Formation of Sub-micron Scale Features Using Electroplated Copper

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The low electrical resistivity of copper which has long made it the material of choice in printed circuit board (PCB) applications has become a key factor enabling faster signal propagation in integrated circuit (IC) interconnects. Copper is now widely accepted as the interconnect material of choice in future integrated circuit device generations. A preferred method for interconnect feature formation utilizes copper electrodeposited onto thin copper layers previously formed by vapor deposition processes. Complete void-free filling of features which may be 5-10 times deeper than they are wide presents a significant challenge to traditional copper electroplating technology. In order to avoid pinch-off and subsequent void formation, an electrodeposition process must proceed at a rate near the base of features which is accelerated to several times the rate of deposition at the top of the feature. Such behavior has been achieved using copper sulfate/sulfuric acid plating solutions in which the rate of deposition is controlled as a function of geometric location by selective adsorption of organic molecules. This paper describes types of organic molecules with catalytic and inhibitory effects on the deposition process which may be added at specific concentrations to electroplating solutions to enable filling of 0.12 micron width, 9:1 aspect ratio features. The effect on filling of various factors, including organic and cupric ion concentrations, will be discussed and mechanisms leading to accelerated bottom-up filling will be described.

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Introduction

Major semiconductor manufacturers are now at stages of the transition from Al to Cu on-chip interconnects varying from development activity to full manufacturing. Numerous press announcements and technical papers [1-3] demonstrate that the interest in copper interconnects is now widespread. Use of a dual-damascene process flow [4] allows construction of the multilevel Cu stack with potentially fewer steps and reduced costs as compared to conventional Al-based interconnects. A new process technology for damascene interconnect fabrication is the electrodeposition of Cu for feature fill. This process is unique among copper deposition methods because it allows filling of high AR features from the bottom up, avoiding the introduction of a center seam or void.

Existing process chemistries developed for printed circuit board (PCB) applications are providing sufficient capability to fill sub-0.25 µm generation integrated circuit features. PCB chemistries were developed to achieve high copper ductility and a uniform thickness distribution across large geometric areas and between the board surface and within high aspect ratio features. These requirements differ distinctly from the IC application which requires a sharply accelerated plating rate within sub-micron IC features in order to achieve void-free fill. While the early success of the PCB chemistries is related to the chemistry properties which improve thickness distribution, the early success can could also be considered coincidental.

Many IC manufacturers are implementing copper at smaller device dimensions where use of these PCB process chemistries do not provide void-free filling. The extendibility requirement for filling smaller geometries has driven extensive development of the copper plating and seed layer deposition processes. As a result, improved seed layer integrity, modifications of plating current waveforms, and new plating process chemistries have led to filling improvements. The success of copper plating to fill high AR features is built upon the achievement of rapidly accelerated Cu deposition at the feature base relative to the field deposition rate. To date, the bottom-up fill process has been described in the literature as being driven primarily by the establishment of a diffusion gradient of suppressing polymers [5]. The effect of leveling additives which may reduce the copper growth rate at the entrance to features has also been widely discussed [6,7]. In this paper, these fill mechanisms, as well as others suggested by the effect of process parameters on fill performance (8), are discussed.

Feature geometry can play a key role in determining the maximum aspect ratio of a feature which can be filled using a given plating chemistry. This is a reflection of the fact that a feature with a narrow and necked opening will tend to close and entrap a void (called a center void) owing to a small but significant rate of deposition at the neck (3). A feature with a generous opening relative to internal dimensions allows for more time before close-off during which bottom-up fill can be established and provide complete filling. Typical examples of combined feature and seed profiles that can produce either voids or complete filling in a single bottom-up fill chemistry are shown in Figures 1a and 1b, respectively.

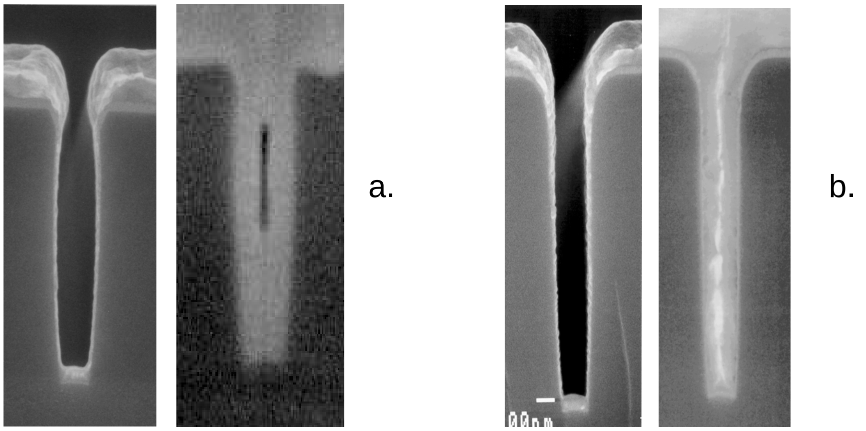


Figure 1 - Seed profile of a trench feature showing (a) pinch off near the opening and fill result following DC plating, and (b) a wide opening and fill result following DC plating.

All electroplating processes require an electrically conductive surface film (seed) to promote nucleation and growth. The seed surface must also be largely free of oxides for efficient charge transfer to begin. PVD copper seed films with thin (10-20 Angstrom), acid soluble oxide layers easily meet this criteria for damascene plating. Existing PVD processes can yield a variety of coverage profiles inside high AR features (Figs. 2 and 3), some of which are discontinuous or exhibit significant agglomeration of Cu material. With a continuous seed layer, plating readily initiates on all surfaces, thereby allowing subsequent bottom-up fill as shown in Figure 2. In contrast, plating onto agglomerated or discontinuous seeds can result in voids near the base which develop when nucleation and plated growth fails on the lower sidewalls or base of the vias. For the seed shown in Figure 3, both a failure to initiate plating and evidence of seed dissolution near the via base lead to the large void at the feature base (bottom void) following plating. A detailed description of the factors related to bottom void formation is given elsewhere.[9].

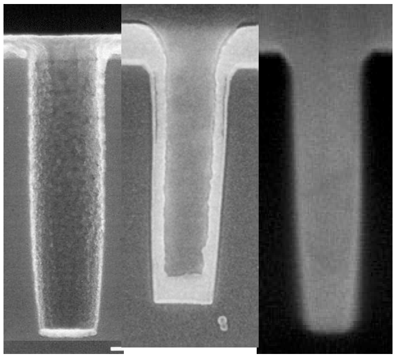


Figure 2 - Cross sectional via images showing (left to right) smooth seed coverage only, metal profile following partial fill by electroplating, and complete fill following electroplating.

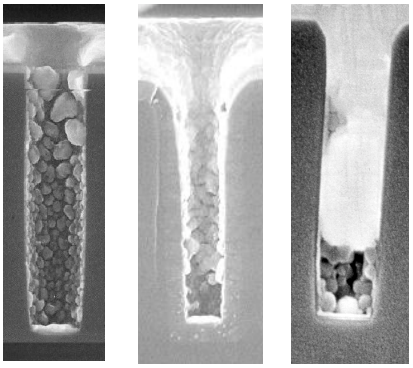


Figure 3 - Cross sectional via images showing (left to right) agglomerated seed coverage, metal profile following partial fill by electroplating, and final fill result following electroplating.

Electroplating methods have been proposed [3,10] which yield some degree of initially conformal deposition to join together isolated agglomerations of seed material, thus allowing subsequent bottom-up fill on a continuous conductive surface. The success of these methods suggests that an initial lack of metallic copper coverage near the via base contributes directly to fill initiation problems. Methods such as these facilitate initial plating on poor seed layers at the expense of increasing the aspect ratio (through conformal deposition) of the feature which must eventually be filled.

Rapid uniform wetting of the wafer surface and the inside of high aspect ratio vias by the plating solution is required for good filling performance. For a solution with good wetting properties (a low contact angle) on the copper surface it can be easily shown that capillary action should force solution several meters into sub-micron features. Contact angle of the plating solution on the wafer surface is a function of both the plating bath chemistry and the oxidation properties of the copper surface. Figure 4 shows contact angle as a function of position between the center and edge of the wafer. It is seen that the plating solution exhibits a much higher contact angle on some seeds and wafer positions than others. In general, oxidation and poor filling performance is associated with high contact angles, however, the nature of the relationship is not fully understood.

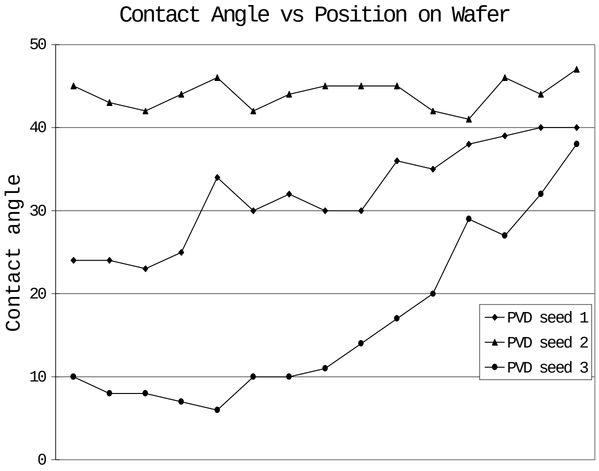


Figure 6 – Contact angle of plating solution on PVD seeds from wafer center (left) to edge (right).

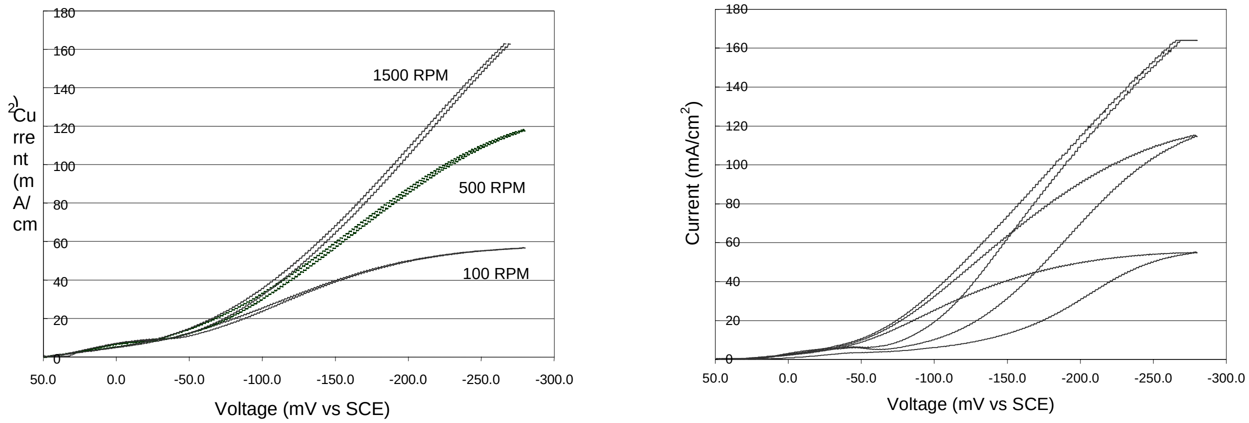
Process Chemistry

Additives present in acid copper plating solutions are responsible for the rapid plating rate within high AR features compared to the plating rate on the adjacent field. Such additives include polymers such as polyethylene glycol which suppress current at a given voltage, levelers such as cationic surfactants and dyes which suppress current at locations to which their mass transfer rate is most rapid, mercapto-containing molecules (brighteners or accelerators) which catalyze current (relative to the suppressors) where they adsorb, and chloride ion which is required for the suppression caused by polymers. To illustrate the effect of these additives, polarization curves measured at a Pt rotating disc electrode for a PCB-type plating solution (8) which is capable of marginal bottom-up fill behavior are shown in Figure 5. In Figure 5a, behavior of the copper electrolyte including sulfuric acid, copper sulfate, and chloride ion is shown as applied potential is swept from 0 to –280 mV. In this simple system, current increases in an approximately exponential manner as potential is increased, until mass transfer of copper to the interface begins to limit overall current (to a degree dependent on the mass transfer associated with electrode rotation). During filling, plating should be carried out at current and mass transfer conditions which avoid copper depletion at the wafer surface because this effect will be exaggerated slightly [10] in small features and can impact fill efficiency.

Figure 5b shows polarization behavior in the presence of a more current-accelerating (catalytic) additive mixture. The electrochemical behavior of this component is dominated by mercapto compounds, but current suppressing polymers are also present. With this additive component, it can be seen that current is not increased relative to the base electrolyte system. The catalytic effect is only observed when this component is used with more suppressing components. Mass transfer behavior in the presence of the catalytic component is similar to the base electrolyte (i.e. current proportionately

5a.) Copper Electrolyte with no Organics

5b.) Copper Electrolyte with 6 ml/L Catalyst additive



5c.) Copper Electrolyte with 3 ml/L Leveler/Suppressor

5d.) Electrolyte + 2 ml/L leveler/suppressor + 6 ml/L catalyst

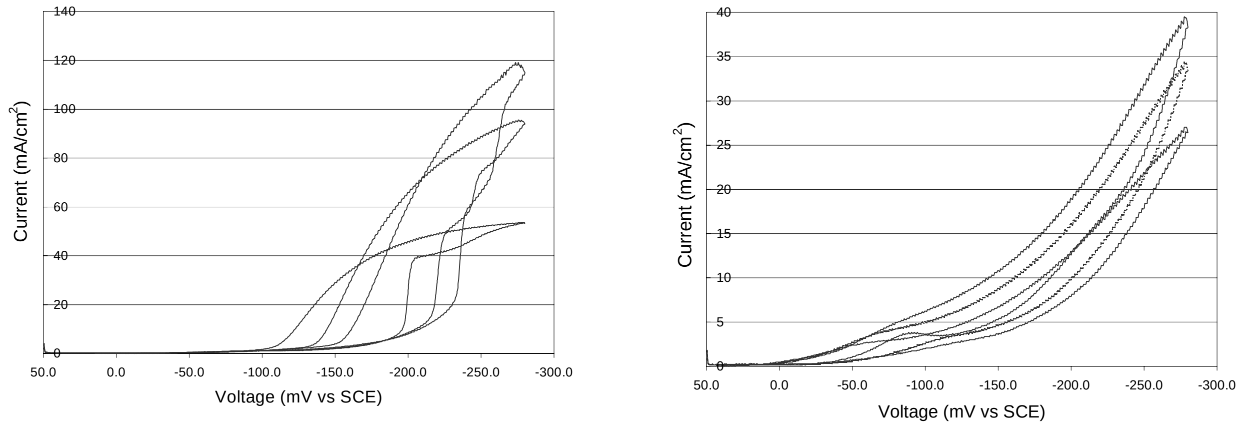


Figure 5 - Polarization curves measured at 100, 500, and 1500 RPM in (a) copper plating solution containing copper sulfate, sulfuric acid, and chloride ion, (b) with addition of 6 ml/L of a catalytic additive to (a), (c) with addition of 3 ml/L of a suppressor/leveler additive to (a), and (d) with addition of 6 ml/L catalytic additive and 2 ml/L suppressor/leveler additive to (a). (All anodic and cathodic scans were taken at 2 mv/sec.)

increases with RPM/flow). However, for the case of the catalyst additive, hysteresis behavior at lower levels of mass transfer is noted between the forward and reverse scans of the plot. When hysteresis is observed the current at a given voltage is lower when scanning toward larger applied voltages than the current when scanning toward zero applied voltage. Hysteresis reflects maintenance of additive adsorption levels existing at a proceeding time, and thus a tendency to maintain an existing current level until surface adsorption re-equilibrates at a mass transfer dependent rate. This hysteresis behavior is a potentially desirable aspect of a process chemistry intended to deliver bottom-up fill since it implies that once an accelerated rate of growth is achieved within a feature it will tend to propagate itself.

Figure 5c shows polarization behavior in the presence of the leveler containing additive mixture. In the presence of this additive, the current at a given voltage is higher at a lower mass transfer rate, except at high currents where mass transfer of copper limits overall current. This behavior reflects the presence of leveling agents which suppress current to a degree dependent on their mass transfer rate to the surface. The suppression of growth achieved by levelers (at areas of high mass transfer such as the wafer field) could contribute to relatively accelerated growth in vias if proper concentration profiles were achieved. Alternatively, levelers which diffuse into damascene features may act to disrupt fill where it eventually adsorbs and suppresses current.

Figure 5d shows polarization behavior in the combined presence of accelerating and suppressing additive components. Starting with this system, further addition of the accelerating or suppressing additive components will increase or decrease, respectively, the current at a given mass transfer and applied potential condition. At the component concentrations shown, the current at a given potential is between the values observed in the presence of suppressing and accelerating species alone only at low voltages. At higher voltages, suppression of current is greater than observed in the presence of the suppressing component alone. This suggests a synergistic suppression effect under certain conditions as has been recently noted [7]. Polarization behavior of the overall additive system will represent current-voltage characteristics on the wafer surface. Maximum differentiation between currents at the wafer surface and within the via can clearly be achieved using a system which causes an overall strong suppression behavior, but which fails to manifest that behavior at the via base.

Fig. 6b -Polarization vs Rotation Rate
Accelerator in Electrolyte

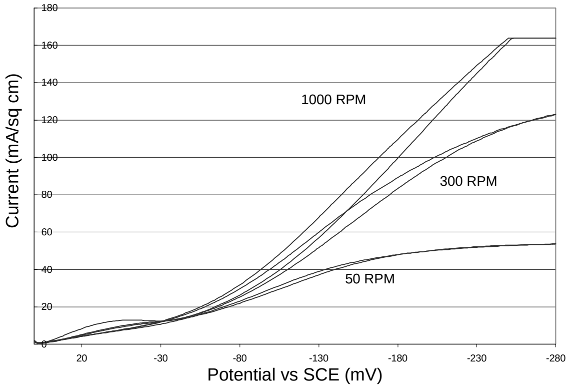


Fig. 6b -Polarization vs Rotation Rate
Accelerator in Electrolyte

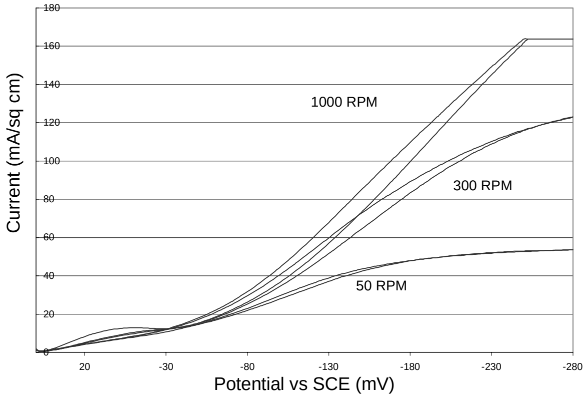


Fig. 6c - Polarization vs Rotation Rate
Nominal Accelerator and Suppressor in Electrolyte

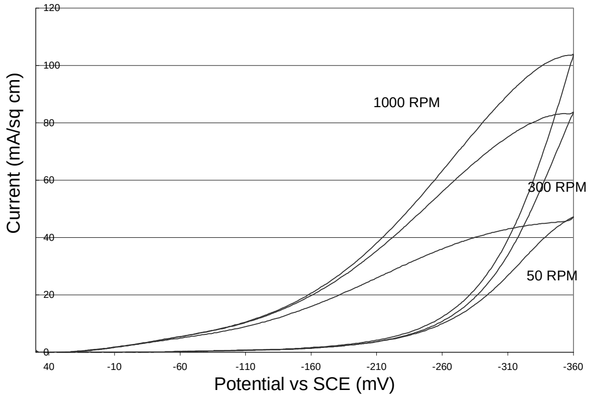


Figure 6 - Polarization curves measured at 50, 300, and 1000 RPM in a copper plating solution containing copper sulfate, sulfuric acid, and chloride ion, (a) with addition of catalytic additive at nominal concentration, (b) with addition a polymer like suppressor additive at nominal concentration, and (c) with addition catalytic additive and suppressor at nominal concentrations. (All anodic and cathodic scans were taken at 2 mv/sec.)

Figure 6 shows polarization curves measured for an additive system developed for IC filling and capable of achieving highly accelerated bottom-up fill. This chemistry contains one accelerating and one polymer based suppressing species. Figure 5a shows polarization behavior in the presence of the accelerating species. As in the case of the PCB chemistry, polarization behavior with the accelerator is not significantly different than observed in the system with no organics present. Absent, however, is the hysteresis in the polarization curves seen for the PCB based accelerator solution (Fig 5b) which also contained some polymer. Figure 6b shows polarization in the presence of the suppressing polymer suppressing polymer added to the base electrolyte. In this case, current is highly suppressed as was observed for the "leveler" type solution used in the PCB chemistry. Absent, however, is any hysteresis indicating rapid polymer adsorption equilibrium is established between the solution and the growing copper surface. Figure 6c shows polarization behavior of the complete IC filing optimized chemistry (accelerator and polymer suppressor). While the polarization behavior of this system is similar to that observed for the PCB system two key differences are observed. First, in the IC filling system the hysteresis between the forward and reverse current sweeps is more pronounced and present over a wider potential range. It is thought this property related to the ability of the chemistry to support distinctly different currents at the feature base and at the wafer surface. Second, the dependence of current on mass transfer rate (rotation) is much greater in the IC fill optimized system reflecting the lack of any leveler species in this chemistry.

Bottom-up fill takes place when the additive adsorption conditions at the base of the via result in a much higher current than the additive adsorption condition on the field adjacent to the via. (Recall that voltage applied at the base of the via is virtually identical to the voltage on adjacent field.) As illustrated in Figure 7, the current at the base of the feature can easily be 5-10X the value on the field if additive adsorption differences exhibiting desired polarization behavior are established at each geometric position. The case shown compares the 500 RPM polarization behavior using the complete additive system to represent field polarization, and polarization behavior in the presence of the more catalytic additive to represent behavior at the via base. Many other combinations are possible, with the most extreme being no additives of any type at the feature base combined with suppressors present at the surface. The ability to achieve this adsorption combination could lead to feature base acceleration rates approaching 100X that of the field (based on the polarization data).

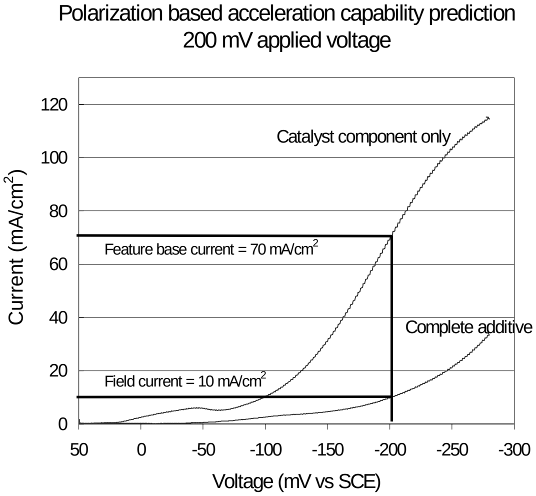


Figure 7 - Polarization behavior of copper electrolyte with catalytic additive only and with complete additive system. Plot shows possible current density differences between wafer areas (feature base vs. field) due to differences in additive adsorption.

Filling Trends and Observations

Any proposed mechanisms for bottom-up fill should explain several measured trends in filling performance as a function of process chemistry conditions. These trends relate strongly to elimination of center voids of the type shown in Figure 1b, and somewhat less to the ability to eliminate bottom voids of the type shown in Figure 3. The following outline of points can be made in summarizing our experience and observations in working with Cu plating bath additive systems.

1. Strongly accelerated fill has not been achieved using suppressing polymers alone or suppressors with chloride ion. Growth in several systems tested appears to be largely conformal as shown in Figure 8.
2. Suppressing polymer concentration can be increased to at least 4X beyond an optimal (plateau) level without impacting fill. These concentrations can extend upwards of 1000 mg/L, well beyond a level at which concentration gradients within features are likely to develop.
3. Bottom-up filling can be achieved in the absence of levelers. A typical time evolution profile using an additive system containing only a polymer suppressor, chloride, and an accelerator is shown in Figure 9. It is seen that an accelerated bottom-up growth component is operative.

4. The addition of levelers to bottom-up filling chemistries often results in top center voids as shown in Figure 10.
5. As chloride ion concentration is increased from zero, the filling acceleration in vias increases to a maximum value then decreases as chloride concentration is further increased. Conformal fill has been noted at very high chloride levels.
6. As accelerator concentration is increased, bottom-up fill increases from near zero to a maximum rate and then diminishes to conformal behavior. This is similar to the trend for chloride ion (point 5).
7. For a given additive system, too low a copper concentration diminishes bottom-up fill capability in high aspect ratio features.
8. In the absence of a leveler-like species, accelerated copper growth continues over a damascene feature following bottom-up fill. Figure 11 shows the metal thickness profile over a set of trenches with and without leveler added to a bath which exhibits bottom-up fill. The nearly 2X thickness increase of copper over dense features reflects a continuation of the accelerated copper growth beyond the time of filling completion. The addition of a leveler component serves to suppress current on the rapidly growing surface once it protrudes above the field, thereby leading to a relatively uniform deposit thickness. A lack of suppressing polymer on the rapidly growing surface (over features)
9. could also contribute to continued rapid growth. To test this in a leveler-free solution, trenches were plated under normal filling conditions until they were approximately flush with the adjacent field. At this time, current was then turned off for 30 seconds. This off-time should allow for complete equilibration of polymer adsorption, a behavior which requires less than two seconds. Following this equilibration period, plating current was resumed using the normal process. The profiles observed were identical to those without the zero current equilibration, indicating accelerated growth following fill results from a strongly adsorbed excess of accelerator species which had accumulated on the surface during bottom-up filling.

Filling Mechanisms

Based on these observations, several mechanisms and factors appear to contribute to bottom-up fill while other possible mechanisms may be only marginally important. The following scenario for the establishment and propagation of bottom-up fill is proposed:

When a wafer is first immersed in a plating solution, a concentration gradient of suppressing and accelerating species may exist on the wafer surface between the via base and the field. This will happen when the quantity of additive species required to form an adsorbed layer on the surface within the via exceeds the amount of additive contained in the solution volume within the via. This effect could account for less suppression at the via base by slow diffusing polymer species when relatively low suppressing polymer concentrations (<100 mg/L) are present in solution. However, a simple calculation indicates that unless a species is consumed rapidly, this concentration gradient will last a second or less for suppressing polymer species which are present at up to several hundred mg/L in solution, and should not exist at all when polymer concentrations exceed 1000 mg/L (where bottom-up fill is still observed). It is well known that most polymer species used as suppressors are not readily consumed or decomposed at the cathode and (as noted above) increasing the polymer level beyond that required for optimal fill does not degrade fill as would be expected for a fill mechanism driven by a polymer diffusion gradient. Beyond this, it is observed that bottom-up fill will take place on a well seeded surface both if a wafer is immersed in a plating solution with the current on and if the wafer is placed in the bath and allowed to equilibrate with the additives in solution for at least 10 seconds. For these reasons, it appears that diffusion-limited adsorption of the polymer is not critical to bottom-up fill in at least some commercially available additive systems.

When current flow begins we will assume that all additive species have reached an equilibrium level on all surfaces of the wafer. This should be expected to lead to initial currents on all surfaces which are approximately equivalent, an effect which agrees with the observed relatively small amount of bottom-up growth seen in the first 5-10 seconds of a filling process (see Figure 9) and the essentially conformal initial growth shown in Figure 2 (center).

After some period of time which depends on current density and chemical concentrations, two phenomena may begin to contribute to fill. First, the accumulation of accelerating mercapto species (or their more accelerating breakdown products) on the surfaces within the features takes place. Accumulation results as surface area within the via decreases and adsorbed mercapto species which are neither incorporated in the deposit or desorbed into solution are concentrated. Current increases in the areas of geometric concentration (bottom corners) as chloride and suppressing polymer is displaced. Too much accelerator in a bath disrupts fill because the accumulation of accelerating species also begins to take place on the wafer surface and differentiation from the via base is lost. The accumulation of catalytic species on the growing surfaces within features is strongly supported by the continued rapid Cu growth above features in the absence of leveler. Such behavior is not interrupted by discontinuing current flow to allow polymer re-equilibration. It is, however, disrupted by reversal of interfacial potential to a value causing oxidation or desorption of the adsorbed catalytic material or by addition of a leveling additive which suppresses current at protruding geometries.

To explain the observed effect of chloride on fill, a second phenomena which contributes to fill initiation may involve the co-deposition of chloride in the Cu film resulting in a depleted chloride concentration within features, <u>or</u> competitive displacement of Cl on the copper surface by the accumulating mercapto species. Low chloride concentration leads to weak or negligible polymer adsorption and higher current for a given potential, as has been well documented in the literature [12]. This effect results in poor suppression of the current at the wafer surface and therefor a lack of possible relative acceleration in the feature. As Cl concentration is increased, good surface suppression is obtained but the levels of Cl within the via may not be adequate maintain polymer adsorption in the presence of the accumulating accelerator mercapto species and good bottom-up fill is obtained. Further increase in Cl may disrupt fill because Cl is able to compete successfully with the mercapto species for adsorption sites and subsequently attract suppressing polymer adsorption within the via.

Finally, once bottom-up fill begins in a bath showing hysteresis behavior between the cathodic and anodic sweeps of a polarization curve (Figure 6c for example), the high current which is initially established will tend to continue.

Many levelers have been found to impede fill, however, fill and surface uniformity improvements should be achievable using a leveling suppressor which is consumed or adsorbed prior to reaching the feature base.

Conclusion

Copper deposition rates within sub-micron features are accelerated up to approximately 10X the rate on adjacent wafer surfaces. Polarizing additives suppress the current on the wafer surface while accelerating additives accumulate within features undergoing internal surface area reduction during initial growth. It is proposed that rapid copper growth begins at the feature base when accelerator accumulation results in displacement of adsorbed suppressor and/or chloride ion. A single rapid growth surface on which organo-sulfur accelerator accumulation continues to occur proceeds upward during bottom-up fill. Accelerated growth can proceed after filling resulting in protrusions over features filled by a bottom-up process. Levelers are not required for rapid bottom-up fill.

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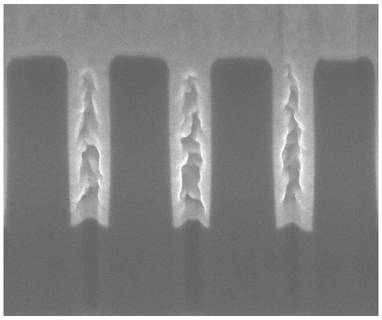

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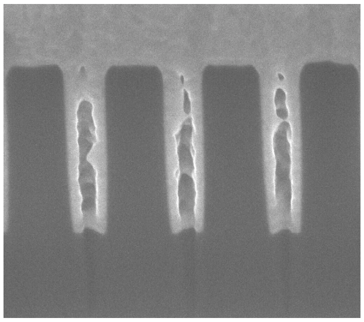

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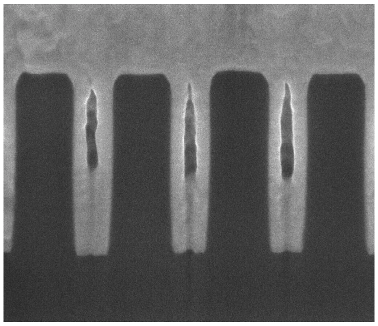

Ultrafill suppressor / Cl only

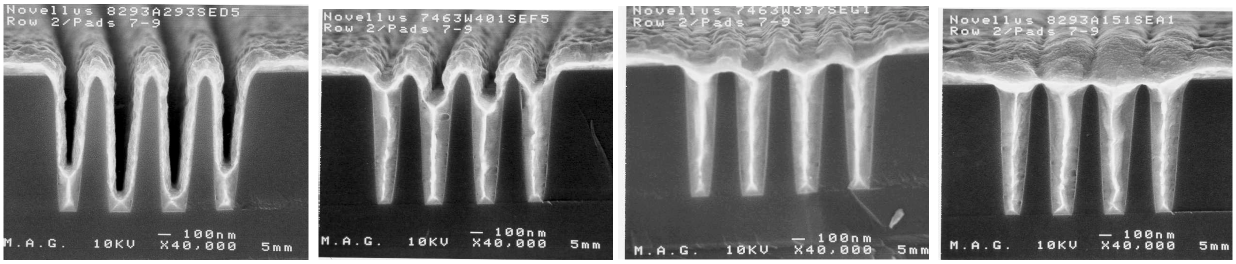

Figure 9 - Fill evolution profile in trenches following 10, 15, 20, and 30 seconds at a current of 10 mA/cm^2.

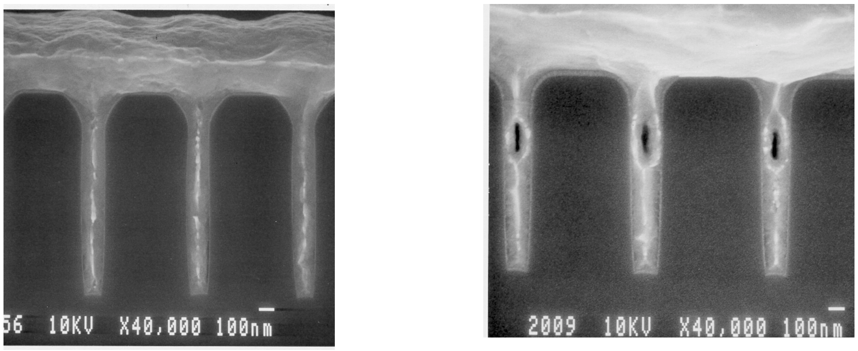

Figure 10 - Trench fill capability of a two-component (polymer suppressor / mercapto accelerator) organic additive plating solution without (left) and with (right) leveler added.

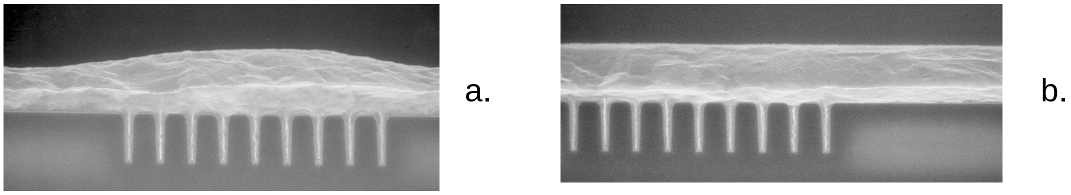

Figure 11 – Metal thickness field profile over dense features following (a) accelerated bottom-up filling, acceleration continues after filling (no leveler present), and (b) following bottom-up filling, acceleration stopped following fill (leveler present).