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Selective Deposition of Copper with Iodine Assisted Growth of MOCVD on an MPTMS Monolayer Surface at a Low Temperature

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We have investigated the selective deposition of Cu films on the mercaptopropyltrimethoxysilane-ocatadecyltrichlorosilane (MPTMS-OTS) patterned glass substrate using (hfac)Cu(DMB) and C_2H_5I as precursors at 110°C. The low temperature deposition of Cu without iodine exhibited the difficulties of Cu nucleation on MPTMS with its low Cu growth rate of 22 nm/min and long induction period of approximately 4 min at 110°C. The addition of iodine significantly enhanced the surface diffusion of Cu adatoms on the MPTMS surface and thus led to increased nucleation and growth rate (28 nm/min) at 110°C. With these advantages, we successfully increased the maximum thickness of Cu selectively deposited on the MPTMS patterned lines from 57 nm to 140 nm without selectivity loss by adding iodine to (hfac)Cu(DMB)(3,3-dymethyl-1-butene) at 110°C. Consequently, the low temperature process for the selective deposition of Cu on the MPTMS-OTS patterned surface can be utilized for the fabrication of flexible electronics.

Keywords: selective deposition, copper, iodine, MPTMS

1. INTRODUCTION

Cu has been widely used as interconnections in the manufacturing of microelectronic devices, such as ultra-large scale integrated circuit devices and thin film transistors for large-area liquid crystal displays (LCDs), as it has lower resistivity and higher electromigration resistance than Al metal; Cu has also benefitted from extensive technology development addressing the drawbacks of Cu use in applications, such as the difficulty with dry-etching of Cu, its poor adhesion to dielectrics, and fast diffusion of Cu into Si and SiO_2.[1-6] In high speed and large scale integrated circuits, the dual damascene process, consisting of Cu deposition into the oxide trenches followed by chemical mechanical polishing of the deposited Cu, has been commonly employed for the patterning of Cu, while in the Cu-based thin film transistors (TFT) process, wet etching of Cu has been used to form Cu electrodes. In addition, both processes include the use of the diffusion barriers / adhesion layers, such as Ta, TaN, TiN, Mo, etc. However, there are still issues that need to be addressed, which include the complexity of the damascene process, a corrosion-related problem due to wet-etching of the Cu/Mo bilayer structure, and the need for thinner diffusion barriers due to the down-scaling of devices. Recently, the combined patterning method of soft lithography printing of self-assembled monolayers (SAM) followed by the selective deposition of metal (or metal oxides) has attracted attention because of its simple process as well as because of the excellent diffusion barrier and adhesion properties of ultrathin SAM monolayers.

Several studies have examined chemical vapor deposition (CVD) of Cu on organosilane SAMs, particularly mercaptopropyltrimethoxysilane (MPTMS), and have reported on the deposition characteristics and material properties of CVD Cu on these SAM surfaces. Sematians investigated Cu nucleation on SAMs by CVD.[7,8] Xin Liu reported the effects of modified SAMs on the enhanced CVD of Cu, which were attributed to the oxidized MPTMS-SAM surface accelerating the rate of ligand protonation in the Cu precursors and ligand desorption.[9,10] There are many reports regarding the deposition of Cu on the SAMs of MPTMS.[11-14] We previously reported on the CVD of Cu on a MPTMS monolayer at a low temperature between 110°C and 160°C.[15-17] However, there are few reports on the selective deposition of CVD Cu on the SAMs of MPTMS in the low temperature region of ≤ 110°C, which is essential for its application to flexible electronics. In addition, selective deposition of Cu has a narrow processing window and thus produces a limited thickness of Cu without selectivity loss. Iodine was reported to act as a surfactant in Cu MOCVD and to enhance the film growth rate of Cu.

As a result, this study examined the effects of iodine on the induction period to nucleate Cu on an MPTMS monolayer and on the selectivity of Cu in the presence of an OTS mono-

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layer. Then, we determined the maximum thickness of Cu obtained with iodine assisted growth of MOCVD Cu at 110°C on an MPTMS monolayer self-assembled on the negative patterns of a pre-printed OTS monolayer.

2. EXPERIMENTAL

The glass substrates were cleaned by dipping them into a cleaning solution ($H_2O:NH_4OH:H_2O_2 = 5:1:1$) at 80°C for 15 min, rinsing them with deionized (DI) water, and then exposing them to UV irradiation ($\lambda = 185$ nm – 254 nm) for 30 min to remove any organic contaminants present on the surface and to activate the surface for the adsorption of the SAMs. The substrate surfaces were treated by dipping them in a 1 mM MPTMS solution in ethyl alcohol and acetic acid at RT for 1 h and then successively rinsing with ethyl alcohol followed by drying in blowing N_2. MOCVD of Cu was conducted on the MPTMS-coated glass at 110°C using (hfac)Cu(DMB)(3,3-dymethyl-1-butene) as a precursor with and without ethyl iodide C_2H_5I. In order to investigate the selective deposition of Cu over an MPTMS monolayer in the presence of an OTS monolayer, a poly-dimethylsiloxane (PDMS) stamp was used to transfer OTS SAM patterns onto the glass substrate and then the MPTMS monolayer was selectively coated on the OTS-free regions by dipping it into the 1 mM MPTMS solution in ethyl alcohol and acetic acid for 1 h at RT, resulting in MPTMS line patterns (5-µm width and 3-um line spacing) on the glass surface. Then, the MPTMS-patterned glass substrate was loaded into a metal-organic chemical vapor deposition (MOCVD) reactor, in which Cu films were selectively deposited on the MPTMS-patterned lines.

A copper MOCVD system consisting of a cold-wall reactor with a halogen lamp heating system and a mechanical pump was used to deposit the Cu. The system was equipped with laser reflectance ($\lambda = 632.8$ nm), which was used to monitor the *in-situ* reflectivity from the substrate surface during the deposition process, which indicates the variation of the surface roughness that is caused by the initial growth of metals on the surface as well as shows the relative induction period needed to nucleate the metal. CVD of Cu was performed on the MPTMS-coated glass surface using (hfac)Cu(DMB) as the precursor at a temperature of 110°C, a working pressure of 0.2 torr, and an Ar flow rate of 7 sccm. Ar was used as the carrier gas. The (hfac)Cu(DMB) metal-organic precursor was loaded into a bubbler and heated to 30°C. The equilibrium vapor pressure of (hfac)Cu(DMB) at 30°C was approximately 1.5 torr. The precursor vapor was introduced to the reactor by the Ar carrier gas and the gas delivery line was maintained at 50°C. Ethyl iodide (C_2H_5I; bp = 72°C) was used to provide iodine atoms on the surface. The vapor pressure of C_2H_5I was high even at RT. Therefore, it was fed directly from a C_2H_5I bubbler at RT into the reactor without the need for a carrier gas. The introduction of C_2H_5I into the reactor increased the processing pressure by 0.005 torr, which was controlled by a metering valve.

The deposited films were characterized using the following techniques: the thickness, surface roughness, and selective deposition of Cu films were examined using atomic force microscopy (AFM); the *in-situ* reflectivity of the substrate surface was monitored by laser reflectance to determine the apparent induction period to nucleate Cu metal on the various surfaces; the sheet resistance of the films was measured using a four-point probe.

3. RESULTS AND DISCUSSION

Figure 1 shows the change of reflectance during the deposition of Cu on the OTS and MPTMS monolayer with the Cu precursor and C_2H_5I at 110°C, respectively. The reflectance remains constant when Cu is deposited on OTS at 110°C, as shown in Fig. 1(a). In contrast with the OTS monolayer, the reflectance starts to increase at approximately 290s after the

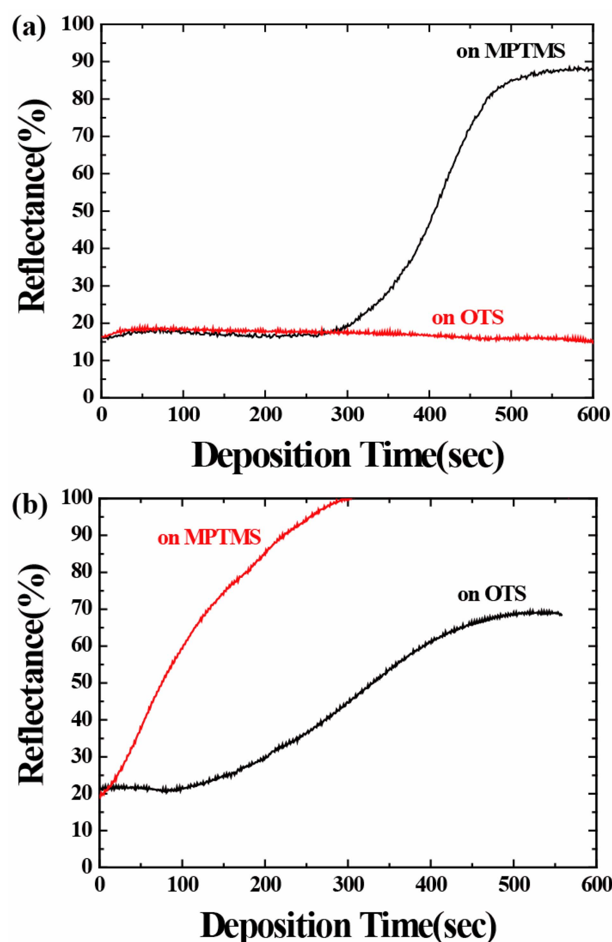

Fig. 1. Reflectance Changes with deposition time during the deposition of Cu on the OTS and MPTMS monolayer (a) with only Cu precursor at 110°C and (b) with the Cu precursor and C_2H_5I at 110°C.

Cu precursor is introduced on the MPTMS monolayer, and then increases to a maximum value at 500 s. This clearly shows the existence of an induction period for Cu nucleation on the MPTMS monolayer upon deposition at 110°C. In order to determine the effect of C_2H_5I addition on Cu nucleation on the MPTMS monolayer, C_2H_5I was continuously added with the precursor and iodine at a volume to feed ratio of approximately 1:1 at 110°C and the change in reflectance was measured as a function of deposition time, as shown in Fig. 1(b). The reflectance increases abruptly immediately after both the precursor and iodine were introduced into the reaction chamber, suggesting that there is no time delay for Cu nucleation on the MPTMS monolayer with continuous iodine addition. However, the reflectance remains almost constant for run with the precursor and iodine on the OTS monolayer. From the results above, it is clear that the addition of ethyl iodide significantly shortened the induction period for Cu deposition on MPTMS. This is attributed to the apparently enhanced surface diffusion of Cu adatoms on the MPTMS surface as a result of the facile dissociation of Cu(hfac) adsorbed on the Cu surface.[15]

Figure 2 shows the variation of Cu film thickness as a function of substrate temperature. For the iodine-assisted Cu deposition on MPTMS, the growth rate rapidly increases from 12 nm/min to 28 nm/min as the temperature increases from 80°C to 110°C, exhibiting the activation energy of approximately 0.16 eV. Further increase of the temperature up to 160°C slightly increases the growth rate to 33 nm/min. For the Cu deposition without iodine, no deposition was observed at 80°C, possibly due to the difficulty with Cu nucleation on MPTMS. As the temperature increases to 110°C, the growth rate of Cu increases to 23 nm/min, which was calculated by considering an induction period of about 4 min. Additional increases of the temperature slowly increases the Cu growth rate. As a result, the addition of iodine effectively enhances the Cu nucleation on MPTMS as well as enhances the Cu growth on the Cu surface. In addition, iodine-assisted Cu deposition enabled the deposition of Cu on MPTMS at the low temperature of 80°C while Cu was not deposited without iodine.

Figure 3 shows the variation of resistivity of Cu films deposited on an MPTMS monolayer as a function of substrate temperature. For non iodine–assisted Cu deposition, the resistivity increases slightly from 3.7 μohm-cm to 3.9 μohm-cm as the temperature increases from 110°C to 130°C. For iodine assisted Cu deposition, a low resistivity of 2.8 mW-cm was obtained even at the low temperature of 80°C. More importantly, the resistivity remains constant at 130°C, indicating the smooth and pure Cu films were deposited at low temperatures (80°C to 110°C) with the addition of iodine.

To directly observe the adhesion improvement, a scotch tape test was carried out and the results are shown in Figs. 4(a) and (b). The images in Figs. 4(a) and (b) show the tapes detached from perpendicularly scratched Cu films on bare glass and MPTMS surfaces, respectively. Again, these images clearly show that the Cu film did not come off of the MPTMS surface at all, whereas the same film nearly came off entirely from the bare glass surface. The strong bonding of Cu-S is responsible for the enhanced adhesion of Cu to the glass substrate and the added iodine is not likely to degrade the adhesion.

Figure 5 shows AFM plane and cross-sectional images of the Cu thin film selectively deposited on the MPTMS patterns (5 mm width and 3 mm spacing) with and without

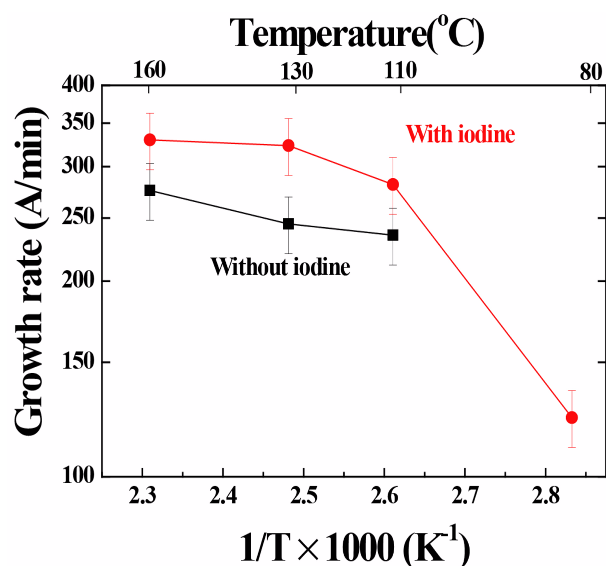

Fig. 2. The growth rate of Cu film on the MPTMS monolayer as a function of substrate temperature; (●) with and (■) without Cu precursor and C_2H_5I.

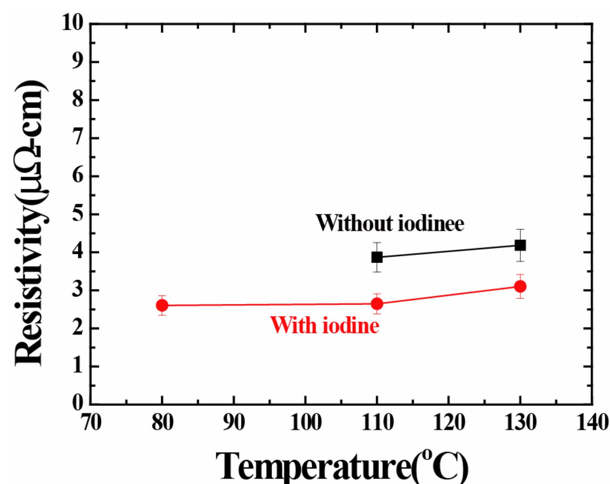

Fig. 3. The variation of resistivity of the Cu films deposited on the MPTMS monolayer as a function of substrate temperature; (●) with and (■) without Cu precursor and C_2H_5I.

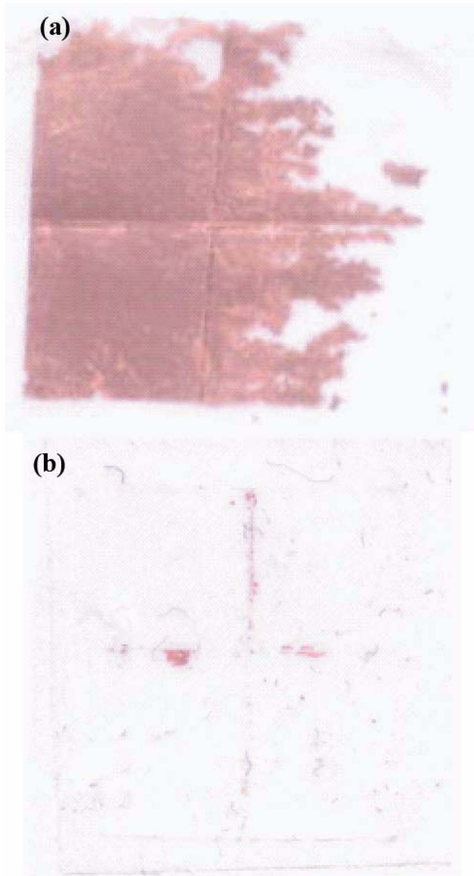

Fig. 4. Optical images (a) and (b) are pieces of Scotch tape detached from Cu films deposited on bare glass and MPTMS surfaces, respectively.

iodine at a deposition temperature of 110°C and pressure 0.2 torr for different deposition times. The selective growth of Cu on the MPTMS patterns via Cu deposition can clearly be seen. However, there is a large difference in the maximum thickness of Cu selectively deposited on the MPTMPS patterned lines between samples with and without iodine: the added iodine significantly increases the maximum Cu thickness from 57 nm to approximately 140 nm as is shown in the cross-sectional images of Fig. 5. This is attributed to the increased growth rate of Cu on the Cu surface as well as the enhanced nucleation of Cu on the MPTMS. Generally, a longer induction period is required to nucleate Cu metal on the MPTMS monolayer at a temperature of 110°C for non iodine assisted Cu deposition, due to the low mobility of Cu on the surface as a result of the high bond strength (72 kcal/mol) of Cu-S.[18,19] For the iodine assisted Cu deposition on the MPTMS patterned lines, the iodine atom that adsorbed to Cu can act as adsorption sites for Cu(I) compounds and also serve as a surfactant to promote the facile dissociation of the adsorbed $[Cu^I(hfac)]_{ad}$ into Cu and (hfac). This leads to the increase in the maximum thickness of Cu selectively deposited on the MPTMS patterns when iodine is added to the Cu precursor. According to the cross-sectional profile, a much steeper edge slope is obtained with iodine.

4. CONCLUSION

This study examined the growth of Cu on the SAMs of MPTMS coated glass surfaces at the low temperature of 110°C, focusing on the effects of iodine on the selective

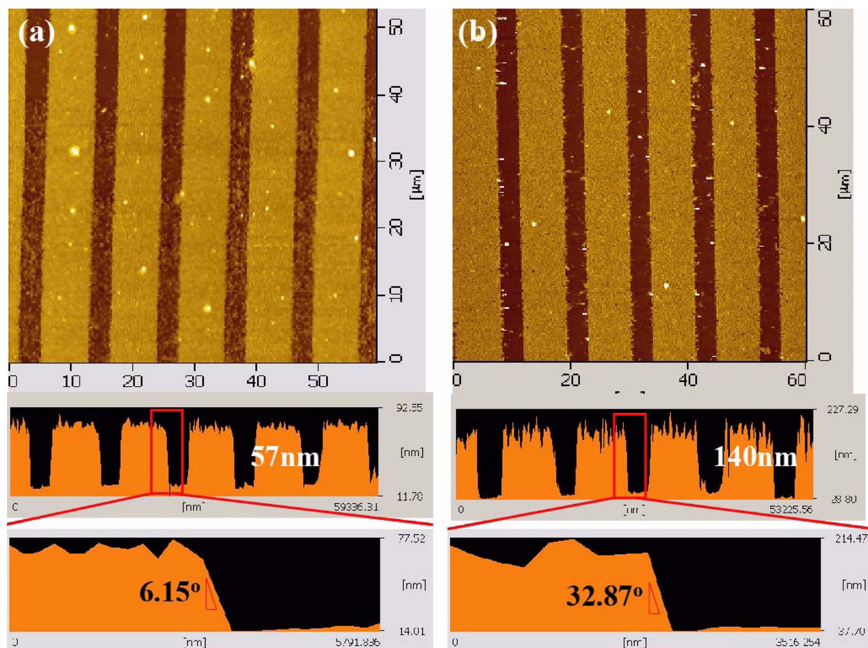

Fig. 5. AFM plane and cross-sectional images of Cu thin film at a deposition temperature of 110°C and pressure of 0.2 torr: (a) without Cu precursor and C_2H_5I, thickness: 57 nm; (b) with Cu precursor and C_2H_5I, thickness: 140 nm.

growth of Cu on the MPTMS patterned lines in the presence of OTS. The strong bonding of Cu-S is responsible for the highly enhanced adhesion of Cu to SiO_2, however, this leads to the low mobility of Cu adatoms on MPTMS causing the difficulty with nucleation, especially at low temperatures. The addition of iodine effectively enhances the mobility of Cu adatoms on MPTMS, and thus facilitating the nucleation and growth of Cu. More importantly, the added iodine does not likely degrade the selectivity of Cu in the presence of OTS. As a result, we can enhance the selectivity of Cu on MPTMS patterned lines while increasing the maximum thickness of Cu from 57 nm to 140 nm without selectivity loss by the addition of iodine.

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