ACD Co-P Interlayers in Soldering with Tin Alloys for Microelectronics

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Autocatalytic cobalt is proposed as a barrier metallization for copper in lead-free soldering. Results about solder reaction and diffusion of autocatalytic cobalt with Sn-Ag-Cu and Sn-Pb alloys are presented. Bonding and solderability of autocatalytic cobalt are discussed.

Solder reaction of autocatalytic cobalt with eutectic tin-lead and tin-silver-copper alloys is characterized by the formation of an homogeneous interface with thin interdiffusion layer. A thick interdiffusion layer is observed between NiP and solder alloy, with formation of brittle intermetallic compounds, mainly Ni_3Sn_4 and Ni_3P. The formation of a very thin interlayer was observed in the case of the cobalt finish, showing a much lower cobalt and tin interdiffusion. The Au layer has a minor role on the soldering behavior of Ni and Co with Sn. Similar results are obtained with BGA balling.

The contact angle of Sn-Pb and Sn-Ag-Cu on CoP/Au after soldering was about 5° in the two cases, while those for SnPb and SnAgCu on NiP/Au were about 5° and 15° respectively. Wetting time is lower for CoP than for NiP for both solder alloys.

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Introduction

Mechanical joining of components in electronics is achieved through soldering with tin based solders alloy. Due to environmental and health concerns, the traditional tin-lead alloy must be replaced with Pb-free solders, i.e. Sn3.8Ag0.7Cu. Lead free solders have high tin content and high melting temperature, leading to a lack of reliability for the electroless nickel/immersion gold ENIG finish. Electroless Ni-P was recognized as diffusion barrier in the copper metallization for the very slow rate of Sn-Ni intermetallics growth and relative low diffusion rate of nickel through gold and copper. The intermetallic compounds Ni_3Sn_2 and Ni_3Sn_4 were recognized as the main constituents of the intermetallic phase between solder and finish [1,2]. During reflowing with Pb-free solders, a new P rich nickel layer is formed along with tin intermetallic compounds. Due to nickel diffusion, phosphorus accumulation at the interface between the Ni-P layer and solder alloy was observed, leading to the formation of nickel phosphide compounds, i.e. primarily Ni_3P [2,3]. Solder joint failure is mostly related to the growth of these compounds and to their brittleness and effects on the mechanical reliability of joints. Phosphides formation at the interface is a relatively new issue in soldering, it is therefore crucial to provide solution to P enrichment and alternatives to the traditional electroless nickel finish.

Unlike nickel, cobalt is less keen to form intermetallic compounds with tin, having a less negative free enthalpy of formation then nickel ($\Delta H_f(Co_3Sn_2)$ = -10 kJ/mol, $\Delta H_f(Ni_3Sn_2)$ = -39 kJ/mol), and Co_2P formation requires more P than Ni_3P. Electroless cobalt can be deposited as nickel from hypophosphite based electrolyte and it is a well known process for magnetic recording layers [4-6].

In this work, an electroless cobalt-phosphorus/immersion gold finish is proposed as diffusion barrier for high tin solders. Cobalt deposition is carried out in a hypophosphite based electrolyte, optimizing experimental condition in order to improve the solderability of the finish and mechanical behavior of the joints.

Experimental

BGA coupons with copper pads defined by solder mask and diameter 0.6 mm were used as substrate for electroless deposition. Reagent grade chemicals and deionized water were used for the preparation of the autocatalytic cobalt solution. Co-P deposition for solderability, mechanical and diffusion evaluation was carried out for 15 minutes at pH = 8 and 95 °C. Ni-P and gold deposition was carried out for 15 minutes in commercial solutions at 85 °C and 88 °C respectively. Thickness was in the range 3-5 μm for Co-P and Ni-P layers, and 0.2 μm for immersion gold.

Contact angle measurements were performed with Optical Contact Angle OCA 20 DataPhysics with TEC 400 heated chamber under Nitrogen flow. Ball soldering was performed in nitrogen atmosphere (oxygen < 150 ppm), with suitable thermal profile depending on solder alloy using Alpha Metals WS1208 gel flux.

Shear test was performed with piezoelectric transducer of WR - WILCOXON RESEARCH, L5 model, S/N 982 (charge sensitivity = 116 pC/Lb; voltage sensitivity = 147 mV/Lb; capacitance = 790 pF, stiffness 0.5x 106 Lb/in) and digital oscilloscope Tektronix 2430; probe diameter 1.2 mm, free fall distance 11.5 +/- 0.5 mm and weight 960 g.

Results and discussion

Electroless Co deposition

Cobalt-phosphorus layers were deposited from a hypophosphite based solution. An electrolyte of the following composition was chosen as a standard for further experiments: cobalt sulfate 0.1 M, sodium hypophosphite 1.5 M, ammonium citrate 0.1 M and glycine 0.1 M. The effect of pH and temperature was investigated.

Below pH = 7.5, deposition was characterized by electrolyte instability, producing irregular and poor deposits. Deposition rate increased with increasing pH up to ten with bright and adherent deposits. Due to hydroxides precipitation and microelectronic industry requirements for circuit preservation, higher values of pH were not taken into account. Phosphorus content in the deposits with values around 4 wt% was slightly influenced by pH variation. This value of P content was evaluated in preliminary studies as the content offering better diffusion barrier properties to the Co-P layer. Morphology of the Co-P layer depending on pH is shown in fig. 1: at low pH, globular three-dimensional structures were detected; at pH higher than 8, well defined grains with size in the range 1-10 μm were observed; at pH = 8, surface was smooth with undefined grains.

X-ray diffraction patterns showed an hexagonal close-packed crystalline structure with slightly broadened reflections. An average value of hardness of 900 HV with an elastic modulus of about 140 GPa was obtained through microindentation measurements on the cross section of the Co-P deposits.

The operative temperature greatly influenced the deposition rate at pH = 8 with a sharp increase at T > 90 °C and a maximum value of 9 mg cm^{-2} h^{-1} measured at 98 °C.

With operative conditions of pH = 8 and T = 95 °C, the influence of the bath dilution was investigated. For both cobalt sulfate and sodium hypophosphite concentration, a maximum for the deposition rate was detected at concentrations 0.1 M and 1.5 M respectively. Phosphorus content of the deposits slightly increased from 2.2 wt% to 5.5 wt% for sodium hypophosphite concentration of 0.5 M and 2 M respectively.

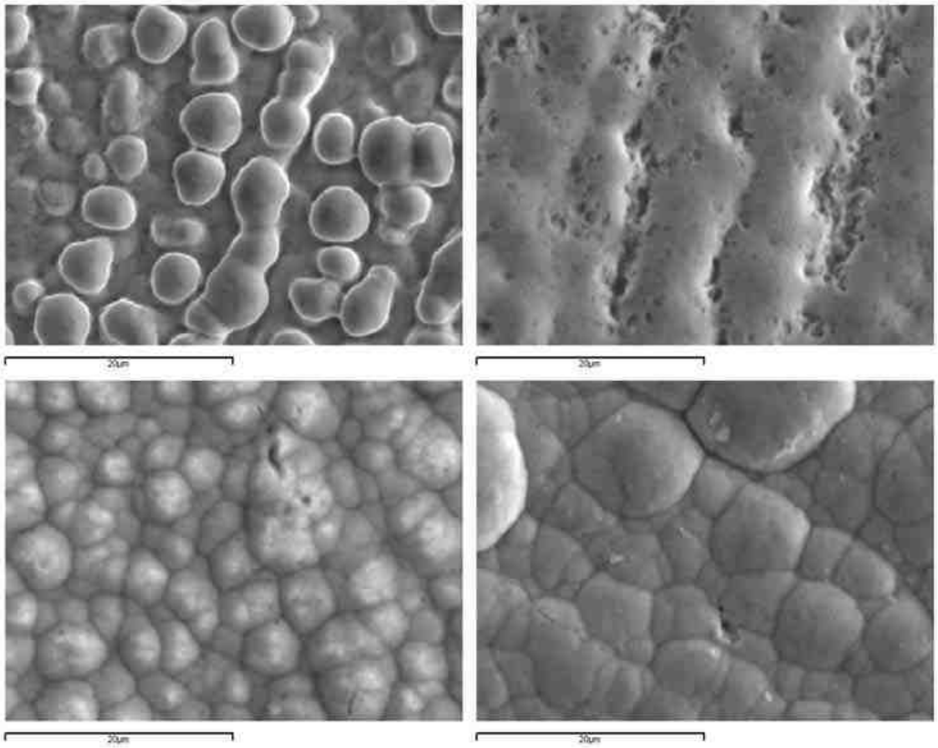


Fig. 1 *- Morphology of Co-P layer depending on pH: a) pH 7.5; b) pH 8; c) pH 8.5; d) pH 9.*

Citrate complexants act on bath stability, deposition rate characteristics of the deposits and buffering of the bath. It is known that a buffering action is produced by the synergic effects of glycine and citrates in presence of ammonia [7]. The deposition rate of Co-P was evaluated as a function of ammonium citrate and glycine concentration. Increasing ammonium citrate concentration produced a slight increase of the deposition rate, but correspondingly a great increase of P content up to 10 wt% at 0.2 M of citrates.

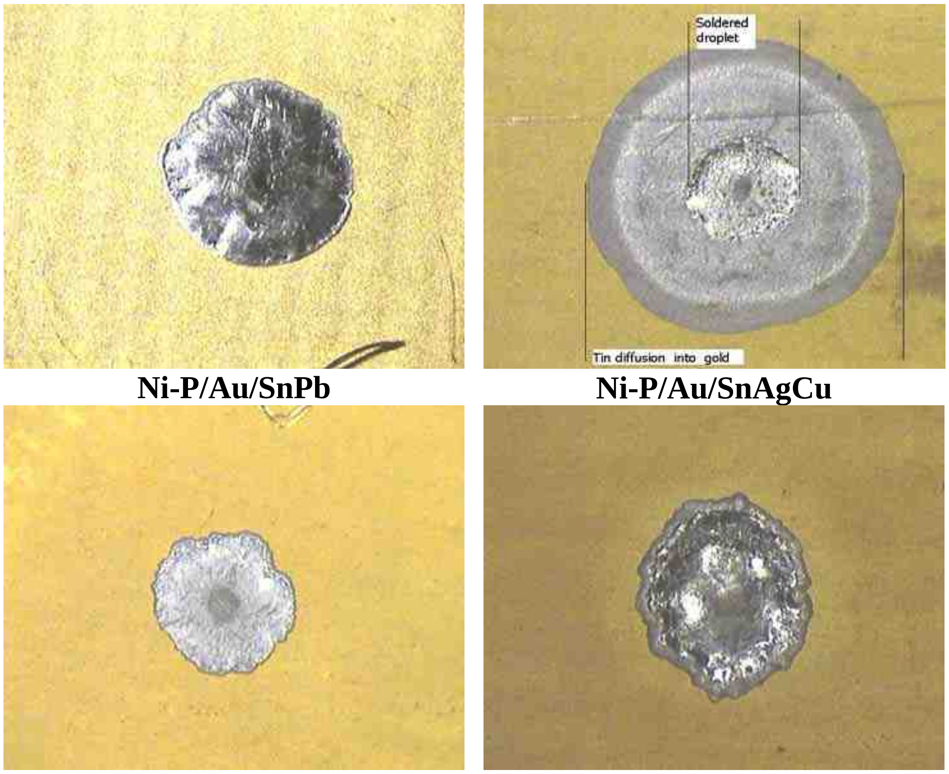
As expected, the increase of glycine in the bath lowered the deposition rate, even if its effect was beneficial for the aspect of the deposits, improving brightness.

Standard electrolyte composition and operative condition (pH = 8, T = 95 °C) were therefore employed for the deposition of barrier layers in soldering, assuring the best conditions in terms of bath stability, deposition rate and P content.

Solderability

Contact angle measurements were carried out to evaluate the solderability of Co-P/Au and Ni-P/Au finishes with Sn-Ag-Cu and Sn-Pb solder balls. High wettability characterised the gold coated electroless nickel if soldered with tin-lead alloy, while solderability was poor if soldered with lead-free alloy: contact angles were 5° and 15° respectively. Gold coated electroless cobalt showed very low values of contact angles with both alloys: 6° and 5° respectively. Figure 2 shows solder balls after reflow. Wetting time, i.e. time to reach final contact angle, was lower for

Co-P/Au than for Ni-P/Au with both the alloys: 22 s and 7 s with Sn-Ag-Cu and Sn-Pb respectively for the former, 30 s and 12 s respectively for the latter.



Ni-P/Au/SnPb **Ni-P/Au/SnAgCu**

Co-P/Au/SnPb **Co-P/Au/SnAgCu**

Fig. 2 *- Solder balls after reflow.*

Diffusion barrier

Figure 3 shows the SEM image of the cross sections of Sn-Ag-Cu/Au/Co-P and Sn-Pb/Au/Co-P joints after soldering with concentration line profiles of elements. Solder interfaces were characterized by irregular shape with presence of cobalt-tin interdiffusion layers. Phosphorus concentration remained constant along the electroless cobalt layer without enrichment at the interfaces and formation of phosphides. A thin interdiffusion layer was observed at the copper-cobalt interface.

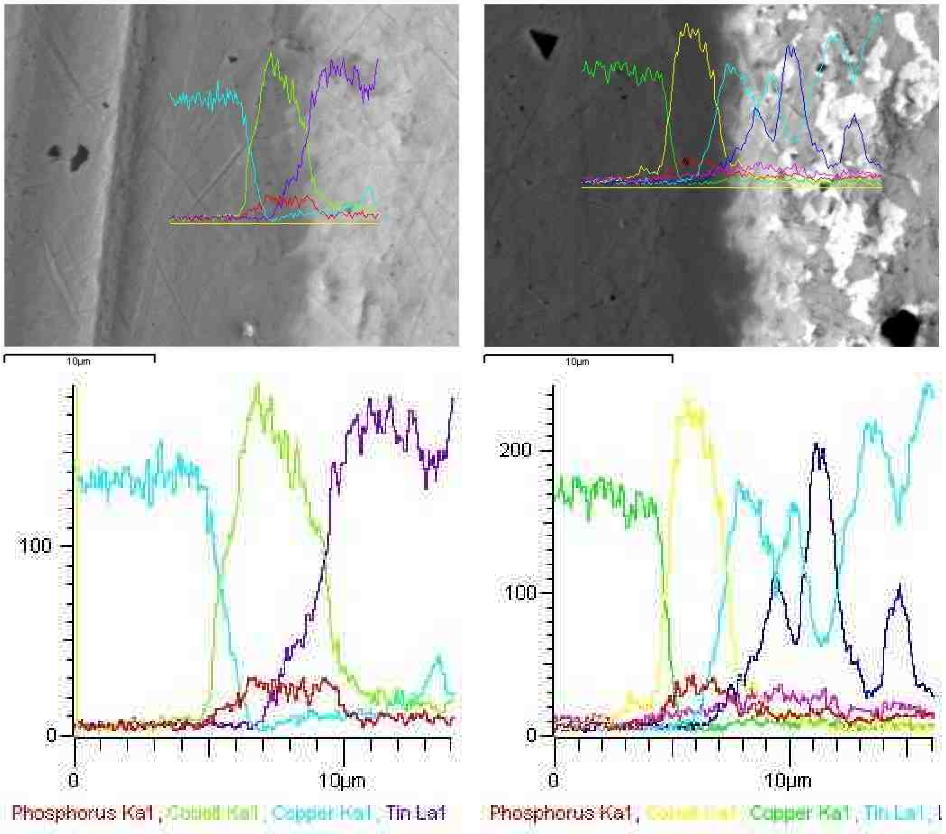


Fig. 3 *- Cross sections of Sn-Ag-Cu/Au/Co-P (left) and Sn-Pb/Au/Co-P (right) joints after soldering with concentration line profiles of elements.*

In fig. 4 SEM image of the cross sections of Sn-Ag-Cu/Au/Co-P and Sn-Ag-Cu/Au/Ni-P joints with concentration line profiles of elements after soldering and heat treatment at 150 °C for 15 minutes are reported.

Thin interdiffusion layers were observed for the Co-P finish at the interface with tin solder without phosphorus enrichment and intermetallic compounds formation. A continuos thick dark layer of intermetallic compounds with P enrichment was visible at the interface between Ni-P and solder. Tin diffusion underneath the Ni-Sn intermetallic compounds layer was also detected.

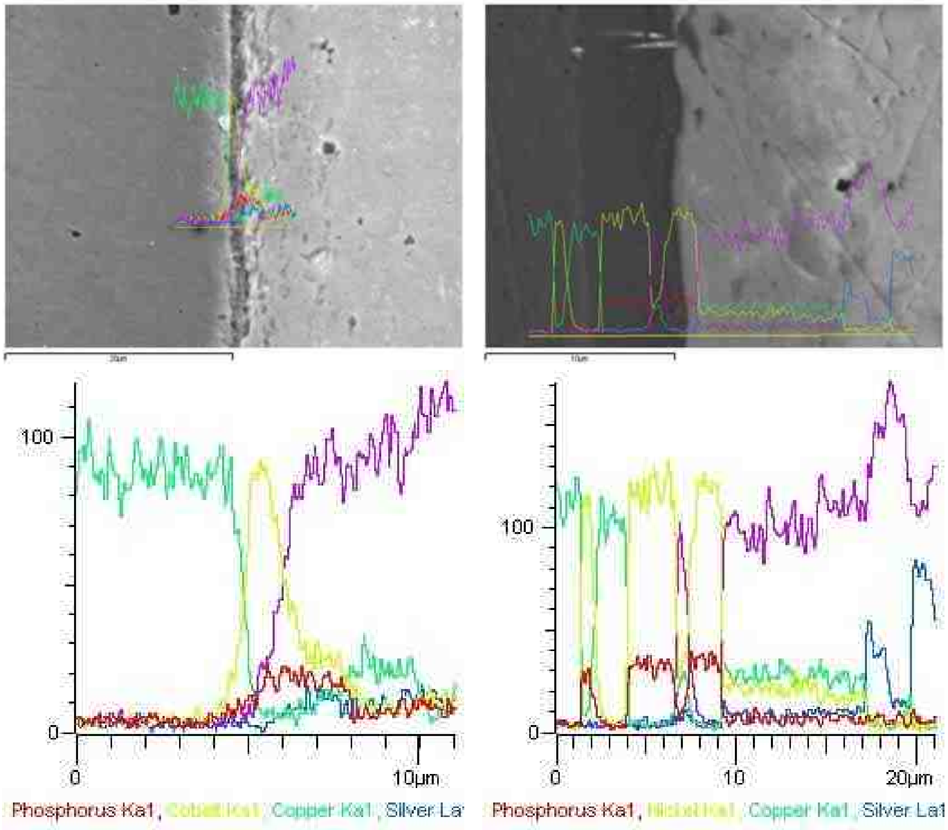


Fig. 4 *- Cross sections of Sn-Ag-Cu/Au/Co-P (left) and Sn-Ag-Cu/Au/Ni-P (right) joints with concentration line profiles of elements after soldering and heat treatment at 150 °C for 15 minutes.*

Mechanical strength of joints

Mechanical joint strength of BGA soldered with Sn-Ag-Cu and Sn-Pb solder paste on Ni-P/Au and Co-P/Au board finishes was evaluated measuring the shear force imposed by a probe of 960 g free falling from a height of 11.5 mm and impacting at board pad-ball interface. A piezoelectric transducer output forces as voltage values: the higher the joint mechanical strength, the higher the voltage value. The average strength value and standard deviation, resulting from sixteen measurements, were respectively for Co-P/Au and Ni-P/Au 67 ± 15 mV and 61 ± 35 mV with Sn-Ag-Cu and 115 ± 27 mV and 130 ± 57 mV with Sn-Pb eutectic alloy. The higher standard deviation given by Ni-P with the two alloys can be explained with the more irregular intermetallic structure and the lower wettability, as reported in the previous sections. However these two factors do not have the same significant effect on the average value.

Conclusions

Autocatalytic Co-P containing about 4 wt% P has been deposited from hypophosphite based solution at pH = 8 and 95 °C. Electroless Co-P/Au finish strongly limits interdiffusion and intermetallic compounds formation with respect to the Ni-P/Au finish with both examined alloys. Contact angle of Sn-Pb solder alloy with Ni-P and Co-P layers is comparable, whilst in the case of Sn-Ag-Cu alloy the angle is much lower for Co-P than for Ni-P layers. Wetting time is lower for Co-P than for Ni-P for both solder alloys. Mechanical joint strength of BGA soldered with Sn-Ag-Cu solder on Co-P/Au and Ni-P/Au board finishes is slightly higher with lower standard deviation for cobalt than for nickel finish

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