# Effect of interfacial interactions on the initial growth of Cu on clean SiO$_2$ and 3-mercaptopropyltrimethoxysilane-modified SiO$_2$ substrates

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## Abstract

The effect of interfacial interactions on the initial growth of Cu on clean $SiO_2$ and 3-mercaptopropyltrimethoxysilane (MPTMS)-modified $SiO_2$ substrates by sputter deposition was studied using transmission electron microscopy, energy dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. Plasma damage during sputter deposition makes surfaces of MPTMS-modified $SiO_2$ substrates consist of small MPTMS islands several tens of nanometers in diameter and bare $SiO_2$ areas. These MPTMS islands are composed of disordered multilayer MPTMS aggregates. The initial growth behavior of Cu on MPTMS-modified $SiO_2$ substrates differs from that on clean $SiO_2$ substrates, although Cu grows in 3D-island mode on both of them. After a 2.5-monolayer Cu deposition on clean $SiO_2$ substrates, spherical Cu particles were formed at a low number density of $1.3 \times 10^{16}$ /$m^2$ and at a long inter-particle distance of 5 nm. In contrast, after the same amount of deposition on MPTMS-modified $SiO_2$ substrates, Cu particles preferentially grow on MPTMS islands at a high number density of $3.9 \times 10^{16}$ /$m^2$ and at a short inter-particle distance of 3 nm, but do not grow on bare $SiO_2$ areas. The increased number density and the decreased inter-particle distance indicate that Cu has a lower mobility on MPTMS islands on MPTMS-modified $SiO_2$ substrates than on clean $SiO_2$ substrates. This difference in Cu mobility is attributed to the enhanced interfacial interactions between Cu and S on MPTMS islands on MPTMS-modified $SiO_2$ substrates via the formation of Cu-S bonds, compared with the relatively weak interfacial interactions between Cu and Si or O on clean $SiO_2$ substrates.

## I. INTRODUCTION

Interfacial interactions of metals with oxide and polymer surfaces play a key role in improving adhesion,[1,2] inhibiting corrosion,[3,4] smoothing surface,[5-7] and achieving selective deposition.[8,9] Among them, Cu-SiO$_2$ system has attracted great interest recently because of its application to catalysis for alcohol oxidation[10] and to interconnect metallization in ultra-large scale integration (ULSI).[11,12] However, Cu however, has a low sticking probability,[13] poor wettability, and poor adhesion[14,15] on clean SiO$_2$ substrates during thermal or sputter deposition, due to the lack of reactivity between Cu and SiO$_2$.[16,17] By enhancing interfacial interactions, methods such as ion bombardment,[18,19] heat treatment[20], and introduction of an intermediate layer[21,22] are effective for improving such thin film properties as surface morphology, wettability and adhesion, etc. However, reports on the mechanism of improvement of these thin film properties are scarce. The effect of interfacial interactions on thin film properties is reflected in the initial growth behavior of thin films. Therefore, the study of the initial growth under different interfacial interactions can clarify the relation between interfacial interactions and thin film properties, and can help predict and control thin film properties during the deposition process.

The purpose of this research is to investigate the effect of enhanced interfacial interactions on the initial growth behavior of Cu. In this study, we introduced an intermediate 3-mercaptopropyltrimethoxysilane (MPTMS, (CH$_3$O)$_3$SiCH$_2$CH$_2$CH$_2$SH) layer between Cu and SiO$_2$ to increase interfacial interactions. n-Alkanethiols have a strong affinity to *1B* elements, such as Au, Ag, and Cu, to form well-ordered self-assembled monolayers (SAMs) on metal surfaces.[23-25] Likewise, organosiloxanes react with hydroxyl groups on hydroxylated SiO$_2$ surfaces to form SAMs, as well.[26,27] Because MPTMS has both siloxane and thiol function groups, it acts as an effective coupling agent between Cu and SiO$_2$.[28] Because of the organic

feature of MPTMS layers, our study of the initial growth of Cu on MPTMS-modified $SiO_2$ substrates will also help clarify interface formation and adhesion improvement between metals and organic thin films applied to low-dielectric materials in future ULSI.[29,30]

In this paper, the surface structure and morphology of MPTMS-modified $SiO_2$ substrates were first investigated using X-ray photoelectron spectroscopy (XPS), contact angle measurements, and atomic force microscopy (AFM). Then, the initial growth of Cu on clean $SiO_2$ and MPTMS-modified $SiO_2$ substrates were compared using transmission electron microscopy (TEM). Finally, the effect of interfacial interactions on the initial growth of Cu was evaluated using energy dispersive X-ray spectroscopy (EDS) and XPS.


## II. EXPERIMENT

### A. Substrate preparation

Si(100) wafers with a sputter-deposited, 10-nm $SiO_2$ thin layer were cut into 2×2 cm substrates. These substrates were hydroxylated via treatment with a 1N $HNO_3$ solution at room temperature (r.t.) for 24 hours, and with an $H_2O_2/H_2SO_4$ (v/v 30/70) mixture at 60-80 °C for 30 min. After this treatment, $SiO_2$ surfaces were considered to have approximately 5 $OH/nm^2$.[31,32] These hydroxylated substrates were then rinsed with deionized (DI) water, and dried by heating in an oven at 100 °C for 30 min. They were then immersed in a 0.01-0.04 M MPTMS solution in benzene at r.t. for 30 minutes under an $N_2$ atmosphere. Finally, these substrates were successively rinsed with benzene, chloroform, methanol, and DI water, and then dried in an $N_2$ stream. All the solvents were of anhydrous grade. Figure 1 is a schematic of the above-described surface modification.

**B. Sputter deposition**

Cu (purity 99.99%) was deposited onto MPTMS-modified $SiO_2$ substrates using a radio frequency magnetron multi-target (Cu and $SiO_2$) sputter system (base pressure $4.0 \times 10^{-5}$ Pa). The deposition was carried out at a power of 15 W in pure argon gas (purity 99.999%) at a total pressure of 0.8 Pa. To study the initial growth of Cu, the deposition rate of Cu was controlled at as low as 0.5 monolayer/s. A single monolayer (ML) is defined as $1.77 \times 10^{19}$ Cu atoms/m$^2$, which is the packing density of a single Cu (111) plane.[33] This deposition rate was determined as the slope of Cu thin film thickness vs. deposition time. To stabilize deposits against electron beam exposure, so that they could be used as specimens for TEM observations, a 10-nm $SiO_2$ layer was continually deposited onto Cu thin films without breaking the vacuum system.

For sputter deposition of Cu onto clean $SiO_2$ substrates, first, a 10-nm $SiO_2$ layer was sputter-deposited onto H-terminated Si(100) substrates that were cleaned with a 1% HF solution, and then Cu was continually deposited onto these $SiO_2$ layers without breaking the vacuum system, under the same conditions used for depositing Cu onto MPTMS-modified $SiO_2$ substrates. Similarly, another 10-nm $SiO_2$ layer was continually deposited onto Cu thin films used as specimens for TEM observations.

**C. Analysis**

XPS measurements were performed using a RIGAKU XPS-7000 photoelectron spectrometer equipped with a monochromatic Mg $K_\alpha$ source ($hv$ = 1253.6 eV). Binding energies were referenced to the C(1s) hydrocarbon peak at 284.8 eV.[24] Water contact angles were measured using a KYOWA FACE CA-DT·A contact angle analyzer. AFM analysis was performed in tapping mode using a Digital Instruments Nanoscope IIIa. Scanning electron microscopy (SEM)

analysis was performed using a HITACHI S-900. Specimens for SEM observations were coated with a 1- to 2-nm Pt layer to avoid the charge-up during electron beam exposure. Plan-view and cross-sectional TEM (XTEM) micrographs were taken in bright-field mode using a JEOL JEM2010F operating at 200 kV. Specimens for TEM observations were prepared by conventional mechanical grinding, polishing, and dimpling, followed by Ar ion milling at an acceleration voltage 4 kV at an incidence angle of 6°. EDS analysis was performed using a built-in a NORAN 663D spectrometer to the JEOL JEM2010F. The probe electron beam used for EDS analysis was focused to approximately 2.5 nm in diameter.

## III. RESULTS AND DISCUSSION

### A. Surface structure and morphology of MPTMS-modified $SiO_2$ substrates

We first clarify the surface structure and morphology of MPTMS-modified $SiO_2$ substrates prior to Cu deposition, because they are important factors to affect interfacial interactions and the initial growth of Cu. Table 1 shows C and S atomic concentrations and water contact angles on $SiO_2$ substrates modified with 0-0.04 M MPTMS. The quantities of C and S on surfaces of MPTMS-modified $SiO_2$ substrates increased with increasing MPTMS concentration. This indicates an increasing amount of MPTMS that reacted with hydroxyl groups on $SiO_2$ substrate surfaces with increasing MPTMS concentration. In addition, with increasing MPTMS concentration, water contact angles also increased from 46° to approximately 80°. Heise *et al.*[34] reported that contact angles of well-ordered SAMs formed on hydroxylated $SiO_2$ substrates by using $NH_2$- and $CH_3$-terminated alkylsiloxanes are 68° and 103°, respectively. Our measured values fall between these two values, suggesting that surfaces of MPTMS-modified $SiO_2$

substrates are possibly covered with disordered MPTMS layers with randomly oriented, distributed thiol groups on the uppermost surface.

Besides surface structure, we also investigated surface morphology of MPTMS-modified $SiO_2$ substrates using AFM. Figure 2 shows that in contrast to the smooth surface of clean $SiO_2$ substrates, many dispersed islands several tens of nanometers in diameter appeared on MPTMS-modified $SiO_2$ substrates. The islands on $SiO_2$ substrates modified with 0.02 M MPTMS were typically 2- to 3-nm high, whereas those on $SiO_2$ substrates modified with 0.04 M MPTMS were mostly higher than 5 nm. Because the height of a single monolayer of MPTMS is approximately 0.5 nm,[28] these islands were apparently not well-ordered MPTMS monolayers, but disordered multilayer MPTMS aggregates, which is consistent with the results from contact angle measurements (see the preceding paragraph). In addition, MPTMS islands did not cover the entire substrate surfaces, and the residual surfaces (i.e., areas that were not covered with MPTMS islands) might be covered with MPTMS monolayers.

Based on these results, the surface structure and morphology of MPTMS-modified $SiO_2$ substrates are summarized as follows. MPTMS monolayers and dispersed MPTMS islands coexist on surfaces of MPTMS-modified $SiO_2$ substrates. The MPTMS islands are composed of disordered multilayer MPTMS aggregates. Thiol groups are randomly oriented and distributed inside and on the surface of each MPTMS island. Because the size of MPTMS islands (several tens of nanometers in diameter) is much larger than that of Cu particles (several nanometers in diameter) formed at the initial growth stage as shown in the next section, the influence of surface morphology of MPTMS-modified $SiO_2$ substrates on the initial growth of Cu is negligible.

**B. Initial growth of Cu on clean $SiO_2$ substrates**

The initial growth behavior of Cu on clean $SiO_2$ substrates was studied using TEM. Plan-view TEM micrographs of Cu on clean $SiO_2$ substrates after various amounts of deposition (Fig. 3) indicate that Cu grew in 3D-island mode. After 1.5 ML Cu deposition, a few nuclei 2- to 5-nm in diameter appeared [Fig. 3(a)]. After 2.5 ML Cu deposition, subsequent nucleation led to the formation of nanoparticles at a number density of $1.3 \times 10^{16}$ /$m^2$ and at an inter-particle distance of 5 nm [Fig. 3(b)]. After 5 ML Cu deposition, due to migration and "liquid-like" coalescence of particles,[35] a linked-island structure was formed [Fig. 3(c)]. Furthermore, after 15 ML Cu deposition, the linked-island structure developed into a percolation structure [Fig. 3(d)]. XTEM micrographs of Cu on clean $SiO_2$ substrates (Fig. 4) indicate that these Cu particles are completely spherical, which means that Cu does not wet on clean $SiO_2$ substrates.

This initial growth behavior indicates high mobility of Cu on clean $SiO_2$ substrates, due to the relatively weak interfacial interactions between Cu and Si or O on clean $SiO_2$ substrates. The closed-shell nature of stoichiometric $SiO_2$ makes it non-reactive to Cu.[16] The main interaction at Cu-$SiO_2$ interfaces is considered to be van der Waals forces. Therefore, Cu adatoms have the high mobility on clean $SiO_2$ substrates. In addition, the surface energy of Cu at room temperature is 1.79-1.83 $J/m^2$,[36,37] whereas that of $SiO_2$ is only 0.62 $J/m^2$.[38] Because interfacial interactions controlled by van der Waals forces are much weaker than Cu-Cu bonding, Cu adatoms easily aggregate into spherical 3D islands that minimize the total energy of Cu-$SiO_2$ system by reducing the fraction of exposed Cu surface.

## C. Initial growth of Cu on MPTMS-modified $SiO_2$ substrates

The initial growth behavior of Cu on MPTMS-modified $SiO_2$ substrates, however, differed from that on clean $SiO_2$ substrates. We first investigated the dependence of the initial growth of

Cu on MPTMS concentration, at which surface modification of $SiO_2$ was carried out. Figure 5 shows plan-view TEM micrographs of Cu on clean $SiO_2$ substrates and on $SiO_2$ substrates modified with 0.01-0.04 M MPTMS after 5 ML Cu deposition. Similar to Cu on clean $SiO_2$ substrates, Cu also grew in 3D-island mode on MPTMS-modified $SiO_2$ substrates. With increasing MPTMS concentration, however, Cu showed a strong tendency to grow preferentially on some areas several tens of nanometers in diameter, but not on other areas. Compared with Cu particles beginning to coalesce on clean $SiO_2$ substrates [Fig. 5(a)], Cu particles on $SiO_2$ substrates modified with 0.01 M MPTMS tended to be more isolated [Fig. 5(b)]. On $SiO_2$ substrates modified with 0.02 M MPTMS, the distribution of Cu particles was more complicated in that two kinds of distributions appeared: one with a low number density and a long inter-particle distance, and the other with a high number density and a short inter-particle distance [Fig. 5(c)]. On $SiO_2$ substrates modified with 0.04 M MPTMS, however, the latter distribution dominated the overall distribution of Cu particles [Fig. 5(d)].

There are two possible reasons why Cu shows different distributions on $SiO_2$ substrates modified with MPTMS at different concentrations. One is the non-uniformity of surface modification of $SiO_2$ substrates with MPTMS. The modification with MPTMS at higher concentrations leads to the formation of more and larger MPTMS islands, which is confirmed by the XPS and AFM analysis (Table 1 and Fig. 2). The more the amount of MPTMS on substrate surfaces, the stronger the influence of surface modification on the initial growth behavior of Cu. The other reason is the plasma damage during sputter deposition (organic substrates are susceptible to plasma[29]). It is possible that large MPTMS islands are etched and remain on substrate surfaces, whereas monolayers and small islands of MPTMS are eliminated from substrate surfaces. This inference is supported by the difference in surface morphology between

SiO$_2$ substrates modified with 0.04 M MPTMS before and after 5 ML Cu deposition (Fig. 6).
Compared with the number and size of MPTMS islands before Cu deposition, the number of
large MPTMS islands decreased and many small MPTMS islands appeared after 5 ML Cu
deposition. Thus, the overall coverage of MPTMS islands decreased. This implies that plasma
damage during sputter deposition causes monolayers and small islands of MPTMS to be
eliminated from substrate surfaces, thus generating bare SiO$_2$ areas, and simultaneously causes
large MPTMS islands to be etched into relatively small MPTMS islands several tens of
nanometers in diameter. As a result, newly generated small MPTMS islands and bare SiO$_2$ areas
coexist on MPTMS-modified SiO$_2$ substrates during Cu deposition. Despite plasma damage, the
randomly oriented, distributed thiol groups exist nevertheless on the uppermost surface of the
remaining MPTMS islands. Therefore, these remaining MPTMS islands still function as an
intermediate "layer" to influence the initial growth of Cu.

We further investigated the initial growth of Cu on SiO$_2$ substrates modified with 0.04 M
MPTMS, because among SiO$_2$ substrates modified with 0.01-0.04 M MPTMS, this kind of
substrates most clearly showed variations in the initial growth of Cu. Figure 7 shows plan-view
TEM micrographs of Cu on SiO$_2$ substrates modified with 0.04 M MPTMS after various amounts
of deposition. After 2.5 ML Cu deposition, Cu showed a relatively high number density of
$3.9 \times 10^{16}$ /m$^2$ and a relatively short inter-particle distance of 3 nm on preferential growth areas
[Fig. 7(a)]. The increased number density and the decreased inter-particle distance indicate that
Cu has a lower mobility on these preferential growth areas than on clean SiO$_2$ substrates. After 5
ML Cu deposition, Cu particles appeared at a relatively low number density on initially non-
growth areas [Fig. 7(b)]. After 10 ML Cu deposition, Cu particles on preferential growth areas
remained isolated, whereas Cu particles on initially non-growth areas began to coalesce to form a

linked-island network structure [Fig. 7(c)]. After 20 ML Cu deposition, the substrate surface was almost completely covered by Cu thin films except for some areas covered with Cu particles that had started to coalesce. Figure 8 shows XTEM micrographs of Cu on $SiO_2$ substrates modified with 0.04 M MPTMS after 5 ML Cu deposition. Cu did not distribute continuously and uniformly at interfaces between Cu and MPTMS-modified $SiO_2$ substrates. Cu preferentially grew on some areas several tens of nanometers in diameter, but not on some flat areas [Fig. 8(a)]; this pattern of growth is consistent with the plan-view TEM observation of the same specimen [Fig. 7(b)]. The high-resolution TEM (HRTEM) micrograph showing a close-up of one preferential growth area [Fig. 8(b)] indicates that the interface between Cu particles and the substrate was not a flat plane, but rather a protrusion approximately 3 nm high and 40 nm in diameter. Cu particles approximately 5 nm in diameter were distributed on the surface of this protrusion.

The similarity in the size of protrusions that have Cu particles and the size of MPTMS islands implies that the preferential-growth protrusion areas are MPTMS islands, whereas the initially non-growth, flat areas are bare $SiO_2$ generated by plasma damage. Therefore, we analyzed the composition at interfaces of Cu and MPTMS-modified $SiO_2$ substrates using EDS. Figure 9 shows that both Cu and S were detected in the protrusion area, but neither Cu nor S was detected in the flat area. This confirms our conclusion that Cu preferentially grows on MPTMS islands, and not on flat bare $SiO_2$ areas.

This initial growth behavior results from the stronger interactions of Cu with MPTMS islands than with bare $SiO_2$ areas. These stronger interactions of Cu with MPTMS islands are demonstrated by the variation in binding energy of S(2p) for MPTMS-modified $SiO_2$ substrates before and after Cu deposition. The binding energy of S(2p) before Cu deposition [Fig. 10(a)]

only showed one component at 163.1 eV, whereas that after 5 ML Cu deposition [Fig. 10(b)] showed two components, at 163.1 and 162.1 eV. Other researchers have also confirmed that S reacts with Cu to form Cu-S bonds.[39,40] The component at 163.1 eV is assigned to RS-H species, and that at 162.1 eV is assigned to RS-Cu species.[25,41] The coexistence of RS-H and RS-Cu species suggests that only the S on the surface of MPTMS islands interacts with Cu, whereas the S inside MPTMS islands does not contribute to interfacial interactions or to the variation of the initial growth behavior of Cu.

Based on these results, we interpret the initial growth behavior of Cu on MPTMS-modified $SiO_2$ substrates as follows. Due to plasma damage during sputter deposition, small MPTMS islands several tens of nanometers in diameter and bare $SiO_2$ areas coexist on substrate surfaces. Due to the stronger interaction between Cu and S on MPTMS islands than that between Cu and Si or O on base $SiO_2$ areas, Cu atoms arriving at the surface of MPTMS islands diffuse through non-S sites and adhere to S-containing sites, whereas Cu atoms arriving at the surface of bare $SiO_2$ areas possibly become weakly bonded, then diffuse and either desorb or reach MPTMS islands and adhere to them. The difference in Cu mobility on MPTMS islands and bare $SiO_2$ areas results in the preferential growth of Cu on MPTMS islands. Therefore, Cu nuclei first appear on MPTMS islands. Compared to this, there is a delay in growth and nucleation of Cu on bare $SiO_2$ areas. Although these bare $SiO_2$ areas are chemically identical to clean $SiO_2$ substrates, the number density of Cu particles on clean $SiO_2$ substrates [Fig. 3(b)] is higher than that of Cu particles on bare $SiO_2$ areas on MPTMS-modified $SiO_2$ substrates [Fig. 7 (a)], after 2.5 ML Cu deposition. This is the evidence that Cu adatoms diffuse through bare $SiO_2$ areas, and preferentially adhere to MPTMS islands. Because the Cu-S interaction also limits the migration and coalescence of Cu particles on MPTMS islands, Cu particles remain isolated at a relatively

high number density on MPTMS islands, whereas they begin to form a linked-island or percolation structure on bare $SiO_2$ areas via particle migration and coalescence.

## IV. CONCLUSIONS

The effect of interfacial interactions on the initial growth of Cu on clean $SiO_2$ and MPTMS-modified $SiO_2$ substrates by sputter deposition was studied using TEM, EDS and XPS. SEM analysis shows that plasma damage during sputter deposition causes the elimination of monolayers and small islands of MPTMS from substrate surfaces, thus generating bare $SiO_2$ areas, and simultaneously causes large MPTMS islands to be etched into relatively small MPTMS islands several tens of nanometers in diameter. Contact angle and AFM measurements suggest that these MPTMS islands are composed of disordered multilayer MPTMS aggregates. TEM analysis shows that Cu grows in 3D-island mode on both clean $SiO_2$ and MPTMS-modified $SiO_2$ substrates. However, Cu particles preferentially grow on MPTMS islands on MPTMS-modified $SiO_2$ substrates at a higher number density and a shorter inter-particle distance than those on clean $SiO_2$ substrates. The increased number density and the decreased inter-particle distance indicate that Cu has a lower mobility on MPTMS islands on MPTMS-modified $SiO_2$ substrates than on clean $SiO_2$ substrates. This difference in Cu mobility is attributed to the enhanced interfacial interactions between Cu and S on MPTMS islands on MPTMS-modified $SiO_2$ substrates via the formation of Cu-S bonds, compared with the relatively weak interfacial interactions between Cu and Si or O on clean $SiO_2$ substrates.

## ACKNOWLEDGMENTS

# REFERENCES

[1] S. W. Russell, S. A. Rafalski, R. L. Spreitzer, J. Li, M. Moinpour, F. Moghadam, and T. L. Alford, Thin Solid Films **262**, 154 (1995).

[2] D. N. Dunn and R. Hull, J. Appl. Phys. **89**, 2635 (2001).

[3] H. J. Grabke, Surf. Interface Anal. **30**, 112 (2000).

[4] C. Y. Rha, W. S. Kim, J. W. Kim, and H. H. Park, Appl. Surf. Sci. **169-170**, 587 (2001).

[5] C. Liu, J. Erdmann, and A. Macrander, Thin Soild Films **355-356**, 41 (1999).

[6] H. Mostéfa-Sba, B. Domenichini, and S. Bourgeois, Surf. Sci. **437**, 107 (1999).

[7] K. W. Lee, S. Lee, and J. W. Park, J. Electrochem Soc. **148**, C131 (2001).

[8] S. Kim, J. M. Park, and D. J. Choi, Thin Solid Films **320**, 95 (1998).

[9] Y. S. Kim, D. Jung, and S. K. Min, Thin Solid Films **349**, 36 (1999).

[10] Y. Han, J. Shen, and Y. Chen, Appl. Catal. A **205**, 79 (2001).

[11] P. C. Pai and C. H. Ting, IEEE Electron Device Lett. **10**, 432 (1989).

[12] L. R. Lloyd and J. J. Clement, Thin Soild Films **262**, 135 (1995).

[13] X. Xu and D. W. Goodman, Appl. Phys. Lett. **61**, 1799 (1992).

[14] C. A. Chang, J. Appl. Phys. **66**, 1163 (1989).

[15] N. Eustathopoulos, B. Drevet, and M. L. Muolo, Mater. Sci. Eng. A **300**, 34 (2001).

[16] J. A. Kelber, C. Niu, K. Shepherd, D. R. Jennison, and A. Bogicevic, Surf. Sci. **446**, 76 (2000).

[17] D. A. Chen, M. C. Bartelt, R. Q. Hwang, and K. F. McCarty, Surf. Sci. **450**, 78 (2000).

[18] K. S. Kim, Y. C. Jang, H. J. Kim, Y. C. Quan, J. Choi, D. Jung, and N. E. Lee, Thin Solid Films **377-378**, 122 (2000).

[19] D. Q. Yang, L. Martinu, E. Sacher, and A. Sadough-Vanini, Appl. Surf. Sci. **177**, 85 (2001).

[20] T. P. Nguyen, J. Ip, P. Le Rendu, and A. Lahmar, Surf. Coat. Technol. **141**, 108 (2001).

[21]S. P. Denise, W. Gerhard, S. Peter, and S. Thomas, Langmuir **15**, 4520 (1999).

[22]K. R. Lee, K. Y. Eun, I. Kim, and J. Kim, Thin Solid Films **377-378**, 261 (2000).

[23]E. T. Vandenberg, L. Bertilsson, B. Liedberg, K. Uvdal, R. Erlandsson, H. Elwing, and I. Lundstrom, J. Colloid Interface Sci. **17**, 103 (1991).

[24]P. E. Laibinis, G. M. Whitesides, D. L. Allara, Y. T. Tao, A. N. Parikh, and R. G. Nuzzo, J. Am. Chem. Soc. **113**, 7152 (1991).

[25]P. E. Laibinis and G. M. Whitesides, J. Am. Chem. Soc. **114**, 9022 (1992).

[26]T. J. Horr and P. S. Arora, Colloids and Surf. A **126**, 113 (1997).

[27]D. A. Styrkas, J. L. Keddie, J. R. Lu, and T. J. Su, J. Appl. Phys. **85**, 868 (1999).

[28]X. Huang, H. Huang, N. Wu, R. Hu, T. Zhu, and Z. Liu, Surf. Sci. **459**, 183 (2000).

[29]M. Du, R. L. Opila, V. M. Donnelly, J. Sapjeta, and T. Boone, J. Appl. Phys. **85**, 1496 (1999).

[30]S. Li, E. T. Kang, K. G. Neoh, Z. H. Ma, and K. L. Tan, Surf. Sci. **454-456**, 990 (2000).

[31]J. M. Madeley and C. R. Richmond, Z. Anorg. Allg. Chem. **389**, 82 (1972).

[32]L. T. Zhuravlev, Langmuir **3**, 316 (1987).

[33]J. Yoshihara, S. C. Parker, and C. T. Campbell, Surf. Sci. **439**, 153 (1999).

[34]A. Heise and H. Menzel, Langumuir **13**, 723 (1997).

[35]H. Shirakawa and H. Komiyama, J. Nanoparticle Research **1**, 17 (1999).

[36]W. R. Tyson and W. A. Miller, Surf. Sci. **62**, 267 (1977).

[37]L. Z. Mezey and J. Giber, Jpn. J. Appl. Phys. **21**, 1569 (1982).

[38]S. H. Overbury, P. A. Bertrand, and G. A. Somorjai, Chem. Rev. **75**, 547 (1975).

[39]C. J. Sandroff and D. R. Herschbach, J. Phys. Chem. **86**, 3277 (1982).

[40]C. K. Kwon, K. Kim, M. S. Kim, and S. B. Lee, Bull. Korean Chem. Soc. **10**, 254 (1989).

[41]C. D. Bain, H. A. Biebuyck, and G. M. Whitesides, Langmuir **5**, 723 (1989).

## TABLE CAPTIONS

Table 1. C and S atomic concentrations and water contact angles on $SiO_2$ substrates modified with 0-0.04 M MPTMS.

| MPTMS concentration (M) | Surface atomic concentration (%) | | Water contact angle (°) |
|---|---|---|---|
| | C | S | |
| 0[a] | 3.9 | 0 | 46 |
| 0.01 | 14.5 | 1.4 | 80 |
| 0.02 | 21.9 | 2.9 | 84 |
| 0.04 | 32.8 | 5.1 | 89 |

[a] Surface modificaiton was done for this specimen using the same procedure as other three specimens, except for no addition of MPTMS.

## FIGURE CAPTIONS

FIG. 1. Schematic of surface modification of $SiO_2$ with MPTMS.

FIG. 2. AFM images showing surface morphology of (a) clean $SiO_2$ and $SiO_2$ substrates modified with (b) 0.02 and (c) 0.04 M MPTMS.

FIG. 3. Plan-view TEM micrographs of Cu on clean $SiO_2$ substrates after (a) 1.5, (b) 2.5, (c) 5, and (d) 15 ML Cu deposition.

FIG. 4. XTEM micrographs of Cu on clean $SiO_2$ substrates after (a) 2.5 and (b) 5 ML Cu deposition.

FIG. 5. Plan-view TEM micrographs of Cu on (a) clean $SiO_2$ substrates and on $SiO_2$ substrates modified with (b) 0.01, (c) 0.02, and (d) 0.04 M MPTMS after 5 ML Cu deposition.

FIG. 6. SEM images showing surface morphology of $SiO_2$ substrates modified with 0.04 M MPTMS (a) before and (b) after 5 ML Cu deposition.

FIG. 7. Plan-view TEM micrographs of Cu on $SiO_2$ substrates modified with 0.04 M MPTMS after (a) 2.5, (b) 5, (c) 10, and (d) 20 ML Cu deposition.

FIG. 8. (a) XTEM micrographs of Cu on $SiO_2$ substrates modified with 0.04 M MPTMS after 5 ML Cu deposition and (b) HRTEM micrograph showing a close-up of one preferential growth area.

FIG. 9. (a) XTEM microgrph of Cu on $SiO_2$ substrates modified with 0.04 M MPTMS after 5 ML Cu deposition, showing two areas analysized with EDS. **1** is the protrusion area that has Cu particles and **2** is the flat area that has no Cu particles. (b) EDS spectra taken from areas of **1** and **2**.

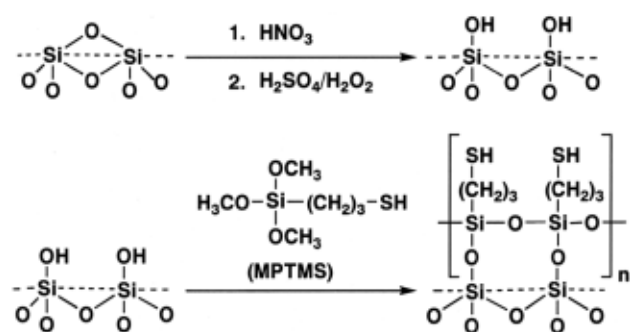FIG. 10. XPS spectra of S(2p) for $SiO_2$ substrates modified with 0.04 M MPTMS (a) before and (b) after 5 ML Cu deposition.
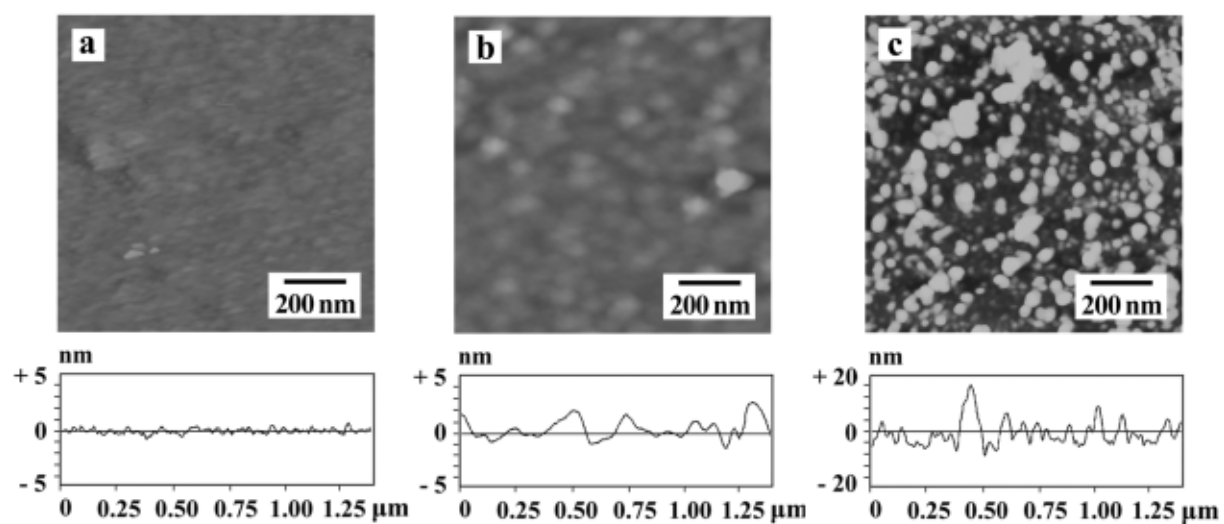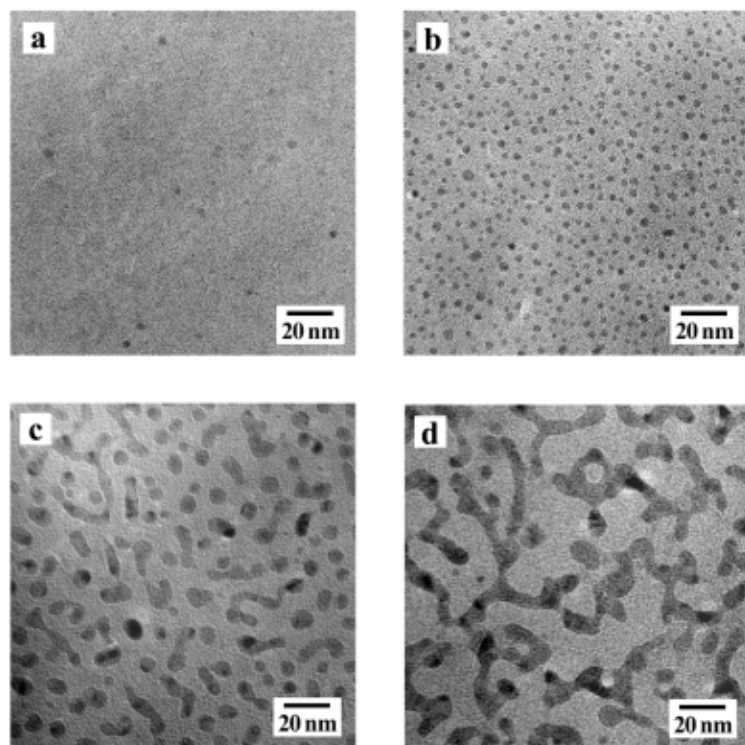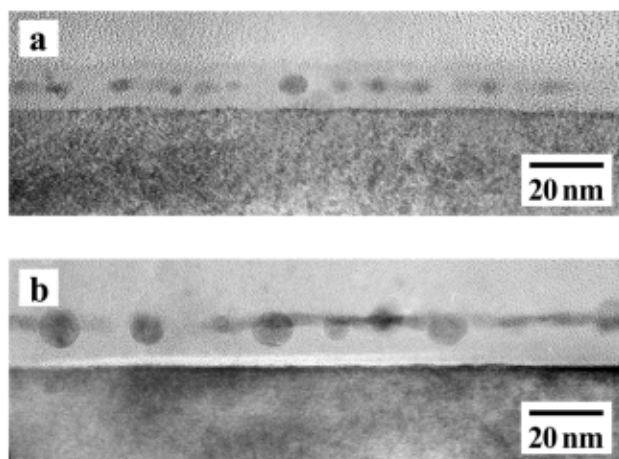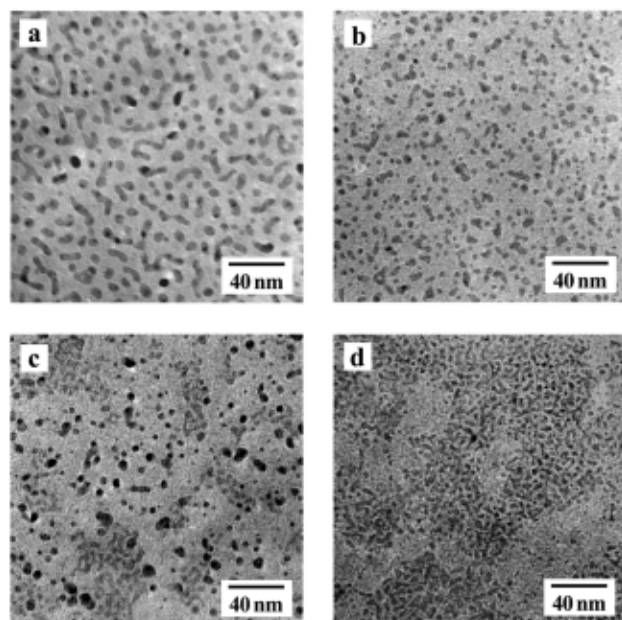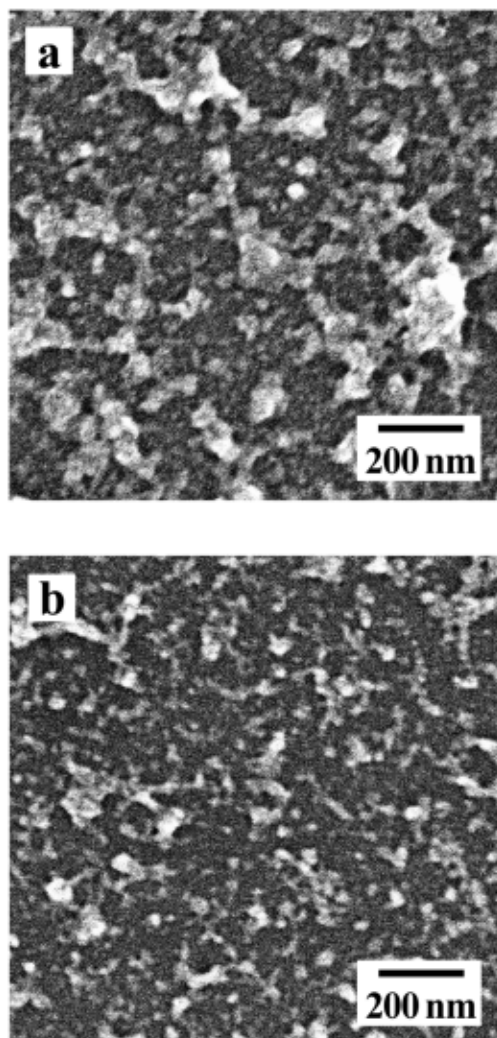
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5



40 nm

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10