Enhancing Productivity for IC-substrate manufacturing by using a novel Copper Electrolyte for Semi Additive Plating

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Abstract

The Semi Additive Process (SAP) has gained more attraction over the past years because it enables very fine lines and spaces for the production of IC-Substrates. When operating with lines and spaces (L/S) of 10/10 µm and less the copper thickness variation is one of the critical parameters which has to be controlled within a tight range in order to avoid reliability problems in assembly or during the lifetime as described in several papers [1], [2] . The key process parameter here is called the copper thickness within-unit distribution (WUD) or copper thickness within-panel-distribution (WPD). Another important parameter is the current density used for the copper plating process. Higher current density operating range of an electrolyte results in in better productivity. But both parameters are usually influencing each other. The existing POR might operate at a current density at 1.5 A/dm² but increasing the current density in order to improve the productivity means the copper thickness variation within the panel will increase. This is not beneficial for the quality of the product, as the market is looking for a tight control of the copper thickness variation on a IC substrate.

Already in 2013 a SAP Electrolyte was introduced to the market which is established meanwhile as a POR at IC-substrate manufacturers. Now in 2017 an upgraded electrolyte was developed in order to overcome this conflict of productivity and copper thickness variation. The novel SAP Copper electrolyte was optimized in its formulation so that higher current densities may be applied while still keeping very good copper thickness within unit distribution (WUD) results. Continuity of innovation and invention as expected by Moore's Law are needed to reduce cost and increase capability. Challenges like within-unit distribution become a critical factor for the subsequent processing steps.

The technical paper will contain results of copper thickness and the copper thickness variation (WUD), microsection pictures, DOE Results, dimple results, filling performance and further data. The novel electrolyte shows capabilities to operate at > 3 A/dm² which brings almost an improvement of the productivity by a factor of 2! The new electrolyte also brings further improvement regarding the Cu thickness variation as tighter tolerances may be realized. This is important for the later process steps during package manufacturing. Other Parameters of the new electrolyte will be shown as well like ductility and copper crystal structures of the new electrolyte.

Introduction

The development objectives of this novel chemical formulation have been focused on maximizing the via filling ability in laser ablated blind micro vias (BMV) and minimizing the metal thickness variation across the substrate surface, both in terms of

within-panel-distribution (WPD) and within unit distribution (WUD). While the first one can be significantly influenced by the specific cell design (primary current distribution), i.e. relative geometries and shape of electrodes, shielding system and fluid dynamic profile, the second one can be set under control of the electrolyte composition (secondary current distribution), i.e. composition of supporting electrolyte and nature and concentration of additive system.

The metal distribution on an electrically non-uniform substrate (pattern layout) is determined by the degree of macroscopic current density uniformity, which can be again controlled, in the limit case, by additive kinetics (uniform distribution under polarization resistance) or by ohmic polarization (non-uniform distribution).The term of ohmic polarization increases with increasing applied current density and has to be counteract by the accurate selection of additive nature and concentration.

The effectiveness of the electroplating process for copper filling application hinges on the ability of the process to generate void free fill of the micron scale features.

It is apparent that for the achievement of a proper filling process the plating rate within via hole should be higher that on the surface and as such the copper electrolyte characteristics are of fundamental importance in creating such differential plating rates.

For this purpose the development of the novel electrolyte focused on the use of proprietary organic additive mixture, consisting of suppressor and anti-suppressor (catalyst) agents, in a inorganic matrix composed by cupric ions sulfuric acid and chloride.

The balanced interaction between the additives gives rise to remarkable deposit characteristic, such as grain refinement, levelling and brightening, and plays a key role in the mechanism of accelerated filling process in direct current plating.

During the development program extensive screening was conducted to find the proper combination of the additives in a significantly operational working range, principally focusing on filling ability and metal distribution which are quantifiable measures used to describe the effectiveness of the process and compare the effect of process and formulation variables.

Development Targets

The following list gives an overview on the main in scope deliverables set as milestones and produced during the development activities of the novel chemistry.

- Higher applicable current density (> 2.5 ASD) compared to POR chemistry
- Superior metal distribution on the unit compared to POR chemistry
- Consistent filling ability in BMV geometries relevant for SAP application
- High quality of copper deposits
- Proper microstructure
- Proper mechanical properties

Results of filling ability and metal distribution within the unit (WUD)

It is known that the composition of the supporting electrolyte has an influence on both filling ability and metal distribution; in general, the combination of high acid and low copper concentration has a beneficial effect on the metal distribution and a detrimental effect on the filling performance. Thus, the applicability of a wide additive working range in a bulk electrolyte containing different acid and copper concentrations at different physical parameters, as current density, have been mandatory studied.

The relationships of each these and the principal effect are presented in this paper and directly compared to the POR chemistry.

The metal distribution on individual unit (WUD) has been defined as difference between maximum and minimum copper thickness on relevant predefined locations and has been calculated according to:

Range = Cu(T)Max – Cu(T)Min

The values of dimple (Fig.1) in 60µm diameter and 35µm thickness BMV laser ablated in pad and plane areas quantify the fill ability of each investigated electrolyte.

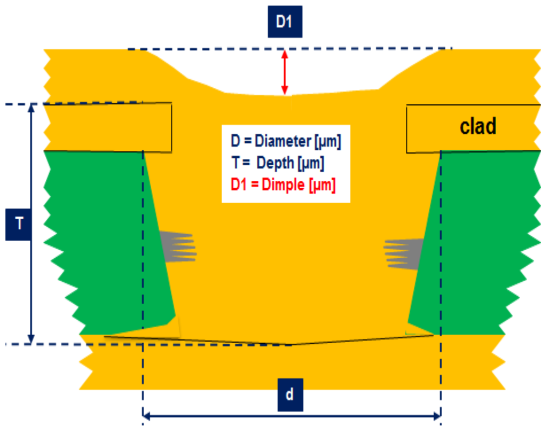

Fig. 1, Principal characteristics of filled BMV

In Figure 2 considerable results of thickness distribution and dimple values obtained at different current densities (1.5 and 3.5 ASD) and with low, medium and high acid and copper concentration have been highlighted.

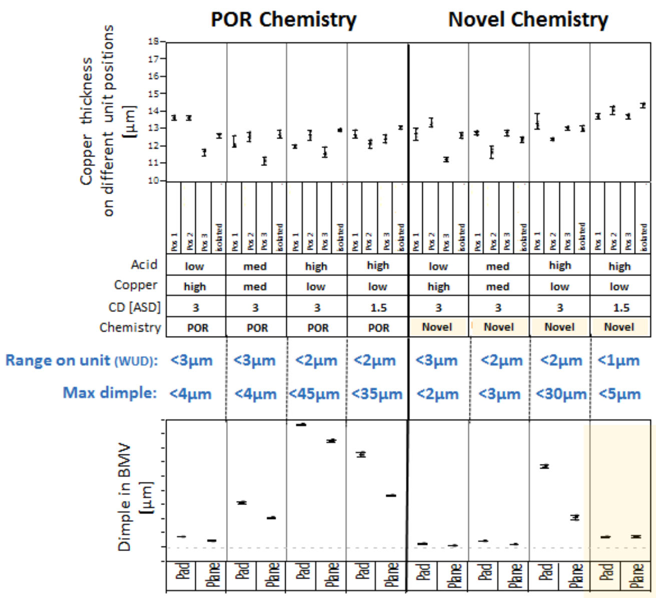

Fig. 2, Comparison between novel chemistry and POR chemistry showing the filling ability and metal distribution within the unit (WUD) at different acid and copper concentrations and current densities.

Common to the investigated electrolytes is a general tendency of filling effectiveness decrease at high acid, low copper and higher current density. However this tendency results to be more pronounced in case of POR chemistry. In contrast to POR electrolyte, at lower current density the novel chemistry is able to promote consistent filling performance even at high acid concentration (dimple values < 5µm).

From the data can be also derived an excellent filling ability of novel chemistry in low and medium acid concentration, slighter superior compared to POR electrolyte.

As result, the novel chemistry manifests superior filling ability in a wider acid and current density regime.

According to the expectations, the current density has an impact on the metal thickness measured on different locations within the individual unit.
Its increase from 1.5 ASD to 3 ASD gives rise to larger Range (Fig 2), i.e. larger copper thickness variation.
Nevertheless, the novel chemistry promotes an improved copper distribution by the combination medium acid/higher CD and high acid/lower CD when compared to the POR Electrolyte.

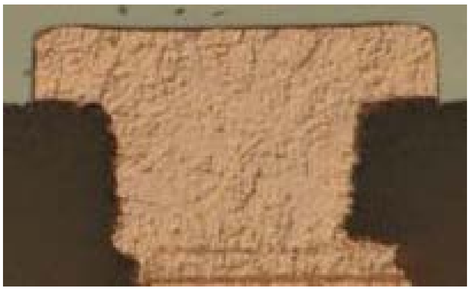

Fig. 3, Micro section of BMV electroplated with the novel chemistry at 3ASD

Fig. 4, Micro section of copper traces electroplated with the novel chemistry at 3ASD

The novel chemistry has been demonstrated to be able to plate high copper quality even at very high deposition rate in direct current.

Fig.5 offers an example of plating performance obtained at 4.5 ASD on SAP layer under following process conditions:

A: medium copper, medium acid, medium accelerator, high inhibitor

B: medium copper, medium acid, high accelerator, high inhibitor

C: medium copper, medium acid, high accelerator, medium inhibitor

D: high copper, medium acid, high accelerator, medium inhibitor

E: high copper, medium acid, high accelerator, high inhibitor

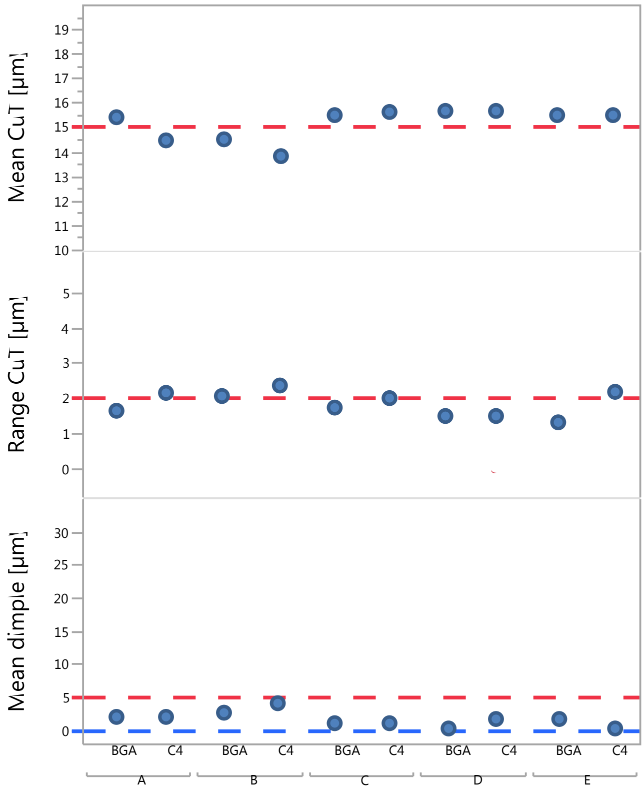

Fig. 5, Dimple and copper Range on individual unit of BGA and C4 side at different plating conditions. Applied current density: 4.5 ASD.

Across the different test conditions both filling ability and metal distribution on the unit have been found to be consistent: mean dimple of < 5µm and copper range between approximately 1 and 2 µm have been measured.

Results of the microstructure

The copper deposits plated at 3 ASD with the novel chemistry exhibit in SEM metallographic investigation of electro polished micro sections (fig. 5) the built up of polycrystalline grains with a polygonal shaped structure without preferential orientation, absence of impurity and grain boundaries defects, together with the presence of a certain degree of twinned planes

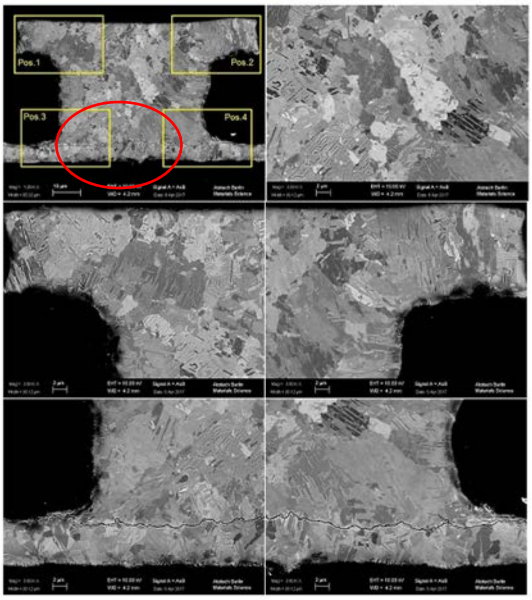

Fig. 6. SEM micrographs of copper structure after annealing (125°C, 4h) deposited at 3 ASD with the novel chemistry.

The micro structure at different BMV locations is polygonal shaped with presence of twinned planes within the grains and absence of grain boundary defects. In this way, it has been demonstrated that the novel chemistry can be operated at higher current density without detrimental effect on the regular formation and growth of the copper grains, as a direct comparison with the micro structure of copper deposits electroplated at 1.5 ASD with the POR chemistry makes evident (Fig 7).

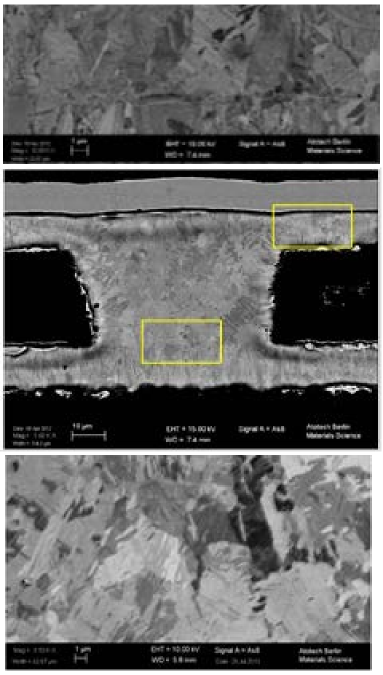

Fig. 7 SEM micrographs of copper structure after annealing (125°C, 4h) deposited at 1.5 ASD with the POR chemistry.

The micro structure at different BMV locations is polygonal shaped with presence of twinned planes within the grains and absence of grain boundary defects.

Results of the mechanical properties

A proper crystal structure of the electroplated copper, as illustrated in the previous chapter, gives rise to different properties of the copper deposits such as mechanical properties and electrical conductivity.

The summary of ductility, tensile strength and deformation work (product of ductility and tensile strength) are properties which give the copper layer enough strength to withstand the expansion of the base material (especially in z-axis) without crack formation and propagation, when the components are subjected to mechanical and/or thermal stress regime.

The novel chemistry exhibits optimal mechanical properties of copper deposits electroplated at 3 ASD (Table 1) as result of a balanced share between ductility and tensile strength.

	Foil thickness (µm)	Ductility (%)	Tensile strength (kN/cm²)	Normalized deformation work (Ncm)
	52.0	26.3	32.0	15.2
	55.0	22.9	33.0	14.5
	55.0	27.1	31.8	15.8
	57.0	24.4	32.2	14.5
	54.0	25.4	32.2	15.2
	58.0	16.7	35.9	10.9
	53.0	23.0	33.3	14.7
	54.0	21.7	34.1	14.1
	55.0	22.7	32.8	14.4
Average	54.8	**23.4**	33.0	**14.4**
Standard deviation	1.9	3.1	1.3	1.4

Table 1. Ductility measurements by hydraulic bulge test. Copper foils plated at 3 ASD with the novel chemistry

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In this way, it has been demonstrated that the novel chemistry can be operated at higher current density without detrimental effect on the mechanical properties, as a direct comparison with the mechanical properties of copper deposits electroplated at 1.5 ASD with the POR chemistry makes evident (Table 2).

	Foil thickness (µm)	Ductility (%)	Tensile strength (kN/cm²)	Normalized deformation work (Ncm)
	60	17.6	34.6	10.5
	58	24.1	31.4	13.7
	56	22.8	31.8	13.2
	57	26.1	31.3	14.7
	50	23.4	30.3	12.8
	50	17.7	34.0	12.6
	49	22.5	31.5	12.6
	50	24.9	33.3	15.3
	48	22.6	31.1	12.7
	48	20.3	32.2	13.1
Average	52.6	**22.2**	**32.2**	**13.1**
Standard deviation	4.6	2.9	1.4	1.3

Table 2. Ductility measurements by hydraulic bulge test. Copper foils plated at 1.5 ASD with the POR chemistry

Conclusions

With the Novel Chemistry a new copper electrolyte was developed which shows many improvements comparing to the existing POR. The results demonstrated that the productivity could be improved because the novel chemistry is able to plate at much higher current densities compared to POR. At the same time the filling and metal distribution abilities could be improved as well. The other properties such as microstructure and mechanical properties could be balanced at the same level like the process of record. Based on these good results the novel chemistry has launched to the market in October 2018.

References

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