A-2-2 (Invited)

Copper Electrodeposition: Principles and Recent Progress

Jonathan Reid

Novellus Systems, Portland Technology Center, Wilsonville, OR 97070 Phone: +1-503-685-8353; Fax: +1-503-685-8399; E-mail: jon.reid@novellus.com

1. Introduction

The capability of copper electroplating to produce void free filling of sub-micron high aspect ratio features has made it the process of choice for copper interconnect formation. Several aspects of copper electrodepositon including the basic electrochemistry and electrochemical kinetics, mass transport phenomona, potential gradients in solution, electrolyte composition, and the influence of various organic additives have been studied for over 50 years. Much of this basic understanding can be applied to development of integrated circuit (IC) copper electroplating processes. Other aspects of copper elecroplating are unique to IC applications. These include the interactions of very thin seed layers with the electroplating process, the basic "bottom-up" filling mechanism needed for seam free filling, and the metallurgical properties of sub-micron scale deposits. Copper electroplating fundamentals relevant to IC fabrication and recent developments unique to IC applications are discussed in this paper.

2. Seed layer impacts

Properties of damascene features determined by the PVD seed layer which impact plating process performance include feature shape, continuity or agglomeration of the seed, and degree of seed oxidation. While the plating process can achieve highly accelerated bottom-up filling a feature shape which is very necked at the opening is difficult to fill because it will plate shut during owing to a finite depositon rate on the sidewall (1). An example is shown in Figure 1.

When PVD films become very thin within high aspect ratio features there is a tendency to form discontinuous or agglomerated Cu layers (1,2). When this takes place the plating process does not initiate at a uniform rate on all surfaces. Typically, this results in accelerated growth beginning above the base of high aspect ratio features and leaves large voids form at the base as shown in Figure 2a. When growth accelerated growth begins at the base of the feature full fill is achieved as shown in Fig 2b.

Finally, the degree of oxidation of the seed layer can play a role in both filling and general deposit quality formed during copper deposition. While some degree of oxidation may enhance wetting in acidic solutions owing to the high solubility of oxide in the acid, excessive oxidation (> \sim 20A) can both entirely consume metallic seed within high aspec ratio features and result in non-uniform wetting on the wafer surface.

3. Process chemistry

Copper electrolating baths are normally formulated using a highly stable base electrolyte solution containing copper sulfate and sulfuric acid. The basic kinetics and solution properties of these solutions have been studied for over 50 years and are well understood. In wafer applications, the sole important criteria for copper sulfate concentrations is the avoidance of depletion of cupric ion within high aspect ratio features during filling processes. Typical cupric ion concentrations in use today range from 17.5 to about 60 grams/liter. Sulfuric acid is usually added to the plating electrolyte (45 - 325 g/L) to increase solution conductivity and improve wetting or oxide dissolution on seed surfaces. In general, more conductive solutions result in a more uniform and cell geometry independent plating thickness distribution, while low acid electrolytes result in a system with less dependence on seed layer resistivity. Seed layer and cell geometry related uniformity dependences are inversely and linearly related to conductivity allowing a wide range of modulation within the 45 to 300 g/L acid concentration range while still maintaining acidity adequate to dissolve oxides and wet adequately.

Organic additives added to copper electroplating baths fall into three categries. Accelerators are mercapto containing species which locally accelerate current at a given voltage where they adsorb. Accelerators are usually present in the plating bath in the concentration range of 1 to 25 parts per million. Carriers are polymers such as polyethylene glycol which tend to form a current suppressing film on the entire wafer surface, especialy in the presence of chloride ion (which can be considered as a co-suppressor). Carriers are usually present in the plating bath at high concentrations (200-2000 ppm) so that their concentration at the interface is not strongly dependent on their rate of mass transfer or diffusion to the surface. Levelers are are a second class of current suppressing molecules which are usually added to the plating bath at a low concentration so that leveler concentration at the interface is mass transfer dependent. In this way, isolated mass transfer locations such as the inside of a via are less suppressed, while protruding surfaces or corners to which mass transfer by diffusion or migration is more efficient are more suppressed.

Bottom-up fill takes place when preferential adsorption of accelerating additives takes place near the base of features while adsorption of suppresing additives takes place in the field. It can easily be shown that voltage drops between the field and the base of any feature will not impact current flow. As shown in Figure 4, it is thus possible to evaluate possible filling acceleration of a plating bath by comparing current – voltage response curves for a complete additive system

(matching the surface of the wafer) with the response in the presence of accelerating additives only (matching possible growth rate at the feature base). In the case shown the fill acceleration based on I-E characteristics at the base of the feature is about 7 times the field frowth rate.

It has been shown that highly accelerated bottom-up fill can be achieved using various accelerator/polymer suppressor systems with no leveler present. Typical fill evolution in a leveler-free system is shown if Figure 5. The mechanism of fill in this system relies on accumulation of accelerating moluecules near the feature base, while the wafer surface remains supressed by polymer adsorption. When levelers are added to these systems fill can either be enhanced by additional suppression of the surface by the leveler adsorption or degraded if leveler diffuses into the feature in adequate concentrations to disrupt accelerated fill.

4. Conclusion

Successful bottom-up filling of IC feaures by electroplating relies on both a high quality copper seed layer film and proper selection of accelerating and suppressing organic additives.

5. Acknowledgement

The prepariation of various seeded structures by the Novellus Metals organization is appreciated.

6. References

- Reid, J., Bhaskaran, V., Contolini, R., Patton, E., Jackson, B., Broadbent, E., Walsh, T., Mayer, S., Martin, J., Morrissey, D., Schetty, R., Menard, S., Proc. INTC, 1999, pp 284-286, May 24-26, 1999.
- Reid, J., Mayer, S., Advanced Metallization Conference Proceedings, II.1, Sept. 28-30, 1999.



Figure 1 - Seed profile of a trench feature showing (a) pinch off near the opening and fill result following DC plating, and (b) a wide opening and fill result following DC plating.



Figure 2 - a.) Cross sectional via images showing (left to right) agglomerated seed coverage, metal profile following partial fill by electroplating, and final fill result following electroplating. b.) Similar fill sequence on continuous seed.



Figure 3. Effect of oxidation of copper on via fill. a.) Ambient oxidation, b.) 50 A cuprous oxide, c.) 100A cuprous oxide.



Figure 4. Current vs potential curves for copper deposition from an electrolyte containing a complete additive system and from an electrolyte containing accelerating additive only.



Figure 5. Partial fill progression during bottom-up filling by copper electrodeposition.