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# COPPER CVD USING LIQUID COINJECTION OF (hfac)Cu(TMVS) and TMVS

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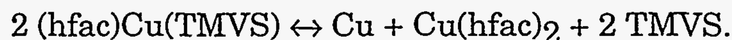
## ABSTRACT

Copper chemical vapor deposition using liquid coinjection of the Cu(I) precursor (hfac)Cu(TMVS) along with TMVS has been demonstrated. The coinjection of TMVS with (hfac)Cu(TMVS) stabilizes the Cu precursor until it enters the reaction chamber, allowing for better control of the deposition and faster deposition rates. Using this technique, we have grown films with as-deposited resistivities of 1.86±0.04 μΩ-cm, independent of film thickness. Deposition rates of well over 100 nm/min are possible. Good step coverage and gap fill down to 0.6 μm lines is demonstrated, with gap fill being limited by the large Cu grain sizes in these films.

## INTRODUCTION

Copper may replace aluminum in ULSI metalizations because of its low resistivity and superior resistance to electromigration. For Cu to be used in such applications, a manufacturable deposition process is required which can meet next-generation requirements in terms of deposition rate, resistivity, and gap fill. Much work has concentrated on chemical vapor deposition (CVD) of Cu since CVD alone is thought to be able to provide the gap fill capabilities required for small dimensions. Recent research has focused on Cu precursors containing the hexafluoroacetylacetonate (hfac) ligand. Both Cu(II) precursors such as $Cu(hfac)_2$ [1], as well as Cu(I) precursors containing another ligand (L), i.e. (hfac)Cu(L) [2], have been studied.

We have used a Cu(I) precursor which uses trimethylvinylsilane (TMVS) as the second ligand [3,4]. This compound, (hfac)Cu(TMVS), also known as Cupra Select®, is a liquid at room temperature, and is coinjected with TMVS into a vaporizer. The coinjection of (hfac)Cu(TMVS) with TMVS stabilizes the Cu precursor by driving the reaction



$$2\,(hfac)Cu(TMVS) \leftrightarrow Cu + Cu(hfac)_2 + 2\,TMVS.$$

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back towards (hfac)Cu(TMVS). This allows, higher vaporizer temperatures to be used. In addition to stabilizing the (hfac)Cu(TMVS) until it reaches the reaction chamber, TMVS is also useful in the liquid delivery system as a solvent, since it will dissolve any solid $Cu(hfac)_2$ built up in liquid lines due to, e.g. overheating.

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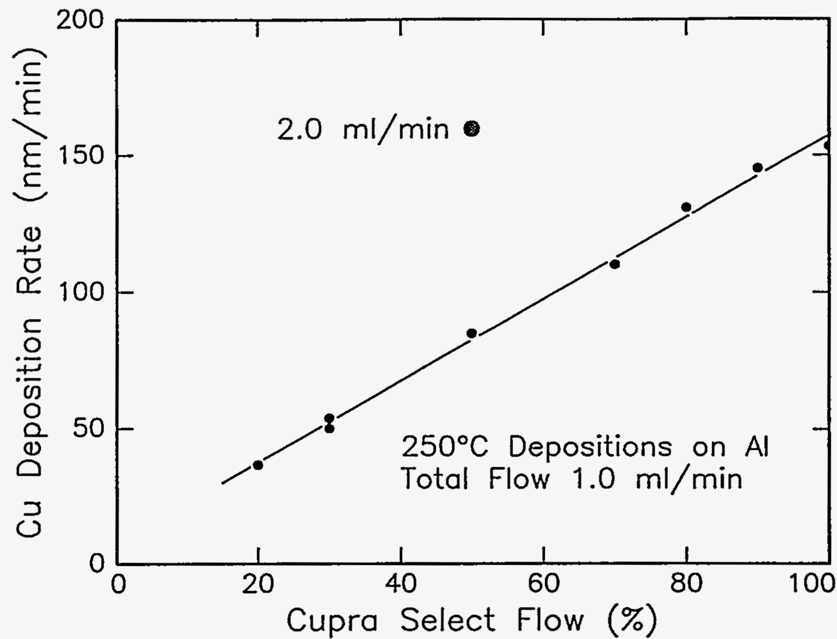


Fig. 1. Deposition rate of Cu at 250°C vs percent of Cupra Select liquid precursor flow. Depositions are on Al substrates to minimize any incubation time. Doubling the total liquid flow rate doubles the deposition rate for a 50:50 Cupra Select:TMVS mixture (denoted by the large filled circle).

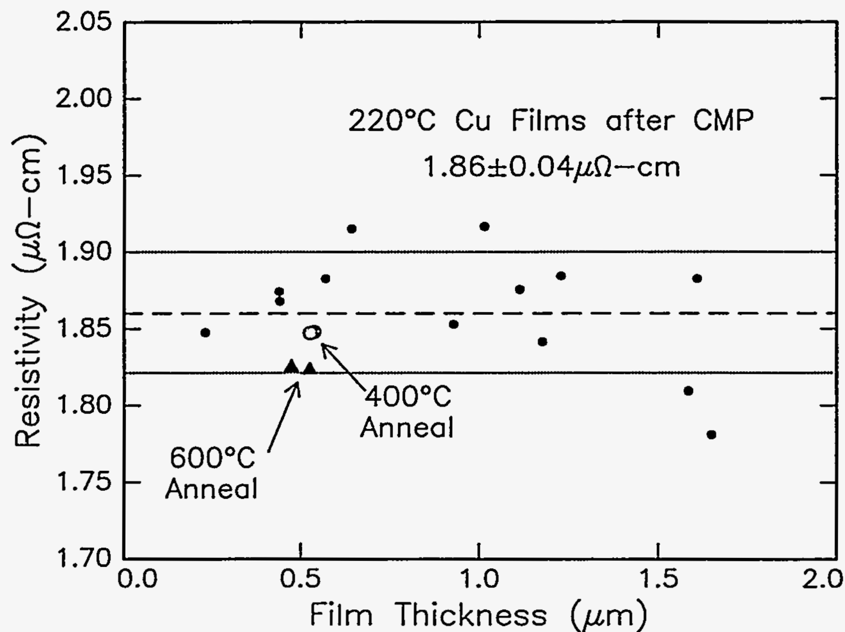


Fig. 2. Measured resistivity vs film thickness for Cu films deposited at 220°C and then chem-mechanically polished. Polishing was performed to ensure an accurate thickness measurement. The average resistivity is 1.86±0.04 μΩ-cm. Vacuum anneals at 400 or 600°C do not result in significant changes to the measured resistivity.

## EXPERIMENTAL

Copper films were deposited on 150 mm wafers in a Watkins-Johnson SELECT 7000P system equipped with an Advanced Technology Materials LDS 300 liquid delivery system. The (hfac)Cu(TMVS) and TMVS precursors were mixed in the liquid phase before injection into the vaporizer. The vaporized precursors are transported to the reaction chamber through heated lines with 50 sccm of $N_2$. Various ratios of TMVS were tried, with optimal liquid delivery system performance and Cu deposition rates obtained for a mixture of 40 – 60 vol.% TMVS.

## RESULTS

Figure 1 shows the Cu deposition rate at 250°C on Al-coated Si wafers vs the ratio of (hfac)Cu(TMVS) in the liquid flow. Depositions were carried out on Al to minimize the effects of incubation time on the results. For a total liquid flow of 1 ml/min, the Cu deposition rate increases linearly with the volume fraction of (hfac)Cu(TMVS) precursor. In addition, for a 50:50 mixture of (hfac)Cu(TMVS) and TMVS, changing the flow rate from 1 to 2 ml/min doubles the deposition rate. This demonstrates that the TMVS does not limit the Cu deposition process, and that the deposition rate could be increased further by increasing the precursor flow rate.

Figure 2 shows resistivity measurements on Cu films of various thicknesses deposited at 220°C after chem-mechanical polishing (CMP). CMP was performed because the relatively large grain sizes in these films results in a rough surface, which leads to inaccurate estimates of the film thickness [4]. The average resistivity of the as-deposited films is $1.86 \pm 0.04$ μΩ-cm. Vacuum annealing at 400 or 600°C (points indicated) may reduce the resistivity slightly, but these data are still within the statistical spread of the unannealed films.

Figure 3 shows cross-sectional focused ion beam images of Cu films deposited onto test structures at 220°C. The large grain size and the resultant rough surface are readily apparent. The upper image shows that for 1 μm geometries, the gap fill obtained is nearly complete. However, for 0.5 μm geometries, the large grain size results in the formation of voids in the deposited films. Deposition at 170°C results in obvious structure-dependent features for the 1 μm gaps, and keyholing in 0.5 μm gaps (not shown).

## DISCUSSION

The use of Cu in ULSI metalization requires a manufacturable deposition process which can meet next-generation demands such as high deposition rate, low resistivity, and good gap fill. By using liquid coinjection of (hfac)Cu(TMVS) and TMVS, we have developed a process which can meet most of these requirements. The addition of TMVS stabilizes the Cu precursor until it reaches the reaction chamber, leading to a more repeatable process. In addition, TMVS can be used to flush the liquid delivery system, removing any $Cu(hfac)_2$ deposits which reduces the amount of preventative maintenance required.

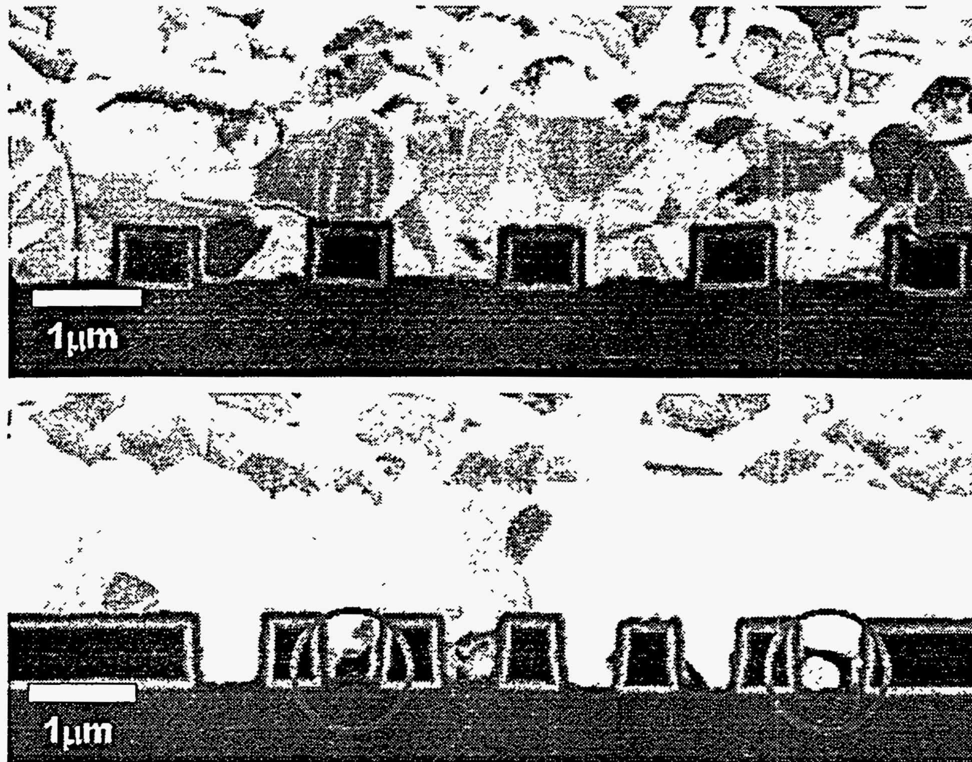


Fig. 3. Cross-sectional focused ion beam images of gap fill test structures with Cu deposited at 220°C. The upper image shows that good gap fill is obtained for 1 μm geometries. However, the bottom image shows that for 0.5 μm geometries voiding occurs because the large Cu grains block deposition in the bottom of the trenches (circled areas). Also note the rough surface of the film which makes accurate resistivity measurements difficult without planarization of the film.

The addition of TMVS does not interfere with the Cu CVD process. As shown in Fig. 1, the Cu deposition rate is a function solely of the liquid injection rate of the (hfac)Cu(TMVS) precursor. Deposition rates in excess of 100 nm/min are easily achievable. These films are 99.98% pure Cu [4], indicating that the addition of TMVS also does not contribute impurities to the film.

The measured resistivities of the Cu films (as-deposited) are 1.86±0.04 μΩ-cm, independent of thickness. Planarization of the films is required to obtain an accurate thickness measurement because of the rough surface of the films. These measured values are higher than the bulk resistivity of Cu (1.68 μΩ-cm), and the reason for this increased resistivity is unclear. Because the impurity level in these films is very low, effects such as surface, grain boundary, and defect scattering must account for the difference.

The remaining difficulty to be overcome is gap fill performance. Integration into future devices will require the ability to fill small vias and lines, certainly at dimensions ≤0.25 μm. For 220°C depositions, these films exhibit unfilled gaps even in 0.5 μm lines (Fig. 3). The principal reason is the large grain size of these films. Nucleation and growth of a grain towards the top of the line can seal off voids below it. Therefore, the grain size has to be reduced substantially, which may be possible to achieve using further chemical additives. Work is currently underway to address this issue.

## CONCLUSIONS

We have developed a Cu CVD process which addresses many of the difficulties with integration of Cu into future ULSI metalizations. Deposition rates in excess of 100 nm/min have been demonstrated. The deposited films are 99.98% pure Cu, and have resistivities of 1.86±0.04 μΩ-cm. Step coverage is excellent. However, the grain size is large, which results in incomplete gap fill for 0.5 μm lines and below. Means of addressing this remaining issue are under study

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