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Silicon Nano-well Arrays for Reliable Pattern Transfer and Locally Confined High Temperature Reactions

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Abstract

Si nano-well arrays, with precisely controlled undercut Si sidewall profiles and flat bottomed pockets, enable uniform nanoscale pattern transfer from resists to metal deposits without degradation of the initial lithographic resolution, as verified by formation of arrays of Au nano-dots with 10 nm diameter. An additional functionality of the Si nano-wells as local nano-reactors, where the patterned material is enclosed in a Si pocket during high temperature reaction, is demonstrated by thermally inducing a phase transformation of the as-deposited A1 phase of FePt nano-dots to the high coercivity, chemically ordered L1₀ phase.

1. Introduction

Nanoscale well (nano-well) arrays which allow confinement of a small volume of liquid or solid are an essential tool to investigate many scientific and engineering phenomena such as individual cellular or molecular behaviors [1-3], array-based biochemical sensing [4-6], crystal growth with controlled sizes [7,8], and so forth. In this report, we present a novel fabrication method and an application of nano-well arrays, which are made using highly reliable nanoscale pattern transfer, to locally confine high temperature reactions. Unlike the numerous methods for generating lithographic patterns in resists, the methods for transferring patterns from resist layers to materials of interest are generally limited to only either lift-off or etching, which each pose their own technical challenges. Lift-off processes need a relatively thick resist film, which could degrade lithographic resolution [9-12] and can require an additional underlying sacrificial polymer layer for generating undercut profiles [13-15]. However, when bilayer resist stacks are used to produce undercut profiles, the control offered by wet chemical etching is often not sufficiently accurate or reliable [16-18]. The development of plasma etching recipes for specific materials or the development of hard masks, made using an extra lift-off process, are imperative for a pattern transfer by plasma etching. Herein we demonstrate a method for pattern transfer from NIL pillars, to PMMA holes, to Si wells, and finally to metallization, which combines lift-off and plasma etching, but without sacrificial resists or metal etching, to produce metal dots enclosed in substrate pockets. The proposed pattern transfer produces Si nano-wells whose well-controlled etch profiles function as reproducible and precise metal lift-off templates, as verified by formation of arrays of Au nano-dots whose diameters range from 100 nm down

to 10 nm. Furthermore, because the patterned nano-dots are located inside etched Si nano-wells, it is feasible to maintain the isolation of individual nano-dots during high temperature processes. Indeed, we demonstrate that thermally induced phase transformations of isolated, multilayered Fe/Pt nano-dots can be accomplished without any deformation of the patterned structure.

2. Experiments

Figure 1 shows a schematic of the overall processing steps. To define the lithographic patterns, first a polymethyl methacrylate (PMMA, Microresist technology GmbH) solution was spin-coated on Si (100) substrate as a 200 nm thick layer and baked on a hot plate at 140 °C for 5 min. Then the coated wafers were subjected to thermal nanoimprint at 180 °C under a pressure of 40 bars for 60 s, using commercial nanoimprint equipment (Obducat NIL 2.5). The imprinting pressure was released sequentially from 40 bar to 20 bar at 180°C, from 20 bar to 10 bar at 160°C, and finally from 10 bar to 0 bar at 100 °C to reduce mechanical damage of imprinted patterns during the demolding step [19]. After nanoimprinting, the residual PMMA layer and the underlying Si substrate were etched by an electron cyclotron resonance (ECR) plasma. A mixture of SF₆ at a flow rate of 26 SCCM, and Cl₂ of 2 SCCM, was used as a source gas for plasma etching (Plasma Quest ECR plasma etcher). The total gas pressure was 10 mTorr, the power for ECR plasma generation was 300 W, and the RF power for ion acceleration towards the Si substrate was 20 W. After defining the Si nano-well array, a Au film or multilayered Fe/Pt film was deposited by using a 1 keV Xe ion beam in a deposition chamber at a pressure of 2.5×10^{-4} Torr. After a lift-off step, Au nano-dot arrays were examined by scanning electron microscopy (XL30 Sirion, FEI), and multilayered FePt nano-dot arrays were annealed at 850 °C for 1 hr at a pressure of 5.0×10^{-6} Torr. Magnetic properties were characterized by alternating gradient magnetometry (MicroMag 2900, Princeton) at room temperature.

3. Results and Discussion

Based on an ion-assisted etching mechanism for Si, chlorine or bromine plasmas result in good anisotropic etching, whereas fluorine based plasmas such as SF₆ or CF₄ are well-known for isotropic etching which has been extensively studied for semiconductor devices and microelectromechanical systems [20-22]. In our study, isotropic SF₆ was used to form an undercut etch profile of Si for a reliable lift-off process, and the secondary Cl₂ gas was added to make a flat bottom for precision layering of deposited metals. Using either of SF₆ or Cl₂ plasma alone caused hemispherically etched well bottoms [22-24], or produced canted, non-undercut sidewalls [22,25,26] which intruded into the nanowell volume, respectively. Since SF₆ etching involves both isotropic etching from ionized gas species such as SF₅⁺, and anisotropic chemical etching by F radicals, variations of etching conditions can, in principle, allow control of the ratio of isotropic to anisotropic components. However, better results were obtained when we independently augmented anisotropic etching by adding Cl₂. This addition of Cl₂ strongly effected the bottom flatness and sidewall angle, with a complete loss of undercut at >25% Cl₂ and the optimum amount of Cl₂ was determined to be fairly small (~7%). The SEM images in Figure 2(a-c) were observed, after nanoimprinting with a somewhat coarse NIL mold (pattern diameter of 100 nm and pitch of 300 nm) and plasma etching for (a) 40 sec and (b,c) 60 sec, and distinctly show the flat bottom and undercut profile of the Si nano-wells thus created. The etch selectivity of ~1.9 was obtained from the relative vertical etch rate of PMMA (1.3 nm/sec) and Si (2.5 nm/sec). The lateral etch rate of Si of 0.7 nm/sec, which was measured at the most deeply undercut regions, is useful to carefully control the undercut depth for the formation of ultrahigh-density patterned arrays. We also confirmed that the proposed method is valid for Si(111) substrates (supplementary data S1). The crystallographic

variation of etch rates is not significant at our experimental conditions, although it is known to affect the etching profile at temperatures below 170 K [27,28].

To demonstrate the pattern transfer from the lithographic resist layer to the Si nano-wells and finally to the target material, a 5 nm thick Ta adhesion layer and then a 50 nm thick Au film were deposited onto etched substrates. Figure 2(d) was obtained after the metal lift-off step and confirms, by comparison with Figure 2(b), that the diameter of Au nano-dot matches the size of the flat bottom of the Si nano-wells. The size of the flat bottom, whose diameter is about 100 nm and is almost the same as the diameter of the initial NIL mold pillars, was not altered in our etching time window (up to 100 sec, supplementary data S2). It is further noted that this method does not obviously degrade the resolution of the initial lithographic pattern during the entire pattern transfer. To explore the resolution limit of this proposed pattern transfer process, we tested a laboratory-made Si NIL mold [25] which has three different Si pillar arrays with diameters of 30, 20 and 10 nm, each with a constant pitch of 100 nm and height of 50 nm. Due to the trapezoidal shape of the NIL mold pillars, whose sidewall angle is about 80° [25], the projected pillar diameters appear to increase by about 20 nm in the plan-view SEM (Figure 3a-c). In this test, 5 nm thick Ta and 10 nm thick Au films were deposited for lift-off. The pattern transfer results presented in Figure 3(d-f) show that the three different patterns of the NIL mold are precisely transferred to the Au nano-dots. In particular, Figure 3(f) clearly shows that this method works very well at a resolution of 10 nm. The off-center appearance of the Au nano-dots in the Si nano-wells occurs due to the slight misorientation between the sample holder and the Au target, which leads to non-normal incidence in our deposition chamber.

As shown in the previous Figures 2(d) and 3, the patterned Au nano-dots are located inside of Si nano-well and are surrounded by the Si substrate. This design is highly useful for isolating these metal nano-dots during high temperature reactions, such as phase transformations or vapor-liquid-solid growth of nanowires from arrayed catalytic nanoparticles, to prevent their agglomeration. To demonstrate the utility of the Si nano-well array for locally confined high temperature reactions, a phase transformation of multilayered Fe/Pt nano-dots was thermally induced and subsequently characterized. The chemically ordered FePt L1₀ phase, which has high magnetocrystalline anisotropy energy ($\sim 7 \times 10^6$ J/m³), has received much attention as one of the most favorable magnetic materials for ultrahigh-density magnetic recording media [29-31]. For the practical use of FePt, however, a high temperature anneal (~ 600 °C) is required to transform the as-deposited, chemically disordered A1 phase to the L1₀ phase [29-31]. Obviously, this high temperature annealing could cause a massive deformation of patterned structures. For example, lithographically defined thin plates on flat surfaces can split into hemispherical particles to reduce their exposed surface area [32]. For the same reasons, closely spaced nanoparticles on flat surfaces can spread and agglomerate during the annealing process [30,33,34], disrupting the positioning and morphology of magnetic patterns which are critical to data storage applications. For deposition into wells, even if the nano-dots melt, the typical tendency to minimize the exposed surface area favors that nano-dots remain within wells. To show that Si nano-wells prevent this degradation, metal multilayers with the structure of Ta 4 nm / (Fe 2.5 nm / Pt 3.2 nm)₈ / Ta 4 nm were deposited inside the Si nano-well array. The thickness ratio of Fe and Pt layers was chosen to give the equivalent atomic composition. Two Ta layers were included for inhibiting surface oxidation and silicide formation of Fe or Pt [35]. After vacuum annealing (without external magnetic field) at 850 °C for 1 hour, the morphology of samples was analyzed using the backscattered electron mode of SEM and in-plane magnetization curves were obtained using alternating gradient magnetometry at room temperature. Although the coercivity value increased from ~ 0.4 to ~ 5 kOe after annealing, as presented in Figure 4(a), the isolated FePt dots appear to be well preserved throughout the annealing process (supplementary data S3). The magnetic moment obtained from the overall

array, with a $4 \times 4 \text{ nm}^2$ patterned area, was measured to be about $60 \text{ } \mu\text{emu}$. From this value, the saturation magnetization (M_S) of the FePt nano-dots with a diameter of 100 nm and height of 46 nm can be calculated to be about 940 emu/cm^3 , which is consistent with previous measurements of $M_S = 700 \sim 1000 \text{ emu/cm}^3$ for the FePt $L1_0$ phase [36-38].

To our surprise, we noted that several plateaus and steps appeared in the magnetization curve in Figure 4(a). As compared to its initial smooth magnetization from an AC demagnetized status, the magnetization reversal process is accompanied by multiple jumps which were qualitatively replicated in different measurements (Figure 4b) and also from different specimens (supplementary data S4). This result can be understood by considering a large distribution of coercivities of each FePt nano-dot from a random magnetocrystalline anisotropy orientation, or a collective reversal motion of magnetostatically coupled nano-dots in arrays [39-41]. Due to strong dipolar interactions between neighboring nano-dots and their competition with the Zeeman energy, magnetic reversal of the overall array could be reached through sequential metastable configurations of magnetic moments with energy barriers between those metastable states [39-41]. Factors which should be critical for practical use of the patterned FePt nano-dot array as a magnetic recording media, such as the alignment of the c-axis of the $L1_0$ phase as well as the control of dipolar interactions by varying nano-dot moment and spacing, will be the subjects of further studies.

4. Conclusions

We have presented a highly reliable and precise pattern transfer utilizing Si nano-well arrays. Well-controlled undercut profiles of sidewalls and the flat bottoms of the nano-wells enable uniform pattern transfer to encapsulated metal dots without any degradation of the initial lithographic resolution. Au nano-dot arrays with 10 nm diameter were successfully generated by these methods. The utility of the nano-well array for locally confined high temperature reactions, in which the patterned material is enclosed in a Si pocket, was also successfully demonstrated through the phase transformation of as-deposited A1 phase of FePt to the high coercivity, chemically ordered $L1_0$ phase. We expect that distinct benefits of the proposed method, including the physical isolation of patterned materials and the reliable transfer of lithographic patterns, can be effective for generating ultrahigh-density patterns with a few tens of nanometers resolution and for non-destructive thermal annealing of locally confined materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. Drake JM, Klafter J. *Phys Today*. 1990; 43:46.
2. Shin K, Obukhov S, Chen JT, Huh J, Hwang Y, Mok S, Dobriyal P, Thiyagarajan P, Russell TP. *Nat Mater*. 2007; 6:961. [PubMed: 17934464]
3. Rettig JR, Folch A. *Anal Chem*. 2005; 77:5628. [PubMed: 16131075]
4. Kim P, Lee BK, Lee HY, Kawai T, Suh KY. *Adv Mater*. 2008; 20:31.
5. Bennett MR, Hasty J. *Nature Rev Genet*. 2009; 10:628. [PubMed: 19668248]
6. Rissin DM, et al. *Nat Biotechnol*. 2010; 28:595. [PubMed: 20495550]

7. Barton JE, Odom TW. *Nano Lett.* 2004; 4:1525.
8. You EA, Ahn RW, Lee MH, Raja MR, O'Halloran TV, Odom TW. *J Am Chem Soc.* 2009; 131:10863. [PubMed: 19624123]
9. Heidenreich RD. *J Appl Phys.* 1977; 48:1418.
10. Mohamad Z, Shirai M, Sone H, Hosaka S, Kodera M. *Nanotechnology.* 2008; 19:025301. [PubMed: 21817538]
11. Sidorkin V, Grigorescu A, Salemin H, van der Drift E. *Microelectron Eng.* 2009; 86:749.
12. Azuma T, Kawamura D, Matsunaga K, Shiobara E, Tanaka S, Onishi Y. *J Vac Sci Technol B.* 1998; 16:3734.
13. Chen Y, Peng K, Cui Z. *Microelectron Eng.* 2004; 73:278.
14. Carlberg P, Graczyk M, Sarwe EL, Maximov I, Beck M, Montelius L. *Microelectron Eng.* 2003; 67:203.
15. Bouchiat V, Esteve D. *Appl Phys Lett.* 1996; 69:3098.
16. Faircloth B, Rohrs H, Tiberio R, Ruoff R, Krchnavek R. *J Vac Sci Technol B.* 2000; 18:1866.
17. Nishida T, Tamamura T. *J Electrochem Soc.* 1993; 140:2414.
18. Vora KD, Shew BY, Harvey EC, Hayes JP. *J Micro-nanolith Mem.* 2007; 6:013003.
19. Wi JS, Wilson RJ, White RM, Wang SX. *J Vac Sci Technol B.* 2011; 29:033001.
20. Plummer, JD.; Deal, MD.; Griffin, PB. *Silicon VLSI technology.* Vol. Ch. 10. New Jersey: Prentice Hall; 2000.
21. Tian WC, Weigold JW, Pang SW. *J Vac Sci Technol B.* 2000; 18:1890.
22. Janseny H, Gardeniers H, de Boer M, Elwenspoek M, Fluitman J. *J Micromech Microeng.* 1996; 6:14.
23. Ignacio Ulacia FJ, McVittie JP. *J Appl Phys.* 1989; 65:1484.
24. Hamaoka F, Yagisawa T, Makabe T. *IEEE T Plasma Sci.* 2007; 35:1350.
25. Wi JS, Lee HS, Lim K, Nam SW, Kim HM, Park SY, Lee JJ, Hong CD, Jin S, Kim KB. *Small.* 2008; 4:2118. [PubMed: 18985672]
26. Rangelow IW, Loschner H. *J Vac Sci Technol B.* 1995; 13:2394.
27. Blauw MA, Zijlstra T, Bakker RA, van der Drift E. *J Vac Sci Technol B.* 2000; 18:3453.
28. Craciun G, Blauw MA, van der Drift E, Sarro PM, French PJ. *J Micromech Microeng.* 2002; 12:390.
29. Inomata K, Sawa T, Hashimoto S. *J Appl Phys.* 1988; 64:2537.
30. Sun S, Murray CB, Weller D, Folks L, Mo A. *Science.* 2000; 287:1989. [PubMed: 10720318]
31. Wang J. *P IEEE.* 2008; 96:1847.
32. Breitling A, Goll D. *J Magn Magn Mater.* 2008; 320:1449.
33. Dai ZR, Sun S, Wang ZL. *Nano Lett.* 2001; 1:443.
34. Li D, Poudyal N, Nandwana V, Jin Z, Elkins K, Liu JP. *J Appl Phys.* 2006; 99:08E911.
35. Yang F, Wang H, Zhang J, Wang Y, Wang H, Zhu J, Li Q, Jiang Y. *J Phys D: Appl Phys.* 2008; 41:235003.
36. Takahashi YK, Ohnuma M, Hono K. *J Magn Magn Mater.* 2002; 246:259.
37. Shima T, Takanashi K, Takahashi YK, Hono K. *Appl Phys Lett.* 2002; 81:1050.
38. Zhao ZL, Ding J, Inaba K, Chen JS, Wang JP. *Appl Phys Lett.* 2003; 83:2196.
39. Stamps RL, Camley RE. *Phys Rev B.* 1999; 60:11694.
40. Kayali MA, Saslow WM. *Phys Rev B.* 2004; 70:174404.
41. Takagaki Y, Ploog KH. *Phys Rev B.* 2005; 71:184439.

Figure 1. Schematic illustration of the overall process used in this study, including steps for nanoimprint lithography, SF_6/Cl_2 plasma etching, metal deposition, and lift-off.

Figure 2.

(a-c) Cross sectional SEM images of Si nano-well arrays after plasma etching for (a) 40 sec and (b,c) 60 sec. (d) Plan view SEM image of Au nano-dots located inside the Si nano-well after the lift-off step. The dotted lines guide the eye for comparison.

Figure 3. Plan view SEM images of (a,b,c) NIL mold and (d,e,f) arrays of Au nano-dots located inside the Si nano-wells. The pitch of Au nano-dots is 100 nm and their diameter is (d) 30 nm, (e) 20 nm, and (f) 10 nm, respectively. The scale bar in insets of (d-f) is 100 nm.

Figure 4.

(a) Magnetic hysteresis loop from the initially multilayered Fe/Pt nano-dot array which was vacuum annealed at 850 °C for 1 hour. Inset graph shows the hysteresis loop from the as-patterned sample before thermal annealing. (Inset x -axis; magnetic field in kOe, y -axis; normalized magnetic moment). (b) Enlarged view of the hysteresis loops from multiple measurements. Red, blue, and black colored lines represent the first, second, and last measurement results, respectively. The external field was aligned in the in-plane direction in every case.