ECWC14
14th Electronic Circuit World Convention

New, advanced soldermask and photoresist pretreatment for significant waste water benefits and low etch depth requirement

B. Gil-Ibáñez, M. Thoms, A. Clicqué, T. Huelsmann, P. Brooks, S. Hotz

Atotech Deutschland GmbH

10553 Berlin, Germany

stephan.hotz@atotech.com

W. Cho, S. Li, Y. Zou

Atotech (China) Chemicals Ltd.

Guangzhou, China

ABSTRACT

Atotech has developed a new ferric-sulfate based microetching process which is both technically and commercially superior to existing POR pretreatment chemistries for Soldermask and Photoresist pretreatment.

The additive combination present in the process creates very deep trenches in the copper surface that ensure an extraordinary adhesion to the resist. These trenches are mainly at copper grains and their size depends on the etch depth: for example, when an etch depth of 0.5 µm is applied, the length of these trenches is around 1 µm. The presence of this characteristic copper surface morphology implies an outstanding adhesion of the copper to the SM even for low etch depth like 0.5 µm. The adhesion performance was confirmed by standard tape test (IPC TM 650 2.4.1.E) when, after immersion Tin or ENIG, none of the coupons with ED 0.5 µm presented any peeling. This excellent adhesion for ultra-low etch depth together with its high copper loading provide another important advantage for the process, because they allow the process to have low bleed within the range of the drag-out, which signicantly reduces waste water volumes.

The clean chemical renegeration of the etchant is another clear advantage of the process. The simple addition of hydrogen peroxide, together with sulfuric acid, permits the fast re-oxidation of Fe(II) to Fe(III) without any undesired side products that might affect the performance of the working bath. This Fe(III) regeneration procedure can be easily controlled and adjusted to the different requirements of the PCB manufacturer.

INTRODUCTION

Commonly used etchants are based on sulfuric acid / hydrogen peroxide or on $CuCl_2$ in combination with different organic additives. Main advantage of these etchant types is the relative low initial cost. However these etchants have several drawbacks. On the one hand, these processes are running with big feed/bleed volumes to maintain a stable copper concentration, which clearly impacts in the final cost. They also generate considerable amounts of chemical waste and thereby require cost-intensive waste treatment. This again bears a cost for the PCB manufacturing and also has considerable environmental impacts. On the other hand, these etchants, especially H_2O_2/H_2SO_4, often exhibit low organic additive stability, which normally means higher dosing amounts and shorter bath lifetimes. This again adds to the cost in use. Also they present some limitations regarding the equipment used during their application, for $CuCl_2$ only Titanium and for H_2O_2 only Stainless steel metal parts, which clearly narrow down the flexibility of these systems.

PROCESS DESCRIPTION

As an alternative etching solution and complete new concept a ferric sulfate based process is introduced to the market by Atotech. The etching solution is based on oxidation of solid copper by iron(III). Because it is based on ferric sulfate, the system is applicable to any spray modules equipped with Titanum and/or Stainless steel metal parts. But this added flexibility is only one of the several advantages this new system presents.

Other of its key advantages is the simplicity of the system: the process only involves two steps: cleaning and etching as it is shown in Figure 1. No further steps like post dips are required, neither to remove residues nor to condition the surface prior to soldermask treatment.

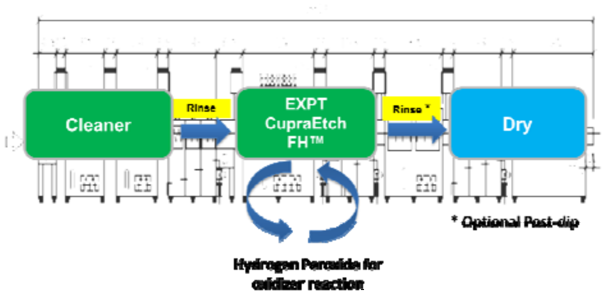

Figure 1: Process flow

Another asset of the system is the high stability the additives exhibit in this iron-based system, especially in comparison to the traditional POR systems using peroxide, where the standard decomposition rates for the organic components are very high. These high performance additives guarantee a much longer life bath, no issues with idle time and the complete absence of sludge, which clearly reduce the running cost for the process. One extra advantage coming from the high stability of the additives is that the bath can hold without any issue a high copper loading, up to 60 g/L Cu. This high copper bath loading together with the ultra-low etch depth (see more details in this regard below) allow the system to be run with small feed/bleed conditions, in the range of the drag-out, which are around four times smaller than those required for the $CuCl_2$ and sulfuric acid / hydrogen peroxide systems. All these advantages of the process certainly reduce the running cost for the process and also minimize the waste water.

The clean chemical regeneration of the etchant is another clear advantage of the process. The simple addition of hydrogen peroxide, together with sulfuric acid, permits the fast re-oxidation of Fe(II) to Fe(III) as it can be seen in the scheme below. This chemical regeneration is taking place immediately which avoids the formation of any undesired side products that might affect the performance and stability of the working bath. This Fe(III) regeneration procedure can be easily controlled and adjusted to the different requirements of the PCB manufacturer.

SURFACE MORPHOLOGY

Apart from the different advantages already described for the process, there is distinct characteristic from the process that stands out over the rest: the very unique surface morphology. For this system, the singular additive combination creates very deep trenches in the copper surface that ensure an extraordinary adhesion to the resist. These trenches are located mainly at copper grains and there homogenously distributed all over the surface. As an example they can be easily seen in the Figure 2 for a sample with an etch depth of 0,5 µm. In the FE-SEM image, a cavernous, brain-like structure can be clearly observed. However, to get a deep look to the unique morphology of the process a FIB cut is required as shown in below (Figure 2). For the case exposed here (ED 0,5 µm) the trenches exhibit values around one micron.

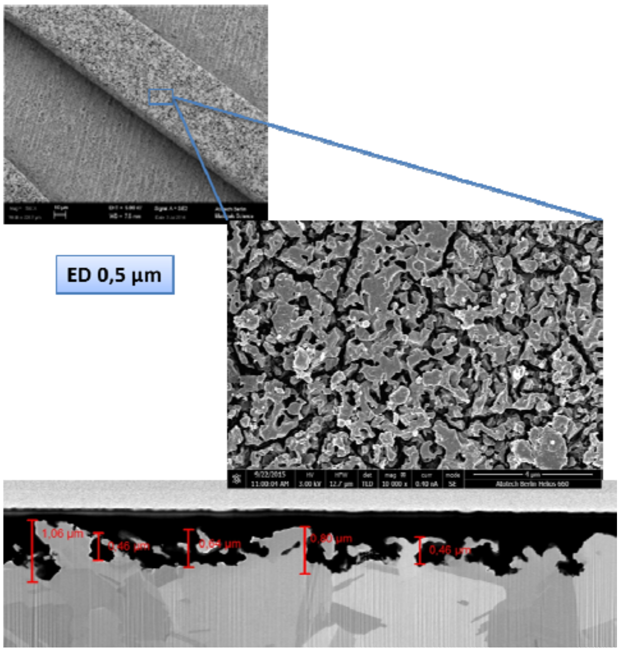

Figure 2: FE-SEM and FIB cut for a sample with ED 0,5 µm

The depth of trenches present on the surface depend on the etch depth. The higher the etch depth, the deeper it is the nature of these characteristic features. For samples with different etch depths, from 0,2 to 0,7 µm, the mean roughness depth (Rz) was measured and represented together with the respective FIB cuts in Figure 3. The relationship between the Rz and the etch depth is almost linear indicating that, within this range, the more it is etched, the more profound are the trenches.

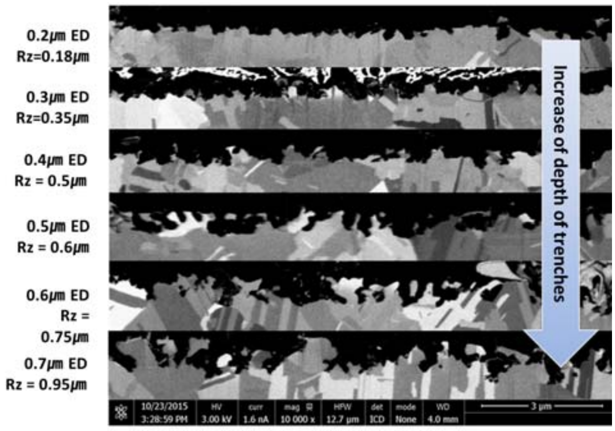

Figure 3: FIB cuts for with different etch depths

PROCESS PERFORMANCE

The presence of this characteristic copper surface morphology implies an outstanding adhesion of the copper to the soldermask. I adhesion performance test by standard tape test (IPC TM 650 2.4.1.E) after immersion Tin and ENIG when using the soldermask Taiyo PSR 4000 G23K and Atotech's internal test artwork for Soldermask. For benchmarking, the results for a competitive CuCl2 pretreatment system have been also included. In the case of ENIG, even with such low etch depths as 0,2 µm no peeling was observed for developed Soldermask features down to 10µm. For the Immersion Tin process, an etch depth of 0,5 µm is sufficient for the process to match the results obtained by the POR system but in that case with an ED 1,3 µm. This excellent adhesion for ultra-low etch depths is a straightforward outcome of its unique surface, where the deep trenches described previously play a key role. The ultra-low etch depths together with its high copper loading allow the process to have a very low bleed within the range of the drag-out, which signicantly reduces the running cost for the process and reduces waste water volumes.

Taiyo PSR-4000 G23K	Items	Competitive $CuCl_2$ system	CupraEtch FH						
	Etch depth	1.3um	0.2um	0.3um	0.4um	0.5um	0.6um	0.7um	0.8um
	Etchrate	1.3um/min	1.2um/min						
	Line Pattern Tape test after FC	>10um	>10um	>10um	>10um	>10um	>10um	>10um	>10um
	ENIG & Tape test	>10um	>10um	>10um	>10um	>10um	>10um	>10um	>10um
	Imm. Tin & Tape test	>30um	>80um	>50um	>40um	>30um	>30um	>20um	>20um

Table 1: Summary of the new process performance with soldermask

CONCLUSIONS

1. On the whole, the new process developed by Atotech, is a new ferric-based in which the additives exhibit a high stability These high performance additives guarantee a much longer life bath , high copper loading of the bath (up to 60 g/L Cu), no issues with idle time and the complete absence of sludge.

2. The clean chemical regeneration of the etchant is another clear advantage. The simple addition of hydrogen peroxide, together with sulfuric acid, permits the fast re-oxidation of Fe(II) to Fe(III) without any undesired side products.

3. The system creates very deep trenches in the copper surface that ensure an extraordinary adhesion to the resist. These trenches are mainly at copper grains and their size depends on the etch depth: for example, when an etch depth of 0.5 µm is applied, the length of these trenches is around 1 µm.

4. The presence of this characteristic copper surface morphology implies an outstanding adhesion of the copper to the SM even for low etch depth like 0.5 µm. This excellent adhesion for ultra-low etch depth together with its high copper loading provide another important advantage for the new process, because they allow the process to have low bleed within the range of the drag-out, which signicantly reduces the running cost for the process and reduces waste water volumes.