

The Processing Windows for Selective Copper Chemical Vapor Deposition from Cu(hexafluoroacetylacetonate)trimethylvinylsilane

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ABSTRACT

To identify the processing tolerance for the selective Cu chemical vapor deposition (Cu CVD) the processing windows were constructed with respect to deposition pressure and substrate temperature over thermally grown SiO₂ vs. various conducting substrates of W, CoSi₂, TiN, TiW, and Al. It is found that the width of selective deposition window decreases as the deposition pressure is increased, and no selective Cu deposition can be obtained as the deposition pressure exceeds 120 mTorr. The lowest temperatures for Cu CVD on various SiO₂ substrates including thermally grown, BPSG, TEOS, and PECVD SiO₂ were determined so that processing windows for selective Cu deposition on variously patterned wafers can be constructed. The selective Cu deposition was also conducted on patterned substrates with submicrometer feature sizes using the PECVD SiO₂ as the interlayer dielectric. The nucleation of Cu on the SiO₂ surface obviously acts as the major limitation for achieving selective Cu CVD. We postulate that the Cu containing adspecies, Cu(hfac), on the insulating SiO₂ surface may combine by surface diffusion, and these assembled adspecies then disproportionate by exchanging electrons with each other rather than transferring electrons through the substrate.

Selective copper chemical vapor deposition (Cu CVD) has been regarded as a potential metallization process in deep submicrometer integrated circuit applications, not only because it deposits Cu films with low resistivity and high electromigration resistance but also because it offers a superior ability for via hole filling of high aspect ratio.¹⁻⁴ In addition, the selective Cu deposition does not need a subsequent etching process, which is a major processing obstacle for applying Cu as interconnection material.⁵⁻⁶ Most of the selective Cu CVD was conducted by using the Cu(R)₂, abbreviated as Cu(II), and Cu(R)L, abbreviated as Cu(I), series precursors, where R is a β-diketone ligand and L is a Lewis base.⁷⁻¹¹ The Cu(R)L precursor has attracted much attention in recent years because of its relatively low deposition temperature and H₂ is not required as a reducing gas. The Cu(I) precursor is usually available in liquid form and delivered by the carrier gas, allowing accurate control of the gas flux. Many Cu(I) precursors have proved to be capable of depositing Cu film with low resistivity and some of these precursors have also exhibited the selective deposition behavior.¹²⁻¹⁵ It has been reported that Cu(I) series compounds deposit Cu by a disproportionation reaction that needs electron transfer between two Cu(R) adspecies.¹⁶ Therefore, the selectivity on conducting vs. insulating surfaces should be existent according to the electron transfer process.

The selective Cu chemical vapor deposition, however, was found to be a complex process. The conductivity of the substrate is just one of the parameters that determines selective deposition. Substrate temperature, reaction pressure, and surface treatment of the substrate all have profound effects on achieving the selective deposition.¹⁷ As the selective deposition is achieved by controlling the relative growth rate of Cu on the conductor and insulator substrate surfaces, any factor that influences the growth behavior of Cu needs to be carefully examined and well controlled; then, the selective Cu CVD can be possibly successful.

This work gives a detailed study on selective Cu CVD using Cu(hfac)TMVS as the precursor, where hfac represents 1,1,1,5,5,5-hexafluoroacetylacetonate and TMVS is trimethylvinylsilane. As one of the most promising precursors for selective Cu CVD, Cu(hfac)TMVS has been extensively studied and verified to be capable of conducting selective Cu film deposition at relatively low temperatures.^{18,19} There are many reports of selective Cu CVD from Cu(hfac)TMVS;^{12,17,20,21} however, selectivity loss was frequently observed. The controversy may result from the dis-

crepancy of the processing apparatus, the widely chosen experimental parameters, and the varieties of sample preparation. In addition, the chemical species and the photoresist that remains on the SiO₂ surface after the processes for pattern generation were also considered to be responsible for the selective loss.¹⁸ A detailed investigation on the selective windows as a function of processing parameters will be helpful in finding the optimum processing conditions for selective deposition of copper.

Because selective Cu CVD is sensitive to the impurities on the substrate surface, selective Cu deposition was first performed on the unpatterned substrates to determine the possible selective processing windows for temperature and pressure. Next, the deposition was carried out on patterned substrates to further investigate the effects of patterning on the selectivity window and to determine process implementation for Cu film deposition. The activation energies of Cu CVD on various substrates were calculated from the Arrhenius plot of deposition rate vs. temperature. The impurity and resistivity of the Cu films were measured and analyzed. The effects of processing parameters on selective Cu CVD were investigated. Finally, discussion was made on mechanism of selective Cu deposition.

Experimental Procedure

Selective Cu deposition from Cu(hfac)TMVS was performed on conducting and insulating as well as patterned and unpatterned substrates. The insulating substrates included the thermally grown SiO₂, borophosphosilicate glass (BPSG), tetraethyl orthosilicate (TEOS) deposited SiO₂, and the plasma enhanced chemical vapor deposited (PECVD) SiO₂, while the conducting substrates included W, TiN, TiW, and Al layers deposited on thermally oxidized Si wafers, and a CoSi₂ layer grown on Si substrate. The layers of W and Al were deposited using an E-beam evaporation system, while the layer of TiW was sputter deposited from a TiW target [Ti 10 weight percent (w/o)]. The TiN film was formed by reactively sputtering a Ti target (99.99%) using a mixed gas of Ar + N₂ (5:1). The CoSi₂ substrate was constructed by thermally annealing an αSi(50 Å)/Co(200 Å)/Si structure at 550°C for 90 min.²²

The patterned substrates contain via holes and fine lines with submicrometer feature sizes. The patterned samples were fabricated on 6 in. diam Si wafers as follows. After an SiO₂ layer was thermally grown, the conducting layer, such as Al, was deposited. This was followed by a deposition of 5000 Å of PECVD SiO₂. Finally, patterns were defined on the PECVD SiO₂ layer by standard photolithographic techniques.

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The apparatus employed for the Cu chemical vapor deposition was described in a previous report.²³ The CVD system is capable of handling a 4 in. diam substrate. Prior to the Cu deposition, all substrates were rinsed in deionized (DI) water but did not go through any chemical cleaning process except the unpatterned substrates of SiO₂. The SiO₂ substrates were cleaned in H₂SO₄ + H₂O₂ (3:1) solution for 20 min followed by DI water rinse and then blown dry in N₂ gas. The samples were loaded into a load-lock and then pumped down to a pressure of 10⁻⁷ Torr before the samples were transferred to the reaction chamber for Cu deposition. It usually took about 1 h for the substrate samples to reach the set temperature before the Cu deposition could be started. When the deposition was finished, the samples were cooled in Ar ambient at a pressure of 10 Torr.

A scanning electron microscope (SEM) was used to observe the surface morphology of the Cu films. The sheet resistance of the Cu films was measured by a four-point probe, and the film thickness was measured by a Dek-Tek surface profiler and also double checked by SEM cross-sectional measurement. Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) were employed for impurity analysis of the Cu films.

Results and Discussion

Copper deposition on the unpatterned substrates.—The CVD Cu films were deposited on the unpatterned conducting substrates of W, CoSi₂, and Al at various deposition temperatures and pressures for a source temperature of 40°C with an Ar carrier gas flow of 20 sccm and also for a source temperature of 60°C with an Ar carrier gas flow of 40 sccm. Figure 1 shows the Arrhenius plots (deposition rate vs. temperature) for Cu CVD on the W substrate at a constant pressure of 10 mTorr for two different conditions of source temperature and Ar carrier gas flow rate. Activation energy E_a of the Cu CVD can be determined from the slope of the linear segments of these Arrhenius plots by the equation $K = A \exp(-E_a/RT)$, where K is the deposition rate, R is the gas constant, and A is known as the Arrhenius pre-exponential constant. The activation energy E_a is determined to be 3.11 and 3.56 kcal/mol, respectively, at temperatures above 200°C for the CVD condition of 60°C source temperature and 40 sccm Ar carrier gas flow and the CVD condition of 40°C source temperature and 20 sccm Ar carrier gas flow; the corresponding E_a values at temperatures below 200°C are determined to be 20.0 and 13.4 kcal/mol. The lower activation energy at temperatures above 200°C indicates that the CVD process becomes mass-transfer limited at high temperature.¹⁶ The Arrhenius plots for the Cu deposition on CoSi₂ and Al substrates are illustrated in Fig. 2 and Fig. 3, respectively. The activation energies for Cu deposition on CoSi₂ and Al substrates are determined to

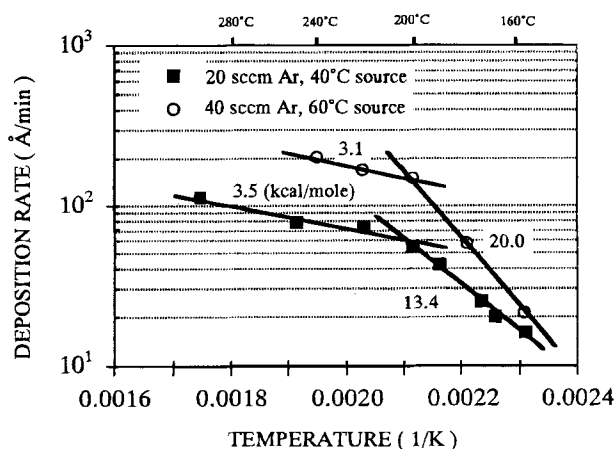


Fig. 1. Deposition rate vs. substrate temperature (Arrhenius plot) for Cu CVD on W substrate at a constant pressure of 10 mTorr. The values of activation energy in units of kcal/mol are indicated in the illustration.

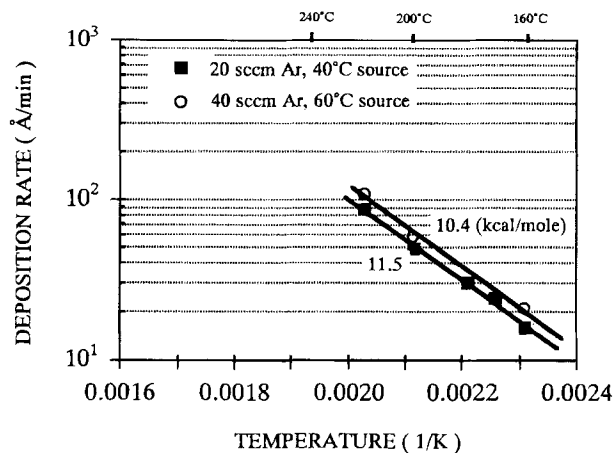


Fig. 2. Deposition rate vs. substrate temperature (Arrhenius plot) for Cu CVD on CoSi₂ substrate at a constant pressure of 10 mTorr.

be 11.5 and 9.7 kcal/mol, respectively, for the CVD condition of 40°C source temperature and 20 sccm Ar carrier gas flow. It was found that the Cu film on the CoSi₂ and Al substrates tended to peel off when the substrate temperature exceeded 220°C. The peel-off of Cu film from the CoSi₂ and Al substrates may result from the discrepancy of thermal expansion coefficient between the Cu film and the CoSi₂ and Al layers. Figure 4 shows the surface morphology of Cu films deposited at a pressure of 10 mTorr for 20 min, on Al substrate at various temperatures. For the 20 min deposition run, copper is still at the nucleation stage on the 160°C Al substrate, while it has become a continuous Cu film on the 170°C substrate. Substantial grain growth can be observed on the Cu film deposited on the 200°C substrate. Apparently, the CVD Cu film is formed by the nucleation and grain growth processes. Thus, once the Cu is nucleated on the substrate surface, it becomes Cu grown on Cu. The surface morphology of CVD Cu film (Fig. 4) also revealed that the compact Cu grains formed a rough surface, and the surface roughness increases with the increase of film thickness and grain size. In addition, the surface often gets scratched during the Dek-Tak measurements. Thus, the Dek-Tak measurements were carried out under the conditions of lightest pressure to avoid scratching. The low density and the rough surface made the thickness measurement difficult and might produce some error in determining the growth rate. To reduce this possible error, a SEM cross-sectional view was employed to check the result of the thickness measurement, and an average value of the thickness was taken as the film thickness for a film with a rough surface. Therefore, the activation energy derived from the Arrhenius plot may be only an approximate value.

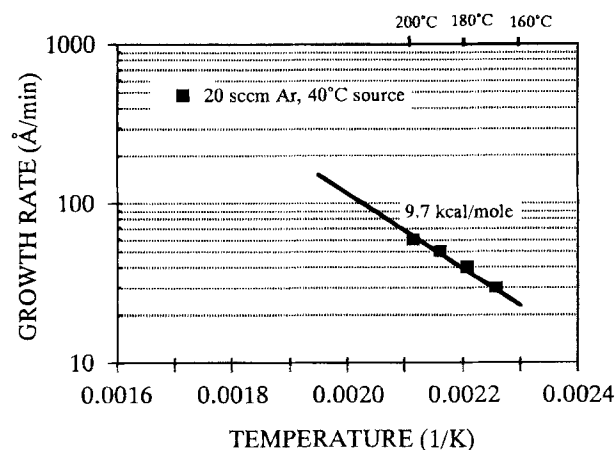


Fig. 3. Deposition rate vs. substrate temperature (Arrhenius plot) for Cu CVD on Al substrate at a constant pressure of 10 mTorr.

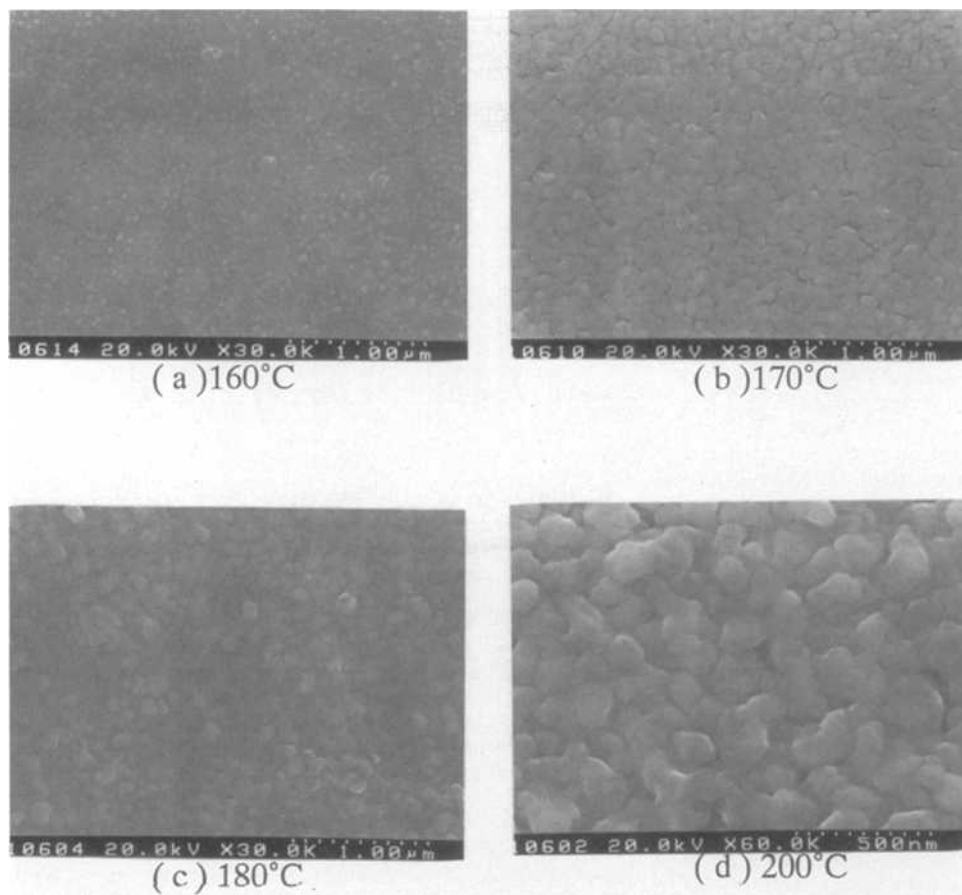


Fig. 4. Surface morphology of Cu films deposited, at a pressure of 10 mTorr for 20 min, on Al substrate at various substrate temperatures of (a) 160, (b) 170, (c) 180, and (d) 200°C.

The Cu CVD on the SiO₂ substrate is very different from that on the conducting substrate. The most marked difference is the higher low-limit-temperature on the SiO₂ substrate. The low-limit-temperature is defined as the deposition temperature below which no Cu nuclei can be discovered by SEM observation (less than 50 Å) at a certain specified deposition condition. For example, the low-limit-temperatures at a pressure of 10 mTorr are 160 and 140°C, respectively, for W and TiW substrates, while the low-limit-temperature for the thermally grown SiO₂ substrate is 200°C at the same deposition conditions. The processing window of selective Cu CVD is based on the difference of low-limit-temperatures between the conducting and SiO₂ substrates.

The selectivity windows for the thermally grown SiO₂ vs. various conducting substrates with respect to the deposition pressure and temperature are summarized in Table I. The processing regions for the Cu CVD on Al and TiW substrates, as shown in Fig. 5, are constructed from the data listed in the table. From Table I and Fig. 5, it is clear that as the deposition pressure is increased, low-limit-temperature for both conducting and SiO₂ substrates decreases, and also does the low-limit-temperature gap between the conducting and SiO₂ substrates. As a result, a triangular region for selective Cu CVD is constructed for each conductor-SiO₂ pair. As shown in Fig. 5, blanket Cu CVD can be carried out at high temperature and high pressure condi-

tion, while selective Cu CVD can be conducted with the condition within the triangle region. For selective Cu CVD in our system, the highest deposition pressure should be limited to 100 and 120 mTorr, respectively, for the Al and TiW substrates, and the corresponding lowest temperature should be limited to 140 and 130°C, respectively.

In multilevel metallization system, CVD SiO₂ layers are employed as the insulating dielectric; low-limit-temperature of the CVD SiO₂ is lower than that of the thermally grown SiO₂ at a given deposition pressure. Table II lists the low-limit-temperatures for various SiO₂ at three different deposition pressures. Thermally grown SiO₂ apparently has the highest low-limit-temperature among the various oxides. Figure 6 shows the processing windows of selective Cu CVD on Al vs. thermally grown SiO₂ and PECVD SiO₂.

Table I. The processing windows for selective Cu CVD on thermally grown SiO₂ vs. various conductive substrates.

	10 mTorr	50 mTorr	100 mTorr
W (°C)	160-200	140-160	130-140
CoSi ₂ (°C)	160-200	150-160	No selectivity
TiN (°C)	150-200	140-160	130-140
TiW (°C)	140-200	130-160	130-140
Al (°C)	150-200	140-160	No selectivity

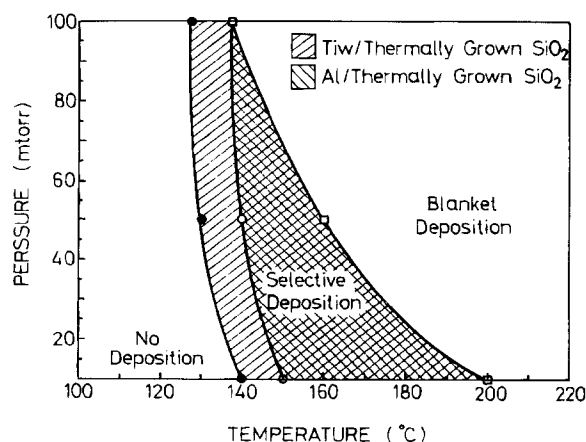


Fig. 5. The processing windows of selective Cu CVD on thermally grown SiO₂ vs. Al and TiW substrates with respect to deposition temperature and pressure for a 20 min deposition.

Table II. The lowest temperatures for Cu CVD on various SiO₂ substrates at three different deposition pressures.

	10 mTorr	50 mTorr	100 mTorr
Thermal SiO ₂ (°C)	200	160	140
BPSG (°C)	180	155	140
TEOS SiO ₂ (°C)	190	160	145
PECVD SiO ₂ (°C)	170	150	140

The deposition rate of Cu has been found to be linearly proportional to the deposition pressure.²³ However, the increase of deposition rate by increasing pressure was achieved at the expense of narrowing the selective window. Nonetheless, the Cu film deposition rate can be increased alternatively by raising the source temperature and the carrier gas flowing rate, as shown in Fig. 1 and Fig. 2. In addition, it is found that the deposition rate of Cu increased by increasing the source temperature (from 40 to 60°C) and the carrier gas flow rate has little influence on the selective window.

The measured resistivity of the Cu film deposited in this work lies in the range of 3-10 μΩ-cm, which is a little higher than that of the bulk material (1.67 μΩ-cm) and that reported elsewhere.^{17,18} The impurities in the Cu film are below the Auger detection limit; that is, the impurity levels are below 1 atomic percent (a/o) in the Cu film. Figure 7 shows the results of impurity analysis by SIMS for the Cu film deposited on the W substrate at 200°C. Several hundred Angstroms of the Cu surface layer were sputtered for removing the surface contamination before the SIMS analysis. The F, O, and C were found to be the major impurities within the Cu film. These impurities may result from incomplete desorption of the hfac ligand. It has been found that the resistivity of the Cu film can be correlated with the surface morphology of the Cu film.²³ As shown in Fig. 4, the CVD Cu film is composed of the compact single grains and thus has a rough surface. Poor connection between the Cu grains will lead to higher resistivity. Furthermore, measurement by four-point probe on a rough surface tends to result in a higher value of sheet resistance.

Copper deposition on the patterned substrates.—The CVD Cu films were deposited on the patterned substrates with submicrometer feature size to further investigate the selective deposition behavior. Figure 8(a) and (b) show the selective Cu CVD on the Al/oxide patterned substrates with 20 sccm Ar carrier gas flow and source temperatures of 40 and 60°C, respectively. Both depositions were conducted for 20 min. The higher source temperature shows a slightly increased Cu nucleation, but the source temperature between 40 and 60°C apparently has little influence on the selective behavior of Cu CVD. Different combinations

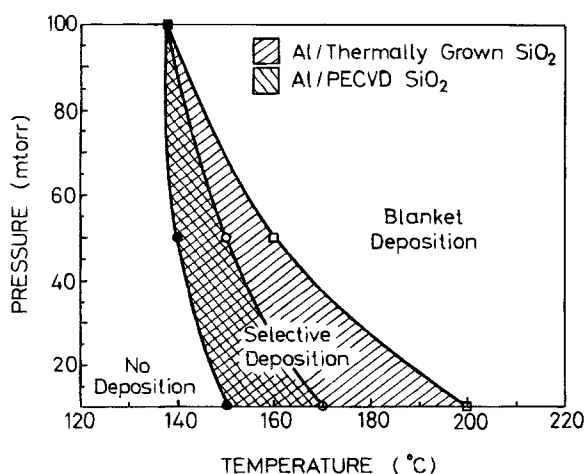


Fig. 6. The processing windows of selective Cu CVD on Al vs. thermally grown SiO₂ and PECVD SiO₂ substrates with respect to deposition temperature and pressure for a 20 min deposition.

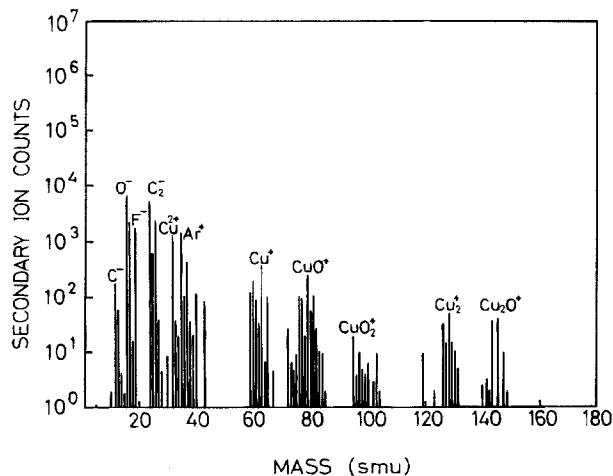


Fig. 7. The mass spectra of SIMS analysis for the Cu film deposited on W substrate at a temperature of 200°C and a pressure 10 mTorr. Cesium (Cs) was used as primary ion beam for the SIMS analysis.

of deposition parameters within the selective deposition window would produce different results of the selective Cu deposition. The SEM micrographs shown in Fig. 9 compare the result of selective Cu deposition conducted at 10 mTorr and 170°C for 20 min with that conducted at 10 mTorr and 150°C for 100 min. Although the deposition conducted at 150°C for 100 min resulted in larger Cu grains, it suffered from selectivity loss. This is because the selective deposition window shown in Fig. 6 is constructed based on the data of the 20 min deposition run. The selective loss [Fig. 9(c) and 9(d)] obviously came from the nucleation of Cu on the SiO₂ surface. Thus, it is preferable to conduct selective Cu CVD at a higher temperature within the tolerance of the selective window so as to shorten the deposition time and avoid the possible selectivity loss.

Mechanism of selectivity loss due to Cu nucleation on SiO₂.—The selective Cu CVD from Cu(hfac)TMVS depends on a number of deposition parameters as well as substrate properties. The substrate temperature, deposition pressure, and surface properties of substrate all have profound effects on the selective deposition.^{19,21,23} The selective Cu CVD on metal/SiO₂ substrate can be achieved by controlling the deposition parameters to produce different Cu nucleation and grain growth behavior on the surface of conducting and SiO₂ substrates. Since the Cu CVD proceeds with Cu nucleation and grain growth procedures, successful selective Cu deposition depends on the appropriate control of Cu nucleation and grain growth behavior. It is believed that Cu CVD starts by breaking the Cu(hfac)-TMVS bond (≈13 kcal/mol) and leaves a Cu containing species, Cu(hfac), on the substrate surface to proceed with further disproportionation reaction.^{19,24} For the cold-wall reaction system employed in this work, the source bath, delivery line, and the gas injector were all kept at a temperature below 60°C to prevent the Cu precursor from decomposing before the precursor reached the substrate surface. The energy for breaking the Cu(hfac)-TMVS bond is supplied from the substrate heating. The molecular flux density condensing on the substrate surface J_a (adsorption rate of molecular) can be expressed as²⁵

$$J_a = nv_a \quad [1]$$

where $n = P_0/kT$ is the number of molecules per unit volume, P_0 is the molecule pressure, and v_a is the root mean square velocity of molecule in the vapor.

The adsorbed molecule may either proceed with further reaction or desorb from the substrate surface. The desorption rate of molecule J_d from the substrate surface can be expressed as

$$J_d = N_0 v_s \exp\left(-\frac{\Delta G_{des}}{kT}\right) \quad [2]$$

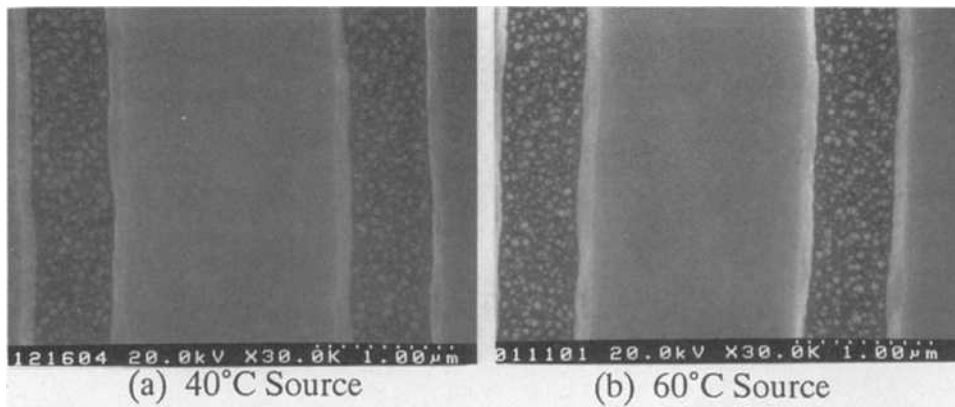


Fig. 8. SEM micrographs showing the surface morphology of CVD Cu deposited on Al/PECVD SiO₂ fine line patterned substrate at a pressure of 10 mTorr, substrate temperature of 170°C, and Ar carrier gas flow of 20 sccm. The deposition was performed for 20 min with source temperature of (a) 40 and (b) 60°C.

where N_0 is the number of adsorbed molecules per unit area, v_s is the surface vibration frequency, and ΔG_{des} is the energy needed for the desorption.

If no nucleation occurs, the rate of desorption must equal the rate of adsorption, and we have

$$N_0 = \frac{P_0}{kT} \frac{v_a}{v_s} \exp\left(\frac{\Delta G_{des}}{kT}\right) \quad [3]$$

Equation 3 gives the molecular density adsorbed on the substrate surface at the equilibrium state. This indicates that the number of adspecies per unit area increases linearly with increasing molecular pressure but would decrease with increasing substrate temperature due to desorption enhancement.

Once the Cu(hfac)-TMVS bond is broken, the adspecies of Cu(hfac) proceeds with the disproportionation reaction in which electron transfer is needed. However, it has been found, in this work, that the substrate conductivity is not such a dominant factor in controlling the behavior of Cu deposition as predicted from the disproportionation reaction. Since the selectivity loss (Cu nucleated on SiO₂) can occur at increased deposition pressure, which in turn increases the adspecies density, the disproportionation reaction on the insulating substrate may proceed through some

other mechanism. Instead of transferring an electron through the substrate that must be conducting, the nearby Cu(hfac) adspecies can exchange an electron to proceed with the disproportionation reaction. In this scheme, the Cu(hfac) adspecies combine by surface diffusion. The surface diffusivity can be expressed as

$$D_s = \lambda^2 v_s \exp\left(-\frac{\Delta G_s}{kt}\right) \quad [4]$$

where λ is the distance between two neighboring surface sites, v_s is the surface vibration frequency, and ΔG_s is the energy required for an adspecies to move to a neighboring site. Although the increase of temperature reduces the surface density of adspecies, it increases the surface diffusivity. Thus, a higher substrate temperature may enhance the selectivity loss.

We have now postulated a consistent mechanism regarding the effects of the processing parameters during the stage of Cu nucleation. The increase of pressure increases the adspecies density on the substrate surface. The increase of substrate temperature prompts the bond breaking of Cu(hfac)-TMVS and enhances the desorption and surface diffusion of the Cu(hfac) adspecies. Although different substrate surfaces provide different bonding energies between

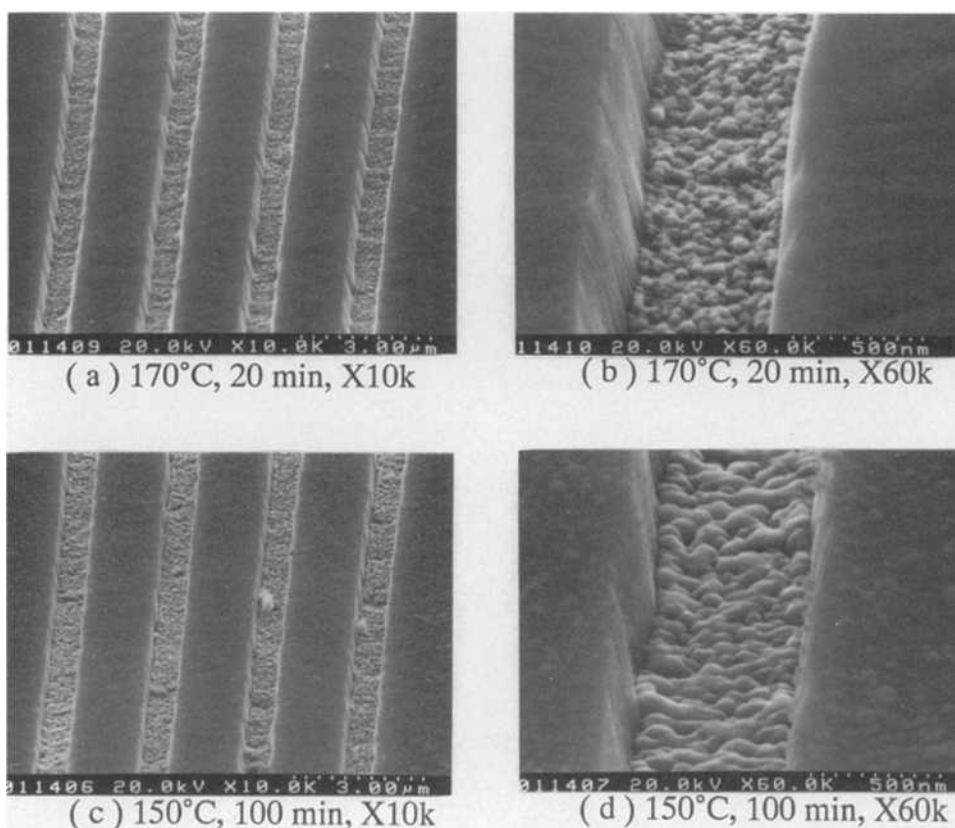


Fig. 9. SEM micrographs showing surface morphology of CVD Cu deposited on Al/PECVD SiO₂ fine line patterned substrate at a pressure of 10 mTorr and with a source carrier temperature of 60°C and Ar carrier gas flow of 20 sccm. The deposition was performed at (a) and (b) 170°C for 20 min, and (c) and (d) 150°C for 100 min.

adspecies and the substrate surfaces, and the conductivity of the substrate may also be helpful for disproportionation reaction, none of them plays a sole dominant role in determining the behavior of Cu nucleation. Thus, a selective window exists on the conducting *vs.* SiO₂ substrates, but the window is narrow.

Conclusion

The chemical vapor deposition process has been studied for selective Cu deposition from a liquid metallorganic compound of Cu(hfac)TMVS using an LPCVD system with a cold-wall vertical reactor. The activation energies of Cu CVD on various substrates of W, CoSi₂, and Al at temperatures below 200°C were determined to be within the range of 10–20 kcal/mol. The resistivity of deposited Cu film was found to lie in the range of 3–10 μΩ-cm; the higher resistivity presumably results from the poorly connected grain structure. The processing window of selective Cu CVD on various conductors *vs.* oxides can be constructed with respect to the deposition pressure and substrate temperature based on the data of low-limit-temperature for various conductors and oxides. Thus, selective Cu CVD can be performed on patterned substrates using the deposition parameters within the processing window. Since the adspecies Cu(hfac) can proceed with disproportionation reaction to nucleate Cu on the SiO₂ surface, the selectivity window of conductor *vs.* SiO₂ substrate is narrow. To widen the processing windows for the Cu CVD, it is necessary to develop either a new precursor that is more sensitive to the surface properties of conductor *vs.* SiO₂ substrate or suitable surface pretreatment procedures that can prevent Cu nucleation on the insulating substrate surface.

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