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Modelling of Surfactant Mass Balance for Microvia Fill Monitoring

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Abstract

The mass balance of surface-adsorbing additives in a microvia filling bath is modeled. The model considers the additives' mass balance between both the solution and the surface-adsorbed layer of additives, as well as on a shape-changing cathode surface, where mass balance of the additives is affected by the surface shape changes. The model is implemented as a finite element model, which applies the arbitrary Lagrange-Eulerian method for tracking the cathode surface shape changes. Further, a weak formulation of the mass balance equations is created in order to enable numerical solution of the model. The model is compared against experiment results.

Introduction

Microvia filling is a process where interstitial interconnections are made between the adjacent layers of a multilayered printed circuit boards (MLBs). As the amount of electronic components increase in a single electronics device, the device size simultaneously decreasing, increased interconnection density becomes evermore inevitable. New manufacturing technologies, such as the via-on-via filling technology, enable creating interconnects between MLB layers straight on top of each other, which further helps achieving greater interconnection density on MLBs. A thorough coverage over the microvia fill and via-on-via technologies is published by Yeh et al. [2].

The electrolytic microvia filling process is a complex electrochemical procedure, where copper ions are reduced from a solution into holes drilled on the MLB, thus to create the necessary interstitial interconnects on the MLB. When applying the via-on-via technology, every microvia needs to be perfectly filled in order to achieve good circuit reliability and thus end-product quality. No void can be left inside the vias, nor can the vias be overfilled or underfilled for the consequent vias to become proper.

The microvia fill process is similar to the electrolytic filling process of sub-micron features in manufacturing of integrated chips (IC). The latter process has been studied extensively in terms of additive mechanisms [10, 5, 9] as well as modelling [17, 6, 1, 3, 13].

Similarly as the electrolytic filling of nano-scale features on silicon wafers in IC manufacturing, also the microvia fill process is governed by the chemistry of surfactant additives. The additives affect the copper ion reduction rate differently on different sites inside and around the microvia, and the magnitude of the additives depends on their local surface coverage. Studies regarding the additive behavior in microvia filling applied in circuit manufacturing have also been carried out by Dow et al. [14, 15]. However, not many computational

models of the microvia fill process have been published and especially not for use in control applications [12, 16]. Because the functioning of the additive chemicals can not be directly measured during plating, modelling the process is a good method to study and develop, and eventually monitor and control the microvia filling process.

Though there are acknowledged similarities between the fill process applied in IC manufacturing and that applied in MLB production, the hundred-fold difference in scales of size and time require re-thinking when modelling of the process. Also the substrate material, the homogenous silicon vs. a very heterogenous glass fiber-reinforced epoxy resin, poses further challenges for process modelling.

This paper presents an advanced method for modelling the surfactant additives' mass balance on the plated cathode surface during microvia filling. The method applies a weak formulation of the related mass balance equations and the method is implemented in a computational model based on the finite element method (FEM) and the arbitrary Lagrange-Eulerian (ALE) method. The modelling results are compared against experimental results.

Modelling

The physical system being modelled includes two copper metal electrodes and a plating bath with aqueous CuSO_4 (760 mol/m^3) and H_2SO_4 (1000 mol/m^3). Plating is done with direct current and a galvanostatic controller keeps the plating current at approximately 215 A/m^2 .

Two organic additive chemicals are added to the bath to obtain the desired fill result. The additives' exact composition is unknown but their effect is known. The first one acts as a suppressors, inhibiting copper reduction and the other one cancels the first one's effect, thus effectively accelerating copper reduction. The generic designations *suppressor* and *accelerator* are used in this paper to refer to the organic additives. Also chloride ions (Cl^-) are added to the bath by using hydro-chloric acid.

Several functioning mechanisms and several additive compositions have been reported, especially within the application domain of microchip manufacturing [9, 14, 7]. For an applicant of the microvia filling apparatus, the exact composition is however often unknown and thus the use of generic additives, specified based on their effect on plating, is justified.

The copper reduction rate is modelled as the plating current density corresponding to the rate of copper reduction (1).

$$i_c = -2i_0 \mu_{\text{Add}}^{\frac{\beta}{\alpha_c}} \mu_{\text{Cu}}^{\beta} \sinh(k\beta H) \quad (1)$$

Equation (1) is a modified Butler-Volmer equation, as documented in [4]. Explanation of all symbols is found in Table1.

Table 1: List of symbols.

Symbol	Property, unit
c	Volumetric concentration, mol/m ³
k	Abbreviated $z_{Cu}F/RT$, 77.887 V ⁻¹
k_i^*	Reaction rate coefficient for species i , reaction *, unit varies
M_{Cu}	Molar mass of copper, 63.55, g/mol
R	Ideal gas coefficient, 8.314 J/mol/K
t	Time, s
T	Temperature, K
H	Driving potential of electrode reactions, V
N	Molar mass flux, mol/m ² /s or mol/m/s
i_c	Cathode current density, A/m ²
α	Apparent transfer coefficient, no dim.
β	$\alpha_c\alpha_a/(\alpha_c + \alpha_a)$, no dim.
θ_i	Proportional surface coverage of surfactant i , no dim.
μ	Chemical term, no dim.
ρ_{Cu}	Density of metallic copper, 8960 kg/m ³
v_T	Tangential velocity of cathode boundary, m/s
∇_T	Tangential derivative operator, no dim.

The cathode surface, Le. the copper deposit front, moves on a velocity determined by the copper metal molar volume and the local plating current density (2).

$$\mathbf{n} \bullet \mathbf{v} = i_c \frac{M_{Cu}}{z_{Cu}F\rho_{Cu}} \quad (2)$$

Because the model is a two-dimensional model, representing the cross-sectional profile of the microvia, \mathbf{v} is a two-dimensional vector, with the components u . and v . The components v_x , and v_y represent the cathode surface movement velocity in the direction of the horizontal and vertical model domain axes, respectively.

As mentioned, during deposition the local cathode current density i is affected by additive chemicals adsorbed on the cathode surface. The effect is included in (1) as the chemical term $\mu_{add} = 1 - \theta_{Supp}$, where θ_{Supp} is the proportional surface coverage of the suppressor additive. Both θ_{Supp} and θ_{Acc} , which is the proportional surface coverage of the accelerator additive, follow mass balance equations of the form (3). The subscript i in (3) becomes *Supp* or *Acc*, depending on whether the suppressor or accelerator additive, respectively, is in question.

$$\begin{aligned} \frac{\partial \theta_i}{\partial t} &= N_i^{ads} - N_i^{des} \\ &- D_i^s \nabla_T^2 \theta_i + v_T \bullet \nabla_T \theta_i - \theta_i (\nabla_T \bullet v_T) \end{aligned} \quad (3)$$

The adsorption and desorption fluxes, N_i^{ads} and N_i^{des} in (3) determine the additives' mass balance between the solution and the adsorbed layer attached on the cathode. In accordance with studies regarding typical electrolytic copper filling additives [2][8], the accelerator additive is modelled so to be able to surpass the suppressor additive in a situation of competitive adsorption (4) and (5).

$$\begin{aligned} N_{Supp}^{ads} - N_{Supp}^{des} &= \\ &k_{Supp}^{ads} c_{Supp} (1 - \theta_{Supp} - \theta_{Acc}) \\ &- k_{Supp}^{des} \theta_{Supp} \end{aligned} \quad (4)$$

$$\begin{aligned} N_{Acc}^{ads} - N_{Acc}^{des} &= \\ &k_{Acc}^{ads} c_{Acc} (1 - \theta_{Acc}) \\ &- k_{Acc}^{des} \theta_{Acc} \end{aligned} \quad (5)$$

The $D_i^s \nabla_T^2 \theta_i$ term represents diffusive migration of surface-adsorbed species along the surface. This movement is evoked by the differences in surface concentration of adsorbed surfactants over the cathode surface. The most right-hand terms in (3), $v_T \bullet \nabla_T \theta_i$ and $-\theta_i (v_T \bullet \nabla_T)$ represent the equation of continuity for mass adsorbed on the surface, which moves with the velocity v_T , and can thus be called the convective part of surfactant mass transfer. v_T is the surface tangential movement velocity, i.e. the velocity of the surface in the direction of the surface itself and ∇_T is the tangential differential operator.

The straight-forward numerical implementation of (3) leads to numerically very noisy solutions due to the surface tangent vector differentials included in $\nabla_T \bullet v_T$, i.e. the surface tangential velocity divergence [11]. A weak formulation (6) of the partial differential equation (3) enables applying the divergence theorem on the divergence of the surface tangential velocity, which rids of the noisy spatial derivatives of the surface tangent vector. By applying this weak formulation the mass balance equations for the additives can be solved fluently and a fast and stable model is achieved.

$$\begin{aligned} \int \hat{\theta}_i \frac{\partial \theta_i}{\partial t} ds &= \\ &\int \hat{\theta}_i (N_i^{ads} - N_i^{des}) ds \\ &+ \int \nabla_T \hat{\theta}_i \bullet (D_i^s \nabla_T \theta_i) ds \\ &+ \int \hat{\theta}_i (v_T \bullet \nabla_T \theta_i) ds \\ &+ \int \theta_i (v_T \bullet \nabla_T \hat{\theta}_i) ds \end{aligned} \quad (6)$$

The content of the terms in (6) is explained thoroughly in [12].

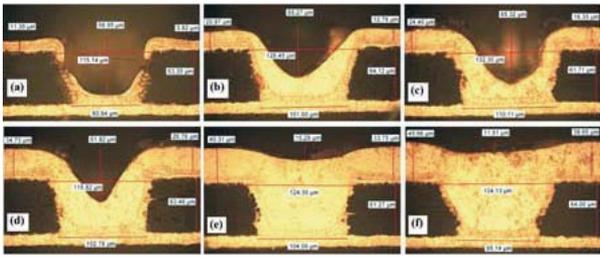


Figure 1: Measured via profiles. Experiment filling times are (a) 15, (b) 30, (c) 45, (d) 60, (e) 75 and (f) 90 minutes.

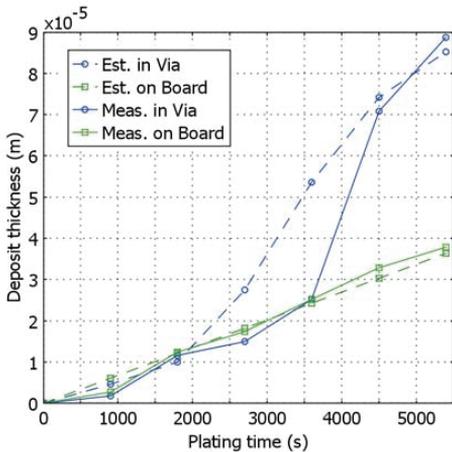


Figure 2: Estimated and measured deposit growth in via center and on flat board.

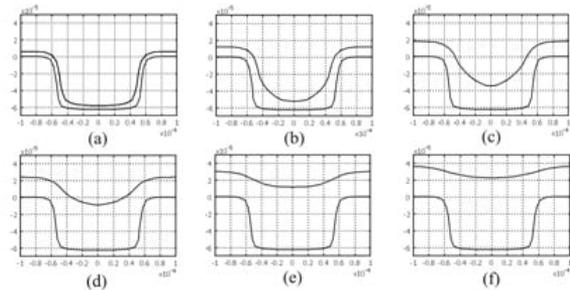


Figure 3: Estimated via profiles. Simulated fill times are (a) 15, (b) 30, (c) 45, (d) 60, (e) 75 and (f) 90 minutes.

Results

The principles explained above are implemented in a FEM model applying the ALE method for tracking the moving cathode boundary. Also via filling experiments were carried out to obtain experimental data in order to verify the modelling results.

The experiments were done in a laboratory-scale apparatus, representing an identical microvia filling bath that is found on the production line of a typical MLB manufacturing plant. To obtain data of the microvia cross-section evolution, microvias were plated in such an electrolyte solution as described earlier for different periods of time. After this the samples were microsectioned and photographed with an optical microscope (500 x magnification). The results of one via fill test series are shown in Fig. 1.

The model was configured with parameters identical to the via fill tests and the obtained via profile evolution estimates at simulation time instants corresponding to the via fill experiments are shown in Fig. 3.

The model can also be compared to the experimental (5) data by comparing measured and estimated thickness of the copper deposit in different locations around and inside the microvia. In Fig. 2 the copper deposit thickness during the deposition process, both on the level board surface as well as in the center point of the via are compared.

Further, a similar model as the one presented in this paper, but where the surfactants' mass balance is not implemented as weak formulations of the mass balance equations is documented in [4]. Also this model predicts the fill end-point correctly but can not follow the via profile evolution during the filling process. Further, severe deformations on the cathode surface, which are not observed in the experiments, are predicted by such a model. Hence, applying the weak formulation to solve the actual mass balance equations for the additives improves the microvia fill model significantly.

Conclusions

A mass balance model of surfactant additives applied in the microvia fill process was created. The mass balance model is based on a set of PDEs formulated in the weak form to enable their smooth numerical solution. The weak formulations are necessary to obtain a stable and accurate model. The model applies the ALE method to track the moving cathode surface and to continuously include the physical effects brought to the system by cathode surface shape changes. The model is compared to experimental data, which verifies the implementation of the mass balance equations.

References

1. W. C., M. S., and R. J. A superfilling model that predicts bump formation. *Electrochemical and Solid-State Letters*, 4(7):C50 C53, 2001. ISSN 1099-0062.
2. Y. C.C., L. K.-H., D. W.-P., H. J.-H., L. C., H. C.H., L. K., C. J., and L. P. Micro via filling plating technology for ic substrate applications. *Circuit World*, 30(3):26 32, 2004. ISSN 0305-6120.
3. W. D., J. D., and M. T.P. Modeling superconformal electrodeposition using the level set method. *Journal of the Electrochemical Society*, 150(5):C302 C310, 2003. ISSN 0013-4651.
4. P. A. J. and T. R. A method for microvia fill process modelling in a cu-cu-electrode system with additives. *J. Electrochem. Soc.*, 000(00):123 123, 12 2007. ISSN 0013-4651.
5. K. K., M. T., and W. K. Role of additives for copper damascene electrodeposition (experimental study on inhibition and acceleration effects). *Journal of the Electrochemical Society*, 151(4):C250 C255, 2004. ISSN 0013-4651.
6. G. M., V. D., S. R. L., and A. R. C. Simulation of shape evolution during electrodeposition of copper in the presence of additive. *Journal of The Electrochemical Society*, 148(1):C54 C58, 2001. ISSN 0013-4651.

7. H. M., T. M., A. K., H. T., and H. K. Copper bottom-up deposition by breakdown of PEG-Cl inhibition. *Electrochemical and Solid-State Letters*, 5(10):C98 C101, 2002. ISSN 0013-4651.
8. L. M., A. G., S. M., T. H., K. M., and H. S. Copper electroplating technology for microvia filling. *Circuit World*, 29(2):9 14, 2003. ISSN 0305-6120.
9. V. P. M., B. R. A., D. H., and A. P. C. The chemistry of additives in damascene copper plating. *IBM J. Res. Dev.*, 49(1):3 18, 2005. ISSN 0018-8646.
10. T. P., C. Y., and W. A. C. Electrochemical and fill studies of a multicomponent additive package for copper deposition. *Journal of The Electrochemical Society*, 148(7):C492 C497, 2001. ISSN 0013-4651.
11. T. R. and P. A. J. Microvia filling with additives: a computational surface coverage model with the ale method. *J. Electrochem. Soc.*, 000(00):123 123, 00 2007. ISSN 0013-4651.
12. P. A. Tenno R. Microvia fill ratio control. 2007. *IEEE International Symposium on Industrial Electronics 2007*.
13. M. T.P., W. D., K. S.-K., and J. D. Curvature enhanced adsorbate coverage mechanism for bottom- up superfilling and bump control in damascene processing. *Elect rochim. Acta*, 2007. Accepted Manuscript, doi: 10.1016 j.electacta.2007.03.025.
14. D. W-P., H. H-S., Y. M-Y., and H. H-C. Influence of convection-dependent adsorption of additives on microvia filling by copper electroplating. *Journal of The Electrochemical Society*, 152(6):C425 C434, 2005. ISSN 0013-4651.
15. W-P. and Y. M-Y. Microvia filling over sifassembly disulfide molecule on au and cu seed layers: A morphological study of copper deposits. *Electrochem. Ss. Lett.*, 8(11):C161 C165, 2005. ISSN 1099-0062.
16. D. W.-P., Y. M.-Y., C. C.-W., L. C.-W., Y. W H., and C. C.-H. Practical monitoring of filling performance in a copper plating bath. *Electrochem. Ss. Lett.*, 9(8):C134 C137, 2006. ISSN 1099-0062.
17. C. Y., T. P., C. R., and W. A. C. Three-additive model of superfilling of copper. *Journal of The Electrochemical Society*, 148(7) :C466 C472, 2001. ISSN 0013-4651.