
Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Fabrication of in situ Patterned Iron Oxide Films using Micro Contact Printing and Selective Deposition

Hyunjung Shin [a] , Hyejin Im [b] , Jong Up Jeon [a] , Eung Soo Kim [c] & Y. Eugene Pak [d]

[a] Nano System Lab., Samsung Advanced Institute of Technology and CRI, Suwon, Korea, 440-660

[b] Department of Ceramic Engineering, Yonsei University, Seoul, Korea

[c] Department of Materials Engineering, Kyonggi University, Suwon, Korea

[d] MEMS Lab., Samsung Advanced Institute of Technology and CRI, Suwon, Korea, 440-660

Version of record first published: 24 Sep 2006

*Mol. Cryst. and Liq. Cryst.*, 2001, Vol. 371, pp. 473-476 



# Fabrication of *in situ* Patterned Iron Oxide Films using Micro Contact Printing and Selective Deposition

HYUNJUNG SHIN[1], HYEJIN IM[2], JONG UP JEON[1], EUNG SOO KIM[3] and Y. EUGENE PAK[4]

[1]*Nano System Lab. and* [4]*MEMS Lab., Samsung Advanced Institute of Technology and CRI, Suwon, Korea 440-660,* [2]*Department of Ceramic Engineering, Yonsei University, Seoul, Korea,* [3]*Department of Materials Engineering, Kyonggi University, Suwon, Korea*

*In situ* patterning of iron oxide thin layers were fabricated via micro-contact printing (μCP) and selective area deposition. μCP is used to pattern two different surface moieties of self-assembled organic monolayers (SAMs) on Au/Cr/Si substrates. An elastomeric stamp is used to transfer hydrophobic (hexadecanethiol (HDT)) SAMs that are to sustain deposition of iron oxide precipitates. Hydrophilic (dithiothreitol, DTT) SAMs were used to induce crystalline iron oxide films. 0.05 M of iron nitrate ($Fe(NO_3)_3 \bullet 9H_2O$) aqueous solutions containing urea under nitric acid (pH < 2) were used. Selective depositions were realized through precipitation of crystalline iron oxides at ambient temperature (80°C) onto the mixed SAM surfaces.

*Keywords*: in situ patterning; micro-contact printing; selective deposition; iron oxide films; self-assembled organic monolayers

## INTRODUCTION

Magnetic oxides, mainly $\gamma$-$Fe_2O_3$ and $Fe_3O_4$ were used most widely for the last few decades in magnetic recording media.[1,2] The fabrication of

materials with nanometer dimensions is the subjects of intense current research. Although several studies have been devoted to the synthesis of nanometer-sized compound semiconductors, relatively little work exists for magnetic materials of similar dimensions. Potential applications for the latter exist in information storage industry.[3]

Microcontact printing (μCP) is a broadly applicable technique for derivatizing surfaces.[4] Using different terminal groups, it is possible to define areas having well-controlled properties on the surfaces. For example, hydrophobic surfaces can be generated with hexadecanethiols (HDT), and hydrophilic surfaces with dithiothreitol (DTT) and so on.

Our strategy for the fabrication of patterned iron oxide films is to combine two key technologies: μCP to generate mixed surface moieties and selective deposition of crystalline iron oxide films onto specific area.

In this study we demonstrated fabrication of *in situ* patterned crystalline $\alpha$-$Fe_2O_3$ films using μCP and selective deposition by thermal hydrolysis of iron nitrate aqueous solutions with urea at 80°C.

## EXPERIMENTAL PROCEDURE

Stamps were prepared from polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning). Thiol SAMs were deposited onto gold surfaces by contacting the PDMS stamps. 0.2 mM of HDT solutions was prepared and the stamps were dipped into the solutions for inking of hydrophobic SAMs. Finally, the prepared samples for the deposition of iron oxide films containing two different SAMs, which are hydrophobic and hydrophilic, respectively, were cleaned with ethanol.

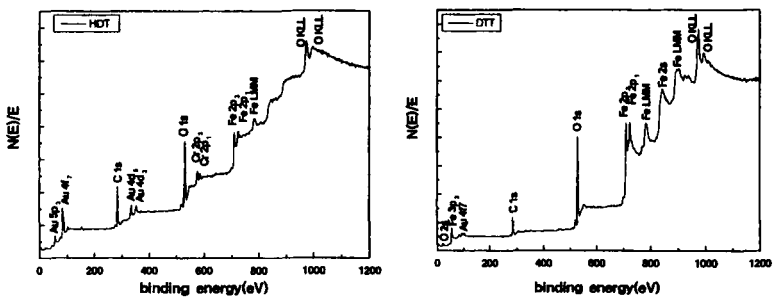
Depositions of iron oxide films were performed through the precipitation of iron nitrate aqueous solutions onto the SAM surfaces. 0.05 M of iron nitrate ($Fe(NO_3)_2 \bullet 9H_2O$) aqueous solutions containing urea under nitric acid (pH < 2) were prepared for the precursor

solutions.

The deposited iron oxide films were characterized using XPS, XRD, AFM and SEM. Magnetic properties were measured by VSM. The patterned films were characterized with SEM and AFM.

## RESULTS AND DISCUSSION

X-ray photoelectron spectroscopic (XPS) results showed that iron oxides were deposited only onto DTT SAMs, but not onto hexadecanethiol (HDT, $CH_3(CH_2)_{15}SH$) SAM surfaces as shown in Figs. 1. It is noted that Au peaks completely disappeared in case of the films deposited on the dithiothreitol (DTT, $SCH_2CH(OH)CH(OH)CH_2SH$) SAM surfaces, whereas exist in case of on the HDT surfaces. Position of Fe 2*p* peaks in multiplex mode showed a good agreement with standard Fe position in $Fe_2O_3$. The narrow peaks for the $\alpha$-$Fe_2O_3$ films are attributed to a single iron oxidation state ($Fe^{3+}$). The binding energy of the Fe $2p_{3/2}$ core level is approximately 710.8 eV. In addition, we observed a shake-up satellite line at 718.5 eV, which is characteristic for $Fe^{3+}$ in $Fe_2O_3$.[5]




Figs. 1 XPS spectrum of the as-deposited $\alpha$ – $Fe_2O_3$ films onto HDT (left) and DTT (right) surfaces, respectively

*Crystallinity of the prepared films was characterized by XRD using* Cu *K*$\alpha$ radiation. X-ray diffraction results implied the as-deposited

films onto DTT SAM at 80°C surfaces were already crystalline $\alpha - Fe_2O_3$. As-deposited $\alpha - Fe_2O_3$ films were converted to $Fe_3O_4$ under $H_2$ at 350 °C for 5h and subsequently transformed to $\gamma - Fe_2O_3$ by careful oxidation at 400 °C for 1h. VSM measurement provided remnant magnetization ($M_r$) of 45 emu/cc, saturation magnetization ($M_s$) of 115 emu/cc, and the coercive magnetization ($M_c$) of 220 Oe in the films. Subsequently, ferrimagnetic $\gamma$-$Fe_2O_3$ films were also synthesized by oxidation of the $Fe_3O_4$ films.

Fig. 2 showed a SEM micrograph of *in situ* patterned crystalline iron oxide films. Width of the white contrast lines, where no iron oxide film was deposited, was about 1 μm. Thiols diffuse from the zones of contact between the stamp and the surfaces to unwanted area where the stamp does not contact the surfaces. This diffusion is highly detrimental to the resolution of μCP and therefore to the patterned iron oxide definition. Experimental conditions of μCP, for example the concentration of the thiolate SAMs in the ink, the applied force during contact processes, and the duration of the contact print, as well as selective depositions should be improved further.

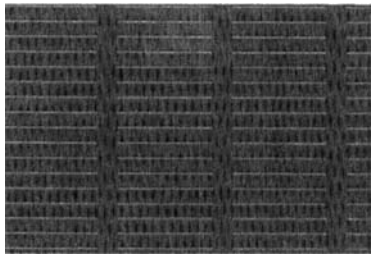


Fig. 2 SEM micrography of patterned (1 μm in width) line *in situ* in $\alpha - Fe_2O_3$ films through micro-contact printing and selective deposition

## *References*

[1] E. Koster, in Magnetic recording technology, C. Denisw Mee and Eric D. Daniel, eds. New York: McGraw-Hill, 1995, 3.37-3.49
[2] S. Dhara, A.C. Rastogi, and B.K. Das, *J. Appl. Phys.*, **74** (11) 7019-21 (1993)
[3] D.D. Awschalom and R.E. Bodnar, *Phys. Today*, **48**, 43 (1995)
[4] Y. Xia and G.M. Whitesides, *Angew. Chem. Int. Ed.*, **37**, 550-75 (1998)
[5] Y. Gao, Y.J. Kim, S.A. Chambers, and G. Bai, *J. Vac. Sci. Technol.* **A 15**, 332 (1997)