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Initial Cu Growth in Cu-Seeded and Ru-Lined Narrow Trenches for Supercritical Fluid Cu Chemical Deposition

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The morphological stability of Cu films in narrow trenches during the initial growth of Cu was studied at temperatures of 140–280 °C for the chemical deposition of Cu in supercritical CO_2. Cu seed layers agglomerated and the deposited Cu and the seed layer coalesced at elevated temperatures. This mechanism resulted in bottom-up like growth at lower temperatures of 160–180 °C. The seed agglomeration was suppressed by starting deposition before reaching the temperature at which agglomeration started of about 150 °C. When Ru-lined trenches were used instead of Cu-seeded trenches, no clear agglomeration or grain coarsening was observed and Cu grew with a conformal topography.

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1. Introduction

A supercritical fluid is a high-pressure fluid that possesses properties of both liquids and gases. The critical point of CO_2 is 73.8 MPa and 31 °C;[1)] above this temperature, CO_2 is a supercritical fluid. Supercritical fluids have zero surface tension and are able to penetrate deep into small features. Supercritical fluids function as an ideal medium for delivering a dissolved substance into such features, because they have moderately high diffusivity and density and thus a high diffusion flux — the diffusion flux of a substance in a medium is proportional to the product of the diffusivity and (the gradient of) the density.

Thin Metal films can be deposited in supercritical fluids using an organometallic compound (precursor). This technology is highly effective for filling high-aspect-ratio features, from LSI vias[2–4)] to carbon nanotubes,[5)] with noble[7,8)] and near-noble metals.[9–13)] It is therefore expected to be the ideal and ultimate solution to solving the gridlock in nanointerconnect fabrication.

In the current damascene vehicle, the potential applications of this deposition technique are threefold: 1) Cu fill, as a replacement for currently used Cu electrochemical deposition, 2) Cu seed layer deposition, and 3) the deposition of refractory barrier metals. The latter two, both of which are replacements for sputtering, may not be straightforward to perform in supercritical fluids, at least at present. In the case of Cu seed layer deposition, deposition is carried out after exposure to air so that reactive barrier metals can be easily oxidized, which leads to poor Cu growth on the seed layer. The deposition of a barrier metal is still a major challenge, as most barrier refractory metals, such as Ti and Ta, are very reactive and precursors containing such elements can react with CO_2 without forming the desired metals or compounds.[6)] For these reasons, we aim to use our deposition technology for filling narrow features with Cu.

We have studied Cu deposition in supercritical CO_2 using copper β-diketonates, such as $Cu(hfac)_2$[9–11)] and $Cu(dibm)_2$,[12,13)] as a precursor [$(hfac)_2$ = bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)hexafluoroacetyl acetonate, $(dibm)_2$ = bis(2,6-dimethyl-3,5-heptanedionato)], and have demonstrated its high effectiveness for filling small vias and trenches with metallic Cu. In this process, a conductive underlying layer is necessary to grow a sound Cu film.[2,10)] The use of a sputtered Cu seed layer employed in electrochemical deposition processes is a practical option. However, sputtered films have a poor coverage, for instance, near at the bottom of the sidewall of trenches/vias. In the electrochemical deposition process, such a thinly deposited part can be easily dissolved with a plating solution. The stability of the seed layer has therefore been of critical concern, and is also still a research subject crucial to understanding supercritical fluid chemical deposition.

For these reasons, we assessed the initial Cu film growth on a Cu seed layer. Ru-lined narrow trenches were used for comparison, because Ru is a stable refractory material regarded as a promising glue in the damascene vehicle.[14,15)]

2. Experimental Procedure

Deposition was carried out using a flow-type processor developed in the laboratory.[12)] $Cu(dibm)_2$ was used as a Cu source and was dissolved in acetone. This solution was injected in a supercritical CO_2 fluid. The CO_2 fluid was then preheated to 150 °C and was supplied to a reactor that was placed in a heating mantle. The internal dimensions of the reactor were 6 cm × 10 cm × 1.5 mm, and the substrate was attached face-down to the reactor wall. Details of the experimental setup are given elsewhere.[12,13)]

Pieces of Cu-seeded and Ru-lined wafer having narrow trenches were used as specimens. The dimensions of the specimens were 7 cm × 1 cm × 0.7 mm. The structure of the Cu seed layer was TaN/Ta/Cu seed layer = 5/8/50 nm and that of the Ru liner was TaN/Ta/Ru = 3.5/3/5 nm.

The standard deposition conditions were a CO_2 flow rate of 3.5 cm^3/min (7.75×10^{-2} mol/min), a pressure of 10 MPa, a reactor temperature of 180 to 280 °C, and a deposition time of 5 min. The molar ratios of H_2, $Cu(dibm)_2$, and acetone were fixed at 1.53%, 292 ppm, and 5.29%, respectively.

The effects of three process patterns on the initial Cu growth were examined for Cu-seeded specimens (Fig. 1). In Experiment A, the specimen was heated to a target temperature without the precursor. Experiment B is the standard process, where the precursor was supplied at the start of temperature holding (usually for 5 min). In Experiment C, the precursor was added when the temperature reached 50 °C

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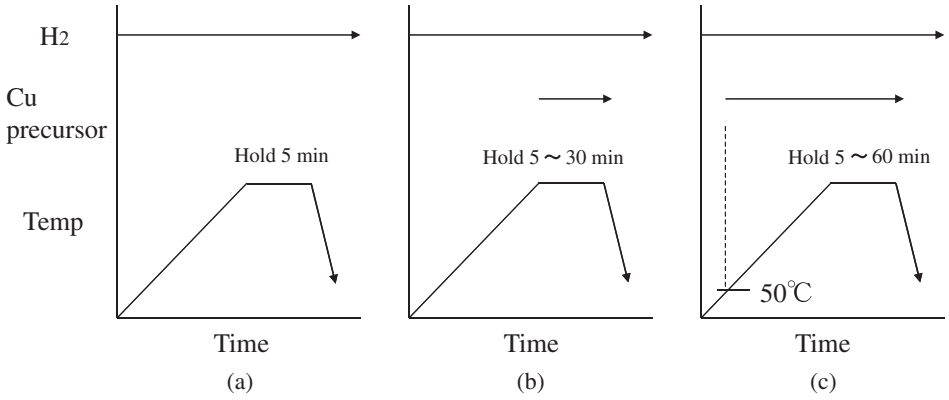

Fig. 1. Three experimental conditions employed in this work: (a) seed layer stability test, (b) standard process, and (c) modified process. See main text.

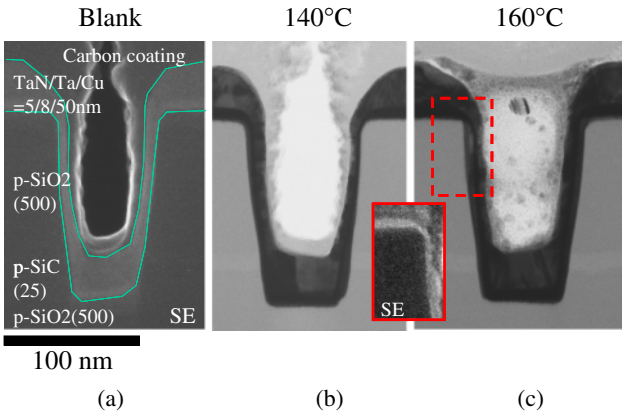

Fig. 2. (Color online) Cross-sectional micrographs of Cu seeded trenches. Secondary electron image of a reference specimen (a), and TEM images of specimens heated to 140 (b) and 160 °C (c) in CO_2+H_2 mixture.

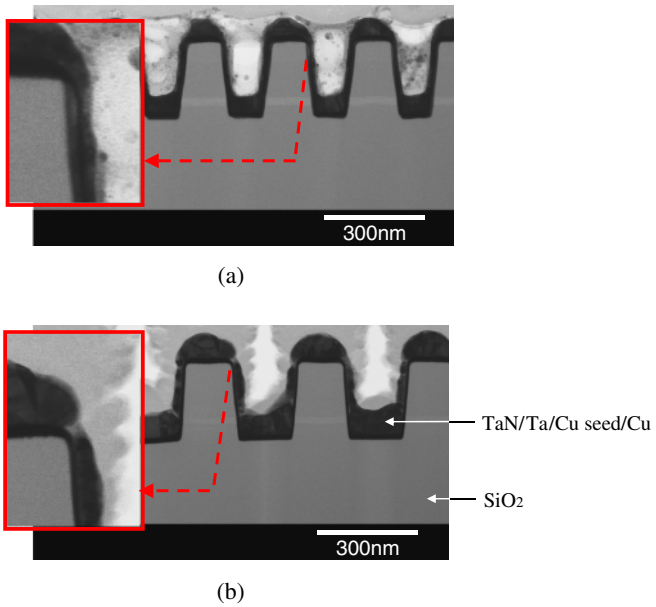

Fig. 3. (Color online) Cross-sectional TEM images of Cu-seeded narrow trenches obtained in standard runs. The holding temperatures were 160 (a) and 200 °C (b).

during ramping. For Ru-lined wafers, the standard procedure (B) was employed.

Cross sections of the specimens were observed with a Hitachi HD 2300C scanning transmission electron microscope (TEM).

3. Results

3.1 Cu-seeded trenches

3.1.1 Experiment A (reference, no precursor)

Figure 2(b) shows a cross-sectional TEM image of a specimen heated to 140 °C. This image shows the same sound surface as that in a nontreated specimen [Fig. 2(a), secondary electron (SE) image taken with the same microscope]. In contrast, in the inset of the high-contrast SE image of a specimen heated to 160 °C, surface wrinkling is clearly observed at a corner of the trench entrance. The TEM image of the same region [dashed box in Fig. 2(c)] is a through-thickness image exhibiting the delamination of the Cu seed layer at the interface with the barrier layer.

3.1.2 Experiment B (standard)

The specimen heated to 160 °C [Fig. 3(a)] showed slight film thickening and partial delamination of the seed layer at the Cu/barrier interface, especially near a corner of the entrance to a trench. Clear agglomeration was observed in the specimen heated to 200 °C, as shown by an increase in the film thickness [Fig. 3(b)]. No change in the seed structure was observed on the specimen processed at 140 °C (data not shown).

3.1.3 Experiment C (modified)

The early addition of the precursor resulted in greater film thickening for the specimen processed at 160 °C [Fig. 4(b)]. The Cu film had a granular structure with grains of 2–5 nm size and a clear interface with the Cu seed layer. No delamination or voiding was observed. Higher temperature and longer holding resulted in more film growth [180 °C and 15 min, Fig. 4(c)]. Cu grains coalesced and the interface between the grown Cu and the Cu seed layer disappeared, especially at a higher temperature of 200 °C [Fig. 4(d)]. This suggests that annealing or active atom diffusion proceeds simultaneously with deposition. No delamination was also observed in this experiment. For reference, a TEM image of a specimen heated to 140 °C is shown [Fig. 4(a)], in which practically no change in the topography can be seen.

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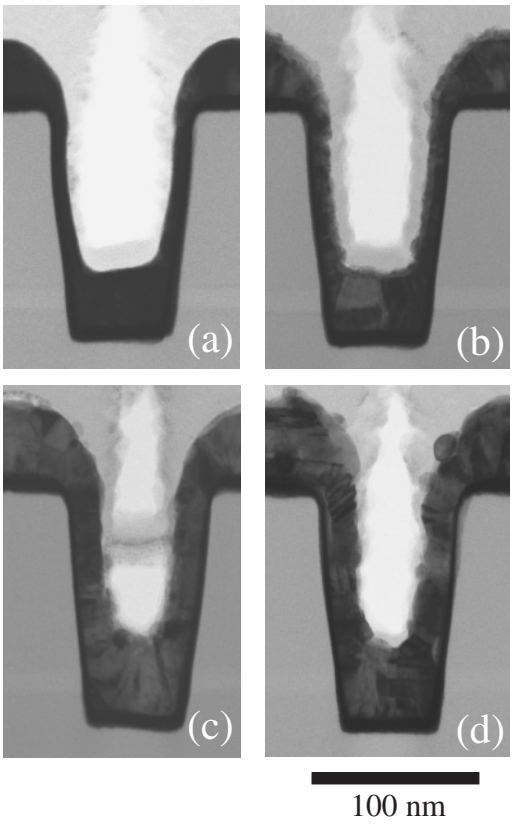

Fig. 4. Cross-sectional TEM images of Cu-seeded narrow trenches obtained in runs with the early addition of precursors with maximum temperatures and holding times of 140 °C and 5 min (a), 160 °C and 5 min (b), 180 °C and 15 min (c), and 200 °C and 5 min (d), respectively.

Table I. Increase in Cu thickness at different positions in Cu-seeded and Ru-lined trenches. The values were determined from electron micrographs. The unit is nm.

	Cu-seeded trenches		Ru-lined trenches	
	Top	Bottom	Top	Bottom
50–140 °C (5 min)	2	2	—	—
50–160 °C (5 min)	2	5	—	—
50–160 °C (60 min)	2	14–33	86	94
50–180 °C (15 min)	21	24	93	93
50–200 °C (5 min)	21	14	—	—

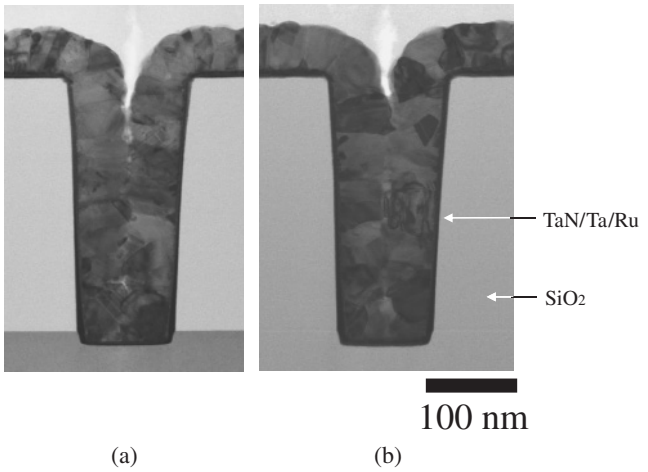

Fig. 5. Cross-sectional TEM images of Cu deposited on Ru-lined narrow trenches as examples of specimens processed by the modified process (Experiment C) with holding conditions of 160 °C and 60 min (a) and 180 °C and 15 min (b).

Table I summarizes the increase in Cu thickness at the bottom and top of Cu-seeded trenches for different runs in Experiment C. An interesting observation here is that preferential Cu thickening occurred at the bottom of the trench, i.e., bottom-up growth, for temperatures of 160 and 180 °C.

3.2 Ru-lined trenches

Figure 5 shows TEM images of Cu in Ru-lined narrow trenches deposited using the modified process (Experiment C) at holding conditions of 160 °C and 60 min (a) and 180 °C and 15 min (b). The Cu layer formed on the barrier/Ru stack exhibits a conformal topography and no delamination at the Ru/Cu interface is observed. Both specimens have a much smoother surface than the Cu-seeded specimens fabricated under similar conditions. Cu grains are elongated normal to the substrate surface, clearly indicating a columnar growth mode. This tendency is much clearer in Fig. 5(a) (160 °C). The grain size is approximately 10–20 nm for growth at 160 °C and 20–40 nm for growth at 180 °C, and the latter specimen appears to have a smaller grain size near the Ru liner, which is evidence of grain growth during deposition. Small voids can be seen at the seam where the grains in contact coalesce with each other. This coalescence does not appear to greatly affect the overall grain structure.

4. Discussion

4.1 Effect of early addition of precursor

It is known that thin Cu films on Ta or TaN can agglomerate and become discontinuous at elevated temperatures.[16–18] The staring temperature of agglomeration decreases as the film becomes thinner. The stability of thin Cu films in supercritical CO_2 has not been well studied. Recently, it was reported that a thin Cu seed layer on TaN becomes discontinuous at approximately 150 °C in a H_2-containing supercritical CO_2 solution.[19] This observation agrees fairly well with our results in terms of the material structure and starting temperature.

In the present work, the early addition of a precursor was effective for suppressing Cu agglomeration. Film thickening was observed at 160 °C [Fig. 4(b)], and this temperature is as low as the staring temperatures of agglomeration [Fig. 2(c)]. Obviously, film thickening during temperature ramping is the reason for the effectiveness.

Note that the temperature required to start Cu deposition on refractory barrier metals from a Cu β-diketonate complex has been reported to be as low as 180 °C.[10,11] We observed a lower starting temperature of deposition in the present study for Cu growth on Cu, which suggests the importance of low interfacial energy in the Cu nucleation kinetics.[16]

4.2 Effect of the underlying layer on Cu morphology

The mechanism described in this subsection is illustrated in Fig. 6. Ideally speaking, Cu nucleates and grows on a Cu seed layer promptly and two-dimensionally because of their perfect miscibility. However, the actual surface of the Cu seed layer has an oxide layer that impedes the nucleation and thus leads to the growth of Cu islands.

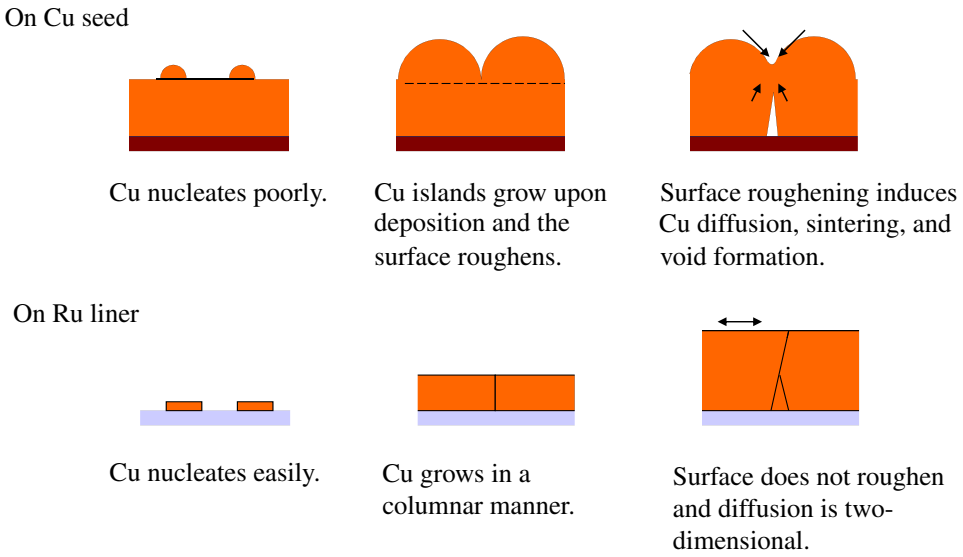

Fig. 6. (Color online) Development of Cu grain structures on Cu seed layer and Ru liner.

Upon the development of the island structure, the islands come in contact with each other to form a rough topography. As is well known, surface atoms diffuse from a convex feature to a concave valley, being driven by the capillary force. In our case, the deposition reaction supplies Cu atoms to the surface so that deposition flux and diffusion flux coexist at the same surface. Therefore, the coarsening and necking of islands proceed continuously, forming new curved portions that function as a source or sink of diffusing atoms. As a result, the surface topography becomes unstable.

Once the instability has became established, this sintering effect 'agitates' the atoms of grains, which leads to the coalescence of the deposited Cu and the seed layer and also to the secondary grain growth or coarsening of Cu.

It is known that the adsorption and desorption of atoms, or condensation and vaporization, respectively, play an important role in the early and low-temperature sintering process.[20] The sorption is an essential physicochemical process in chemical deposition and showed therefore be also actively involved in the agglomeration process.

Compared with Cu, Ru is a nobler element, has greater resistance to oxidation, and is known to adhere well to Cu.[16–18] For these reasons, the two-dimensional nucleation of Cu on Ru is expected to occur with a very high nucleation density.[16] The top surface of the growing islands becomes aligned parallel to the substrate, and as a result, a columnar grain structure develops while keeping a smooth surface and a conformal topography.

4.3 Bottom-up Cu fill

Generally, when the surface reaction dominates the growth kinetics, which is usually the case for lower deposition temperatures, conformal deposition is expected to occur. We reported that the growth rate is limited by the surface reaction for a temperature range of 200 to 260 °C under the same deposition chemistry.[12] Indeed, we observed good conformal growth in the Ru-lined specimens at 160 and 180 °C as stated above [see Fig. 5].

However, when Cu-seeded specimens were used, preferential Cu thickening was observed to occur at the bottom of the trench, especially at lower temperatures of 160–180 °C (Table I). These temperatures are slightly higher than the temperature at which seed layer agglomeration starts and much lower than the temperatures at which grain coarsening and surface roughening occur. In such a case, the surface diffusion flux exceeds the Cu deposition flux and Cu migrates towards the concave bottom, leading to preferential thickening at the bottom. When the deposition temperature is higher, for instance, at 200 °C, the Cu deposition flux becomes relatively large compared with the Cu diffusion flux, and bottom-up growth does not take place.

The above-mentioned bottom-up behavior depends on the trench width. The smaller the dimension, the larger the change in size (thickness) is expected to occur upon the same degree of coalescence. (For this reason, we speculate that this mechanism of bottom-up growth may be partly involved in examples of superior narrow-feature fill reported so far.[3,4,7]) The Ru-lined trenches we used have larger dimensions than the Cu-seeded trenches; however, this difference in size does not simply account for the absence of bottom-up fill in the Ru-lined trenches. So far we have discussed is the effect of roughness on the migration of atoms, and the migration obviously occurs actively when the Cu seed layer was used. Indeed, the Ru-lined specimens had a larger surface roughness than the Cu-seeded specimens of a similar thickness (data not shown).

5. Conclusions

We studied the initial Cu film growth on Cu-seeded layer and Ru-lined narrow trenches for supercritical fluid chemical deposition.

A thin Cu seed layer became discontinuous at about 150 °C when no precursor was added. When Cu was deposited on the seed layer, grain coarsening and surface roughening occurred, especially at higher temperatures. The associated bottom-up growth was observed at lower temperatures. The agglomeration can be suppressed by depositing Cu on the seed surface, which was performed by starting the precursor supply during temperature ramping.

The use of a Ru liner resulted in the highly conformal growth of Cu, and no significant grain coarsening was observed.

These behaviors were discussed in terms of nucleation and sintering theory. Deposited Cu forms a coarse island structure on the Cu seed layer, and the resulting differences in surface curvature drive atom diffusion. Deposition proceeds concurrently with this sintering process, which enhances surface roughening. As a result the surface topography becomes unstable and the grains and the seed layer coalesce. In contrast, on the Ru liner, nucleation occurs in a two-dimensional manner and the film grows conformally without grain coarsening/coalescence.

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