated by selective removal of the native oxide layer on the irradiated area, followed by dissolution of the interior substrate.

Figure 2(a) shows a cross-sectional TEM image of metallic glass irradiated with 30 keV Ga^+ ions at a dose of $110 \mu\text{C}/\text{cm}^2$. A layer that is approximately 40 nm wide can be observed at the surface [marked A, Fig. 2(a)]. This layer is considered to result from a change in the density and/or the presence of Ga^+ ions from ion implantation. However, no crystalline phase could be observed in this layer, and the substrate remains amorphous, as seen in the enlarged image of Fig. 2(b). Figures 2(c) and 2(d) show electron diffraction images of a metallic glass substrate irradiated with 30 keV Ga^+ ions at doses of 28 and $1100 \mu\text{C}/\text{cm}^2$, respectively. Both images show a diffuse ring pattern, and therefore reveal that the irradiated area remains amorphous at every ion dose. A secondary ion mass spectrometry analysis shows the peak density of Ga^+ ions at a depth of approximately 8 nm, and irradiated Ga^+ ions were not detected at depths greater than 80 nm. The result indicated that the surface layer includes high density Ga^+ ions. Therefore, the FIB-irradiation-induced etching enhancement does not result from a change in crystallography, and a structure can be fabricated with the substrate remaining amorphous.

The dependence of the depth of the structure on ion dose, after etching in HN solution for 3 s, is shown in Fig.

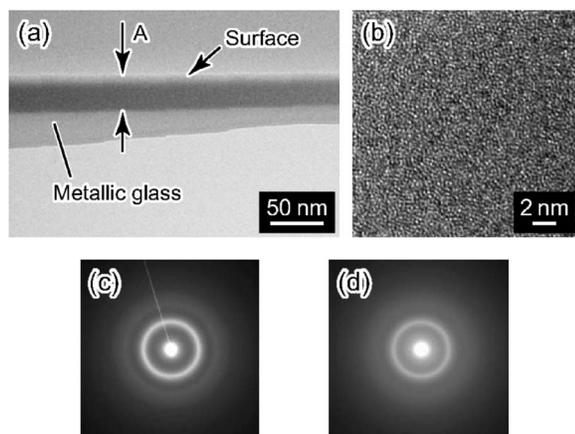


FIG. 2. (a) Bright field cross-sectional TEM image and (b) enlarged TEM image of 30 keV Ga^+ irradiated area at a dose of $110 \mu\text{C}/\text{cm}^2$. Electron diffraction pattern of Ga^+ irradiated metallic glass substrate at doses of (c) $28 \mu\text{C}/\text{cm}^2$ and (d) $1100 \mu\text{C}/\text{cm}^2$.

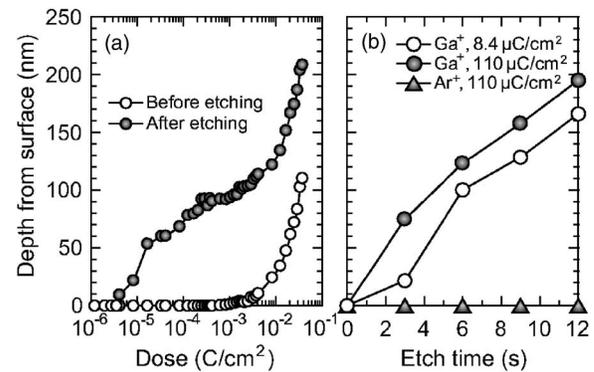


FIG. 3. (a) Change in depth of the irradiated area at various doses, before and after etching in HN solution for 3 s. (b) Change in depth of the irradiated area by irradiation with 30 keV Ga^+ and 30 keV Ar^+ ions plotted as a function of etch time.

3(a). For doses less than $633.6 \mu\text{C}/\text{cm}^2$, no change is observed after irradiation. For greater dose values, the irradiated area becomes spattered. The irradiated area is etched when the dose is over $4.2 \mu\text{C}/\text{cm}^2$, and concave structures are fabricated from the etching. The depth of the irradiated area after etching increases continuously with the increase in the dose. For the fabrication of a structure with a depth of 80 nm on an area of $5 \times 5 \mu\text{m}^2$, the direct ion milling process requires an irradiation time of 112 s. However, the method proposed here requires an irradiation time of only 0.46 s, over 200 times faster than the ion milling method. This indicates that the proposed method is effective for fabrication of a structure on a metallic glass surface.

Change in depth of the irradiated area is plotted as a function of etch time and is shown in Fig. 3(b). To investigate the effect of the species of irradiated ion, both Ga^+ and Ar^+ ions were irradiated. In the case of irradiation with Ar^+ ions, the irradiated area is scarcely etched in HN solution for all etch times, whereas the Ga^+ irradiated area is etched at 3 s. This indicates that the etching enhancement effect depends on the species of irradiated ion, and Ga^+ ion plays an important role in the fabrication of structures. For the Ga^+ ion irradiation, the etch rate of the surface region of the metallic glass substrate, which has greater levels of implanted Ga^+ ions, is faster than that of nonimplanted sub-

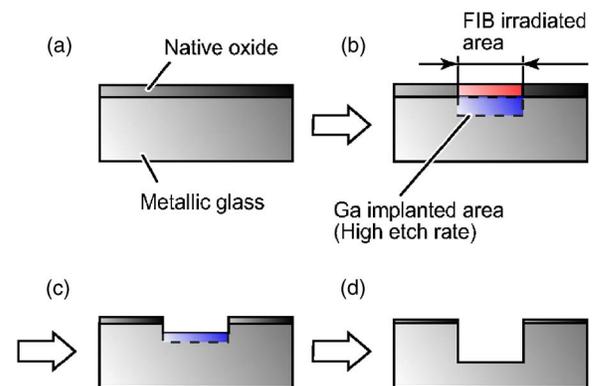


FIG. 4. (Color online) Schematic diagrams showing the mechanism of nanofabrication using FIB irradiation and wet chemical etching. (a) Metallic glass with native oxide. (b) After FIB irradiation. Ga^+ ions are implanted into the substrate, and corrosion resistance of the implanted area decreases. (c) After etching in HN solution. The native oxide implanted with Ga^+ ions is selectively etched, and the etching is enhanced at the Ga^+ implanted substrate. (d) Fabrication of a concave structure.

strate. This result indicates that the presence of Ga^+ ions enhances the etch rate of the metallic glass substrate. It is considered that the change in the etch rate of a Ga^+ implanted metallic glass substrate is the result of the low etch resistance of Ga^+ itself and/or the change in the composition of substrate atoms, which induces a decrease in etch resistance. However, the Ar^+ implanted area does not show etching enhancement due to a difference in chemical characteristics from the presence of Ga^+ ions when using HN as the etchant.

Figure 4 shows schematic diagrams for the mechanism of nanofabrication considered from the results obtained in this study. Bulk metallic glass is covered with a native oxide layer [see Fig. 4(a)]. After irradiation with Ga^+ ions, the irradiated ions are implanted into the native oxide layer and metallic glass substrate, and corrosion resistance of the implanted area is decreased [see Fig. 4(b)]. After etching in HN solution, the native oxide layer implanted with Ga^+ ions is selectively etched, and a concave structure is fabricated on the irradiated area [see Fig. 4(c)]. The etching is enhanced for the Ga^+ ion implanted substrate. After dissolution of the implanted substrate, the etch rate becomes that for an untreated metallic glass substrate, and the depth keeps increas-

ing until the native oxide layer on the nonirradiated area is removed.

This letter proposes a rapid method of nanopatterning on a metallic glass surface using a combination of FIB irradiation and wet chemical etching. This simple and rapid process can fabricate a structure with a depth of several tens to hundreds of nanometers. This phenomenon is dependent on the species of irradiated ion and results from the presence of Ga^+ ions that induce a change in the etching characteristics of a metallic glass surface.

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