

Tech Talk

Fine Lines in High Yield (Part CLV)

Advances in Copper Plating (Part B)

Karl H. Dietz (for CircuiTree Magazine, August, 2008)



Karl Dietz is the development manager at DuPont's Electronic Materials Laboratory, Research Triangle Park, NC. His responsibilities include application studies for printed circuit materials. Karl has 35 years of experience in a variety of R&D, manufacturing and quality control functions and holds a PhD. in organic chemistry from the University of Frankfurt, Germany. If you would like to participate in the exchange or if you have any questions, Karl Dietz can be reached at 919-248-5248, fax: (919) 248-5132, or via e-mail <Karl.h.dietz@usa.dupont.com>.

Last month's Tech Talk covered several advances in copper plating, including environmental advances, and new applications such as copper pillar plating on wafers. But the focus was on "bottom-up" via fill processes for plating microvias shut and the metallization of TSVs (through silicon vias).

The mechanism of bottom-up plating into blind vias was discussed for additive systems that feature accelerators, inhibitors, chloride, and optionally leveler. Additional studies on filling microvias and plated through-holes (PTH) with plated copper, using other additive systems, and a method to minimize the degradation of additives is being covered in this article.


Dow and Chen (Ref. 1) point out that a copper plating bath containing carrier, brightener and level in a composition that was optimized for blind via "bottom-up" filling gave unsatisfactory results with plated through-holes. They developed a new composition for DC plating that gave good results with both blind vias and through-holes. The new composition was not disclosed in the article.

More recently, Dow, Yen and Chen (Ref. 2) introduced a novel plating bath composition that was optimized for Through-hole filling. It does not contain a carrier such as polyethylene glycol nor does it contain an accelerator. Instead, it contains two strong inhibitors, one quaternary amine and one amide that both rely on chloride ions to be attached to the copper surface, in the case of the amide in form of a protonated species. The authors point out that the adsorption of chloride to the copper surface is strongly potential dependent and this potential dependency in turn is chloride concentration dependent. Given the typical potential profile on the copper surface and in the through-hole, more chloride is adsorbed on the surface and near the through-hole entrances than near the center of the through-hole. Thus, more inhibitor is anchored where more chloride is adsorbed and plating is more inhibited in these areas. Consequently, the highest plating rate is seen near the center of the hole. Strong forced bath convection will level the concentration gradient of the adsorbed inhibitors, equalizing plating rates and leading to plating voids in the through-hole.

H. Dyar and others (Ref. 3) introduced a novel low cost blind via metallization/planarization process that uses an electrically-mediated (pulse plating) technique. The only additives in the bath are polyethylene glycol (PEG) and chloride. The electrically-mediated waveform shows forward modulation, reverse modulation and off-time. Complete copper filling of the blind vias with only minimal surface plating is achieved by alternating uniform (conformal) copper deposition with non-uniform copper etching whereby more copper is etched on and near the surface than at the



The miracles of science™



bottom of the blind via. This is achieved by creating different types of diffusion layers during plating and etching cycles. During plating, the hydrodynamic diffusion layer is thin relative to the surface profile in which case the diffusion layer follows the contours of the surface profile in uniform thickness. Since plating is diffusion limited, the plating is conformal, i.e. of uniform thickness. This thin, uniform diffusion layer is formed when a high cathodic peak current is employed for a relatively short time. During etching, a thicker diffusion layer is created which has a flat surface and therefore is thinner over the copper surface than over the microvia. Thus the etch rate during the anodic cycle is faster on the surface and near the opening of the microvia than it is at the bottom of the via. This thicker diffusion layer is achieved by employing a low anodic peak current and a relatively long on-time. The alternating plating and etch cycles result in completely filled blind vias with little surface copper.

Cheng-Ching Yeh, Wei-Ping Dow and others (Ref. 4) did a comprehensive study on the impact of different plating process parameters on microvia and through-hole filling, confirming many of the findings mentioned in last month's Tech Talk. The authors concluded that optimizing the microvia fill as well as through-hole filling is difficult since high copper/ low acid concentration favors the microvia fill process whereas low copper/high acid is the preferred condition for through-hole plating. Low current density plating gave better bottom-up filling performance, but to shorten the plating cycle, the current density was doubled in the second phase of the plating cycle, yielding a reasonable trade-off between productivity and microvia fill percentage. The effects of different additive components were studied but the discussion of the results describes the additive system only as a new type. It was found that when insoluble anodes were used, which is often the case in periodic reverse pulse plating, the consumption of additives increases greatly. A method to reduce this undesirable side-effect is described below (Ref. 5).

The insoluble anodes are typically made of titanium that is coated with mixed oxides. Oxygen is formed at the insoluble anodes during plating. This oxygen degrades (oxidizes) organic additives in acid copper plating baths. The organic additives are either cationic species or carry a positive charge due to protonation and therefore migrate to the negatively charged cathode. These additives also reach the anode because of bath agitation.

Menard and Wurm reported much reduced additive consumption with a modified anode. The basic idea was to make it more difficult for the additives to reach the anode by shielding the anode surface from the fluid movement due to agitation. The beneficial effect of reduced additive consumption has been observed for many years when anodes were "bagged" to prevent anode film particles from contaminating the bath. Menard and Wurm considered different shielding materials and constructions. They dismissed diaphragms and membranes because they can deteriorate with time and have a tendency to plug. First, a plastic grid was used as a shield. The grid had only very small contact points with the anode to preserve a large active anode surface area. The additives trapped between the grid and the anode degraded fast but additive replenishment due to agitation was much reduced so that additive consumption at the anode was also much reduced. When the plastic mesh was replaced by a non-active titanium mesh of similar configuration, a threefold further reduction in additive consumption was observed. This effect was explained by the fact that the metal shield, being in contact with the active anode, acquires the potential of the anode and thus repels the positively charged additives before they can get near the anode.

Another beneficial effect was observed. The shielding of the anodes resulted in a more uniform plating thickness across the panel. The rising oxygen bubbles act as a shield at the upper portion of the anode that reduces the current density in this region and leads to lower plated copper thickness in the upper portion of a panel. It was observed that in the presence of an anode shield, larger bubbles form. The total bubble cross section area is therefore much smaller with large bubbles for a given volume of gas and therefore the shielding effect near the top that reduces the current density is much reduced, leading to improved copper thickness uniformity.

References

1. A novel copper electroplating formula for laser-drilled micro via and through hole filling, Wei-Ping Dow and Hsiang-Hao Chen, Circuit World, 30/3 (2004) pgs. 33-36
2. Through Hole Filling by Copper Electroplating for SiP, Wei-Ping Dow, Ming-Yao Yen, and Hsiang-Hao Chen, CircuitTree Magazine, February 2007, pg. 13
3. A low cost semiconductor metallization/planarization Process, H. Dyar et al, Plating & Surface Finishing, March 2004, pg. 32
4. Micro via filling plating technology for IC substrate application, Cheng-Ching Yeh, Kuo-Hsing Lan, Wei-Ping Dow et al, Circuit World, 30/3 (2004), pgs. 26-32
5. Reduced additive consumption in base metal plating baths, S. Menard and J. Wurm, Circuit World, 30/3 (2004), pgs. 17-20



The miracles of science™