Development and qualification of a vacuum pumping system for metalorganic vapor phase epitaxy copper precursors

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Semiconductor devices incorporating copper interconnects are set to revolutionize the performance and functionality of integrated circuits. Copper interconnects enable faster and more reliable circuitry at sub-0.25 μm dimensions with lower resistivity and excellent resistance to electromigration. Numerous methodologies exist whereby copper can be deposited, with chemical vapor deposition (CVD) being one such technique. A vacuum pumping system that effectively and efficiently handles the process byproducts from the CVD precursor Cu(hfac)(TMVS) has been developed and qualified. It is shown that a standard dry pump used in conjunction with additional apparatus in the vacuum system results in the safe handling of process byproducts. The performance of each component of the vacuum system has been individually qualified and the abatement performance of the overall system shows >99% destruction efficiency of process effluent. © *2000 American Vacuum Society.* [S0734-211X(00)10306-3]

I. INTRODUCTION

The semiconductor manufacturing industry is beginning to exploit new materials and manufacturing technologies in order to meet the demand for smaller and faster integrated circuitry. As dimensions continue to shrink into the sub-0.25 μm range the materials selected for device manufacture become increasingly critical to overall performance. Aluminum has traditionally been the metal selected for device interconnects, but as device dimensions continue to shrink its continued viability is brought into question. Aluminum has a relatively high resistivity (2.65 μΩ cm) and susceptibility to electromigration when compared with other metals such as copper.[1] In contrast, copper enables the manufacture of faster, more reliable devices with lower resistivity (1.67 μΩ cm) that exhibit excellent resistance to electromigration. Increasingly, copper appears to be the metal that will eventually replace aluminum for device interconnects and is one of the most rapidly growing areas in semiconductor device manufacture.

Two widely used techniques for deposition of device quality copper films are physical vapor deposition (PVD) and chemical vapor deposition (CVD). CVD techniques are becoming the preferred method since they offer additional benefits over PVD techniques, such as excellent step coverage and fast film growth rates. The solid precursor $Cu(hfac)_2$ can be used to deposit device-quality copper films in low temperature plasma-assisted CVD (PACVD).[2] A carrier gas (usually hydrogen, nitrogen, or argon) is passed through a sublimator (held at a temperature in the range of 50–100 °C) to deliver the precursor into a reaction chamber where hydrogen reduction of the precursor deposits a film of pure copper.[3,4] However, inherent problems associated with precursor delivery from solid sources, such as control accuracy and reproducibility, have restricted the development of solid precursor based processes and led to the development of alternative liquid precursor based processes.

Liquid precursors for the deposition of copper films can be prepared by mixing Cu(II) complexes with suitable solvents. The liquid precursor is delivered to a reaction chamber using liquid delivery systems (LDS) that offer improved accuracy and reproducibility (over solid precursor sources) with a level of performance that is comparable with traditional gas delivery systems. Liquid delivery of Cu(II) complexes in conjunction with PACVD techniques are used to deposit high quality copper films in the temperature range 160–170 °C with high accuracy and reproducibility.[5]

Cu(I) complexes mixed with solvent produce an alternative liquid precursor that offer a number of additional benefits over the Cu(II) variety. These include the growth of high quality copper films with faster deposition rates at lower temperatures. In addition, the use of plasma to assist with the deposition is not required. One method to deposit copper films is by CVD from liquid precursors that contain copper bearing species. Cu(hfac)(TMVS) is one such liquid precursor that is produced commercially by the addition of trimethylvinylsilane (TMVS) to the Cu(I) complex $Cu(hfac)_2$. The precursor is delivered to the reaction chamber using direct liquid injection (DLI) whereupon thermal decomposition (most efficient at approximately 200 °C) deposits films of pure copper (preferentially on metallic surfaces) via the thermally activated disproportionation reaction:[6]

$$2Cu^{+1}(hfac)(TMVS) \rightarrow Cu^0 + Cu^{+2}(hfac)_2 + 2(TMVS). \quad (1)$$

Copper films deposited in this manner show high levels of accuracy and reproducibility to give high purity (99.99% pure) copper with resistivities of 1.85 μΩ cm.[7]

A vacuum system on this copper deposition process is required to pump the effluent from the reaction chamber. These will include unreacted precursor Cu(hfac)(TMVS) in

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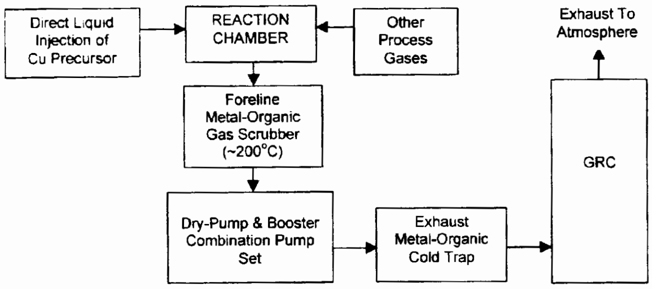

FIG. 1. Schematic diagram showing the components of a vacuum pumping system for MOCVD copper precursors.

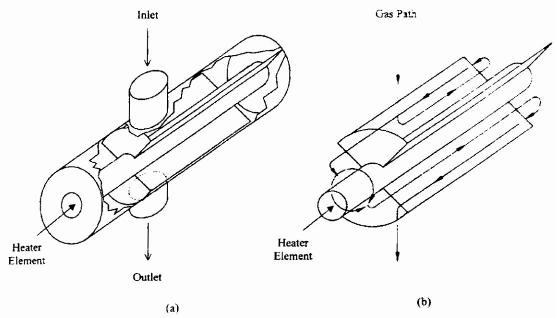

FIG. 2. Schematic diagram showing the design of a metalorganic gas scrubber detailing the gas path; (a) the exterior construction and orientation of the scrubber indicating the insertion port for the heating element; (b) the construction of the internal parallel thermal planes (the baffles are omitted in this schematic for clarity) and shows the gas path through the scrubber, the inclusion of the baffles will generate a more tortuous gas path ensuring intimate contact of the effluent gas with the hot central element.

addition to the reaction byproducts $Cu(hfac)_2$ and TMVS. Although the reduction of Cu(hfac)(TMVS) occurs most favorably at 200 °C it has been reported to occur under reduced pressures at temperatures as low as 40 °C.[8] The swept volume of a standard semiconductor dry pump is entirely metallic and typically runs at temperatures in excess of 40 °C thereby presenting an ideal environment for further reduction of any unreacted precursor. Further reduction will plate the internal surfaces of the swept volume with copper thereby reducing the clearance tolerances and eventually lead to rapid pump failure. Hence, the admittance of the unreacted precursor to the pump should be avoided. The $Cu(hfac)_2$ and TMVS byproducts are in the vapor phase as they exit the reaction chamber. Under normal conditions the TMVS will remain in the vapor phase throughout the vacuum system. However, the $Cu(hfac)_2$ can condense on surfaces where the temperature falls below 80 °C. Under normal operating conditions the temperature within the pump body is in excess of 80 °C thereby ensuring that condensation of $Cu(hfac)_2$ will not occur. Condensation of the $Cu(hfac)_2$ byproduct will occur in room temperature exhaust lines and may lead to exhaust line blockages. An exhaust temperature management system (TMS) is required to avoid such blockages in the exhaust lines. In addition, the inclusion of a cold trap in the exhaust line will provide the ability to trap and recover the $Cu(hfac)_2$ byproduct in a controlled and safe manner. A gas reactor column (GRC) is included for final stage abatement to remove any remaining copper-bearing species and to abate the TMVS component in the gas stream before exhausting to the atmosphere at environmental emission standards.

II. APPARATUS AND EXPERIMENTAL

A feasibility study has been undertaken to evaluate the performance of a vacuum system that protects the pump from copper plating and facilitates process byproduct recovery in a manner suitable for recycling. Figure 1 outlines schematically the main components of such a system evaluated on the CVD Cu(hfac)(TMVS) process. It consists of a hot metalorganic gas scrubber at the pump inlet, a standard BOC Edwards iQ80/500 dry-pump booster combination (run with N_2 gas ballast and shaft seal purges), an exhaust metalorganic cold trap and a BOC Edwards Gas Reactor Column (GRC) for final-stage abatement. The components of this vacuum system are in agreement with a similar system for this process detailed elsewhere.[9] Process conditions were simulated by delivering the precursor into the reaction chamber at a flow of 0.5 $g\,min^{-1}$ with a helium carrier gas flow in the range 200–500 sccm. The reaction chamber was at ambient temperatures at all times ensuring no reduction reaction occurred within the chamber thereby maximizing the flow of unreacted precursor into the foreline scrubber (i.e., a worst case scenario from the pumping perspective).

A schematic diagram detailing the construction of the foreline metalorganic gas scrubber[10] is shown in Fig. 2. The scrubber sits atop the booster pump in a horizontal orientation with a footprint comparable to that of the pumpset. The inlet and outlet of the scrubber are adjacent thereby allowing it to be inserted into existing vacuum lines with the minimum of disruption; see Fig. 2(a). It consists of a horizontal tubular component into which is inserted concentrically a pipe to which are attached a number of parallel running vanes; see Fig. 2(b). At regular intervals along the length of the vanes strategically positioned baffles (shown in the image of Fig. 3) connect adjacent vanes in a manner to direct the gas flow towards the central core. The flow of gas through the scrubber is also detailed in the schematic of Fig. 2(b). A removable heating element is located along the central core of the scrubber to maintain an internal temperature of approximately 200 °C, while the temperature of the outer casing never exceeds 85 °C. Unreacted precursor entering the scrubber is therein reduced via the disproportionation reaction and deposits copper on the internal surfaces. The inter-

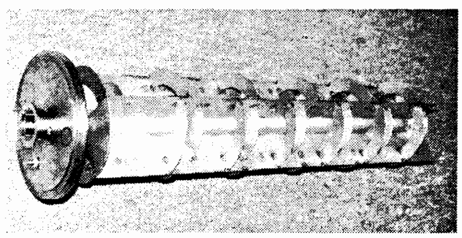

FIG. 3. Image showing the internal construction of the metalorganic gas scrubber showing both the parallel thermal planes and the thermal baffles attached between adjacent planes that are perpendicular to the gas-flow path.

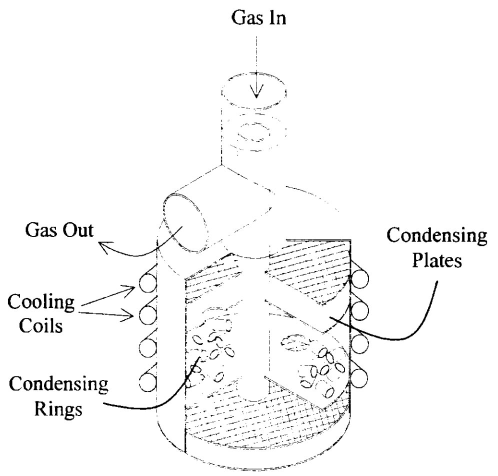

FIG. 4. Schematic diagram detailing one possible configuration of the cold-trap placed in the exhaust line. The thermal characteristics of this trap design are such that condensation of material occurs preferentially on the cooler walls towards the outer trap body.

nal construction is such that copper deposits on the central core and grows concentrically outwards thereby ensuring good conductance is maintained.

If the temperature within the pump and the exhaust pipework is sufficiently hot (i.e., in excess of 80 °C) then the $Cu(hfac)_2$ will not condense. However, this material is valuable and it can be recovered from the effluent gas flow for recycling. Figure 4 shows a schematic of one embodiment of a metalorganic cold trap utilized for condensing the $Cu(hfac)_2$. The cold trap is watercooled and is inserted in the exhaust line between the pump and the GRC. It is fitted in close proximity to the pump and precedes any silencer in the exhaust line. Heating the exhaust line from the pump to the trap inlet port to approximately 120 °C ensures that material does not condense in either the exhaust lines or at the trap inlet. Conduction of heat along the length of the cold-trap inlet feed line (which is attached to the inlet port) maintains it at a higher temperature than the main trap body. Hence, condensation of $Cu(hfac)_2$ byproduct in the inlet feed line is restricted thereby reducing the possibility of an inlet blockage of the cold trap.

The GRC is included in the vacuum system to provide final stage abatement of the remaining effluent components. This will consist mostly of the organic solvent TMVS but may also contain some residual traces of $Cu(hfac)_2$ or unreacted Cu(hfac)(TMVS).

III. RESULTS

A. Foreline scrubber

To evaluate the operating efficiency of the foreline scrubber the quantity of unreacted precursor, Cu(hfac)(TMVS), entering the scrubber inlet is compared with that at the scrubber outlet. Thermal deposition monitors placed at the inlet and outlet of the foreline scrubber are used to obtain a relative measure of unreacted precursor entering and exiting the scrubber, respectively. Each deposition monitor is comprised of a heating block, cartridge heater, thermocouple, and deposition shield. They are maintained at a temperature of 200 °C and oriented so that the monitoring faces are perpendicular to the gas flow. Upon completion of each simulated process run the thickness of copper deposited on the surfaces of each thermal monitor is measured using a Dektak Profilimeter. The relative performance of the scrubber is determined by calculating a ratio of the thickness of copper deposited on the inlet monitor with that deposited on the outlet monitor.

TABLE I. Profilimeter measurements taken on heated copper deposition monitors placed at the inlet and outlet of the foreline scrubber following each design iteration. A relative scrubbing efficiency is calculated from the profilimeter measurements.

Foreline scrubber	Internal design	Inlet step height (μm)	Outlet step height (μm)	Scrubbing efficiency (%)
A	Parallel vanes only	10.3	1.48	85.6
B	Addition of baffles	8.8	1.11	87.4
C	Double number of baffles	8.7	0.92	89.4
D	Same as C	8.2	0.79	90.4
E	Reduce clearances	5.7	0.11	98.1

The foreline scrubber was evaluated a number of times throughout its development cycle. The efficiency of the initial basic design of scrubber was measured to be 85%. After a number of design improvements were implemented the efficiency of the scrubber rose to approximately 98%, see Table I. The inclusion of baffles as employed in *Scrubbers B, C,* and *D* resulted in a slight improvement in efficiency. Reducing the clearances between the parallel vanes and the inner wall of the main scrubber body was found to produce a significant improvement in performance. The foreline scrubbers evaluated in the course of this work were all prototype designs. Internal inspections of the pump set after each test run employing each scrubber detailed in Table I in the foreline showed no visible evidence of copper metal deposition within either the booster or the dry pump.

B. Exhaust metalorganic cold trap

The performance of the cold trap was evaluated by measuring the amount of copper present in the gas stream at the trap outlet. A sample of the gas stream is extracted at a rate of 100 sccm from the effluent and passed through an impinger filled with 20 cc of 4M HCl. The gas stream is sampled in this manner for 60 min while the Cu(hfac)(TMVS) is flowing at a rate of 0.5 $g\,min^{-1}$ into the process chamber. Upon completion of the sampling period the solution in the impinger is neutralized and mixed with a reagent to provoke a color change in the solution. A Cu low-range colorimeter is used to quantify the color change, the intensity of which is indicative of the amount of copper present in the mixture. The absolute quantity of copper present in the gas flow is thereby calculated in grams per minute ($g\,Cu\,min^{-1}$) or as parts per million (ppm) as a volume measurement (v/v Cu).

TABLE II. Colorimeter measurements of copper species detected at the cold-trap outlet and an overall system efficiency rating for the removal of copper bearing species from the gas stream.

Exhaust trap	Copper admitted to system (mg Cu min^{-1})	Copper detected at outlet of cold trap (mg Cu min^{-1})	System efficiency (%)
A	85.5	1.45	98.3
B	85.5	3.96	95.4
C	85.5	1.06	98.8
D	85.5	1.26	98.5

A flow rate of 0.5 g min^{-1} of the copper precursor Cu(hfac)(TMVS) will deliver approximately 85.5 mg min^{-1} of elemental copper to the process chamber. The combined efficiency of the foreline metalorganic scrubber and the metalorganic cold trap at removing copper species from the gas stream can be calculated from the colorimeter measurements taken at the outlet of the cold trap. Table II shows the absolute quantity of copper bearing species measured in the gas stream at the exhaust of the cold trap and an efficiency measurement relating to the reduction of copper in the overall effluent gas stream.

Visual inspection of the cold trap after each test run showed that the majority of the $Cu(hfac)_2$ byproduct deposited within the main trap body. An extremely light dusting of green $Cu(hfac)_2$ powder at the outlet could often be identified. Approximately 70%–90% of the expected $Cu(hfac)_2$ byproduct could be recovered from within the trap body.

C. Evaluation of gas reactor column scrubbing capabilities

The abatement function of the gas reactor column (GRC) is twofold. It is required to abate the volatile organic TMVS component in the exhaust effluent and any remaining traces of copper-bearing species that may also be present. Hence the abatement performance of the GRC needs to be qualified for both TMVS and Cu. The abatement of TMVS [i.e., $Si(CH_3)_3$] to environmentally compatible release gases occurs in the following manner:

$$Si(CH_3)_3+9O_2 \longrightarrow 5CO_2+6H_2O+SiO_2. \quad (2)$$

Mass spectrometry measurements at the outlet of the GRC are used to qualify the GRC abatement efficiency for TMVS. The GRC has been found to be capable of abating the TMVS to sub-10 ppm levels (within environmental release criteria) in the exhaust gas stream with delivery rates of TMVS up to 1.0 g min^{-1} at the GRC inlet.[11]

The GRC efficiency for copper abatement has been evaluated using the colorimeter technique outlined above. The quantity of copper measured in the gas stream at the GRC inlet is compared with that measured at the outlet to give a relative efficiency rating for the GRC performance (with respect to copper abatement). Table III shows the absolute quantity of copper measured at the GRC inlet and outlet and the calculated relative efficiency rating for three consecutive simulated process runs. The efficiency of the GRC (as a stand-alone device) to abate copper in the gas stream is consistently >99% and the absolute quantity of copper measured in the exhaust gas from the GRC is sub-0.1 ppm (v/v Cu).

D. Overall system abatement efficiency

The efficiency of the overall vacuum system for copper abatement is a function of the combined efficiencies of the metalorganic gas scrubber, the exhaust metalorganic cold trap, and the GRC. An overall abatement efficiency rating can be calculated by relating the quantity of copper in the gas stream at the GRC outlet with that admitted to the reaction chamber. The precursor Cu(hfac)(TMVS) is admitted to the reaction chamber at a rate of 0.5 g min^{-1}. This is equivalent to copper entering the system at a rate of approximately 85.5 mg Cu min^{-1}. The quantity of copper in the gas stream at the GRC outlet during three process runs was measured and an efficiency value calculated (see Table IV). The overall efficiency of the vacuum system at removing copper species from the gas stream is calculated to be 99.99%.

IV. CONCLUSION

A feasibility study has been performed on a vacuum system to pump Cu(hfac)(TMVS). The system consists of a foreline metalorganic gas scrubber to reduce unreacted precursor in the reaction chamber effluent gas stream to $Cu(hfac)_2$ and TMVS. A metalorganic cold trap is inserted in the exhaust line to condense and recover the $Cu(hfac)_2$ byproduct. A GRC with a modified reaction cartridge provides final stage abatement of the TMVS and residual traces of $Cu(hfac)_2$ and unreacted Cu(hfac)(TMVS) in the gas stream. These components used in conjunction with a standard dry-pump booster combination pump set (with N_2 gas ballast and shaft seal purges) have been qualified for pumping the Cu(hfac)(TMVS) MOCVD process.

The performance of the overall vacuum system has been qualified to show that the abatement efficiency is 99.99% for copper. In detail, we have shown that the foreline metalor-

TABLE III. Levels of copper bearing species measured at the inlet and exhaust of the GRC from the Cu(hfac)(TMVS) process.

Test run	GRC inlet (g Cu min^{-1})	GRC inlet (v/v Cu) ppm	GRC exhaust (g Cu min^{-1})	GRC exhaust (v/v Cu) ppm	Cu abatement efficiency (%)
1	1.45×10^{3}	10.9	4.77×10^{-6}	0.03	99.70
2	3.96×10^{-3}	29.8	3.09×10^{-6}	0.02	99.93
3	1.06×10^{-3}	7.9	9.87×10^{-6}	0.07	99.10

TABLE IV. Efficiency of the complete vacuum system at removing copper components from the overall gas stream.

Test run	Copper admitted to system (mg Cu min^{-1})	Copper detected at outlet of GRC (mg Cu min^{-1})	System efficiency (%)
1	85.5	4.77×10^{-3}	99.99
2	85.5	3.09×10^{-3}	99.99
3	85.5	9.87×10^{-3}	99.99

ganic gas scrubber is up to 98% efficient at reducing unreacted Cu(hfac)(TMVS) in the process effluent gas stream. The metalorganic cold trap condenses and removes the remaining copper from the gas stream to an efficiency of 98%. The GRC shows 99% abatement efficiency for copper resulting in sub-0.1 ppm emissions of copper and an ability to abate the TMVS organic solvent to sub-10 ppm levels in the gas exhaust stream with delivery flows of up to 1.0 g min^{-1} of TMVS. The system described above has been commercialized into an integrated product, the Copper Exhaust Management Systems (CEMS), and is suitable for CVD processes using Cu(hfac)(TMVS) or similar organic copper precursors.

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