ELECTROCHEMICAL APPROACHES FOR MICRO AND NANO SCALE FABRICATION OF ARRAYED FUNCTIONAL STRUCTURES

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Introduction

Precise fabrication process for micro and nanoscale structures is fundamental for manufacturing advanced devices and systems. In particular, the fabrication process for well-ordered, arrayed structures is significant for their broad area of application such as semiconductor devices, MEMS, microreactors and analytical systems, etc. These structures have been fabricated mainly using physical (dry) processes such as sputtering, reactive ion etching (RIE) and deep reactive ion etching (DRIE) in combination with photolithographic processes. On the other hand, electrochemical processes have advantages for precise controllability and low energy consumption with high productivity, and numbers of approaches have been proposed to fabricate functional micro and nano structures [1]. In this paper, electrochemical fabrication processes for functional micro and nano structures are described, mainly focusing upon the arrayed structures.

Fabrication of magnetic nanodot array

Fabrication of arrayed magnetic dots with submicrometer scale is one of the key processes for the preparation of ultra-high density magnetic recording media, such as bit-patterned media (BPM). Processes for their preparation have been studied mainly using the dry processes, such as sputtering and reactive ion etching [2]. On the other hand, we have attempted to apply the wet processes to fabricate the BPM [3-5], in combination with the formation of nano-patterned substrates using electron beam lithography (EBL) and nanoimprint lithography (NIL).

For the NIL, either UV-curable resin or spin-on-glass (SOG) was applied as mold material. After the formation of the patterned substrates, magnetic dots were formed using electroless deposition or electrodeposition, followed by chemical mechanical planarization (CMP). The surface microstructure of the specimens was observed using a scanning electron microscope (SEM). Magnetic properties of the deposits were evaluated by a superconducting quantum interference device (SQUID) and a magnetic force microscope (MFM).

Figure 1(a) shows representative SEM image of the CoPt nanodots deposited into the nano-patterned substrate fabricated by EBL, showing that CoPt was successfully deposited into the pores so that the nanodot arrays with high areal recording density can be fabricated by the electrochemical process.

It was also confirmed that the CoPt nanodots can be successfully formed into the nano-patterned NIL-patterned substrates, as is seen in Fig. 1(b). From these results, it is indicated that the nanodot arrays with high areal density with shape accuracy can be fabricated by using the wet processes.

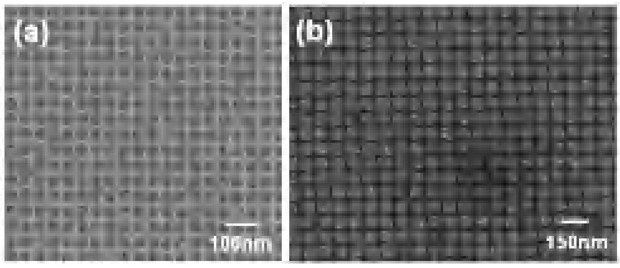

Fig. 1 SEM images of electrodeposited CoPt magnetic nanodot arrays using (a) EBL-patterned and (b) NIL-patterned substrates.

Area-selective formation of macropore array at Si wafer surface and its modification

Electrochemical etching or anodization process, typically for aluminum, has been extensively studied for fabricating arrayed pore structure [6]. Such a process is applicable to Si wafer to form high aspect ratio pores. Since the porous Si layer possesses photo and electroluminescence properties and can be oxidized ca. 100 times faster than conventional Si (100) layer, it has been widely studied for the applications of luminescence devices as well as manufacturing of SOI (Silicon On Insulator) structures applied for advanced ULSI devices [7,8]. Furthermore, formation process of high aspect ratio array of straight macropores with several micrometer diameter using n-type Si (100) wafer was proposed [9, 10]. Based on these processes, we have achieved uniform formation of the macropore array at selected microarea [11], as is shown in Fig. 2. Using this structure, fabrication of various functional microstructures was attempted. One significant feature of the electrochemical process is that, it can perform both deposition (reduction) and etching (oxidation) in the same apparatus by alternating the applied potential, which is advantageous to develop the process to fabricate various micro and nanostructures which requires both etching and deposition. From this view point, we attempted to develop "single-batch" process, consisting of the area-selective formation of arrayed pores by the Si electrochemical etching followed by metal deposition into the pores by electrodeposition [12]. In order to achieve such a process, metal source, for example Ni was added in the etchant for the anodization described in the previous chapter, and after completing the pore formation, the applied bias was switched to negative to initiate metal electrodeposition.

Figure 3(a) shows representative cross-sectional SEM image of the specimen after the Ni electrodeposition. It clearly shows that Ni was successfully filled into c.a. 200 µm depth Si pores without voids. Then the sample was immersed into tetramethylammonium hydroxide (TMAH) aqueous solution to dissolve the Si and release the Ni microstructure, as is shown in Fig. 3(b).

Another application of the arrayed pore structure is to fabricate the miniaturized “test tubes” with pL (pico litter) volume [13]. After the formation of the pore array, the specimen was treated with wet-thermal oxidation to form SiO_2 layer at the surface. Then, the Si_3N_4 and SiO_2 layer at the front and back surfaces were removed by precise polishing. In order to expose the top and bottom part of the "test tubes," bulk Si part was partially removed using TMAH aqueous solution. Figure 5 shows representative SEM images of the array of pL volume SiO_2 tubes fabricated by this process. Well-ordered, uniform array of the tubes, which exactly follow the uniformity of the shape of the macropore array, is formed. It was also confirmed that aqueous solution could be easily introduced into these tubes due to the hydrophilic nature of SiO_2 and capillary force, and could be applied as microscopic reactors.

Conclusion

Electrochemical processes to fabricate functional micro and nano structures, such as arrays of nano dots and pores, have been introduced. As described, array of metal nanodots and macropores can be successfully fabricated using electrochemical deposition and etching processes, and are applicable for further modification to form various structures. These processes demonstrate capability and possibility of the electrochemical processes for micro and nano fabrication, and further precise processes can be developed for various applications, with deep understanding of the mechanism of the reactions for these processes.

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References

[1] J.W. Schultze, A. Heidelberg, C. Rosenkranz, T. Schäpers and G. Staikov, Electrochim. Acta, 2005, 51, 775.
[2] T. Aoyama, S. Okawa, K. Hattori, H. Hatte, Y. Wada, K. Uchiyama, T. Kagotani, H. Nishio, I. Sato, J. Magn. Magn. Mater., 2001, 235, 174.
[3] J. Kawaji, F. Kitaizumi, H. Oikawa, D. Niwa, T. Homma, T. Osaka, J. Magn. Magn. Mater., 2005, 287, 245.
[4] T.Ouchi, Y. Arikawa, T. Homma, J. Magn. Magn. Matter., 2008, 320, 3104.
[5] T.Ouchi, Y. Arikawa, J. Mizuno, S. Shoji, T. Homma ECS. Trans., 2009, in press.
[6] For example, H. Masuda, Oyo Butsuri, 2003, 72, 1280.
[7] A. G. Cullis, L. T. Canham, P. D. J. Calcott, J. Appl. Phys. 1997, 82, 909.
[8] K. Imai, Solid-State Electron. 1981, 24, 159.
[9] V. Lehmann, J. Electrochem. Soc. 1993, 140, 2836.
[10] A. Sato, Jpn. J. Appl. Phys. 2000, 39, 1612.
[11] T. Homma, H. Sato, K. Mori, T. Osaka, S. Shoji, J. Phys. Chem. B, 2005, 109, 5724.
[12] H. Sato, T. Homma, K. Mori, T. Osaka, S. Shoji, Electrochemistry, 2005, 73, 275.
[13] H. Sato, T. Homma, K. Mori, T. Osaka, S. Shoji, Electrochim. Acta, 2005, 51, 844.

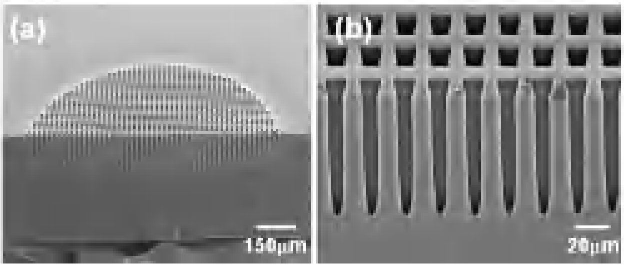

Fig. 2 Cross-sectional SEM images showing the macropore arrays area-selectively formed at Si wafer surface (a) wide view, (b) close-up view.

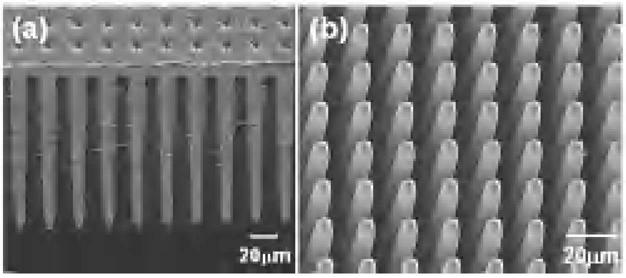

Fig. 3 SEM images of the Ni filled into arrayed macropore at Si wafer surface, (a) cross-sectional view, (b) after removing Si using TMAH.

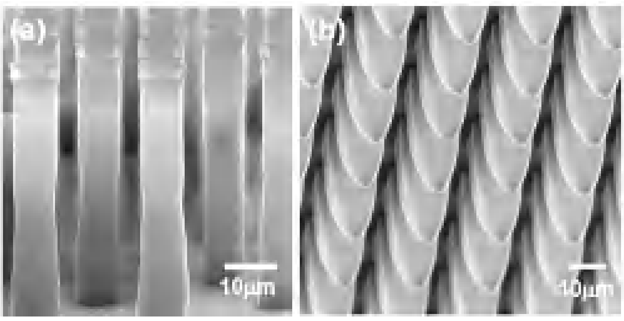

Fig. 4 SEM image of the arrayed SiO2 tubes, (a) side view, (b) bottom view.