Conjointly address stringent device specifications, long bath life considerations, and HSE/ESG standards for specific copper seed wet etching applications

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The paper details the development of a specialized wet etchant for Cu Pillar applications, designed to meet various process specifications, including compatibility with a wide range of materials, a short processing time, minimal feature undercut (<1µm), wafer uniformity, and extended bath life, all while minimizing HSE impacts. Examining existing Cu seed etchants such as H2O2/H2SO4, nitric, phosphoric/phosphonate, persulfate, KI/I2, and FeSCN-based solutions, it becomes evident that none of these legacy blends address both current and future technical and environmental requirements.

Collaborative efforts involving chemical formulators, equipment specialists, online monitoring metrology, and advanced chip engineers have led for significant enhancements and advantages in the wet Cu seed etching process which are reported hereafter.

-General solution attributes

Through etchant development initiatives conducted by Technic' R&D group on various metals such as Ti, TiN, Ag, Ni, Nb, In, and Au, a range of highly effective and environmentally responsible active ingredients were pinpointed in table 1. These components were utilized to create a stable mixture with low peroxide content. The resulting acidic formulation, when utilized, exhibits remarkable selectivity toward numerous metals including Sn, SnAg, Ni, Al, Ti, and AlN (refer to Figure 1), minimal Cu (ECD) roughening and a shallow undercut (<1µm) Figure 2.

TechniEtch Cu-Select ingredient functionalities

• Oxidative species	H2O2
• Cu Chelating agent	Hydroxyl-Carboxylic acids
• Bubble nucleation quencher	Polycarboxylic alkyl acids
• H2O2 stabilizer	…
• Wetting agent	Anionic surfactant
• Solvent	water

Table 1- TechniEtch Cu Select active ingredients.

ER in nm/min @ 25C	Immersion	Selectivity
Cu (PVD)	>180	1
Cu ECD	90-100	2
TiW	<10	>18
SN	<2	90
Al(5%Cu)	<0,2	750
Ni, Bi, In	<0,2	750
Ti/TiN/Au	<0,2	750
Ta/TaN	<0,2	750
Ag	<0,8	187,5
Undoped Si, SiO2	<0>	

Figure 1- Cu Select compatibility /selectivity

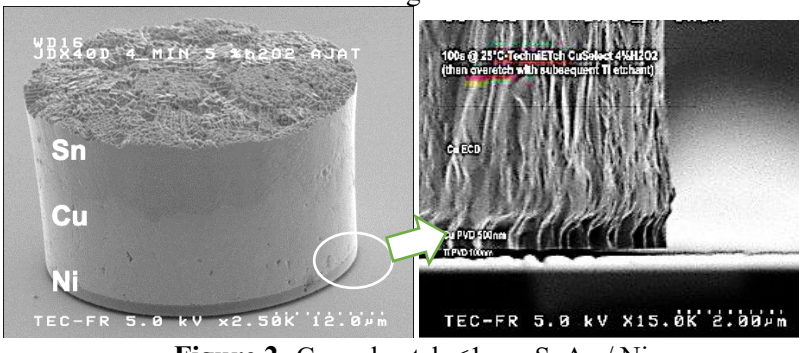

Figure 2- Cu underetch <1µm, SnAg / Ni

Conjointly, in response to a growing concern about environmental impact, Technic is committed to developing eco-conceptualized solutions and collaborating with partners to explore bath monitoring assistance. The goal is to extend the bath life of Technic's surface preparation solutions and reduce waste generation during large-volume chip manufacturing. This involves initiatives such as:

- Real-time monitoring metrology- Adjustment of key ingredients at the point of use.
  - Interestingly, it was observed that the ER profile (Figures 3) is exhibiting a very

slow steady decreases over one week trial to reach an equivalent of 4x 12”x400nm fully dissolved Cu wafers and an ER change of less than 20%. By measuring H2O2 in solution throughout the experiment, it turned out that the stoichiometry of the expected reaction $H2O2+Cu \rightarrow Cu^{2+}+1/2O_2+H2O$ was not respected. That interesting observation let suggest that the poly-carboxylic mixture is conjointly part of the Cu reaction mechanism itself and the quenching of the fast degradation/reaction H2O2 in presence of copper. Those observations would be further studied to optimize online bath monitoring and define the composition of the spike (H2O2, solution make-up or both) to extend bath life.

- End-point detection metrology (Figure 4) was explored over one week experiment.
  - With a process time changing by around 30% over a week, EPD assistance permit to overcome ER change while maintaining process specification. (uniformity, undercut). This approach ensures efficient use of resources and contributes to a better control of the process specifications.
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-Process optimization

By integrating the solution to an acid spray tool with 20% over-etch process recipe on patterned wafers proved sufficient to ensure complete removal of Cu seed and debris, affirming the solution's excellent ability to rapidly eliminate the non-uniform native metal oxides, Cu PVD layer and control Seed undercut down to 1m through its effective wetting and sequestering properties.

Notably, the Cu etching rate was increased by 30% when dispense through a spray nozzle compared to immersion trial under agitation, without compromising wafer-to-wafer ER repeatability letting foresee very reliable and high throughput using cassette batch spray process under 2 mins process. Figure 3 also presents the stable etch rate measurement in nm/min over an experiment included a large number of wafers over 24 hours trials. Additionally, experiments over 72 hours and hundreds of wafers showed a merger 19% ER drop over the trials, confirming the etchant stability in terms of metal content and process time compared to standard H2O2 based etchant which could be offset by applying EPD and/or online monitoring.

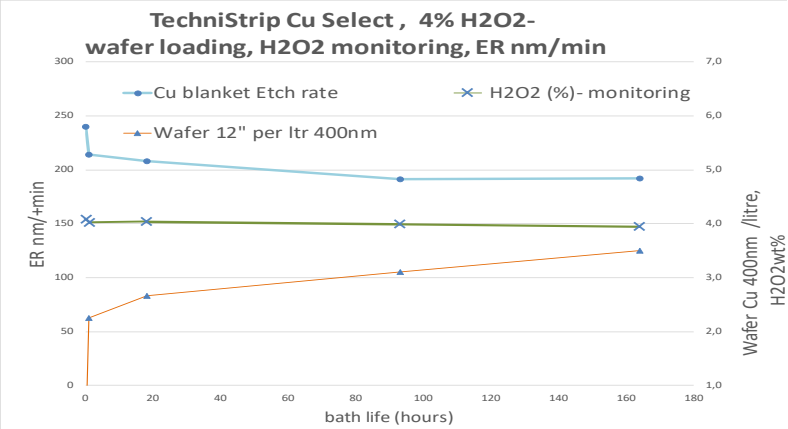

Figure 3- ER stability, H2O2% monitoring, wafer loading

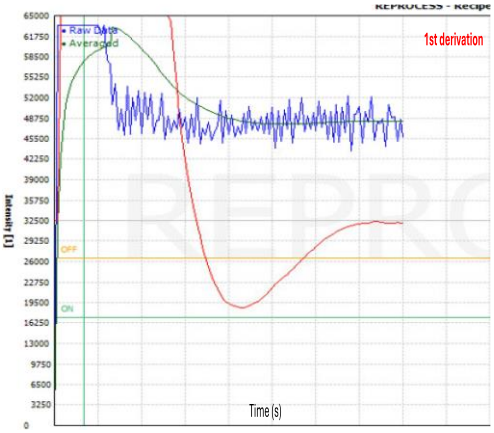

Figure 4- EPD on Siconnex

-Summary

The study underscored significant performance indicators and attributes, including materials compatibility, process window, uniformity, and etching time in batch spray. Additionally, it provided valuable insights into extending the solution bath life through online monitoring (EPD, Online analysis). The team is presently refining the process and actively seeking further enhancements in process reliability, robustness, and preventing intermetallic attacks which will be presented.

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Technic expresses sincere appreciation for the comprehensive support received by the tool partner, Siconnex and end users.