

CU FILM DEPOSITION FROM SUPERCRITICAL CARBON DIOXIDE FLUIDS FOR 3D-IC THRU VIA FORMATION

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1 INTRODUCTION

As miniaturization proceeds, new metal-wiring (interconnect) technologies are required for the fabrication of high-performance LSIs. One of the crucial technological targets is the formation of MEMS-based thru silicon vias (TSVs) of 3D IC. Cu electroplating is the most popular of the deposition technologies currently under investigation, but its plating technology does not seem to be able to perform defect-free Cu filling in high-aspect via holes with sufficient step coverage. Technology for deposition in supercritical fluids is becoming of crucial interest as a replacement for electroplating because of the excellent penetration capabilities of supercritical fluids. Supercritical carbon dioxide (scCO₂) demonstrates a unique combination of gas and liquid properties above the critical points (304 K, 7.2 MPa). Additionally, it has as high a density as liquids, as high a diffusivity and as low a viscosity as gases, zero surface tension, and solvent capabilities. Because of these unique properties, scCO₂ impregnates and delivers a metal precursor dissolved into scCO₂ into high-aspect-ratio gaps, trenches, and TSVs. The metal deposited on these topographies demonstrates good gap-filling and step coverage. Technologies using scCO₂ are very attractive for the fabrication of new metal wiring. We developed a flow-type deposition processor designed to enable the independent control of deposition parameters and long-term deposition in which a precursor dissolved in scCO₂ is continuously supplied to a reactor while the deposition characteristics of the film are studied [1]. This paper reports the Cu deposition characteristics of scCO₂ using Cu(dibm)₂ in our developed flow-type reaction system.

2 EXPERIMENTAL

A schematic diagram of our flow-type reaction system is shown in Figure 1. Liquid CO₂ cooled at 0°C was pressurized using a high-pressure pump to above the critical point of CO₂ and was supplied to a H₂ mixing unit designed to enable the admission of a low-pressure (max. 1.5 MPa) gas to a high-pressure fluid, typically continuous 10 MPa. A precursor, copper(II)bis-diisobutylmethanate or Cu(dibm)₂, was dissolved in acetone and supplied continuously to a hot-wall reaction chamber via a pre-heating system that heats CO₂. Deposition

pressure was kept constant using an automatic pressure controller. $\text{Cu}(\text{dibm})_2$ was purchased from Kojundo Chemical Laboratory Co., Ltd. (Sakado, Japan) and used as received. The substrates used were TaN-coated Si wafer coupons with gap-fill test patterns 10 μm in dia. x 90 μm in depth. Before deposition, Au thin film, nom. 50 \AA in thickness, was sputtered to the wafer in order to generate nuclei for Cu deposition. Film thickness was measured using a Dektak³TM surface profiler. Film sheet resistance was measured by a four-point probe method using a HIOKI 3239 Digital HitesterTM. The deposition conditions were as follows: temperature 200-280°C, pressure 10 MPa, hydrogen concentrations 0.4 and 1.2 mol%, precursor concentrations 3-300 ppm, acetone concentration 6 mol%, and deposition time 1-8 hrs. Figure 2 shows the dimensions of the reaction chamber. The thin channel arrangement enabled one-dimensional flow. The substrate was positioned at the midpoint of upper heat in a facedown manner.

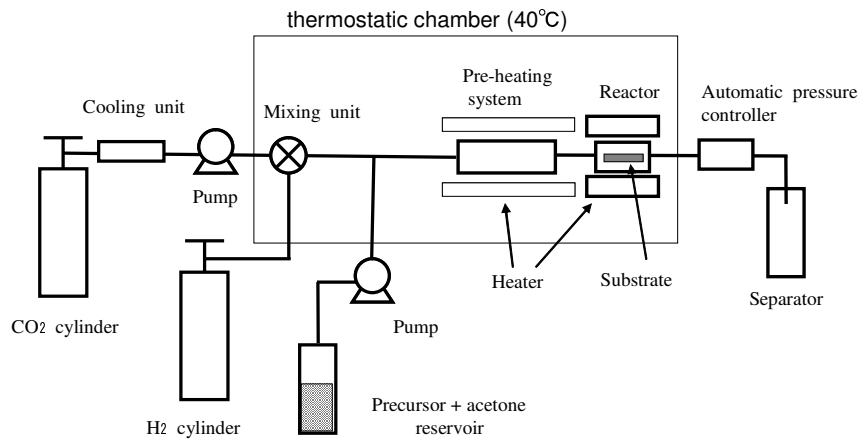


Figure 1. Schematic diagram of the flow-type reaction system designed to enable long-term deposition. A precursor dissolved in acetone was continuously supplied to the reaction chamber.

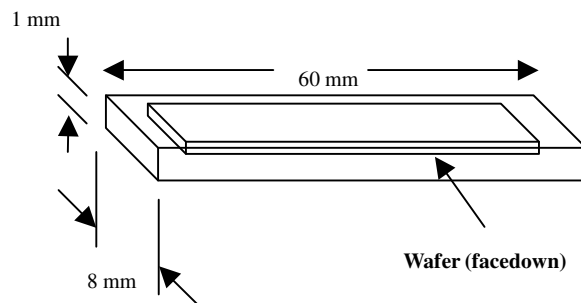


Figure 2. Schematic diagram of the reaction chamber with a built-in heat block. A substrate is positioned at the midpoint of the heat block and faced toward the flow.

3 RESULTS AND DISCUSSION

For long-term deposition, the precursor must be supplied continuously. Liquid precursors, such as Cu(I)(hexafluoroacetylacetonate)trimethylvinylsilane or Cu(hfac)tmvs, seem suitable for this purpose, but they are troublesome in handling because they react easily with oxygen, which changes their structure. Although copper(II)bis-(hexafluoroacetylacetonate), Cu(hfac)₂, has good solubility in scCO₂ (around 35.2g/L), this precursor is not acceptable due to its inclusion of the environmentally unfriendly fluorine. Cu(dibm)₂ has a considerable low solubility of only 3.32 g/L and therefore cannot be used directly as a precursor in deposition.

In our experiment, Cu(dibm)₂ was dissolved in different organic solvents and supplied to the reaction system. In order to determine the efficiencies of different solvents, Cu(dibm)₂ was dissolved in solvents such as ethanol, propanol, hexane, acetone, and cyclohexane. Figure 3 shows the solubility of Cu(dibm)₂ in solvents of volume 1 ml. Hexane, acetone, and cyclohexane had good solubilities; cyclohexane in particular dissolved Cu(dibm)₂ excellently. Depositions from scCO₂ using these solvents were carried out one at a time. Figure 4 shows film thickness and (111)/(200) relative intensity. Acetone demonstrated thicker and better microcrystallinity, with a relative intensity higher than that of any other solvent. The resulting best solvent was thus acetone.

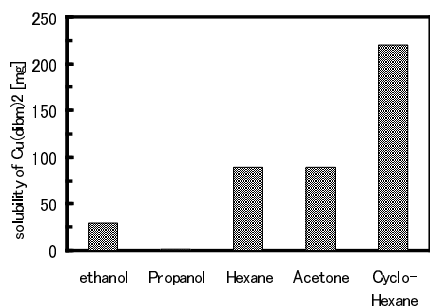


Figure 3. Solubility of Cu(dibm)₂ in solvents such as ethanol, propanol, hexane, acetone, and cyclo-hexane.

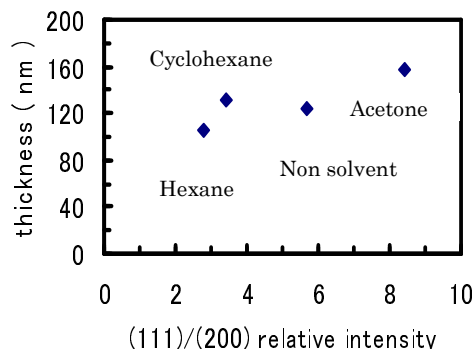


Figure 4. Acetone was thickest and had the highest (111)/(200) relative intensity. Acetone is thus the best solvent.

Figure 5 shows the dependence of temperature between the inlet and midpoint of the reaction chamber on the pre-heating system temperature. The temperature difference between the inlet and midpoint decreases as pre-heat temperature increases and above 150°C, inlet temperature nearly reached the midpoint temperature. The pre-heating system must heat the chamber to slightly above 150°C. Temperatures of 180°C and above are not acceptable because they would initiate deposition in the pre-heating system and thereby consume the precursor.

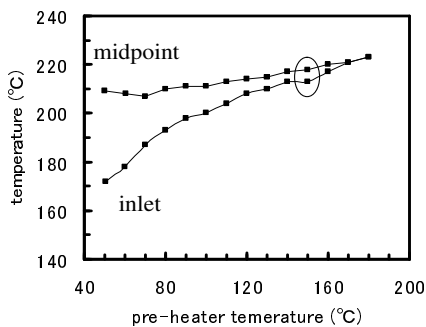


Figure 5. Temperature difference between inlet and midpoint of the chamber decreases above a pre-heater temperature of approx. 150°C.

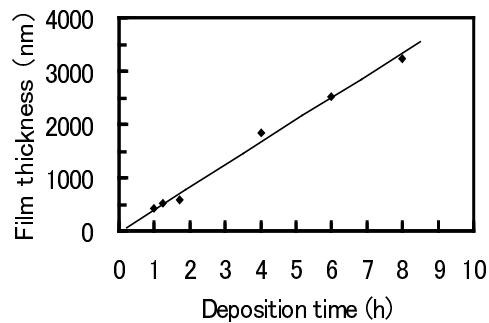


Figure 6. Deposition time dependence of copper film thickness over 1-8 hrs at 240°C, 10 MPa, with H₂ and Cu(dibm)₂ concentrations of 1.2 mol% and 57 ppm, respectively.

The deposition time dependence of copper film thickness is shown in Figure 6. Deposition was carried out at 240°C, 10 MPa, and H₂ and Cu(dibm)₂ concentrations of 1.2 mol% and 57 ppm, respectively, and deposition time varied from 1 to 8 hrs. Film thickness increased with deposition time, and a good upward linear relationship was observed in the range of 1-8 hrs. The film growth rate was 6.95 nm/min. The film thickness after 8 hrs of deposition was 3.2 μm. A long-term deposition was performed using our developed flow-type reaction system to enable the continuous supply of a precursor over a long period of time and to allow the independent and precise control of deposition parameters such as deposition temperature, time, pressure, and the concentrations of H₂ and the precursor. High deposition rates such as those around 30 nm/min are thus conceivable if these parameters are adjusted to optimum conditions. High growth rate and thicker film are critical to MEMS processing design. Figure 7 shows the temperature dependence of the copper film growth rate between 200°C and 260°C. Deposition conditions were 10 MPa, 60 min, precursor concentration 57 ppm, and H₂ concentrations of 0.4 ml% and 1.2 mol%. The calculated activation energies for the H₂ concentrations were 0.38 eV for 0.4 mol% and 0.41 eV for 1.2 mol%. The activation energies obtained in this study were slightly lower than the values we reported previously (approx. 0.45 eV [2]; see dashed lines in Fig. 7). In our previous study, copper(II)hexafluoroacetylacetonate was also used as a precursor, but without the addition of a co-solvent. The lowering of activation energy observed in this

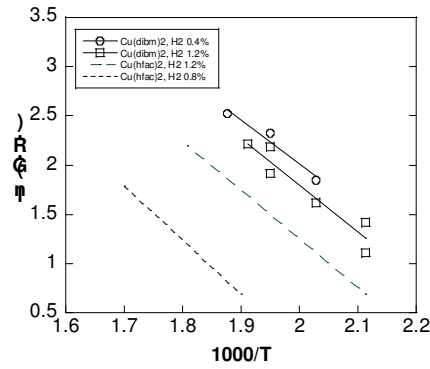


Figure 7. Temperature dependence of film growth rate between 200°C and 260°C, 10 MPa, 60 min, $\text{Cu}(\text{dibm})_2$ concentration of 57 ppm, and H_2 concentrations of 0.4 mol% and 1.2 mol%.

study is assumed to be the effect of the co-addition of acetone as a solvent.

Freestanding films obtained from a long-term deposition are shown in Figure 8. The deposition conditions were: 240°C, 10 MPa, 57 ppm $\text{Cu}(\text{dibm})_2$, 1.2 mol% H_2 ; the left film was deposited over 4 hrs and the right over 8 hrs. The copper film deposited on the heat block and later removed was shiny, showed good uniformity, and was approx. 1.6-2.7 μm in thickness. The overall film was about 40 mm in length and 8 mm in width.

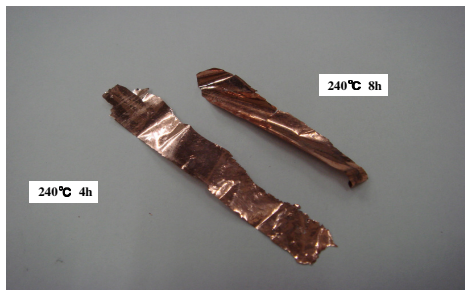


Figure 8. Freestanding thick Cu films obtained from a long-term deposition of 4-8 hrs. 40 mm length x 8 mm width x 1.6-2.7 μm thickness.

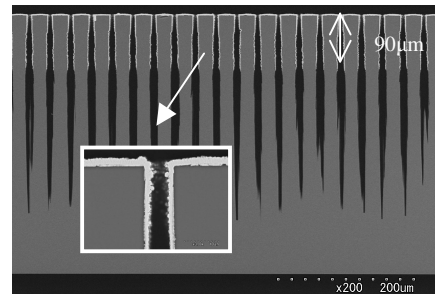


Figure 9. A cross-sectional SEM image of Cu filling in vias with 10 μm dia. x 90 μm depth. The inset shows a close-up of a via.

Figure 9 displays a cross-sectional SEM image of Cu films deposited inside vias 10 μm in diameter and 90 μm in depth. The inset shows a close-up of a via with 2 μm of film (in thickness) deposited at the top, but the film thickness deposited on the wall of the via decreased as depth increased. Deposition was carried out under the following conditions: 240°C, 8 hrs, 10 MPa, 57 ppm $\text{Cu}(\text{dibm})_2$, and 1.2 mol% H_2 . Adjusting the deposition parameters to optimum

values caused the growth rate to increase even more, and thus the excellent filling of gaps in vias several μm in diameter now appears to be a possibility.

4 CONCLUSION

We studied the deposition characteristics of Cu film from scCO_2 using $\text{Cu}(\text{dibm})_2$ dissolved in acetone and long-term deposition. Our flow-type deposition processor was designed to enable the independent control of deposition parameters and long-term deposition, wherein a precursor dissolved in acetone is continuously supplied to a reactor chamber. Results of our study indicate that a long-term deposition was successfully completed and that a thick film was obtained. Through the optimization of the deposition parameters, we expect to enable further increases in the growth rate and the creation of thicker films. We believe that it will be possible to enable the formation of MEMS-based thru vias of 3D IC using our processor.

5 REFERENCES

- [1] M. Matsubara and E. Kondoh, 39th Autumn Meeting of Society of Chemical Engineering Japan, (Sep. 2007)
- [2] E. Kondoh and J. Fukuda, J. Supercritical Fluids, in printing (accepted manuscript became available online on 27 December 2007).