Electroless plating of copper at a low pH level

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A new process for electroless copper plating at a pH level of ≤9 is described. The process uses amine borane reducing agents and ligands based on neutral tetradentate nitrogen donors. The use of a variety of buffer systems is demonstrated. Electroless bath performance over a wide range of conditions is presented. The quality of the plated copper is comparable to that obtained by currently used electroless plating processes, and has a resistivity of about 1.8–2 μΩ-cm, depending on bath composition and process parameters. Use of the process is illustrated for forming conductors and filling via holes having submicron minimum dimensions.

Introduction

Electroless copper deposition is widely used in electronic packaging for high-aspect-ratio through-hole plating and for selective metal deposition [1–10]. The electroless copper plating process in current use is based on EDTA or tartarate as the complexant with formaldehyde as the reducing agent, and on the well-known Fehling's-type solution reduction reaction. The literature regarding electroless copper plating describes variations of this approach and generally involves the use of different additives to achieve desirable metallurgical properties for electronic applications [11–15]. In addition, the formaldehyde-based process operates at pH levels above 11.5. In view of the environmental and material compatibility issues associated with the current process [16–18], there is a need to develop more versatile chemical systems for electroless plating, with special emphasis on achieving wide operating conditions, efficient process control, and effective bath regeneration to improve manufacturing efficiency and obviate environmental concerns and waste disposal problems. In this paper we describe the development of an electroless copper process which is specifically useful at pH levels of ≤9 [19]. Process performance and some applications are also illustrated.

Experimental methods

The chemicals used to develop the process were reagent grade. Copper sulfate and triethanolamine were obtained from Aldrich, and the complexing agents were obtained from Strem and from Fluka. Dimethylamine borane was obtained from Fluka. Plating rates were determined by weight gain measurements on copper coupons with and without palladium seeding. Rates reported were averaged over a plating time of one hour or more to avoid the

effects of variations in initiation times. Initial optimizations were carried out with bath volumes of 1 liter. Subsequently bath performance was evaluated at 5-liter and 60-liter volumes. Virgin polypropylene without any filler materials or pyrex glass was found to be the material most compatible with the bath components. Bath replenishments were accomplished by measurements of the concentrations of copper ions, the reducing agent, and the additive. Specific procedures were established and implemented as described later in this paper. The process was designed to eliminate frequent adjustments in pH level. In a typical experiment, the pH level is adjusted after about eight hours of plating. Bath temperature is controlled to within ±1°C by means of a water thermostat, and air is bubbled into the bath to improve its long-term stability, as is generally the practice in electroless copper plating systems. The increased oxygen level due to the bubbling prevents the growth of small copper nuclei formed as a result of homogeneous reactions triggered by dust, and prevents the extraneous deposition of copper in crevices in the plating tank and part holders. Four-probe room-temperature resistivity measurements were carried out on copper layers plated on Si wafers containing vacuum-deposited Cr (20 nm) and Cu (50 nm) seed layers. The concentrations in the bath of copper and the additive 2,2′ dipyridyl were analyzed by optical spectroscopy. The instruments used to obtain uv-visible spectra were a Perkin Elmer Model 330 spectrometer and a Brinkmann fiber optic colorimeter, the latter for on-line measurements. The dimethylamine borane concentration was measured by iodimetry. Corrections for copper interference were made by means of a blank titration with no dimethylamine borane present in the bath. Potentiometric titration for dimethylamine borane was performed with an Orion titroprocessor.

- *Bath composition*

The major components of an electroless plating solution are the metal ions in a suitable oxidation state, the complexing agents, a reducing agent, and a buffer. The solution also contains additives and surfactants in order to achieve the desired quality of the deposited metal layer. In the case of the conventional electroless copper plating process, the reducing agent is formaldehyde. The actual reducing specie in this plating process has been shown to be the methylene glycolate anion formed by reaction of formaldehyde with the hydroxyl ions [20]. The formation of the methylene glycolate anion is favored at high pH levels; reasonable plating rates for use in the industry are obtained at pH ≥ 12. With the increasing use of alkali-sensitive dielectrics such as polyimides and aluminum nitride in electronic packaging and experimental VLSI interconnection structures, the use of conventional additive processes for metallization has become less attractive. Operation at lower pH levels requires the use of other reducing agents, such as hypophosphite and dimethylamine borane. Earlier attempts to use hypophosphite for depositing thick layers of high-purity copper of low resistivity were largely unsuccessful [21–24]. Amine boranes are strong reducing agents and are stable in neutral and alkaline media. The pH range between 7 and 10 provides the optimal environment, in which most alkali-sensitive dielectrics are not significantly affected. Efforts were then made to develop an electroless copper plating process in the pH range of 7–10. Amine boranes are useful reducing agents in this pH range, and since the Cu–B phase is generally less favorable thermodynamically, deposition of high-purity copper appears feasible. Boranes with different amine moieties such as t-butylamine, morpholine, and dimethylamine were found to be suitable. Dimethylamine borane was used in most of the experiments because of its ready availability.

The electroless metal deposition reaction by amine boranes results in the generation of protons, and a pH change is expected as plating progresses. Thus, strong buffers are essential in order to provide a stable environment and to reduce the chances of homogeneous decomposition as a consequence of the pH decrease from the plating reaction and increased dissociation of copper complex. In the conventional process, EDTA serves as the chelating agent as well as the buffer, even though EDTA is a strong chelating agent but a weak buffer. As a result of the weak buffering action, frequent pH adjustment is necessary for stable bath operation. To avoid this problem, we decided to use different systems to satisfy the two needs. We chose strong buffering systems which are relatively poor complexants and strong chelating agents which are not efficient buffers. For example, when EDTA or triethanolamine was individually used both as a buffer and as a ligand at pH 9, poor bath stability led to homogeneous formation of metallic particles throughout the bath. When EDTA was used (strong complexant) with triethanolamine (excellent buffer, good complexant), marked improvements in stability were observed at pH 9. In this case, mixed ligand complexes of Cu with EDTA–triethanolamine are formed, and triethanolamine also acts as a good buffer at pH 9.

Strong complexing agents are also essential to keep the metal ion in solution at this pH level and to reduce the possibility of spontaneous homogeneous decomposition. After our initial studies with EDTA-based systems, we focused our attention on the multidentate nitrogen donors, which form strong complexes with copper. The nitrogen donor systems are versatile ligands for copper, and a large variety of these are available. Examples of multidentate nitrogen ligands capable of strongly complexing copper are shown in **Figure 1**. The electroless copper plating solutions were formulated with copper sulfate, a tetraaza ligand, and

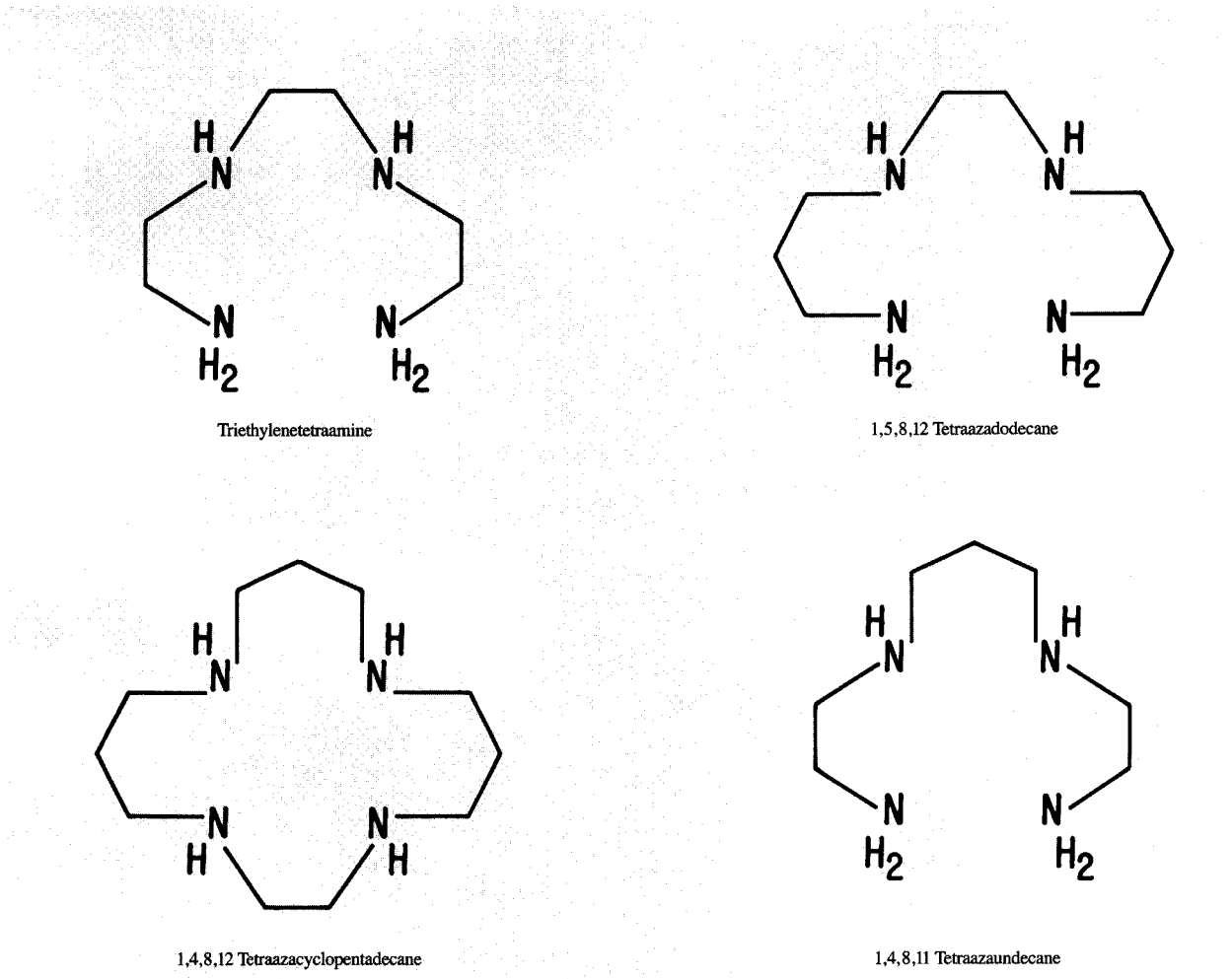

Figure 1

Examples of strong nitrogen donor complexants for Cu^{2+}.

a suitable buffer such as triethanolamine or substituted triethanolamine. The choice of the buffer was based on the pH of operation and, hence, the pK_a of the buffer. In general, the tetraaza ligand used in the present study complexed copper strongly, and no complexation by the buffers could be discerned from the visible spectra obtained.

Several different tetradendate nitrogen ligand systems were investigated. Triethylene tetramine and 1,5,9,13 tetraazatridecane were poor complexing agents for sustained stable electroless copper plating at pH levels of 7 to 10. Baths containing these systems were unstable, and homogeneous decomposition was observed. The complexing agents 1,4,8,11 tetraazaundecane and 1,5,8,12 tetraazadodecane proved to be suitable for stable electroless copper bath operation. The complexing ability from stability-constant data increased in the order 1,5,9,13 tetraazatridecane < triethylene tetramine < 1,5,8,12 tetraazadodecane < 1,4,8,11 tetraazaundecane [25]. Because of its commercial availability in large quantities and its low cost, 1,5,8,12 tetraazadodecane was chosen as the complexing agent for extensive study of low-pH electroless copper plating. The use of a strong multidentate ligand such as tetraazadodecane (a poor buffer at pH 9) along with triethanolamine (a strong buffer at pH 9) resulted in excellent bath stability. This approach of having two components play separate and independent roles permits the use of the same ligand system over a range of pH by simply using different buffer systems. For operation in the pH range between 8 and 10, we used triethanolamine

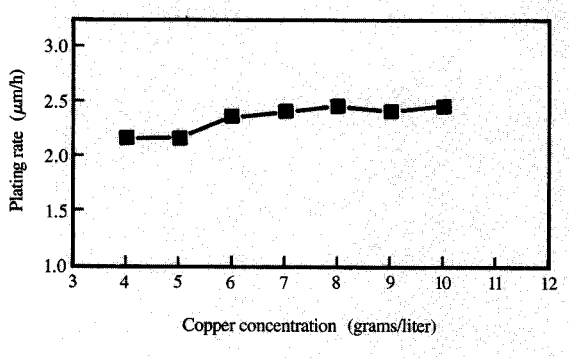

Figure 2

Plating rate at 65°C as a function of copper concentration, in a bath containing dipyridyl (100 ppm), tetraazadodecane (0.04 M), triethanolamine (0.3 M), and dimethylamine borane (0.067 M).

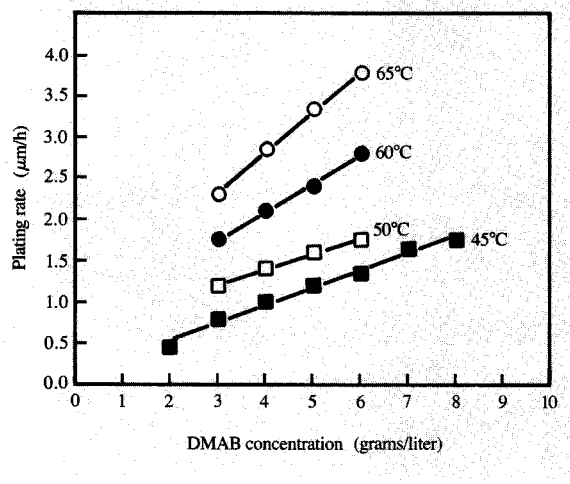

Figure 3

Plating rate as a function of dimethylamine borane, in a bath containing only phenanthroline (10 ppm) as an additive.

and borax buffers with no discernible difference in plating rate and quality. However, the use of triethanolamine was found to result in a lower fluctuation in pH level as plating progressed, in comparison to the borax buffer system, indicating a poor buffer capacity of the borax buffer.

Additives are essential for enhancing bath stability and improving the metallurgical quality of the plated copper. Accordingly, experiments were conducted with the diimine-based additives commonly used in the electroless copper formaldehyde system. The additive 2,2′ dipyridyl was found to be superior to 1,10 phenanthroline. The resistivity of a 2-μm-thick electroless plated copper film was found to be 2.3–2.6 $\mu\Omega$-cm when 1,10 phenanthroline was used at a concentration of 10 to 100 ppm. The resistivity was 1.83–1.95 $\mu\Omega$-cm when 2,2′ dipyridyl was used at a concentration of 30 to 300 ppm. In general, a hydrophobic, less soluble additive is more likely to adsorb on a substrate and affect the metallurgical properties of the deposit. We have found that 4,4′ dimethyl 2,2′ dipyridyl, which has a lower solubility, is as effective as 2,2′ dipyridyl at the lower concentration range of 10–30 ppm in providing low-resistivity copper. The addition of a soluble hydrophilic system such as 4,4′ dicarboxy 2,2′ dipyridyl, with carboxylic acid moiety in the dipyridyl ring, resulted, in all concentrations, in the production of dark, powdery deposits. The long-term bath stability at a load factor of 100 cm^2 per liter depended on the additives used, in the following order: 1,10 phenanthroline < 2,2′ dipyridyl < 4,4′ dimethyl − 2,2′ dipyridyl.

On the basis of the above results, it was concluded that a preferred electroless copper bath for scale-up and long-term operation should be based on the following composition: copper sulfate (0.032 M), 1,5,8,12 tetraazadodecane (0.04 M), triethanolamine (0.3 M), and dimethylamine borane (0.067 M). The additive of choice is 2,2′ dipyridyl in a concentration range of 30–300 ppm. The pH of the bath should be adjusted to 9 at 20°C. The rates of deposition in such a bath as a function of copper, dimethylamine borane, and dipyridyl concentrations are shown in **Figures 2**, **3**, and **4**. In general, deposition rates of about 2–3 μm per hour are observed with stable bath operation for several days. The plating rate increases with temperature; a plating temperature of 65°C is recommended for most applications. The plating rate drops with increasing dipyridyl concentration, but above 150 ppm there is no discernible effect on plating rate and deposit quality. The plating rate is essentially independent of copper concentration in the range examined.

- *Process monitoring and control*

The electroless plating process can be visualized as a homogeneous redox system in chemical equilibrium. The electroless deposition system is designed in such a manner that heterogeneous electron transfer (plating) is favored over homogeneous electron transfer (bath decomposition). The concentrations of the bath components and operating conditions are carefully optimized initially to enhance the plating process and inhibit homogeneous decomposition. However, there is always a finite possibility that homogeneous decomposition may occur. Variations in process parameters can disturb this dynamic solution equilibrium and trigger homogeneous decomposition.

As the plating proceeds, concentrations of the metal ions, the reducing agents, and the additives decrease, and concentrations of the reaction products increase, eventually leading to bath instability. Thus, even a well-designed bath has a finite lifetime because of the depletion of reactants and the accumulation of products arising from the disturbance of the homogeneous redox equilibrium. The bath life can be extended considerably by replenishing the critical components and keeping the composition as close to the initial concentration as possible.

Thus, for successful long-term operation, it is essential to establish a monitoring and control strategy for the critical components of the bath. This is especially true of the additives, since variations in their concentrations affect bath stability, metallurgical quality, and process performance. During the very early stages of the present effort, we decided to investigate and select bath components that are amenable to monitoring. The major components requiring monitoring were the copper ions, the reducing agent, and the additive 2,2′ dipyridyl. While it was found that many thio compounds such as 3,3′ dithiodipropionic acid and 2,2′ thiodiglycollic acid performed as well in preliminary experiments, bath optimization was restricted to 2,2′ dipyridyl or its derivatives as additives because of the relative ease of monitoring. Copper concentration was monitored by visible spectroscopy. Dimethylamine borane concentration was monitored by titration with potassium iodate using potentiometric detection. A correction procedure was necessary to eliminate inaccuracies due to the interference from Cu ions. The 2,2′ dipyridyl concentration was monitored by uv spectroscopy after the addition of dilute sulfuric acid to the bath sample. The uv absorbance as a function of 2,2′ dipyridyl concentration was linear in the 250–330-nm range. Since hydrolysis of dimethylamine borane was kinetically slower than copper decomplexation, precipitation of copper particles occurred during acidification. The dimethylamine borane was oxidized by adding ammonium persulfate in sulfuric acid to avoid copper reduction and complications from the presence of copper particles.

The long-term performance of the process was evaluated in 5-liter and 60-liter volumes. Copper foils were plated for about 7–8 hours to simulate high-throughput conditions. The surface-to-volume ratio was 100 cm^2 per liter. The Cu concentration was monitored continuously, and Cu was replenished as required by an *in situ* fiber optic monitoring and control system developed in our laboratories. The absorbance vs. concentration of copper ions was linear in the visible region at 570 nm. By using a mnemonic developed from earlier experiments, dimethylamine borane was replenished in relation to the amount of copper plated. Thus, for every mole of copper ions replenished, two moles of dimethylamine borane was added. This

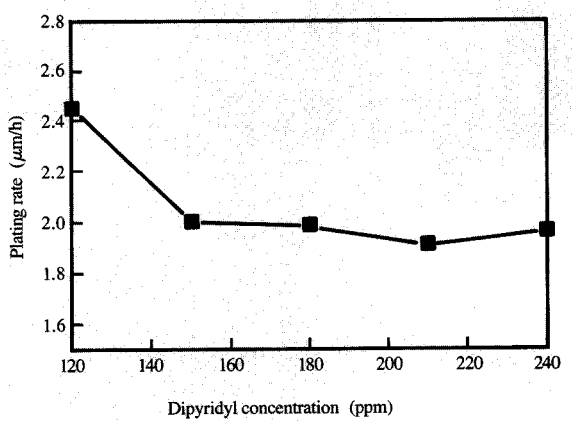

Figure 4

Effect of dipyridyl concentration on plating rate at 65°C, in a bath containing copper sulfate (0.032 M), tetraazadodecane (0.04 M), triethanolamine (0.3 M), and dimethylamine borane (0.067 M).

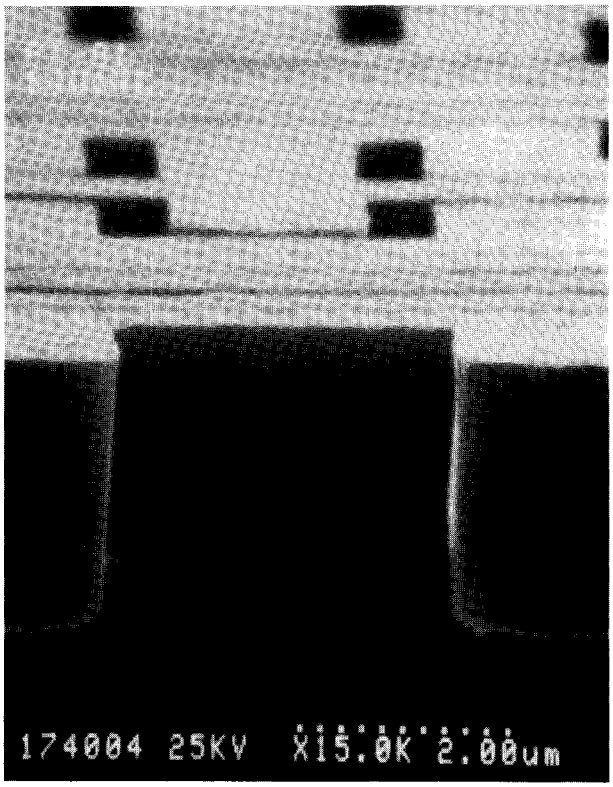

Figure 5

Scanning electron micrograph of an interconnection structure having submicron minimum dimensions, after removal of pattern-defining polyimide layer (by reactive ion etching).

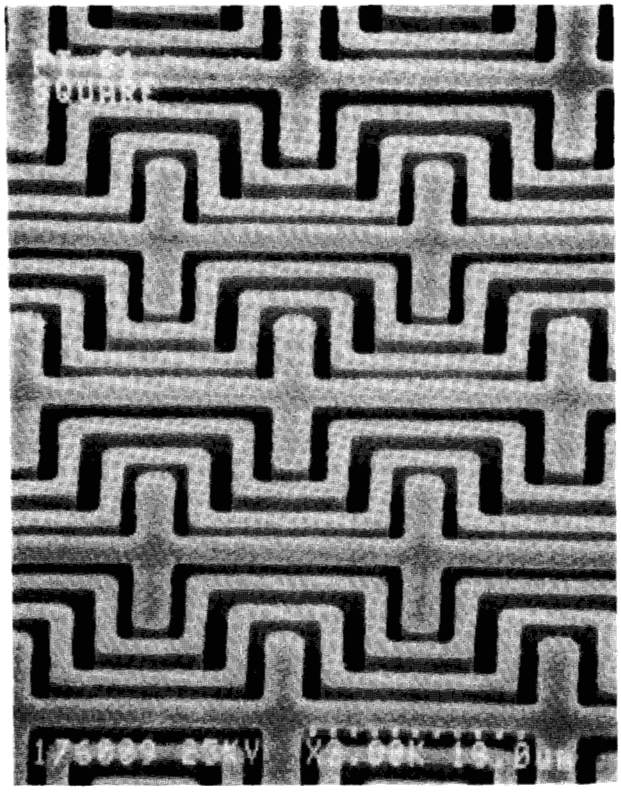

Figure 6

Scanning electron micrograph of a structure similar to that shown in Figure 5.

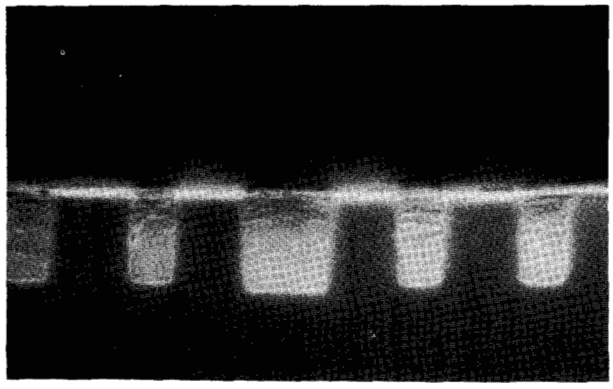

Figure 7

Scanning electron micrograph of polyimide trenches (0.7 μm wide, 1.9 μm deep) filled using electroless copper plating (aspect ratio of 2.7).

relationship was empirically determined in long-term experiments with a 5-liter bath. The concentration was also verified by analysis every four hours of operation. The additive concentration was kept within 300 ± 20 ppm by periodic analysis. Because of the efficient buffering action, rapid fluctuations in pH were not observed. In a typical experiment, a decrease of 0.2 units of pH was observed for every 0.25 turnover in Cu concentration. Bath pH was retained within ±0.2 units with sodium hydroxide. For sodium-free operation, tetra alkyl ammonium hydroxide or the ligand tetraazadodecane was used. With the implementation of this process control strategy, the bath could be operated for several weeks, yielding up to eight turnovers in copper concentration and the formation of good-quality deposits.

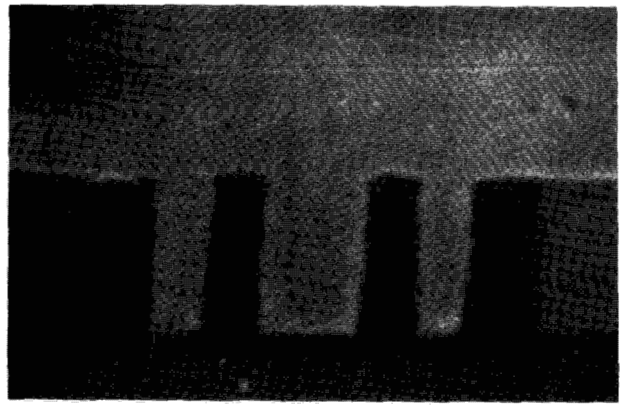

Figure 8

Scanning electron micrograph of polyimide trenches (0.7 μm wide, 2.8 μm deep) filled using electroless copper plating (aspect ratio of 4).

Potential application to microelectronics

The advantages of the combined use in electronic interconnection of metallic conductors with low resistivity and insulators with low dielectric constants are well recognized [26]. Because of the low capital investment and operating costs and the relatively high throughput associated with electroless plating, it seemed appropriate to explore the feasibility of using the process described here for forming conductors and filling via holes in microelectronic structures. Illustratively, **Figures 5–8** show scanning electron micrographs obtained using the process. Excellent via-hole filling at submicron dimensions (700 nm) up to an aspect ratio of 4 has been achieved, as indicated in Figures 7 and 8.

Summary

A new electroless copper bath based on the use of multidentate nitrogen donor ligands for copper ions in solution has been demonstrated. Amine borane reducing agents permit its operation at a pH level of ≤9. It is a potential replacement for the conventional formaldehyde-

based electroless copper plating bath, and has been used to obtain high-quality copper deposits. The use of the bath to form interconnection structures having submicron minimum dimensions has been illustrated. Process control and scale-up strategies have been demonstrated.

Acknowledgments

We wish to thank G. Wandy, R. Knarr, D. Canaperi, and D. Rath for technical assistance, P. J. Bailey for the scanning electron micrographs, and K. Ruffing for metallurgical studies. We gratefully acknowledge the support provided by S. Greco, K. Srikrishnan, A. Sugerman, C. Uzoh, S. Mathad, C. Jahnes, and M. Russak in the fabrication of the submicron interconnection structures.

References

1. W. A. Alpaugh and J. M. McCreary, *Insulation/Circuits* **24**, 27 (1978).
2. J. R. Bupp, L. N. Chellis, R. E. Ruane, and J. P. Wiley, *IBM J. Res. Develop.* **26**, 306 (1982).
3. C. R. Shipley, *Plating & Surf. Fin.* **71**, 92 (1984).
4. M. Baker-Pole, *Circuit World* **10**, 8 (1984).
5. R. Keeler, *Electron. Pkg. Prod. (U.S.A)* **30**, 70 (1990).
6. J. W. Balde, *J. Electron. Mater.* **18**, 221 (1989).
7. T. G. Tessier, I. Turlik, G. M. Adena, D. Sivan, E. K. Yung, and M. J. Berry, *Proceedings of the 1989 International Electronics Packaging Symposium*, International Electronics Packaging Society, San Diego, p. 248.
8. T. Ohsaki, T. Yasuda, S. Yamaguchi, and T. Kon, *Proceedings of the IEEE International Electronic Manufacturing Technology Symposium*, Anaheim, 1987, p. 178.
9. S. S. Wong, J. S. Cho, H. K. Kang, and C. H. Ting, *Proceedings of the Electronic Packaging Materials Science Symposium*, Materials Research Society, Pittsburgh, 1991, p. 347.
10. Y. Shacham Diamond, A. Dedhia, D. Hoffstetter, and W. G. Oldham, *Proceedings of the 8th International IEEE VLSI Multilevel Interconnection Conference*, Santa Clara, CA, 1991, p. 109.
11. F. Pearlstein, "Electroless Copper Plating," *Modern Electroplating*, F. A. Lowenheim, Ed., John Wiley & Sons, Inc., New York, 1974, pp. 474–476.
12. L. N. Schonberg, *J. Electrochem. Soc.* **118**, 1571 (1971).
13. F. Pearlstein, U.S. Patent 3,222,195, 1965.
14. R. M. Lukes, U.S. Patent 2,996,408, 1961.
15. F. Pearlstein and R. F. Weightman, *Plating* **60**, 474 (1973).
16. R. Jagannathan, M. Krishnan, and G. Wandy, U.S. Patent 4,818,286, 1989.
17. J. Darken, Patentschrift (Switzerland) CH 671037A, 1989.
18. H. Honma, M. Komatsu, and T. Fujinami, *Hyomen Gijutsu* **42**, 914 (1991).
19. R. Jagannathan, R. F. Knarr, M. Krishnan, and G. P. Wandy, U.S. Patent 5,059,243, 1991.
20. T. M. Tam, *J. Electrochem. Soc.* **132**, 806 (1985).
21. D. R. Ferrier, U.S. Patent 4,325,990, 1982.
22. P. E. Kukanis, J. J. Grunwald, D. R. Ferrier, and D. A. Sawoska, U.S. Patent 4,209,331, 1980.
23. A. Hung, *Plating & Surf. Fin.* **75**, 62 (1988).
24. A. Hung, *Plating & Surf. Fin.* **75**, 74 (1988).
25. R. Barbucci, L. Fabrizzi, P. Paoletti, and A. Vacca, *J. Chem. Soc. Dalton Trans.*, p. 1763 (1973).
26. R. J. Jenson, J. P. Cummings, and H. Vora, *IEEE Trans. Components, Hybrids, Manuf. Technol.* **CHMT-7**, 384 (1984).

Received February 26, 1992; accepted for publication December 9, 1992

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