Electrochemical Fabrication of Magnetic Nanostructures - analysis, control, and design of deposition processes -

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In this paper, we will describe our approaches to fabricate functional micro/nano structures using electro-chemical deposition processes, mainly focusing upon the magnetic nanostructures such as ordered array of nanodots for the use of bit patterned media (BPM) for Terabit/inch^2-level ultra-high density magnetic data storage system [1, 2].

In order to fabricate the BPM, substrates with arrayed nanoscale pores are required. For this, electron beam lithography (EBL) and UV-nanoimprint lithography (UV-NIL) were employed. The EBL has capability to form single-nm scale patterns, while the NIL has advantage for productivity. Electrodeposition (CoPt) and electroless deposition (CoNiP) processes, both can form the ferromagnetic Co alloys with high perpendicular magnetic anisotropy, were applied to deposit the magnetic nanodots [3, 4]. In both cases, formation of c-axis perpendicularly oriented hcp structure with high crystallinity is required to obtain required magnetic properties, such as high coercivity, and for the case of electrodeposition of CoPt, it was found that application of very thin (< 5 nm thick) Cu(111) underlayer considerably improve the crystal orientation of the CoPt, resulting in high perpendicular magnetic anisotropy from the initial deposition stage.

Figure 1 shows representative SEM images of the CoPt nanodot array deposited into patterned substrates fabricated by UV-NIL and EBL processes, showing uniform formation of the nanodots without defects. We are trying to fabricate the array of further smaller dots, down to < 10nm diameter scale, as shown in Fig. 2. In addition, we are investigating the initial nucleation and growth process of the deposits in such small scale patterns.

Then attempt was also made to form the nanodot array using the electroless CoNiP system. However, the Cu underlayer was not applicable for this case since Cu surface is known to be catalytically inactive for the reaction of hypophosphate ion, which is the reducing agent for this system [5]. Thus we tried to add the second reducing agent which could react at Cu surface, and it was found that addition of hydrazine worked well for this system to obtain high crystallinity and crystal orientation of the CoNiP from initial deposition stage (< 20 nm thick) as shown in Fig. 3, to obtain high coercivity of ca. 3000 Oe. The results of electrochemical analysis showed that the hydrazine effectively acts to initiate the deposition at Cu surface, followed by the reaction of hypophosphite to proceed the film growth, and that the presence of hypophosphite even enhanced the reaction of hydrazine. In situ surface enhanced Raman spectroscopy for the solution containing the reductants was carried out as shown in Fig. 4, and the results indicated the shift in the peaks for hydrazine adsorbed on Cu surface in the presence of the hypophosphate, suggesting the interaction between these two species. The results of DFT calculation for the Raman spectra also supported such an interaction of these species.

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[1] H. J. Richter, A. Y. Dobin, O. Heinonen, K. Z. Gao, D. Weller et al., *IEEE Trans. Magn.*, **42**, 2255 (2006).
[2] H.Sato, T.Homma, *J.Nanosci.Nanotech.*, **7**,225 (2007).
[3] T. Ouchi, Y. Arikawa, Y. Konishi, T. Homma, *Electrochim. Acta*, **55**, 8081 (2010).
[4] T. Ouchi, N. Shimano, T. Homma, *Electrochim. Acta*, **56**, 9575 (2011).
[5] I. Ohno, O.Wakabayashi, S.Haruyama, *J. Electrochem. Soc.*, **132**, 2323 (1985).

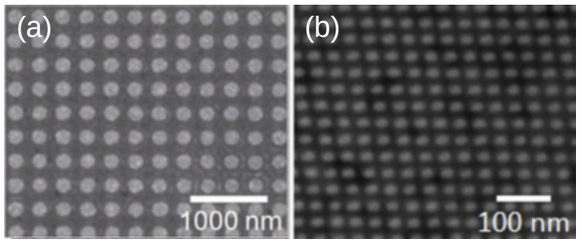

Fig. 1 SEM images of CoPt nanodot array deposited into patterned substrates fabricated by (a) UV-NIL (150nm diameter - 300 nm pitch) and (b) EBL (20 nm diameter - 35 nm pitch).

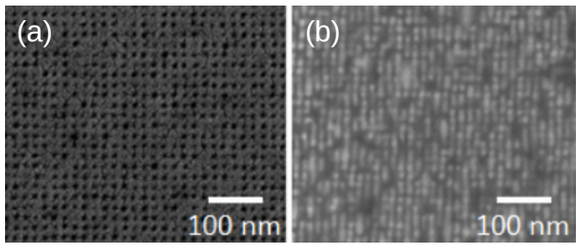

Fig. 2 SEM images of the 8 nm diameter-18 nm pitch patterned substrate (a) and after the CoPt deposition(b).

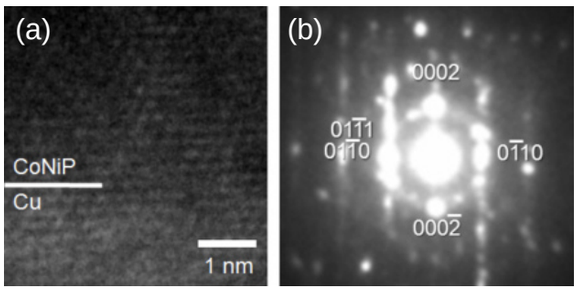

Fig. 3 Cross sectional TEM bright field image (a) and corresponding THEED pattern (b) of the initial deposition region of CoNiP on Cu substrate.

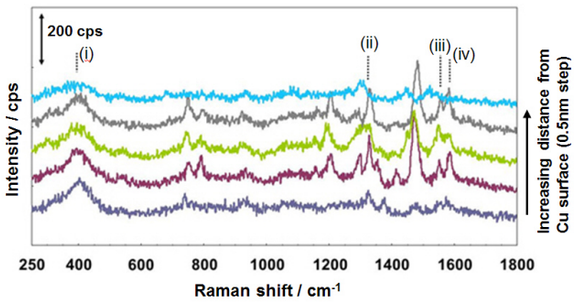

Fig. 4 In situ Raman spectra of the solution containg hydrazine and hypophosphite on Cu substrate surface. The peaks correspond to (i) N-Cu, (ii) NH_2 twist, (iii) and (iv) NH_2 scissor, respectively.