Copper rich Cu_{1-x}Ni_x Alloys (0.05 < x < 0.15) Electrodeposited from acid Sulfate-Based Electrolyte with Benzotriazole additive for Microbump metallization for 3D Stacked Integrated Circuits (SIC).

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Abstract

In this paper we report on electrodeposition of CuNi alloys with low Ni content for applications in three-dimensional stacking of integrated circuits (SIC). For practical reasons related to compatibility with SIC processing, a common sulfate-based electrolyte solution was chosen and the high copper/low nickel content in the deposited alloys was achieved through the introduction of organic additive benzotriazole (BTA). BTA is known as a strong inhibitor for Cu deposition, but its effects on CuNi alloy deposition were not known before. We hypothesized that, in addition to bringing the onset potential of Cu closer to that of Ni deposition, the slower diffusion through the BTA passivation layer could enable improved control of the composition of the deposited alloy as well as the current distribution over the substrate. Our hypotheses were tested through systematic electrochemical measurements combined with ex-situ imaging and chemical analysis techniques. As such, CuNi alloys with Ni content between 5 - 15 at.% were successfully fabricated from a sulfate-based CuNi electrolyte solution with BTA as an organic additive.

Introduction

In stacked integrated circuit (SIC) technology, increased computational power is achieved by stacking chips on top of each other and interconnecting them via microbumps,¹⁻³ which have the dual role of electrical contacts and physical adhesive between the chips. Microbumps are formed by joining opposing metal stages, also known as under bump metallization(s) or UBM, using a solder layer between them. When Cu and Sn, typical UBM and solder materials, respectively, are brought in contact, an intermetallic compound (IMC) will form at the interface and provide a physical connection between the two. The IMC growth rate depends on temperature and contact pressure to which SIC's are exposed during fabrication and operational use. In the case of Cu/Sn microbumps, a Cu_6Sn_5 IMC will develop at the Cu/Sn interface first, followed by formation of Cu_3Sn at the Cu/ Cu_6Sn_5 interface.⁴⁻⁶ The latter continues to grow when the chip is in use due to electromigration and increased temperatures during device operation.^{7,8} The growth of Cu_3Sn results in microvoids at the Cu/ Cu_3Sn interface, which compromises the electrical and mechanical properties of the microbump. Furthermore, the electrical properties of IMC are inferior to those of the elements, and if allowed to grow excessively, it will decrease the feature's electrical reliability.⁹⁻¹³ The ability to control the IMC growth in microbumps is essential, especially when they are being downscaled in size to increase the computational power per area. To improve the control over IMC growth rate, multiple alternative UBM/solder combinations are considered. In this work the emphasis is on fabrication of a CuNi alloy that could be used as an alternative UBM material. Ni is known to inhibit the formation of microvoids and IMC growth, but replacing a Cu UBM by Ni UBM alone still results in reliability issues over time.¹⁴⁻¹⁶ Various combinations of Cu and Ni layers have also been investigated^{17,18} and while they do offer further improvements in controlling IMC growth rates, Ni is harder than Cu and transfers more pressure to the chips during bonding, thus creating a different processing issue. As an alternative to layered Ni/Cu structures, we explore the feasibility of using an electrochemically deposited CuNi alloy as UBM. Hao Yu *et al.* studied the thermodynamic effects of CuNi alloys on the formation of Cu_6Sn_5 and Cu_3Sn intermetallics and concluded that a CuNi alloy, with approximately 10 at.% Ni, prevented Cu_3Sn formation.¹⁹ Therefore, this CuNi alloy is expected to improve the reliability of micro-bumps and thus increase the

operational lifetime of the chip.

The main challenge in co-deposition of Cu and Ni is a relatively large difference in their standard reduction potentials.²⁰ As a consequence, alloy deposition currents largely exceed the limiting current for Cu deposition, resulting in dendrite-like Cu deposits.^{21,22} A common approach to address this challenge is to use complexing agents, such as citrates, to bring the reduction potentials closer together. However, citrate-based CuNi electrolytes are incompatible with some of the SIC processing steps, and thus a different approach is required to maintain similar level of control of alloy composition and surface morphology.^{23–26} A sulfate-based CuNi electrolyte was targeted as both Cu and Ni sulfate-based electrolytes are, or have been used, in SIC manufacturing and are compatible with current SIC manufacturing process steps. Instead of complexing agents, we used benzotriazole (BTA), an organic additive known for its excellent copper passivation properties. The BTA molecules bond specifically to Cu through its nitrogen group and, depending on BTA concentration, a rather thick Cu(I)-BTA film can grow over time on a copper surface.^{27–29} We hypothesized that BTA could have a twofold role in CuNi alloy electrodeposition from sulfate-based electrolytes. First, as the adsorbed BTA can strongly polarize the copper deposition onset potential on a Cu substrate,^{30,31} it could also significantly reduce the difference in copper and nickel onset potentials, provided BTA does not affect the partial nickel deposition current. Secondly, a thick Cu(I)-BTA layer could act as a barrier for ion transport from the electrolyte to the surface of the Cu electrode, and influence deposition rate of both metals. We combined in-situ electrochemical methods and ex-situ imaging techniques to test both hypotheses and fabricated CuNi alloys with Ni content varying from 5 – 15 at.% from a sulfate-based CuNi electrolyte with BTA as an organic additive. We focused on constant current deposition techniques since wafer-scale production-line plating tools preferably operate under current-control mode.

Experimental and Methods

The development of the deposition bath started from a conventional high throwing power $\text{CuSO}_4 + \text{H}_2\text{SO}_4$ bath in which the CuSO_4 concentration was lowered to 76 mM. This concentration allows for Ni to co-deposit with Cu in a 9:1 ratio at -20 mA cm^{-2} , a common

current density for Cu deposition. NiSO_4 , H_3BO_3 and H_2SO_4 were added to this bath sequentially to investigate their respective effects on the Cu^{2+} reduction. BTA was added to this bath and its effectiveness in inhibiting the Cu deposition, was tested by means of voltammetry. Whether or not BTA forms a rate inhibiting layer on the Cu substrate, was investigated by determining the limiting currents for Cu^{2+} reduction at the rotating disc electrode (RDE).

For the voltammetry experiments, a 3 mm diameter Pt rotating disc electrode was used on which a 150 nm Cu layer is pre-deposited from a CuSO_4 bath, described in Table 1 A. After each experiment the Pt substrate was first electrochemically stripped from all deposits and then cleaned with a piranha solution ($\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$ in a 3:1 ratio). The galvanostatic depositions were performed on custom made, removable, 4 mm diameter copper metal disk pellets in the rotating disk electrode (RDE) setup shown in Figure 1. The cell was sealed by a cover with tight fitting openings for the RDE, reference electrode, counter electrode, N_2 purge line, N_2 headspace line and an additional exhaust hole to release vapor and N_2 gas (Figure 1). This setup allowed to purge the solution with N_2 gas before every experiment and purge the headspace with N_2 during the experiment to avoid additional perturbations of the liquid flow. The water jacketed cell was heated to 45°C using a circulating thermostatic bath to prevent precipitation of boric acid (H_3BO_3).

To design our CuNi alloy deposition bath, NiSO_4 bath components typical for the Watts bath (Table 1, B) were added to a typical high throwing power CuSO_4 bath (Table 1, A). However, the pH was adjusted to accommodate the co-deposition and NiCl_2 was omitted as the chloride concentration was kept at 1mM using KCl. This concentration is required to improve the bonding of BTA to the Cu surface.^{29,32} An overview of the bath compositions, used in the described experiments, can be found in Table 1.

The cell setup shown in Figure 1 was connected to a Parstat 4000 potentiostat (Princeton Applied Research, AMETEK Scientific Instruments), controlling all the electrochemical measurements. For linear sweep voltammograms (LSV's) the scan rate was 15 mV s^{-1} . The potentials were measured versus Ag/AgCl reference electrode (0.205 V vs SHE) and later converted to the standard hydrogen electrode scale. IR correction was performed by the built-in software function for each experiment separately.

The morphology and the elemental composition of galvanostatically deposited CuNi layers were examined by using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The pellets were removed from the RDE after electrochemical deposition experiments, dried, and then loaded into the SEM (Fei Nova NanoSEM) equipped with EDS (Oxford Instruments NCA Pentafet x3). SEM imaging was performed using a 15 kV accelerating voltage, while all EDS measurements were performed in a ‘top-down’ mode at 15 keV. Monte Carlo simulations showed that less than 2% of electron trajectories penetrated deeper than 700 nm into the surface^{33–35} and since the deposits were at least 1 μm thick, an overestimation of the Cu contents was not expected. The kinematic viscosity of the electrolytes was measured using an Ubbelohde type viscometer (SI Analytics) with a capillary diameter of 0.47 mm and a K (calibration number) of 0.003222, calibrated according to DIN 51562-1, ISO 3105. The standard deviation from five consecutive viscosity measurements on each bath composition (defined in Table 1) varied between 0.07% and 0.31%.

Results and Discussion

The effects of NiSO_4 and H_3BO_3 on the deposition limiting current density and the ability of BTA to inhibit the Cu deposition were investigated using linear scanning voltammetry (LSV) on a Cu RDE (Figure 2). The experiments were performed at pH -0.25 (left), which is the unchanged pH of the combined CuSO_4 and NiSO_4 bath, and pH 1.75 (right, the H_2SO_4 concentration was decreased to 0.019 mol L^{-1}), which is more suitable for Ni deposition. An even higher pH (> 2) is preferred for optimal Ni^{2+} reduction, but in a solution of 0.076 mol L^{-1} CuSO_4 and a pH over 1.85, BTA ($>100 \text{ ppm}$) reacted with Cu^{2+} in solution, resulting in a Cu(I)BTA suspension.^{28,36,37} A pH of 1.75 was chosen to avoid formation of the suspension during experiments. In the Cu-only electrolyte ($\blacktriangle$), which served as a reference solution, the onset of Cu^{2+} reduction is at 0.25V, close to the equilibrium potential ($U_{\text{eq}} = 0.26 \text{ V}$), for both pH values. The deposition current density plateau is at -0.023 A cm^{-2} at pH -0.25 and $-0.033 \text{ mA cm}^{-2}$ at pH 1.75 at 60 rpm. A steep increase in current density at potentials more negative than -0.3 V for pH -0.25 and -0.4 V for pH 1.75 is due to H_2 evolution.

The addition of $1.14 \text{ mol L}^{-1} \text{ NiSO}_4$ (◆) to the Cu-only bath raised the current density plateau from -0.023 to $-0.015 \text{ mA cm}^{-2}$ at pH -0.25 and from -0.033 to $-0.015 \text{ mA cm}^{-2}$ at pH 1.75 . The onset of Ni^{2+} reduction is observed at -0.38 V and -0.45 V for pH -0.25 and 1.75 respectively ($U_{\text{eq}} = -0.25 \text{ V}$). When 0.728 mol L^{-1} of H_3BO_3 is added as well (▼), no significant effects on the reduction of Cu^{2+} or Ni^{2+} were observed. The addition of 1000 ppm BTA (●) to Cu-Ni-BA bath results in a shift of the onset potential of Cu^{2+} from 0.25 V to -0.3 V at pH 1.5 and demonstrates that BTA inhibits the Cu deposition reaction even in the presence of NiSO_4 and H_3BO_3 . One has to note though that BTA suppression is more effective when H_3BO_3 is not present at pH 1.75 (■). In the latter bath the onset potential of Cu^{2+} is shifted more negative by at least 0.26 V at which point the H_2 evolution masks the Cu^{2+} reduction onset. At pH -0.25 there is only a small shift in the onset from 0.13 to 0.15 V . H_3BO_3 is a key ingredient in Ni electrolytes since it prevents immediate passivation of electrodeposited Ni and its presence in our CuNi electrolyte is deemed a must, even though BTA is more efficient without it. Current-potential curves for the Cu-Ni-BA-BTA bath (●) show that the addition of BTA also causes the shift in the onset of Ni^{2+} reduction from -0.45 V to -0.56 V . The small peak and plateau that were observed at -0.72 V are expected to be formation of Ni hydrides mediated by BTA.³⁸ The background LSV's of the baths with and without H_3BO_3 and BTA, at pH -0.25 and 1.75 , are shown in Figure S1.

The shifts in Cu and Ni deposition onsets as a function of BTA concentration in a Cu-only bath (●) and a CuNi bath (▲) are summarized in Figure 3a. By adding 100 ppm BTA to the Cu-only bath (●) the onset potential shifts 300 mV more negative. Incremental increase in BTA concentration up to 1500 ppm lead to an approximately linear change in the onset potential with a negative slope of about 25 mV per 100 ppm BTA. Addition of NiSO_4 and H_3BO_3 to the Cu-BTA bath (▲) had no effect on the onset of Cu deposition. However, the solution pH strongly affected the onset potential as shown in Figure 3b. The Cu deposition onset potential for the baths without BTA was about the same irrespective of solution pH in the pH range between -0.25 and 1.75 . The Cu^{2+} reduction onset potential shifted approximately linear with increasing pH from 0.16 V at pH -0.25 to -0.37 V at pH 1.75 . Interestingly, at pH -0.25 BTA (1000 ppm) only realizes a negative potential shift of 0.09 V indicating a dramatic decrease in effectiveness of the suppressing effect of BTA with

decreasing pH. These observations can be explained by the protonation of BTA at low pH (equations 1 and 2):

When the pH is decreased from 1.75 to -0.25, the fraction of BTAH decreases the fraction of $BTAH_2^+$ increases. The latter is not reactive towards Cu while BTAH can adsorb on Cu surface and form Cu(I)BTA complexes.^{27,39-48}

The onset potential for Ni deposition (combined with H_2 evolution) (Δ) is also shifted by BTA but not as efficiently as the onset of Cu deposition. The original potential difference between the onset potentials for Cu and Ni deposition is 0.65 V but at 1000 ppm of BTA this difference is reduced to 0.25 V. At 1500 ppm BTA the Ni reduction onset potential has shifted beyond the H_2 evolution onset potential so that the onset potential of Ni^{2+} cannot be accurately determined.

Although it was demonstrated that the onset of Cu^{2+} reduction could be shifted even more at higher BTA concentrations, the 1000 ppm BTA concentration was chosen for further experiments for two reasons: the onset of Ni deposition also shifts to more negative potentials for higher BTA concentrations, and at this concentration the onset of Cu deposition does not yet overlap with the H_2 evolution. It is also of interest to keep the additive concentrations as low as possible since they could get incorporated in the deposited film and have a detrimental effect on the alloy properties.

Figure 4 shows Levich plots for Cu deposition in all tested electrolyte formulations at pH 1.75: Cu-only bath, the Cu-Ni bath, and the corresponding baths containing H_3BO_3 and BTA. Two groups of data can be distinguished based on the slope values $\Delta i_L / \Delta(RPS^{-0.5})$ listed in Table 2. The presence of $NiSO_4$ in the electrolyte decreases the slope of the Levich plots by 50%, indicating a reduced dependency on rotation rate for Cu^{2+} reduction. If H_3BO_3 is present, a smaller decrease of about 8% occurs. When comparing corresponding solutions with and without BTA, no significant decrease in rotation dependency is measured.

Changes in the slopes, and therefore changes in rotation rate dependency, can be attributed to changes in kinematic viscosity (ν) and diffusion coefficient (D). The change in D of Cu^{2+} alone could point to changes in mass transport in the vicinity of the electrode (due to presence

of BTA). The diffusion coefficient of Cu^{2+} is calculated from the Levich equation (Equation 3):

$$i_L = 1.554 \cdot nFD^{2/3}c_B \cdot \nu^{-1/6} \cdot \sqrt{w} \quad (3)$$

where i_L is the limiting current density of a species, n is the number of electrons transferred in the cell reaction, F is the Faraday constant, c_b is the concentration of CuSO_4 in the bulk ($7.6 \cdot 10^{-5} \text{ mol cm}^{-2}$), ν is the kinematic viscosity, w is the rotation rate in s^{-1} and D is the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$. The viscosity of the different electrolytes was measured at 45°C using an Ubbelohde and the results are listed together with the Levich slopes and calculated diffusion coefficients in Table 2.

ν increases by 74% when NiSO_4 is present in the bath ($\Delta\square\circ$ vs $\blacktriangle\blacksquare\bullet$, respectively). Adding H_3BO_3 ($\Delta\blacktriangle$ vs $\square\blacksquare$, respectively) to the electrolyte causes an average increase in kinematic viscosity of 7%, regardless of whether NiSO_4 is present or not. The decrease in D for NiSO_4 containing baths ($\Delta\square\circ$) is most prominent when compared to the baths without NiSO_4 ($\blacktriangle\blacksquare\bullet$). The presence of NiSO_4 reduces D on average by 61%. To evaluate the effect of BTA on D , the Cu-BA ($\square$) and Cu-Ni-BA ($\blacksquare$) baths are compared to the Cu-BA-BTA ($\circ$) and Cu-Ni-BA-BTA ($\bullet$) baths respectively. D decreases by 11% when BTA is added to the Cu-BA bath ($\square$ vs $\circ$) and by 3.7% when BTA is added to the Cu-Ni-BA bath ($\blacksquare$ vs $\bullet$). D and ν were raised to the power $2/3$ and $-1/6$, respectively, to reflect their contributions to the rotation rate dependency of the Cu^{2+} reduction, as derived from the Levich equation (3) (Figure 5).

Figure 5 shows that the large difference in ν between baths with and without NiSO_4 is reduced to an average difference of 9% for $\nu^{-1/6}$ ($\Delta\square\circ$ vs $\blacktriangle\blacksquare\bullet$). Between these baths $D^{2/3}$ decreases on average by 46%. $D^{2/3}$ increased by 7.2% when BTA is added to the Cu-BA bath ($\square$ vs $\circ$) and decreased by 2.5% when BTA is added to the Cu-Ni-BA bath ($\blacksquare$ vs $\bullet$).

It can be concluded that BTA does suppress the Cu^{2+} reduction kinetics, but no proof was found for the twofold mechanism where BTA would also act as a diffusion inhibiting layer. Also, the difference in rotation rate dependency was only noteworthy between baths with and without NiSO_4 . Comparing $\nu^{-1/6}$ and $D^{2/3}$ shows that the difference in Levich slopes can almost be completely attributed to the change in D in these baths.

Two approaches to ‘pre-assembly’ of the inhibiting BTA layer on a Cu substrate have also been tested: dipping the Cu-substrate in a Cu-Ni-BA-BTA (1000 ppm) bath for different

periods of time, and electrodeposition of the Cu-seed layer from the Cu-Ni-BA-BTA (1000 ppm); both followed by alloy electrodeposition experiments.

Following a 60 s dip in the BTA-containing bath, LSV was recorded in a Cu-Ni-BA electrolyte, showing that Cu^{2+} reduction kinetics were suppressed by 66 mV (Figure 6). The shift was a factor 9 smaller when compared to having 1000 ppm BTA in solution (590 mV shift). This observation was in line with that of Mansfeld *et al.*⁴⁵ who found that BTA which adsorbed on Cu during dipping of the substrate in a BTA containing bath, partially desorbs when the substrate is brought in contact with the BTA-free electrolyte. On the sample where the Cu-seed was electrochemically pre-deposited (approximately 150 nm thick layer deposited at -70 mA cm^{-2}) from the BTA-containing Cu solution there was no shift in the initial reduction onset of Cu^{2+} . However, the second onset occurs at 0.0 V (Figure 6). We speculate that plated Cu seed layer was only partly covered by BTA, causing the Cu deposition to start in the BTA-free areas first. In both approaches, BTA layer, that might have been present after a dip or after a pre-deposition, did not inhibit Cu deposition as effectively as when BTA was present in the CuNi electrolyte. Therefore, BTA must be present in the CuNi electrolyte to achieve the maximum inhibition.

Since our goal is to up-scale the CuNi alloy deposition process from coupon- to a wafer-level, and since production-line plating tools operate mostly in current-control mode, we focused on galvanostatic deposition experiments (Figure 7).

Figure 7A shows potential-time responses for the Cu-Ni deposition from a Cu-Ni-BA-BTA bath with varying BTA concentration (0 – 1000 ppm) at pH 1.75. Two current densities were chosen for this experiment: -21.5 mA cm^{-2} (—), which is 10% over the limiting current of the Cu^{2+} reduction (at 100 RPM), and -40.5 mA/cm^2 (---), expected to lead to a higher Ni content in the alloy. Please note that the time axis is interrupted at about 5 seconds and that two time segments are plotted in a different scale to allow easier observation and analysis of phenomena in both initial and late stage of deposition. The steady state potential is reached after 4.5 s at -21.5 mA cm^{-2} and after 1 s at -40.5 mA cm^{-2} in BTA-free electrolyte. Similar potential-time responses were obtained for Ni deposition from Ni-BA-BTA electrolyte (Figure 7B). However, Ni deposition from BTA-free electrolyte does not follow the same trend, and potentials in the early and late stages are similar, *i.e.* there is no ‘plateau’ at more

positive potentials in the early stage of deposition. By combining LSV and galvanostatic deposition measurements we can conclude that Cu deposition on the Cu substrate is favored over Ni deposition during the initial stages of deposition. The rate at which the Cu^{2+} concentration at the electrode surface decreases is proportional to the applied current density, shortening the time to reach the steady state from approximately 4.5 s at -21.5 mA cm^{-2} to about 1 s at -40.5 mA cm^{-2} . When BTA is present in the electrolyte, the onset of the Cu deposition is shifted to more negative potentials. Similar trend is observed in the Ni-only bath, and during galvanostatic deposition at -21.5 and -40.5 mA cm^{-2} . However, one must be cautious when interpreting galvanostatic measurements in Ni-only electrolyte, since used current-densities both belong to the Ni-hydride formation regime and a transition from Ni deposition to Ni-hydride formation³⁸ could be reflected in the transients' shape. For comparison, Ni was deposited from the same electrolyte at -12 mA cm^{-2} (at which no hydride formation is expected) and the plateau at more positive potentials in the early stages of deposition was not observed (Figure 7B).

The effect of BTA on the morphology and chemical composition of the deposit was investigated using SEM and EDS. Elemental Cu and Ni were deposited from the BTA-containing electrolytes and served as a sort of a reference for description of alloy morphologies. Figure 8 shows images of Cu film deposited from Cu-BA-BTA (1000 ppm) on a 150 nm Cu seed at -21.5 mA cm^{-2} (Figure 8a) and -40.5 mA cm^{-2} (Figure 8b and 8c). Ni films were deposited from the Ni-BA-BTA solution and they are shown in Figures 8a, 8b, and 8c. The difference in grain size is striking with Cu grains being on average 4 times larger than the Ni grains. At -40.5 mA cm^{-2} , Cu grains are also not completely coalesced, yet, resulting in a rougher surface when compared to the Ni layer. Based on our measurements described above, one can conclude that these differences in morphology are due to BTA having a significant effect on Cu deposition, while no, or very little, effect on Ni deposition.

SEM images of CuNi alloys deposited at -21.5 mA cm^{-2} and -40.5 mA cm^{-2} from electrolytes having different BTA concentration are displayed in Figure 9. For both current densities, dendrite-like features are transformed into a smoother granular morphology with increase in BTA concentration. The grain sizes, shape, and roughness of the alloy features deposited at these two current densities were generally comparable.

The cross section perspectives of the CuNi deposit in Figure 10.a and b reveal that the grains are not spherical but elongated in vertical direction. For the layer deposited at -21.5 mA cm^{-2} the Ni content was about half that compared to the layer deposited at -40.5 mA cm^{-2} and the height-to-base diameter ratio is approximately 1.5 (Figure 10.a) while for the latter it is between approximately 2 and 4 (Figure 10.b). When Cu is deposited from Ni-free electrolyte containing 1000 ppm BTA, no elongated grains are observed (Figure 8.c), indicating that the presence of Ni is at least partly responsible for this phenomenon. Increasing the BTA concentration to 2000 ppm, while keeping all other experimental parameters unchanged, lead to suppression of the vertical growth rate and the grains were not elongated any more (Figures 10.c and d). However, there was an unwanted side-effect: EDS analysis revealed that the amount of Ni in the alloy was below detection limit of the tool (0.1 at.%). This observation gives further indication that Ni is somehow causing grains to grow faster in the vertical direction, but also that the amount of Ni in the deposit depends on BTA concentration in the solution.

Figure 11 shows Ni content in the deposited alloy as a function of BTA concentration, pH, and current density. With increase in BTA concentration from 0 to 1000 ppm, the amount of Ni decreased from 11.5% to 0.2% at -21.5 mA cm^{-2} and from 30% to 1.5% at -40.5 mA cm^{-2} . This decrease in the amount of Ni in the deposit with increasing BTA concentration is in line with the observation that BTA also shifts the onset of the Ni^{2+} reduction to more negative potentials. When pH of the Cu-Ni-BA-BTA (1000 ppm) bath was increased to 2.5 (at which point the solution became a sol) Ni content in the deposited alloy increased from 0.2% to 4% at -21.5 mA cm^{-2} , and from 1.5% to 6.6% at -40.5 mA cm^{-2} . It is also noteworthy that no significant amounts of C or N, indicating the presence of BTA, were detected in any of the analyzed samples with respect to deposition from BTA-free electrolytes. At this point in time, we do not have the explanation for the elongated shape of CuNi alloy grains, and we can only speculate that this is due to a complex interplay between the experimental deposition parameters, electrolyte composition, Cu and Ni nucleation and growth phenomena, and mass transport limitations. Based on all the results presented above, a promising path forward would be to further explore electrodeposition from electrolytes containing 2000 ppm BTA, to increase the Ni at.% to 10 without destabilizing the sol to a suspension and while maintaining

the current surface morphology.

Conclusions

We have explored electrochemical deposition of CuNi alloys with low Ni content from sulfate-based electrolytes with BTA as an organic additive. We have studied the effect of BTA on alloy deposition kinetics, surface roughness, its interactions with other bath components, and its sensitivity to pH changes. We explored possible multiple roles of BTA in deposition of CuNi alloys, such as deposition inhibitor, a diffusion layer for ions in the electrolyte, and ability to suppress dendrite formation. While BTA strongly inhibited Cu deposition, and the surface roughness decreased with increasing the amount of BTA in the electrolyte, we did not find a definitive proof that it could act as a diffusion barrier for mass transport of ions to the electrode. This however, did not prevent us from controlling and manipulating the composition of CuNi alloys. Other noteworthy results include the inverse dependence of the Ni at.% in the alloy on the BTA concentration in the solution, and alloy grains having higher growth rate in the vertical direction when Ni was present in the electrolyte. Alternative approaches to assembly of inhibiting BTA layer on a Cu substrate, such as dipping of the substrate in a BTA containing electrolyte, or substrate fabrication from Cu electrolyte containing BTA, were not as effective as having BTA present in the solution during alloy deposition.

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Tables

Bath compositions with component concentrations in mol L ⁻¹						
	[CuSO ₄]	[NiSO ₄]	[KCl]	[H ₂ SO ₄]	[H ₃ BO ₃]	[BTA]
A. High throwing power CuSO ₄ bath ²⁹	0.376		1.0 × 10 ⁻³	1.84		
B. Watts type NiSO ₄ bath		1.141			0.728	
C. Cu-only (virgin Cu)	0.034 – 0.38		1.0 × 10 ⁻³	1.8 × 10 ⁻²		
D. Cu-BTA	0.076		1.0 × 10 ⁻³	1.8 × 10 ⁻²		8.39 × 10 ⁻³
E. Ni-BA		1.141	1.0 × 10 ⁻³	1.8 × 10 ⁻²	0.728	
D. Cu-Ni ¹	0.076	1.141	1.0 × 10 ⁻³	1.8 × 10 ⁻²		
E. Cu-Ni-BA ¹	0.076	1.141	1.0 × 10 ⁻³	1.8 × 10 ⁻²	0.728	
F. Cu-Ni -BTA ¹	0.076	1.141	1.0 × 10 ⁻³	1.8 × 10 ⁻²		0 – 0.0126 ²
G. Cu-Ni-BA-BTA ¹	0.076	1.141	1.0 × 10 ⁻³	1.8 × 10 ⁻²	0.728	0 – 0.0126 ²

¹ The H₂SO₄ concentration for solutions with pH -0.25, 0.00, 0.75 and 1.75 was 1.84, 1.00, 0.18 and 1.8E-2 mol L⁻¹ respectively.

² 0.0126 mol L⁻¹ BTA corresponds to 1500 ppm

Table 1. Electrolytes used in this work. In the coded names (A to G) Cu corresponds to the presence of CuSO₄, Ni to NiSO₄, PC to Potassium Chloride, SA to Sulfuric Acid, BA to Boric Acid and BTA to 1H-Benzotriazole. The products used to make these electrolytes were CuSO₄: Sigma Aldrich, powder, anhydrous 99.99%; NiSO₄: Alfa Aesar, powder, hexahydrate, ACS, 98.0%; KCl; Merck, for analysis EMSURE®, ACS; H₂SO₄: KMG, 96%; H₃BO₃: Alfa Aesar, ACS grade, 99.5%; 1H-Benzotriazole: Acros Organics, 99%.

Diffusion coefficients calculated from kinematic viscosities and Levich slopes at 45°C			
	Diffusion coefficient (10 ⁻⁶ cm ² s ⁻¹)	Kinematic viscosity (10 ⁻³ cm ² s ⁻¹)	Levich slope (10 ⁻²)
Cu-only (Δ)	16.4	6.41	3.41
Cu-BA (□)	14.8	6.79	3.16
Cu-BA-BTA (○)	16.4	6.81	3.39
Cu-Ni (▲)	6.44	11.1	1.67
Cu-Ni-BA (■)	6.11	11.8	1.60
Cu-Ni-BA-BTA (●)	5.90	11.9	1.56

Table 2. Diffusion coefficients of the indicated bath compositions as calculated from corresponding kinematic viscosities and Levich slopes at pH 1.75. No Levich slopes for Cu-BTA nor for Cu-BA-BTA were calculated as the limiting currents of Cu²⁺ for these baths weren't reached before the H₂ evolution onset.

Figure Captions

- Figure 1. Schematic drawing of the cross-section view of the RDE setup. The inset shows the bottom-up view of the used RDE-tips with the exposed surface of the removable working electrode pellets.
- Figure 2. Linear sweep voltammogram (0.015 V s^{-1}) at the Cu rotating disc electrode (60 RPM) in 76 mM CuSO_4 (Cu) + KCl + H_2SO_4 with the addition of NiSO_4 (Ni), boric acid (BA) and benzotriazole (BTA) (Table 1), at pH -0.25 (a) and pH 1.75 (b). The potential was measured with IR correction versus a Ag/AgCl reference electrode (0.205 V vs SHE) and converted to reference versus the standard hydrogen electrode (SHE).
- Figure 3. (a) Onset of Cu^{2+} and Ni^{2+} reduction potentials at pH 1.75 in a Cu-BTA bath (●) and a Cu-Ni-BA-BTA bath (▲ and Δ respectively) as a function of BTA concentration. (b) Onset of the Cu^{2+} reduction potential in a Cu-Ni-BA-BTA bath (▲) as a function of pH.
- Figure 4. Levich plots for all tested electrolytes at pH 1.75. The calculated slopes are tabulated in Table 2.
- Figure 5. Block diagram representation of the contributions of the diffusion coefficient and kinematic viscosity to the Levich slope in each of the indicated bath compositions. D and ν are raised to the power $2/3$ and $-1/6$ respectively to reflect their contributions to the rotation rate dependency of the Cu^{2+} reduction as derived from the Levich equation (5).
- Figure 6. LSV's (0.015 V s^{-1}) at the Cu RDE (60 RPM) of Cu^{2+} reduction in a Cu-Ni-BA bath (◆: 60 RPM and pH 1.75), a Cu-Ni-BA-BTA bath (●), in a Cu-Ni-BA bath after the substrate was dipped in a Cu-Ni-BA-BTA bath for 60 seconds (▲) and in the same bath after the 150 nm Cu seed layer was pre-deposited from a Cu-BA-BTA bath (■).

Figure 7. (a) Potential-time responses of CuNi depositions with BTA concentrations 0, 10, 100 and 1000 on Cu pellets ($\varnothing$ 4 mm, 1 μ m thick deposits) at -21.5 (---) and -40.5 mA cm⁻² (—). The first 5 seconds are shown on a different time scale for easier analysis of the initial stages of deposition. (b) Potential-time responses for Ni deposition from Ni-BA and Ni-BA-BTA electrolyte on Cu pellets ($\varnothing$ 4 mm, 1 μ m thick deposits) at -21.5 (---), -40.5 mA cm⁻² (—) and -12 mA cm⁻² (only for Ni-BA-BTA,). Initial 5 seconds are shown on a different time scale.

Figure 8. SEM images of a Cu and a Ni layer deposited on Cu from a Cu-BA-BTA (a, b and c) and from a Ni-PC-SA-BA-BTA bath (d, e and f). Top down perspectives of the layers deposited at -21.5 mA cm⁻² (a and d) and at -40.5 mA cm⁻² (b and e). 45° tilted perspective of the layers deposited at -40.5 mA cm⁻² (c and f).

Figure 9. SEM images of CuNi alloys deposited from a Cu-Ni-Ba-BTA bath on Cu at -21.5 mA cm⁻² using BTA concentrations of 0, 10, 100 and 1000 ppm at -21.5 mA cm⁻² (a to d respectively) and at -40.5 mA cm⁻² (e to h respectively). For each sample a top-down (a, b, c, d, e, f, g and h) and a 45° angle perspective (a', b', c', d', e', f', g' and h') is presented.

Figure 10. Cross section SEM images of the elongated CuNi grains, deposited from a Cu-Ni-BA-BTA (1000 ppm) bath at -21.5 mA cm⁻² (a) and at -40.5 mA cm⁻² (b). SEM images of a CuNi on Cu deposited from a Cu-Ni-BA-BTA bath with 2000 ppm BTA from a top-down (c) and a 45° tilted perspective (d).

Figure 11. Atomic percentages of Ni, determined by EDS, in deposits at -21.5 mA cm⁻² (●) and -40.5 mA cm⁻² (◆) as a function of the BTA concentration. For the experiment with 1000 ppm BTA, the pH was increased to 2.5 to evaluate the effect of pH on the Ni content in the deposit (○ and ◇)

Figure S1. Linear sweep voltammogram (0.015 V s⁻¹) at the Cu rotating disc electrode (60 RPM) in KCl + H₂SO₄ with the addition of boric acid (BA) and benzotriazole (BTA) at pH -0.25 (a) and pH 1.75 (b). The potential was measured with IR correction versus a Ag/AgCl reference electrode

492 (0.205 V vs SHE) and converted to reference versus the standard hydrogen
493 electrode (SHE).

Bottom view RDE

Pt RDE

Cu pellet RDE (Removable)

Pellet side view

Side view cell

a **b**

a **b**

a **b**

-21.5 mA cm⁻²
Top down

a

5 μm

-21.5 mA cm⁻²
Top down

d

5 μm

-40.5 mA cm⁻²
Top down

b

10 μm

-40.5 mA cm⁻²
Top down

e

10 μm

-40.5 mA cm⁻²
45° angle

c

2 μm

-40.5 mA cm⁻²
45° angle

f

2 μm