Site-Selective Deposition of Magnetite Particulate Thin Films on Patterned Self-assembled Monolayers

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Magnetite micropatterns were successfully fabricated by the site-selective deposition technique using self-assembled monolayers (SAMs) as templates. Magnetite particles were selectively deposited on Pd catalysts which were adsorbed to the $-NH_2$-terminated surface of a SAM, in an aqueous solution containing iron nitrate and dimethylamine−borane. Pd colloid catalyst particles were adhered to the amino group of a patterned SAM by electrostatic interaction. Crystalline Fe_3O_4 (magnetite) particulate films were then deposited on amino-group regions by the effect of metal Pd catalyst. Site-selective deposition of crystalline Fe_3O_4 was thus realized in an aqueous solution. The deposition mechanism of Fe_3O_4 is discussed in detail in comparison with the deposition of γ-FeOOH in the solution.

Introduction

Fe_3O_4 is well-known as a magnetic material used for recording media and magnetic heads, etc. Recently, magnetite has been attracting much attention as a tunneling magnet resistance material due to its half-metal nature and high polarity. Usually, magnetite films are obtained by using the PVD method, although some methods of deposition from aqueous solution have been reported. In many cases by using a liquid-phase deposition technique, FeOOH films were deposited first and then heated to make magnetite.[1−4] However, there have been few reports in which magnetite film was obtained directly from aqueous solution without a heating process.[5−8] Substrates which are susceptible to heat treatment such as polymers are available by using a solution-deposition process, which in terms of “green chemistry” is superior to the usual heating processes because less energy is required. Lin et al. reported that magnetite film was prepared by providing NH_3 gas to Fe solution through a Langmuir monolayer.[5] Abe et al. set a tube close to the substrate and sprayed a fresh solution of Fe and alkali continuously onto the substrate through the tube, to prepare the magnetite film.[6,7] Izaki et al. succeeded in achieving Fe_3O_4 deposition from an aqueous solution at low temperature by using the reduction of nitrate ions;[8] Pd catalyst particles were adsorbed on the substrate and reducing agent, such as dimethylamine−borane complex, thus reducing nitrate ions on the catalyst and increasing pH at the surface locally. This reaction resembles electroless deposition, although a film was directly deposited not by reduction but by the rise of pH.

Patterning techniques are very important for fabricating thin film devices, but it is usually difficult to etch metal oxides because of their high corrosion resistance which is one of the features of ceramics. Magnetite also has high corrosion resistance and it is often used for protecting steel surfaces from corrosion. Although the liftoff method can be used to solve the second problem, it also needs many processing steps, which increases the cost.

We have succeeded in micropatterning ceramic thin films such as TiO_2,[9,10] SnO_2,[11] ZnO,[12] ZrO_2,[13] Ta_2O_5,[14] and $SrTiO_3$,[15] using self-assembled monolayers (SAMs) as templates and liquid-phase deposition techniques at low temperature.

SAMs are organic monolayer films that are chemisorbed on substrates such as silicon wafers or native oxide films on metal substrates. SAMs have many applications to immobilize a catalyst[16] or macromolecules including DNA,[17] proteins, and cells.[18] Moreover,

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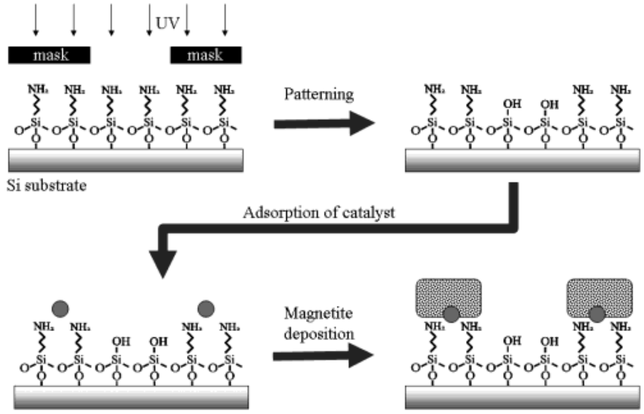

Figure 1. Schematic diagram of the fabrication process for magnetite patterning.

the use of SAMs for reducing stiction in MEMS[19] and as resist materials in etching have been reported.[20] Calvert et al. developed selective metal deposition by using electroless metal deposition on various SAMs, which were patterned to have an Si−OH surface and a functional-group surface such as an amino-group surface.[21,22] Metal film grew on the Pd catalyst adsorbed only on the functional-group surface.

Here, we report the site-selective deposition of iron oxide Fe_3O_4 “magnetite” on a self-assembled monolayer. We used this site-selective Pd catalyst adsorption technique and iron oxide deposition technique for deposition on the surface of a substrate with a catalyst. Figure 1 shows the outline of our experimental procedure. We prepared a patterned SAM and adsorbed Pd catalyst particles onto the amino-group region site-selectively. Iron oxide film was deposited on the Pd catalyst site-selectively and thus a micropattern of iron oxide Fe_3O_4 “magnetite” particulate thin film was successfully fabricated in an aqueous solution.

Experimental Section

SAM Preparation. A p-type Si[100] wafer (1−50 Ωcm, Newwingo Co., Ltd.) was used as a substrate, which was cleaned ultrasonically in acetone, ethanol, and deionized water. The substrate was then cleaned with UV light (wavelength of 185 and 254 nm) and ozone gas by using UV/ozone cleaner (PL21-2100, SEN Lights Corp.) to remove organic contamination from the wafer surface. Following the cleaning, the substrate was immersed into a 1 vol % solution of aminopropyltrimethoxysilane [APTS; $H_2NC_3H_5Si(OCH_3)_3$] in CH_3OH/H_2O (95:5) containing 1 mM CH_3COOH for 20 min at 50 °C. The substrate was then rinsed with methanol and baked at 120 °C for 5 min.[21]

UV light was irradiated on an APTS-SAM through a photomask by using a low-pressure mercury lamp (Figure 1). UV-irradiated regions became hydrophilic silanol regions to prepare patterned APTS−SAMs which have amino-group regions and silanol-group regions.

Catalyzing Procedure. Catalyst solution containing Na_2PdCl_4 (0.38 mM) and NaCl (0.01 M) in a 0.01 M 2-morpholinoethane sulfonate pH 5 aqueous buffer was prepared. The details of preparation of this solution are described in ref 23. Hydrolyzed Pd colloids were formed in this solution.[24] The patterned APTS-SAM was immersed into the colloidal dispersion of catalyst at 25 °C for 30 min and catalyzed APTS−SAM was rinsed with water.

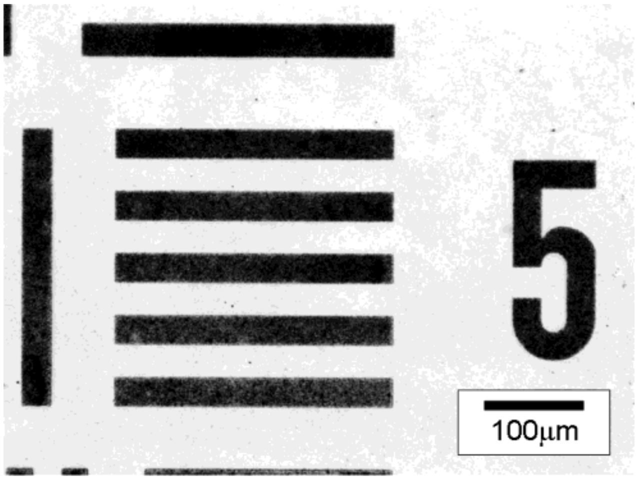

Figure 2. Optical microscope image of as-deposited film. Black regions and white regions show the films deposited on UV-irradiated and non-UV-irradiated regions, respectively.

Magnetite Film Preparation. Catalyzed SAM was immersed in an aqueous solution containing iron(III) nitrate (0.0025 M) and dimethylamine−borane (DMAB) (0.03 M) and kept at 80 °C using a water bath for 30 min to deposit magnetite particulate thin film.[8] DMAB was used to reduce nitrate ions, giving rise to OH^- ions and hence raising the solution pH to precipitate Fe_3O_4.

Characterization. Deposited films were observed by a scanning electron microscope (SEM; S-3000N, Hitachi Ltd.) and an optical microscope (OM; BX51WI, Olympus Optical Co., Ltd.). Structural information of films was obtained by X-ray diffraction analysis (XRD; RAD-1C, Rigaku; 5° incident angle, Cu Kα, 40 kV, 30 mA, scanning speed 1°/min). X-ray photoelectron spectroscopy (XPS; ESCA3200, Shimazu Corp.; 1×10^{-5} Pa Mg Kα) and energy-dispersive X-ray analysis (EDX; Falcon Imaging System, EDAX Inc.) and secondary ion mass spectroscopy (SIMS; TOF−SIMS IV, ION-TOF GmbH; 2.4 pA Ga^+, 25 keV) were used for surface analysis. The particle size of colloids and surface ζ-potential of substrates and colloids were measured by an electrophoretic light-scattering spectrophotometer (ELS-7300K, Otsuka Electronics Co., Ltd.) at 25 °C. Surface ζ-potential of a SAM was determined by measurement of electrophoretic mobility of polystyrene latex monitor particles with diameter of 520 nm on the SAM surface. The monitor particles were coated with hydroxypropyl cellulose (MW = 300000). Surface ζ-potential of colloids was evaluated from electrophoretic mobility in a quartz cell. Catalyst colloid solution was measured as it was. NaCl aqueous solution (10 mM), adjusted to the desired pH by HCl, was used for surface ζ-potential measurement.

Results and Discussion

Site-Selective Deposition of Iron Oxide. A black colored iron oxide film selectively deposited onto regions of the APTS-SAM that had not been exposed to UV radiation following application of the Pd catalyst dispersion. Figures 2 and 3 show an OM image and a SEM image of as-deposited films, respectively. Black contrast

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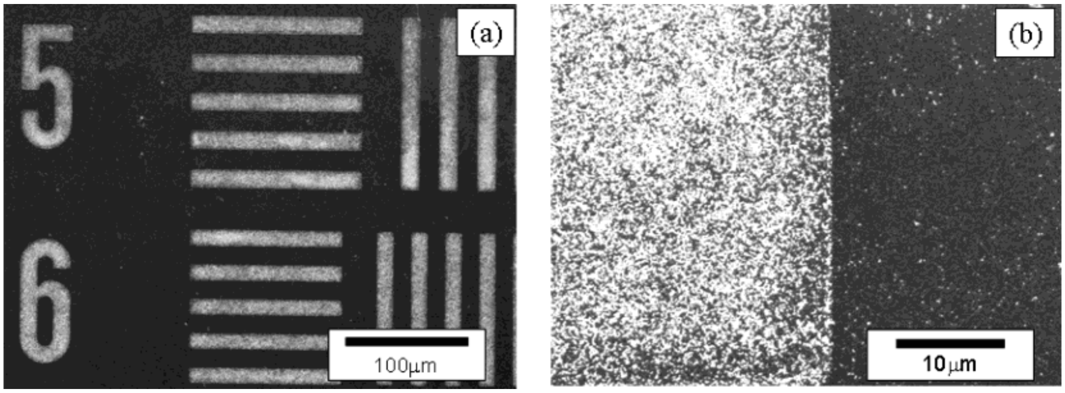

Figure 3. SEM images of (a) as-deposited films and (b) magnified area of (a). Black and white regions correspond to UV-irradiated and non-UV-irradiated regions, respectively.

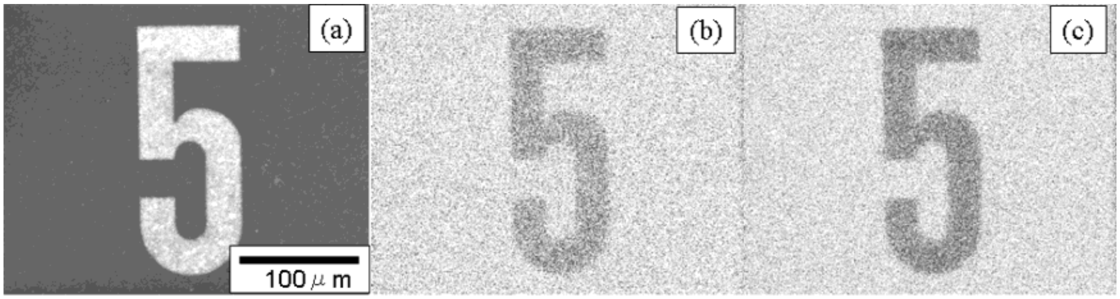

Figure 4. EDX analysis of as-deposited film on patterned APTS-SAM: (a) SEM image and characteristic X-ray images of (b) Fe and (c) O.

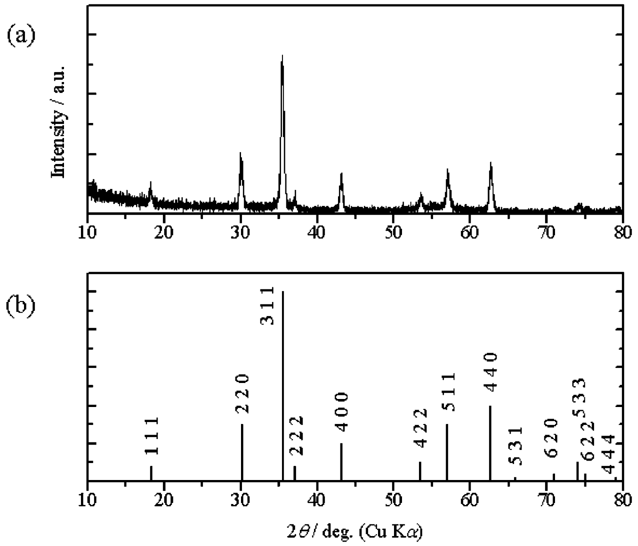

Figure 5. X-ray diffraction pattern of (a) as-deposited film on catalyzed APTS-SAM and (b) the JCPDS card data of Fe_3O_4 (No. 19-0629).

represents a deposited film in an optical microscope image (Figure 2), whereas the white contrast shows deposited films in SEM images (Figure 3). The EDX mapping images shown in Figure 4 indicate the films deposited on the amino-surface regions, showing mapping images consisting mainly of iron and oxygen. The XRD pattern (Figure 5) of the thin film deposited on the whole surface of the APTS-SAM clearly indicates that it is a magnetite (Fe_3O_4) film composed of randomly oriented crystallites of about 20 nm in diameter, which was evaluated using the Scherer equation.

These evaluations show the successful fabrication of a micropattern of crystalline magnetite films in an aqueous solution using a patterned APTS-SAM and Pd colloid catalysts adsorbed on amino-group ($-NH_2$) regions of a SAM.

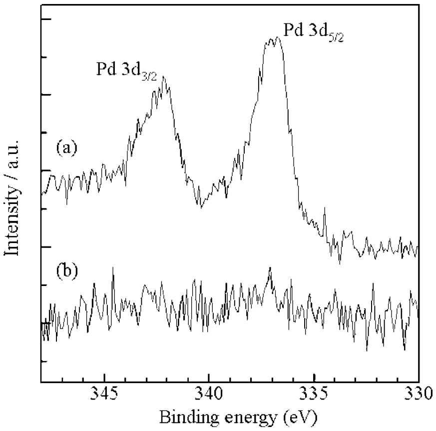

Figure 6. XPS spectra for Pd 3d of (a) catalyzed APTS-SAM and (b) catalyzed UV-APTS-SAM.

Adsorption Mechanism for Pd Catalyst. Pd catalyst plays an essential role in depositing magnetite films because no magnetite deposition was observed when Pd catalysis was not performed. To clarify the adsorption mechanism for Pd catalyst, Pd catalyzation was performed on an APTS-SAM and a UV-irradiated APTS-SAM (denoted as UV-APTS-SAM hereafter). Figure 6 shows XPS spectra of Pd 3d for (a) APTS-SAM and (b) UV-APTS-SAM after Pd-catalyzing treatment. While an intense peak of Pd $3d_{5/2}$ was observed for APTS-SAM at 337.1 eV (Figure 6a), no peak was detected for UV-APTS-SAM (Figure 6b), indicating that Pd was adsorbed selectively to the amino ($-NH_2$) surface. Referring to an earlier report,[24] the spectrum of Pd $3d_{5/2}$ in Figure 6a can be divided into Pd−N (338.7 eV),[29] Pd−Cl

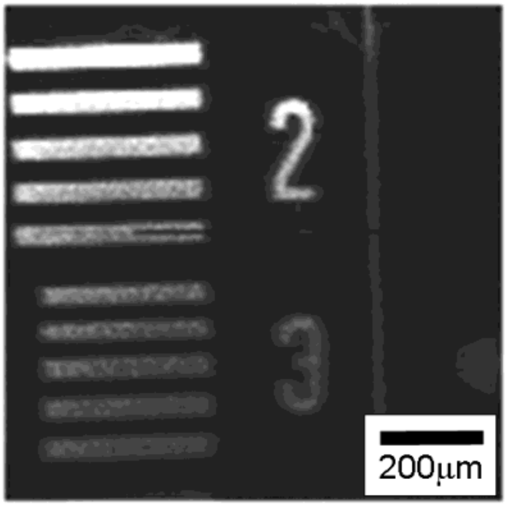

Figure 7. SIMS mapping image of Pd ($m/z = 104, 105, 106, 108, 110$) on patterned APTS-SAM. White contrast represents the presence of Pd.

(337.8 eV),[30−32] and Pd−O (336.9 eV)[33] to be Pd−N:Pd−Cl:Pd−O = 0.012:0.105:0.883. Pd on the APTS-SAM was mainly combined with O as Pd−O (336.9 eV). This result indicates that Pd colloids on APTS-SAM consist of Pd−O or Pd−OH as well as a small amount of Pd−Cl. Although the Calvert group reported that the hydrolyzed Pd particles make covalent bonds with other SAMs which have amine groups,[24] the Pd−N bond was hardly observed in our XPS experiment because of Pd colloid particles hiding Pd−N bonds. Pd−N bonds might have been present also in our case. However, only XPS can analyze the surface state of a few nanometers in depth, and hence it might have been hard to observe the contact regions of surface amino groups and Pd colloid particles whose size was 30 nm in diameter. Furthermore, site-selective adsorption of Pd was clearly observed by TOF-SIMS mapping as shown in Figure 7. Bright regions due to Pd ($m/z = 104, 105, 106, 108$, and 110) are observed on the APTS-SAM surface, while no Pd signal is seen on the UV-APTS-SAM surface. These results clearly indicate that site-selective adsorption of Pd catalyst occurred on the APTS-SAM surface.

Light-scattering measurements indicated that the catalyst solution contained colloid particles of ~30 nm in diameter. Surface ζ-potentials measured by an electrophoretic light-scattering spectrophotometer (pH = 5) were +27 mV for APTS-SAM, −33 mV for UV-APTS-SAM, and −31 mV for Pd colloid particles. The particle size and the surface charge of catalyst are in good agreement with earlier work.[23,25] This result clearly suggests that Pd particles with negative surface potential adsorb only to APTS-SAM with positive surface potential due to strong electrostatic attractive force, while electrostatic repulsion force should keep Pd catalyst particles away from UV-APTS-SAM.

Deposition Mechanism for Fe_3O_4. Izaki et al. proposed the following reaction schemes for the chemical deposition of Fe_3O_4 film:[8]

$$Fe(NO_3)_3 \rightarrow Fe^{3+} + 3NO_3^- \quad (1)$$

$$(CH_3)_2NHBH_3 + 2H_2O \rightarrow BO_2^- + (CH_3)_2NH + 7H^+ + 6e^- \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (4)$$

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow (Fe^{2+}, Fe^{3+})(OH)_8 \quad (5)$$

$$(Fe^{2+}, Fe^{3+})(OH)_8 \rightarrow Fe_3O_4 + 4H_2O \quad (6)$$

Starting trivalent iron ions are reduced to divalent ions owing to the presence of the reducing agent, $(CH_3)_2NHBH_3$ (reactions (1)−(3)). Electrons generated according to reaction (2) are also expected to reduce nitrate ions to nitrite ions as shown in reaction (4), which is promoted by the presence of a catalyst on a substrate. Then, the pH in the vicinity of catalyst particles rises locally and Fe_3O_4 (magnetite) becomes deposited according to reactions 5 and 6.

Magnetite is composed of Fe^{2+} and Fe^{3+} ions and cannot be obtained from the solution containing only Fe^{3+} ions. However, the initial solution involved Fe^{3+} ions only, and hence Fe^{2+} ions are considered to be produced by reaction 3. Shortly after preparation of an aqueous solution for magnetite film deposition, the color of this solution was orange. This solution became transparent and colorless after some minutes, suggesting the progress of reaction 3 because Fe^{3+} solution is yellow and Fe^{2+} solution is colorless.[26] The colorless solution gradually changed to yellow and the magnetite film was deposited in the solution at 80 °C.

Additionally, dark green film was deposited from the solution at less than 60 °C. Shortly after taking out this dark green film from an aqueous solution, it gradually changed to orange color. XRD measurement revealed this orange film was of γ-FeOOH (lepidocrocite) or a mixture of lepidocrocite and magnetite. Lepidocrocite is synthesized by oxidizing a solution containing Fe^{2+} at pH $\simeq$ 7 through the formation of green rust.[27] In contrast, magnetite is synthesized from Fe^{2+} salt solution at higher temperature under alkaline conditions.[27] Reaction (4), which produces OH^-, would progress slowly at low temperature, and hence pH did not become high locally on the surface of a substrate at low temperature, rather causing the deposition of γ-FeOOH. Fe^{3+} would be reduced to Fe^{2+} in the solution because γ-FeOOH cannot be produced from an Fe^{3+} aqueous solution. This is consistent with the progress of reaction (3) in the solution.

Furthermore, although Fe^{2+} is expected to be reduced to Fe in the solution, Fe metal film was not deposited

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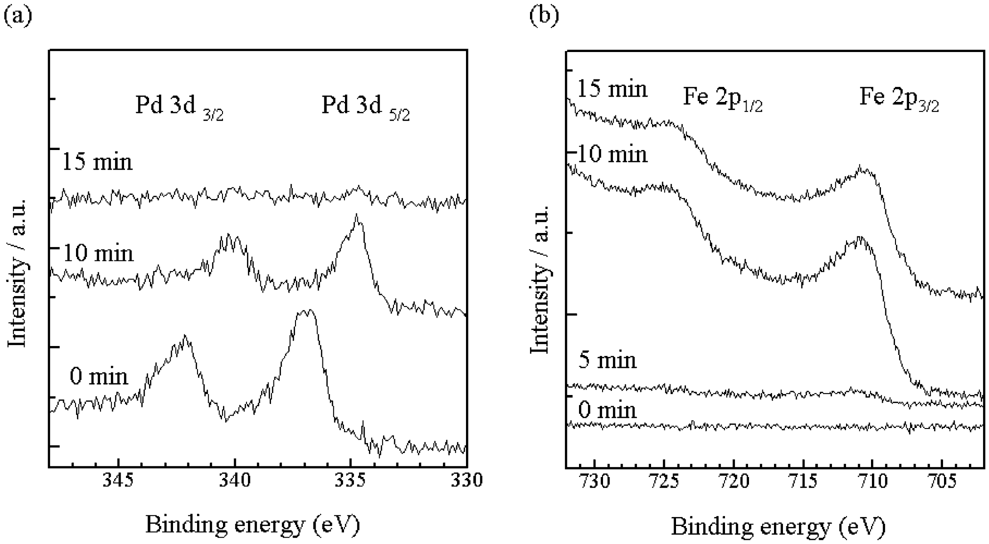

Figure 8. (a) Pd 3d and (b) Fe 2p region of the XPS spectra taken at different deposition times. After 10-min immersion, Pd 3d peaks shift to the lower energy side because Pd ions were reduced to metal.

in this system. Standard electrode potentials vs that of the hydrogen electrode (SHE) of the present reactions are as follows:[28]

$$\mathrm{Fe^{3+} + e^- \rightarrow Fe^{2+}} \qquad E° = +0.771 \text{ V vs SHE} \quad (3)$$

$$\mathrm{NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-} \qquad E° = +0.01 \text{ V vs SHE} \quad (4)$$

$$\mathrm{Fe^{2+} + e^- \rightarrow Fe^0} \qquad E° = -0.44 \text{ V vs SHE} \quad (7)$$

Reaction (4) would progress preferentially because its standard potential is higher than that of reaction (7). Reduction of Fe^{3+} to Fe^{2+} would have priority compared with the reduction of nitrate ions since the standard potential of (3) is higher than that of (4). Accordingly, reduction of Fe^{3+} ions (reaction (3)) progresses before the pH rises (reaction (4)) or the reduction of Fe^{2+}, to Fe (reaction (7)), which gives rise to appropriate conditions for the deposition of Fe_3O_4 (magnetite).

To further elucidate the deposition process, specifically the role of Pd catalyst, the state of Pd was analyzed by XPS, which was conducted as a function of Fe_3O_4 deposition time. Figure 8a shows the XPS spectra of Pd $3d_{3/2}$ and Pd $3d_{5/2}$ taken from three different samples, for which the deposition time was counted from the initial immersion of a catalyzed SAM substrate into a magnetite deposition solution. “0 min” means the time just before immersing the sample into a solution containing iron nitrate and DMAB. Two peaks at 342.2 and 336.9 eV observed at 0 min correspond to those of oxidized Pd, possibly PdO or Pd hydroxide.[33] After 10-min immersion, these two peaks shifted to the lower energy side, 340.1 and 334.8 eV, indicating that Pd ions were reduced to form metal particles.[33] Further immersion for 15 min made both peaks disappear because the deposited magnetite particles covered almost the entire surface, inhibiting the release of photoelectrons from Pd particles. It should be noted that Fe_3O_4 (magnetite) begins to deposit only after Pd ions are reduced to metal particles according to the XPS spectra of Fe 2p measured simultaneously with Pd 3d as shown in Figure 8b. This observation firmly indicates that reduced metal Pd acted as a catalyst and reduced nitrate ions to nitrite ions in the amino surface region to deposit Fe_3O_4.

Conclusion

We successfully fabricated patterned magnetite films directly by using patterned functional groups of SAM. Pd colloid catalysts were adsorbed on amino-group regions of a patterned SAM by electrostatic interaction between substrates and catalysts, causing site-selective adsorption of catalyst. It was possible that adsorbed colloidal Pd particles on APTS-SAM made covalent bonds with amino groups. Pd catalyst caused the reduction of nitrate ions, which culminated in an increase of pH, and the crystalline magnetite was deposited only on amino-group regions on which Pd existed. Consequently, site-selective deposition of crystalline magnetite films was realized in an aqueous solution. This process can be used for nano-/micropatterning of films deposited by using a catalyst.

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