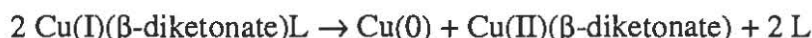
Chemical Vapor Deposition of Copper for Microprocessor Applications

Jason Lee Literature Seminar November 11, 1997

Copper is a promising material for interconnects in semiconductor devices due to its lower resistivity and better electromigration resistance relative to currently used aluminum alloys.[1] However, implementation of copper poses significant challenges such as a high contact resistance with silicon and detrimental diffusion into the silicon substrate. Recent advances in barrier layers and chemical-mechanical processing provide reasonable methods for fabricating interconnects provided an adequate method for blanket coverage of copper can be developed.[2,3] Chemical vapor deposition is of interest for immediate applications into microchip fabrication because of its conformal filling of sub-micron dimension gaps. However, chemically important aspects involving precursor stability and film quality need to be properly addressed.[4]

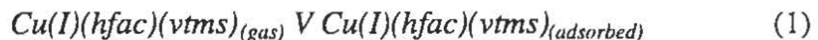
In typical chemical vapor deposition conditions, the copper precursor is transported to the reaction chamber in the vapor phase. High purity copper metal can be deposited at rates of ~200 nm/min and temperatures from 165°C to 205°C with complete filling of 0.3 μm wide gaps with 6:1 height-to-width aspect ratios.[5] This is not currently possible with copper sputtered physical vapor deposition.[6] The most documented family of precursors for copper CVD has the general form Cu(I)(β-diketonate)(Lewis base adduct).[7] An increase in the volatility is seen with the use of fluorinated β-diketonate ligands such as 1,1,1,5,5,5-hexafluoro-2,4-acetylacetonate (hfac).[8] Different Lewis bases, such as alkenes, dienes, alkynes, phosphines, and amines have been used to stabilize the Cu(I) complex. The vinyltrimethylsilane (vtms) derivative of the Cu(I)(hfac)L is an attractive precursor because it remains a liquid at room temperature and has an elevated vapor pressure relative to other derivatives.

Cu(I)(β-diketonate)L precursors deposit copper via thermally-induced disproportionation rather than thermal decomposition.

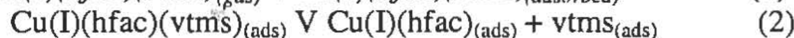


$$2\ \mathrm{Cu(I)(\beta\text{-}diketonate)L} \rightarrow \mathrm{Cu(0)} + \mathrm{Cu(II)(\beta\text{-}diketonate)} + 2\ \mathrm{L}$$

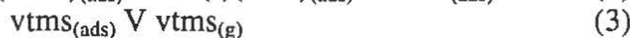
Thermally induced disproportionation has the advantage over thermal decomposition that it should be possible to avoid significant impurity incorporation in the growing copper film.[8] The disproportionation reaction at the surface is believed to take place following the proposed mechanism.[10]



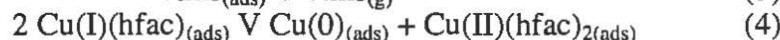
$$Cu(I)(hfac)(vtms)_{(gas)}\ V\ Cu(I)(hfac)(vtms)_{(adsorbed)} \quad (1)$$



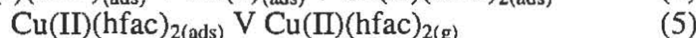
$$\mathrm{Cu(I)(hfac)(vtms)_{(ads)}\ V\ Cu(I)(hfac)_{(ads)} + vtms_{(ads)}} \quad (2)$$



$$\mathrm{vtms_{(ads)}\ V\ vtms_{(g)}} \quad (3)$$



$$\mathrm{2\ Cu(I)(hfac)_{(ads)}\ V\ Cu(0)_{(ads)} + Cu(II)(hfac)_{2(ads)}} \quad (4)$$



$$\mathrm{Cu(II)(hfac)_{2(ads)}\ V\ Cu(II)(hfac)_{2(g)}} \quad (5)$$

Experimental evidence indicates that the surface disproportionation reaction in step 4 is rate limiting.

Copper films deposited from mixtures of Cu(I)(hfac)(vtms) and water vapor nearly double their rate of deposition and substantially reduce their nucleation time.[11] Excess water vapor, however, significantly increases the resistivity due to copper oxide incorporation, and eventually the deposition rate slows to a gradual halt.[12] The incorporation of copper oxide is completely suppressed by the introduction of hfacH vapor along with the precursor and water vapor during CVD. Selective vapor-phase etching of the copper oxide with the hfacH yields volatile reaction products of $Cu(II)(hfac)_2$ and water vapor.[13]

Selective deposition occurs in favor of metallic substrates such as TiN over insulated surfaces such as SiO_2. Kinetic analysis of the surface nucleation of Cu(I)(hfac)-(vtms) over various substrates produces activation energy values that are reversibly proportional to the electric conductivity of the surface.[14] The nucleation phase of copper film growth has an important influence on structure and morphology of the resulting film.[15] Modifying surface regions with chemical passivating agents to favor adhesion failure results in patterned microstructures with copper CVD.[16]

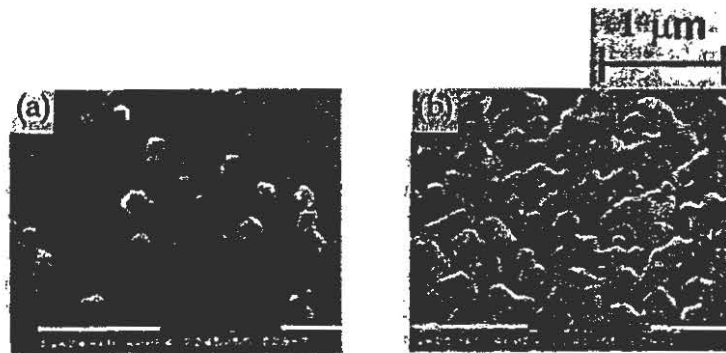


Figure 1. SEM photographs of the copper films deposited from Cu(I)(hfac)-(vtms) at 180°C under 0.5 Torr for 20 min on: (a) SiO_2 and (b) TiN.[17]

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