

Selective Deposition of Iron Oxides Thin Layers on Si(100) from Aqueous Solutions

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Chemical solution deposition (CSD) is used widely to deposit thin inorganic films on account of its simplicity and low cost. Moreover, this method can be easily scaled up, which is in contrast up other film deposition techniques, such as vacuum evaporation,¹ sputtering,² spray pyrolysis³ and chemical vapor deposition.⁴ Combined with micro-contact printing (μ CP) of OTS (octadecyltrichlorosilane), CSD has been applied to micro patterning of a variety of inorganic thin films,⁵⁻⁹ where the OTS layers play a role of an organic resist to develop characteristic surface properties. In the ranges of selectivity obtained by various deposition techniques, CSD often produces thin film patterns with rather low selectivity and poor resolution because the OTS layers are influenced by the solution pH during deposition. This letter reports the development of micrometer scale patterning methods of α -Fe₂O₃ (hematite) and β -FeOOH (akaganeite) thin films using μ CP and CSD, where the pattern resolution of thin films was enhanced using a buffer solution as the reaction media.

Si(100) substrates were treated with a piranha solution for 10 min and washed with deionized water, acetone, and 2-propanol and dried with a stream of nitrogen. Iron oxide thin films were deposited at 75 °C on patterned OTS on 3 × 3 cm² sized Si substrates in an aqueous solution, where the iron oxide precipitates are also formed during the deposition process. Stamps with a micron-size patterned relief structure were prepared by mixing polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) with a curing agent for 30 min, followed by

curing at 80 °C for 1 h. A solution of OTS in anhydrous hexane (10 mM) was used as an “ink” and applied to the stamp using a spinner at 3000 rpm for 30 s. The inked stamp was placed in contact with Si and held in place for 30 seconds, yielding OTS thin films with approximately 30 Å mass coverage.¹⁰

Fe(NO₃)₃·9H₂O and FeCl₃·6H₂O were used as starting materials to produce hematite and akaganeite, respectively. The hematite thin films were deposited from a 0.05 M iron nitrate solution. The akaganeite thin film was deposited from 0.05 M iron chloride in 0.1 M acetate buffer solution. The OTS-patterned Si substrates were immersed in the solution for 2 h at 75 °C with constant stirring. The final pH range of the iron nitrate and iron chloride-acetate buffer solutions was 1.5 ~ 1.7 and 2.5 ~ 3.0, respectively. The color of the nitrate and chloride solutions was red-brown and light ochre, respectively. Both precipitates and thin films were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Figure 1(a) and (c) show SEM images of the precipitates and thin film prepared in Fe(NO₃)₃ solution. The deposited thin film was densely covered with hematite nanoparticles with spherical shapes with an average size of 20 - 50 nm. XRD of both the powder and film showed three predominant peaks at 33.2, 35.6, 65.4° 2 θ , which were assigned to (104), (110) and (214) for the hematite phase.¹¹⁻¹³ At pH < 2, the formation of a hematite phase was more favorable than the other phases, such as goethite.^{14,15} Figure 1(b) and (d) show spindle-like particles and thin films prepared in the FeCl₃ solution. The powder sample was comprised of monodisperse 350 nm particles, and the thin films on Si contained a thin conformal layer of large particles, 500 nm in size, overlying on the layer. The bottom layer also showed spindle-like particles, approximately 200 nm in size, imbedded on the layer deposited on Si. XRD of both the powder and film showed peaks for the akaganeite phase corresponding to the (200), (400), (600), (110) and (310) planes.¹¹ In the presence of Cl⁻, the formation of the akaganeite phase was more favorable than the other phases.¹⁶

Figure 2(a) and (b) show area selective deposition of iron oxide thin films on OTS patterned Si. Figure 2(c) shows the surface profilometry scan of the patterned iron oxide film, where the 500 μ m patterns show two separate hematite layers, 80 μ m wide and 120 nm thick. The edges of the film are quite sharp, even though the surface roughness of the hematite layer is approximately 30 nm. The chemical composition of the akaganeite film was analyzed by Auger electron spectroscopy at a 10 keV beam voltage on a 15 μ m × 15 μ m area after Ar⁺ ion sputtering for 10 seconds. In Figure 2(d), the akaganeite covered

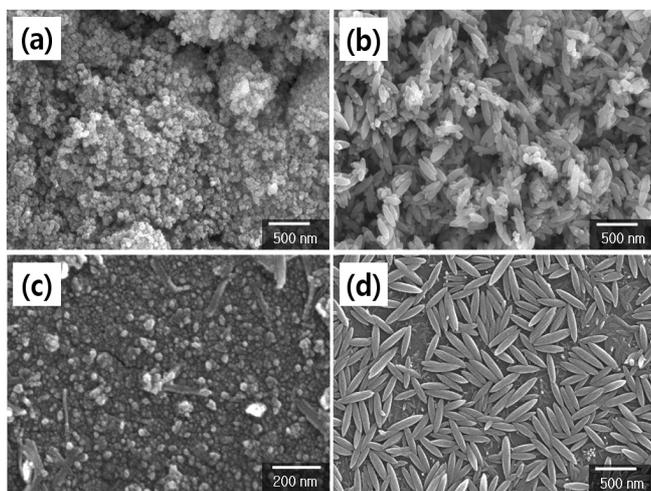


Figure 1. SEM images of (a) hematite powder, (b) akaganeite powder, (c) hematite thin film and (d) akaganeite thin film.

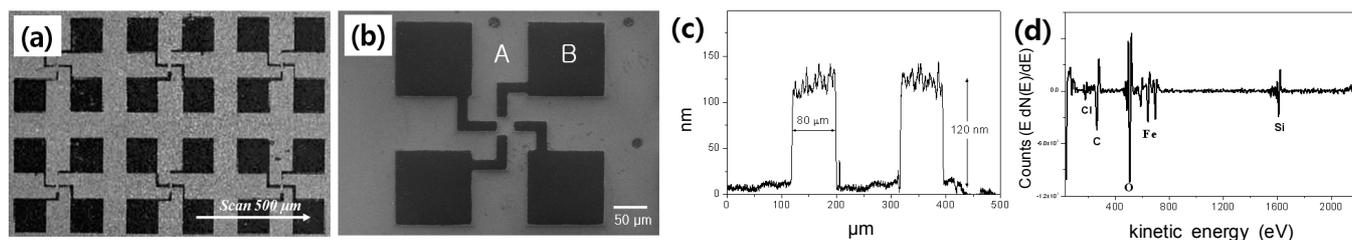


Figure 2. (a) Optical microscopy image of patterned hematite thin films, (b) SEM image of akaganeite thin film, (c) Surface profile of a selected area in figure (a), and (d) Auger electron spectra of area (A) in figure (b).

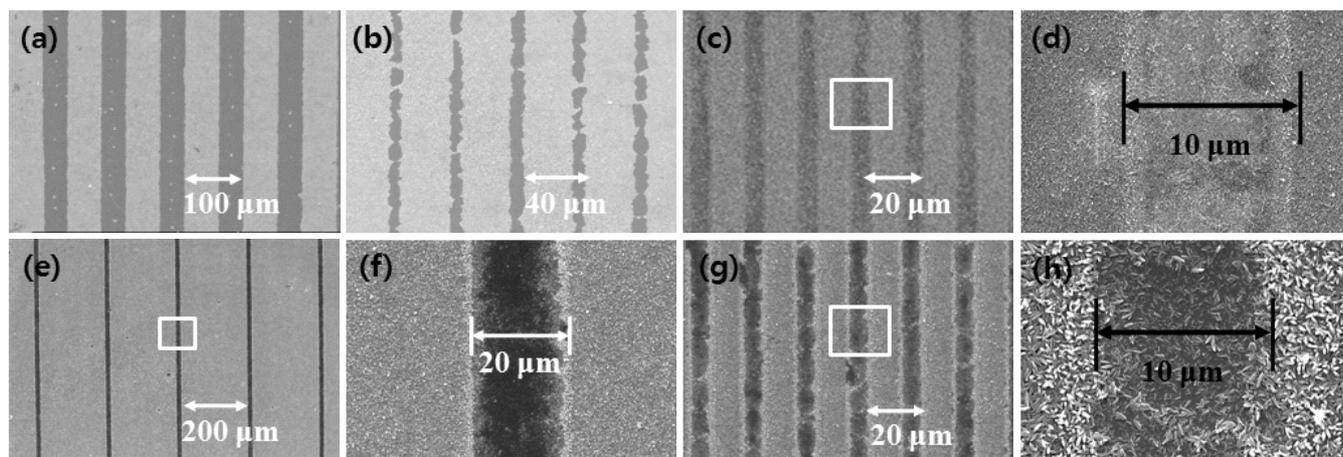


Figure 3. SEM images of hematite (a) ~ (d) and akaganeite thin films (e) ~ (h) with different printed OTS line widths.

region (A) shows peaks for Fe, O, Cl, C and Si, while region (B) showed Si and O along with some C and Fe impurity. The peak for Cl from region (A) was assigned to Cl^- ions in the three-dimensional tunnel of the akaganeite phase.^{17,18} The strong peak for carbon in region (A) may be due to the hydrocarbons of OTS, which shows that iron oxide thin films were deposited exclusively on the OTS printed area.

Figure 3 shows that the surface morphology and edge sharpness of the iron oxide films on the OTS printed Si depend strongly on the pH and starting materials. The bright regions in the SEM images are iron oxide films on the OTS printed area and the dark ones are the Si surfaces. In the case of hematite shown in Figure 3(a) ~ (d), the areas of the films are larger than that of the akaganeite films shown in Figure 3(e) ~ (h). The size of the original OTS printed line patterns of the PDMS stamps shown in Figure 3 (b) was 20 μm with a 20 μm space. However, the width of the hematite films was 30 μm ; the iron oxide films were extended approximately 5 μm wide along both sides. In the case of the 10 μm line and 10 μm space shown in Figure 3(c) and (d), the entire surface was covered with a hematite films with no clear edges. In contrast, the akaganeite films shown in Figure 3 (e) ~ (h) were approximately 2 μm wide along both sides of the lines. SEM also showed that the akaganeite layers in the boundaries were thicker than that in the center, which was attributed to the diffusion of the OTS moiety during μCP .^{10,19} In the 10 μm OTS line with a 10 μm space shown in Figure 3 (h), the entire surface was covered with an akaganeite layer but with clear boundaries. Therefore, the area selectivity of thin film deposition increases with increas-

ing ionic strength in the buffer solution. Correlation between the edge-resolution of the films and the buffer strength of the starting solution will be discussed. In addition, the present synthetic method does not require complicated multi-step modifications to perform μCP for iron oxide film patterns, as reported earlier.¹⁹

In conclusion, micrometer scale patterns of two types of iron oxide layers were obtained successfully using microcontact printing of OTS on Si. The iron oxide thin layers were formed on the OTS printed area, which was assigned to the catalytic etching of OTS under the acidic experimental conditions, or to the heterogeneous nucleation on OTS layer.²⁰ It was also found that the high ionic strength of the reaction media helped increase the edge-resolution of the thin film patterns during pattern formation, particularly at low pH. Overall, this patterning method can be applied to other solution deposition processes.

Experimental Section

Materials and reagents. The Sylgard 184 kit was purchased from Dow Corning. The p-type Si(100) wafers were obtained from Buysemi Co., Korea. OTS (Octadecyltrichlorosilane, 99%), Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98%), Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 98%), Sodium acetate buffer (0.1 M, pH 7.0) and *n*-hexane (HPLC grade, 97%) were purchased from Aldrich St., Louis USA. All chemicals were of analytical grade and obtained commercially.

Characterization. The iron oxide films were first assessed

by optical microscopy. Selected samples from the optical microscopy inspection were studied by scanning electron microscopy (SEM, Phillips XL30FEG), surface profilometry (Tencor R-step 500), Auger electron spectroscopy (VG Scientific MicroLab 310-B, 10 keV) at a 10 keV beam voltage after Ar⁺ ion sputtering for 10 seconds. X-ray diffraction (XRD) patterns were measured with a Rigaku X-ray diffractometer, D/MAX-2000 Ultima, on $\theta \sim 2\theta$ scanning mode. The measurements were performed under the conditions of 40 kV, 30 mA, and Cu-K α ($\lambda = 1.5405 \text{ \AA}$). All XRD spectra of the films were calibrated using Si (200) peak from substrates ($2\theta = 32.9^\circ$, $d = 2.74 \text{ \AA}$).

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