Development of Bi Electrodeposition Process for Fabricating Microabsorber Array for High Sensitive X-ray Imaging Sensor

Hiroataka SATO,^a Hideomi KOBAYASHI,^a Hiroyuki KUDO,^b Toshimitsu IZUMI,^b Takayuki HOMMA,^{a*} Tetsuya OSAKA,^a Shuichi SHOJI,^b Yoshitaka ISHISAKI,^c Ryuichi FUJIMOTO,^d and Kazuhisa MITSUDA^d

^aDepartment of Applied Chemistry and ^bDepartment of Electrical Engineering and Bioscience, Waseda University (Okubo, Shinjuku, Tokyo 169-8555, Japan)

^cDepartment of Physics, Tokyo Metropolitan University (Minami-Osawa, Hachioji, Tokyo 192-0397, Japan)

^dHigh Energy Astrophysics Division, Institute of Space and Astronautical Science, Sagami-hara (Kanagawa 229-8510, Japan)

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Microscale Bi electrodeposition process was developed to fabricate the array of mushroom-shaped absorbers for the high sensitive X-ray imaging sensor, so called X-ray microcalorimeter array. The bath composition and operating conditions for Bi electrodeposition was optimized, and sufficient bath stability and surface smoothness of the deposits were achieved by applying the additives such as diethylenetriamine pentaacetic acid and sodium n-dodecyl sulfate with appropriate concentration. By applying the two-step exposure steps for the “stem” part and the “roof” part, the mold to deposit the mushroom-shaped microstructure was formed from single-layered photoresist coating. The absorber array was successfully fabricated by the sequential processes of Bi electrodeposition into the mold, precise polishing, and mold removal.

Key Words : Bi Electrodeposition, MEMS, Micromachining, X-ray Imaging

1 Introduction

In the field of astronomy, X-ray spectroscopy has attracted much attention for exploring unknown high energy phenomena in the space, which requires precision tool for X-ray sensing.¹⁾ We have attempted to develop X-ray microcalorimeter, which is expected to be one of the most sensitive X-ray sensors,^{2, 3)} by detecting the X-ray photon energy from temperature rise of several mK caused by its incidence. The multi-pixel array of the X-ray microcalorimeters can be applied to X-ray imaging sensor for next generation X-ray telescope system.^{2 - 5)}

Figure 1 illustrates schematic design of single pixel of the X-ray microcalorimeter. It consists of an X-ray absorber, a temperature sensor, and a membrane, which acts as a thermal insulator. A Au/Ti bilayer with Al interconnects is used for the temperature sensor, which is called “transition edge sensor (TES)” since its electric re-

sistivity is extremely temperature-sensitive at the temperature around the superconducting transition edge and shows high energy resolution of several eV.^{2, 4, 5)} In order to minimize the “dead area” where the incident X-ray photons can not be reached to the TES part, the mushroom-shaped structure with 10 μm thick roof part is formed onto each TES element. The absorber material is desired to have low specific heat in order to maximize the transfer rate of the heat from the top of the absorber to the TES part. At the operating temperature of X-ray microcalorimeter (0.3 K), Sn has low specific heat of $1.5 \times 10^{-8} \text{ J K}^{-1} \text{ cm}^{-3}$ due to its superconducting state. Therefore, we have been investigating to fabricate the X-ray microcalorimeter using Sn electrodeposition process,^{2, 3)} and the energy resolution of $136.5 \pm 3.5 \text{ eV}$ at 6 keV of X-ray photon was achieved. On the other hand, the Sn turns to be the superconducting state at the operating temperature, and under such a state, it is generally known that quasiparticle with relatively long lifetime is formed, which makes the energy resolution lower. Thus as an alternative approach, we attempt to apply the material which does not become superconducting state at the operating temperature, and focused upon Bi as a candidate, which has relatively low specific heat of $2.4 \times 10^{-7} \text{ J K}^{-1} \text{ cm}^{-3}$ and does not become superconducting state at 0.3 K. Application of Bi to the fabrication of the absorber for the X-ray microcalorimeter has been investigated using dry processes such as evaporation.⁶⁾ On the other hand, in the present work, we attempt to develop

Fig. 1 Schematic design of single pixel of the X-ray microcalorimeter ; (a) X-ray absorber, (b) temperature sensor, (c) Al interconnects, and (d) membrane for thermal insulation.

the microfabrication process of the absorber array for X-ray microcalorimeter using Bi electrodeposition.

2 Experimental

We used 625 μm thick n-type Si (100) substrates, whose surface was cleaned by dipping in methanol for 2 min, dichloromethane for 20 min and methanol for 2 min again to remove the residual contaminants. After drying by an oven at 135°C for 15 min and natural cooling, the "mold" for the mushroom-shaped microstructure array was formed by photolithographic technique. In this work, the positive photoresist of PMER P-LA 900 PM (Tokyo Ohka Kogyo), whose compositions are 40 wt% of novolak resin and 60 wt% of propylene glycol mono methyl ether acetate (PGMEA) and viscosity is 900 mPa s, was used to form the mold. The 20 μm thick photoresist coating was spin-coated on the substrate. Following the pre-bake at 110°C for 8 min, ultraviolet light (UV) from mercury lamp (65 mW cm^{-2}) was irradiated to the coating to form the mold pattern, whose details will be described later. After the exposure, the specimens were dipped in PMER developer (P-7 G, Tokyo Ohka Kogyo), which contains 3 wt% of tetra methyl ammonium hydroxide aqueous solution with 2 wt% of anion surfactant, for 3 min at the room temperature, followed by rinsing with deionized water for 3 min. A conductive seed layer of 100 nm thick Au on 20 nm thick Cr was formed on the mold by electron beam evaporation. Then Bi was electrodeposited into the mold up to 30 μm thick using a potentiostat/galvanostat (Hokuto-Denko, HAB-151). Table 1 shows basic composition and operating conditions for the Bi electrodeposition, whose details will be described in the following section. After the deposition, the Bi layer surface was polished down to the designed thickness to form separate elements of the array using an automatic rotational polishing machine (Musashino Denshi, MA-200 D, rotational speed : 110 rpm, load : 200 g), using a nylon polishing cloth (Heraeus Kulzer, Orange) and polycrystalline diamond slurry (Engis, PC-S-4889, grain size : *c.a.* 1 μm). Finally, the photoresist mold was removed with acetone.

Following the procedure, the fabricated microstructures were observed by a scanning electron microscope (SEM, Hitachi, S-4700). Some specimens were treated by a focused ion beam milling (FIB, Hitachi, FB-2000 A) to observe the cross sectional regions under the roofs of the mushroom-shaped structures.

Table 1 Basic composition and operating conditions of Bi electrodeposition.

Chemicals	Concentration/ g l^{-1}
Bi_2O_3	20.3
HClO_4	54.7
Diethylenetriamine pentaacetic acid	0 - 45
Sodium n-dodecyl sulfate	0 - 500 ppm
Current density	25 mA cm^{-2}
Bath temperature	35°C
pH	2.0 (adjusted by NH_4OH)

3 Results and Discussion

The conditions of Bi electrodeposition were optimized prior to the fabrication of the mushroom-shaped absorbers. Figure 2 shows representative SEM images of the surface morphology of the deposited films from various bath compositions. Initially, the bath only containing Bi_2O_3 and HClO_4 was used. However, the bath was quite unstable and formed precipitates immediately after the preparation. Moreover, the deposited film possessed dendritic feature, as is shown in Fig. 2(a). By adding diethylenetriamine pentaacetic acid (DTPA, $[(\text{HOOCCH}_2)_2\text{NCH}_2\text{CH}_2]_2\text{NCH}_2\text{COOH}$), which is reported to stabilize Bi^{3+} in aqueous solution⁷⁾ to the bath, it was confirmed that the formation of the precipitation was inhibited. However smooth surface was not obtained as is seen in Fig. 2(b). On the other hand, when sodium n-dodecyl sulfate (SDS, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3\text{Na}$) was added to the bath together with the DTPA, flat and smooth surface was obtained (see Fig. 2(c)). After systematic survey, it was found that the optimum concentrations of DTPA and SDS were 45 g l^{-1} and 500 ppm, respectively, which were employed for the following investigation. The Bi deposition rate is 560 nm min^{-1} at constant current density of 25 mA cm^{-2} , which is sufficient to fabricate the structure such as the mushroom-shaped absorber array with 20 μm thick.

Next, we attempted to fabricate the mushroom-shaped absorber array using the procedure described above with the Bi electrodeposition. In our previous study, the molds for the stem part and the roof part were sequentially formed by two-step coating of the photoresist.⁷⁾ In order to simplify the process, we developed a new photolithographic technique with single resist coating, as is shown in Fig. 3. The exposure requires two-step UV irradiation; first is for the stem part of the mushroom and second is for the roof. The roof parts were exposed mod-

Fig. 2 Representative SEM images of the surface of films obtained from the Bi baths at 25 mA cm^{-2} for 15 min using additives; (a) additive-free, (b) 45 g l^{-1} of DTPA, and (c) co-addition of 45 g l^{-1} of DTPA and 500 ppm of SDS.

Fig. 3 The two step mold formation process for the mushroom-shaped microabsorber array; (a) UV irradiation for the stem part, (b) UV irradiation for the roof part, and (c) after the two steps of irradiations.

Fig. 4 SEM image of the bilayer mold for the mushroom-shaped microabsorber array.

erately so that the exposed depth would be equal to the thickness of roof part and not reached to the bottom, as is schematically shown in Fig. 3(b). As a result of exposure optimization, it is clarified that UV irradiation steps of 400 mJ cm^{-2} for stem part and 315 mJ cm^{-2} for roof part are suitable conditions to form the fine mold as is shown in Fig. 4 of SEM image.

Figure 5 shows SEM image of the sample after the Bi electrodeposition, precise polishing, and acetone dipping. The array of uniformly formed mushroom-shaped microstructure can be observed in Fig. 5. We fabricated microscopic openings on some roof parts to observe the stem regions underneath them using the FIB and confirmed that there was no residual photoresist, clarifying that the free-standing mushroom-shaped absorber array was successfully fabricated by the Bi electrodeposition process. It is expected that the electrodeposition process can be applied to fabricate various three-dimensional, functional microstructures.

4 Conclusion

In the present work, Bi electrodeposition process for microfabrication of the mushroom-shaped absorber array for X-ray microcalorimeter was developed. In order to improve the bath stability and surface morphology of the deposition film, the conditions of Bi electrodeposition were optimized. As a result, applying DTPA and SDS to the bath was found to prevent precipitation and smooth the surface. In fabrication process of the absorber, the bilayer mold for the mushroom could be formed by controlling UV irradiation region and exposed depth with single-layered photoresist coating in photolithographic technique. Then, Bi was filled into the mold by the Bi electrodeposition. Following surface polishing and photoresist removal with acetone, it is confirmed that the designed Bi absorber array was successfully fabricated. It is

Fig. 5 SEM image of the mushroom-shaped microabsorber array fabricated by the Bi electrodeposition process.

expected that the electrodeposition processes are widely applied to fabricate various three-dimensional nano- and microstructures for functional microsystems.

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