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Surface Preparation of Aluminum for Plating by Zincating

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Abstract

The objective of this work is to gain better understanding of the influence of zincate bath chemistry on zincating morphology of Aluminum bond pads to provide reference for zincating chemistry design and process control for wafer bumping applications.

Keywords: Metallization , Electrolss nickel , Zincate.

الخلاصة:

أن الهدف من هذا العمل هو للحصول على معلومات متقدمة في فهم وأستيعاب فكرة الطلاء بالزنك اللاكهربائي على طبقة من الألمنيوم (الأساس) علماً بأن الألمنيوم يتميز بتغطيته الذاتية وذلك بتكوين أوكسيد الألمنيوم ذات المقاومية الكهربائية وسرعة التكوين. أن طبقة الزنك اللاكهربائي المرسبة (مدار البحث) هي طبقة وسطية لترسيب الطبقات السطحية الأخرى على الألمنيوم ذات التطبيقات الواسعة في الصناعات الألكترونية بمختلف أنواعها.

1- Introduction

Electroless nickel (EN) metallization or bumping of silicon wafers is gaining interest in flip chip packaging applications because of its relatively low cost and simple process [1-10]. Additional impetus for using EN as under bump metallurgy (UBM) materials may come from the adoption of copper-containing lead-free solders as the bump materials. Significant dissolution of copper into the lead-free solder from its copper bearing UBM (Cr/Cu, TiW/Cu, for example) could change the physical properties of the solders, as the copper content in the solders is rather low. The intermetallic compound formation between the solders and commonly used UBMs with copper finishing may also raise reliability concerns. This work presents the low cost process for UBM formation on aluminum pads of single die/dice for Flip Chip applications. The UBM (Under Bump Metallization) is required in solder bump structure to provide adhesion/diffusion barrier layer, solder wettable layer, and oxidation barrier layer between the bonding pads of the die and the bumps. Typically, UBM is deposited on the whole wafers by sputtering, evaporation, or electroless plating. These deposition techniques are not practical for UBM formation on single die/dice, thus preventing Flip Chip technology from being applied in applications where the whole wafers are not available [1].

Nickel, be it chemically (EN) or physically (sputtered) deposited, would be an ideal UBM component material as it is not a constituent element in the popular lead-free solder system, and its dissolution into solders is much slower than that of copper. Aluminum, with minor doping of other elements, is the

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dominant material for IC bond pad metallization. This will remain true for sometime, even taking into consideration the newly emerged copper metallization schemes. Aluminum is catalytic for electroless nickel deposition. However, Aluminum rapidly oxidizes during rinsing and/or when exposed to air, and the oxide films produced will completely suppress metallization or prevent the formation of Al-Ni intermetallic bonds, resulting in adhesion failure. Zincate treatment of Aluminum bond pads is thus an essential process step in electroless nickel bumping that activates the pads for subsequent EN deposition. Zincation of Aluminum relies on the electrochemical exchange reaction between zinc complexes in solution and Aluminum metal, depositing zinc crystallites at the expense of Aluminum dissolution (etching). Previous studies have shown that zincating operations have significant impact on the morphology of a resultant zinc layer on Aluminum pads [10,11] and the zincate morphology has direct correlation with the quality of EN bumping [11, 12 , 13]. Zincate treatment of bulk Aluminum and Aluminum alloys has been extensively studied and documented in the past [12- 14]. However, commercial solutions and process conditions for treating bulk Aluminum have been found not suitable for wafer bumping [11] and similar studies on zincation of Aluminum bond pads are lacking. Aluminum bond pads on silicon wafers have two distinct features: tiny in area and thin in material. This necessitates special considerations on the chemistry design and operation condition selection of zincate bath. There is no published study yet on the role of zincate chemistry in achieving good zinc morphologies for wafer bumping applications. In this work a series of systematic experiments were designed and conducted in this work. A zincate bath has been optimized with the (DOE) approach. The information presented here will provide insight into the zincate chemistry and zincate process control in wafer bumping applications.

2-Experimental Significances

Although electroless nickel has been widely used in wafer bumping and package substrate manufacturing and many laboratory research and industrial success stories published, the understanding on the unique requirements posed by the specialties in electronics packaging to the plating process is not sufficient. Any fundamental understanding with respect to the EN process will be useful in improving product quality or in applying the process to new applications. For the particular zincating process step in wafer bumping or metallization, a zincate bath and its interaction with different types of real semiconductor metallizations is quite complex. The results obtained may[not be a generic solution for all cases]. However, the information presented may serve as a reference for other zincate chemistry designs and zincate process control in EN wafer bumping for flip chip packaging applications.

3– Experimental Work

The test of specimens used in this study was prepared from blank wafers. Silicon wafers with 5000 angstrom thick silicon oxide were cleaned by soaking in pure nitric acid

at room temperature for 3 minutes followed by rinsing with deionized (DI) water, blowdring with pure nitrogen. A pure aluminum film of about one micron thick was deposited onto the polished side of the wafers with an unbalanced magnetron sputtering system.

The test wafers were then diced into smaller segments for experiments. Different pad geometry and arrangements were adopted to check their possible influence to zincate quality.

Basic zincating ingredients for treating bulk Aluminum were reported in the literature[13] to include zinc oxide (5 ~ 50 g/l), sodium hydroxide (50 ~ 500 g/l), potassium sodium tartrate (10 ~ 50 g/l), sodium nitrate (0 ~ 1 g/l) and ferric chloride (1 ~ 2 g/l). There were also solutions containing nickel compounds (e.g., NiSO4 10 ~ 30 g/l) instead of ferric chloride. The functions of these components in the solution are: zinc oxide provides zinc source, ferric chloride in conjunction with the tartrate ion improves adhesion of deposits, sodium nitrate limits the amount/thickness of deposits, and sodium hydroxide maintains desired pH level. Most currently available commercial zincate solutions are for bulk Aluminum material and are generally based on these chemicals with different concentrations and proprietary additives depending on the supplier. The selection of chemicals to make up our experimental solutions is based on these literature reports. A DOE experiment of 5 components (ZnO, NaNO3, C4H4KNaO6, FeCl3 and NiCl2) with 6 levels of concentration was carried out to identify the influence of each key components and obtain the best concentration ranges and combinations. The solution concentration levels in the DOE are shown in Table 1. The five components and their six levels. The concentration ranges selected here are much lower than commonly reported values because our previous studies [12, 16, 17, 18, 19] have shown that 10 to 20 times dilution of the commercial solutions for bulk Aluminum was necessary to produce acceptable zincate quality and hence good EN bump quality on Al pads. NaOH content was kept at 40 g/l for all the experiments.

A standard double zincate procedure [11,15] was followed in all the zincate experiments as follows:

1. Mild etching/cleaning with weak alkaline cleaner .
2. Rinsing with deionized (DI) water, room temperature (RT);
3. First zincating; 45 s, RT
4. Rinsing with DI water, RT
5. Nitric acid dip; 20% HNO3, 15 s, RT
6. Rinsing with DI water, RT
7. Second zincating; 15 s, RT
8. Rinsing with DI water, RT
9. Nitrogen blow dry.

4- Results And Discussion

4-1- Quantification of Zincate Morphology

Effect of zinicate quantification morphology typical optical microscopic views of the zincate morphology associated with various DOE bath compositions are shown in Fig.1 which shows in (a) a homogeneous and smooth coverage of the Al pad by zinc crystallites. and (b) to (d) show increasingly rougher surfaces, compared to (a), on which the agglomeration of zinc crystallites can be seen. It was noticed that the bump size and their patterns had no

influence on the resultant zincate morphology.

A good quality zincate is characterized by fine zinc crystal grains, homogeneous crystallite distribution, smooth coverage of the whole pad and no nodular agglomeration of zinc crystallites. The zinc crystallite agglomeration is especially detrimental to the adhesion of EN plating to the Aluminum pad[16] because the adhesion of EN to the agglomerated zinc metal is much weaker than that of EN to Aluminum. Based on the collective perception of a good zincating treatment, a quantitative quality number, Q, was

calculated for each sample using the relationship

Q = % coverage – % Agglomeration . .. . . .(1)

where '% of coverage' is the ratio of the area covered by zinc crystallites (including the Zn agglomerates) over the total area examined, and %Agglomeration the ratio of the areas covered by the zinc agglomeration spots over the total area. Hence, Q represents the effective coverage of the aluminum surface by fine zinc crystallites and a higher Q value would thus imply better zincate quality. The measurement results and the Q values for all the samples are listed in Table 2.

4-2 Effect of Design

The factorial effect of the five solution components was analyzed with an established method [16].

i) ZnO

Fig. 3 shows the variation of the zincate morphology with ZnO concentration while keeping that of the others constant. These micrographs show that as the ZnO content increases the zinc crystallites become larger. Agglomeration of zinc crystallites appears when the ZnO content is above 0.2 g/l. here fore, ZnO concentration should be below 0.20 g/l to produce smooth, homogeneous and agglomerate free zincate morphology.

ii) FeCl3 and NiCl2

The experimental results for FeCl3 show that its concentration should be kept below 0.015 g/l. At higher concentration, zinc crystallite agglomeration, similar to that shown in Fig. 3d, appears and further addition could result in a morphology as shown in Fig. 1d. Similarly, the concentration of NiCl2 should be kept below 0.075 g/l. This seems to suggest that the iron or nickel ions could also promote zinc crystallization on zinc nuclei – high concentrations of Fe^{3+} or Ni^{2+} would speed up the zinc crystallization on existing zinc crystallites, making nucleation of zinc on free aluminum surface more difficult.

iii) $C_4H_4KNaO_6$

The main function of potassium sodium tartrate is to complex with the iron or nickel ions to prevent them from precipitation by hydrolysis. The experimental results showed that the concentration ratio of the tartrate over ferric chloride should be kept below 40 (or below 15 for NiCl2), to avert zinc agglomeration. It appears that the tartrate can also function as a zinc crystallization promoter or it can enhance the activity of iron or nickel ions.

iv) NaNO3

The optimum level of sodium nitrate was found to be around 0.025 g/l. Lower than this the effect was not obvious but at much higher levels (above 0.4) zinc crystallites become coarse and agglomerates start to grow.

An average quality number, Qav for each concentration level of a particular component is obtained by averaging the Q-values of the 6 samples with that level along the column of the component. The QAv values of the five solution components at different levels are shown in Fig. 2. The variation in QAv of a component indicates the existence of factorial effect of the component and, the larger the variation, the more profound the effect of the component, according to the orthogonal experimental theory. The result show that all the components have influences on the zincate quality but ZnO has the most prominent effect. The best concentration levels corresponding to the highest point on the curves in Fig. 2 are listed in table.3 as below:

Ferric chloride and nickel chloride have the same function of promoting adhesion [12] and it is interesting to notice that the best level for NiCl2 is level 1, corresponding to

zero addition of the chemical. This indicates that there is actually no need to add in NiCl2 chloride is present in the bath, or vice versa.

4-3 Optimization Effect

Further optimization nail down the optimum concentration of individual components, the concentration of a particular component was changed around the best DOE-determined values given above, while keeping those of the others constant. Ferric chloride and nickel chloride were not used together in this round of experiments. Samples for the following variations were prepared in table.4.

4-4 Optimum bath Composition

Optimum bath chemistry by summarizing the results from individual optimization experiments, an optimum bath composition was identified as table 5 .

The performance of the bath was confirmed. Full coverage of the Al surface with fine grained and agglomerate-free zinc crystallites was achieved. A typical view of the zincate morphology resulting from the optimal zincate bath is given in Fig. 4.

5 – Conclusions

Influence of the basic ingredients and their concentrations in a zincate solution on the zincate morphology of Al bond pad has been experimentally studied with a design of Experiment (DOE) approach. An optimum bath composition was established which produced the desired zincate morphology, i.e., nearly full coverage of the Aluminum pad surface with fine-grained and agglomerate-free zinc crystallites. The low concentration levels of the major ingredients in such a zincate bath distinguish it from conventional zincate baths formulated for bulk Al applications.

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Table 1. Concentration levels of the components in the DOE experiment, g/l.

Level	NiCl2	ZnO	NaNO3		KNa	FeCl3
1	0.375	0.0125	0.87	0.0		0.0
2	0.450	0.0175	1.00	0.01		0.05
3	0.525	0.0225	1.13	0.02		0.1
4	0.600	0.0275	1.25	0.03		0.15
5	0.675	0.0325	1.38	0.04		0.20
6	0.750	0.0375	1.50	0.05		0.25

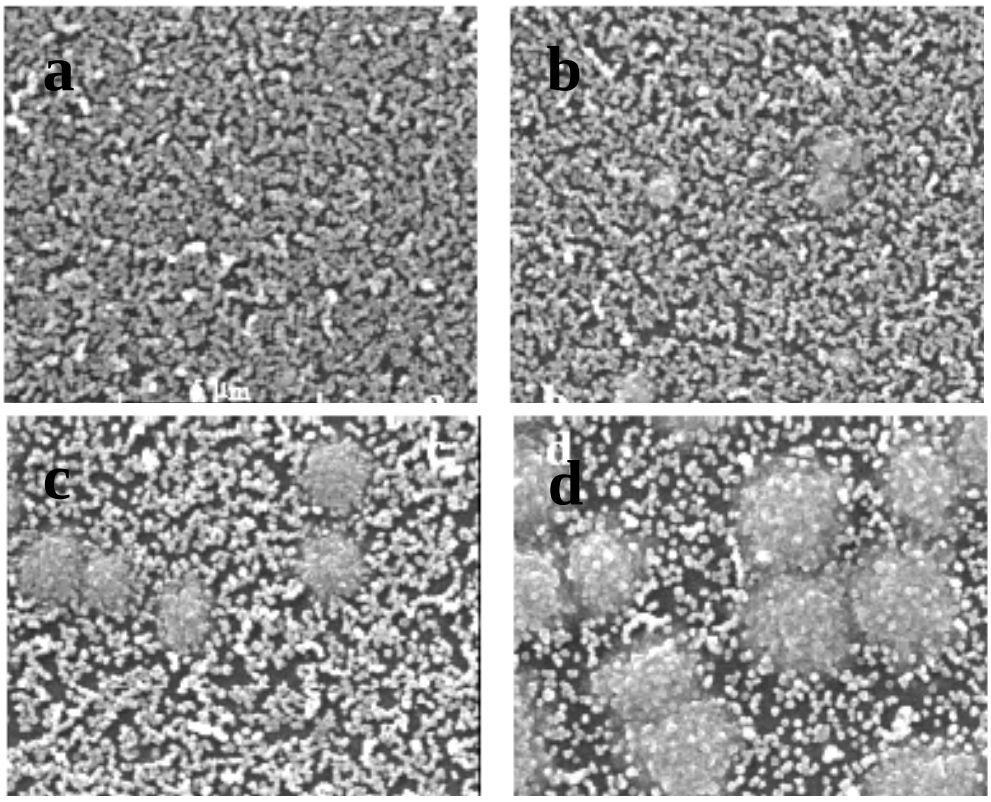


Fig.1. Optical microscopic Picture of the zincate morphologies (1000X).

Table 2 The orthogonal L_{36} Matrix and Quality Quantification of the DOE samples

Sample ID	Concentration levels					%Coverage	%Agglomeration	Q
	ZnO	$NaNO_3$	KNa*	$TeCl_4$	$NiCl_2$			
1	1	1	1	1	1	90	3	87
2	1	2	2	2	2	96	0	96
3	1	3	3	3	3	95	3	92
4	1	4	4	4	4	80	15	65
5	1	5	5	5	5	80	3	77
6	1	6	6	6	6	75	5	70
7	2	1	2	3	4	85	5	80
8	2	2	3	4	5	95	0	95
9	2	3	4	5	6	95	5	90
10	2	4	5	6	1	90	0	90
11	2	5	6	1	2	55	10	45
12	2	6	1	2	3	85	10	75
13	3	1	3	5	1	80	15	65
14	3	2	4	6	2	90	8	82
15	3	3	5	1	3	85	6	79
16	3	4	6	2	4	80	6	74
17	3	5	1	3	5	75	15	65
18	3	6	2	4	6	85	5	80
19	4	1	4	1	4	75	10	65
20	4	2	5	2	5	92	6	86
21	4	3	6	3	6	60	10	50
22	4	4	1	4	1	85	10	75
23	4	5	2	5	2	70	15	55
24	4	6	3	6	3	80	8	72
25	5	1	5	3	1	75	10	65
26	5	2	6	4	2	90	15	75
27	5	3	1	5	3	70	10	60
28	5	4	2	6	4	65	20	45
29	5	5	3	1	5	80	30	50
30	5	6	4	2	6	80	20	60
31	6	1	6	5	4	65	10	55
32	6	2	1	6	5	60	50	10
33	6	3	2	1	6	60	15	45
34	6	4	3	2	1	70	15	55
35	6	5	4	3	2	85	10	75
36	6	6	5	4	3	60	50	10

* $C_4H_4KNaO_6$

Table.3. Relation between component , level and concentration

Component	Level	Concentration, g/l
ZnO	1	0.375
NaNO3	2	0.0175
C4H4KNaO6	4	1.25
FeCl3	2	0.01
NiCl2	1	0.0

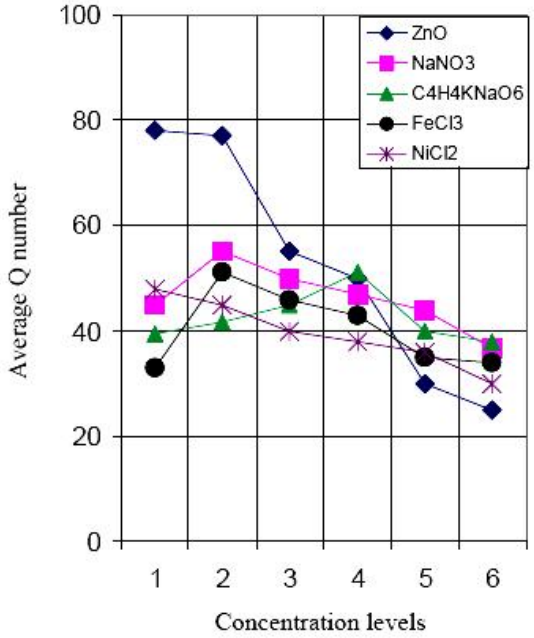
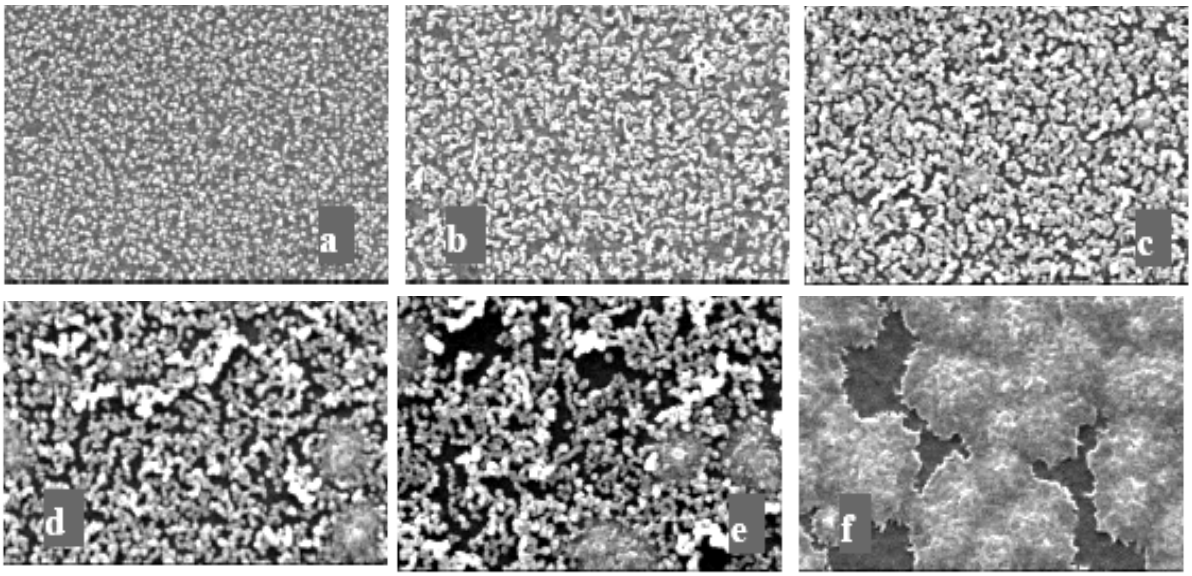


Fig. 2. Average Q number, QAV, for the components at different concentration levels.

Table.4. Relationship between component, Concentration range and Increment.

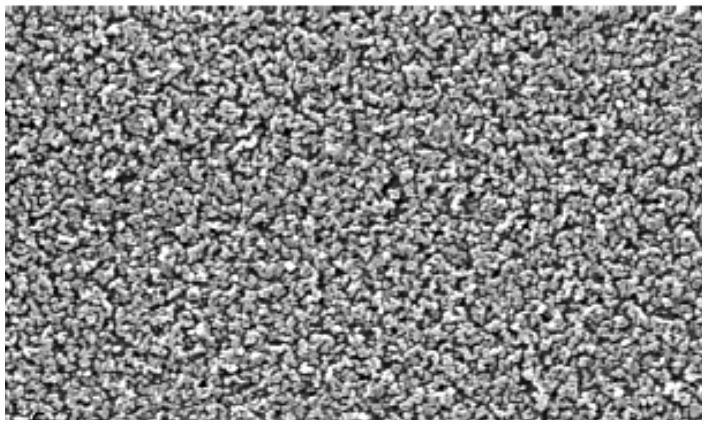
Component	Concentration range	Increment g/l
ZnO	0.05 ~ 0.75	0.05
NaNO3	0.0125 ~0.0425	0.005
C4H4KNaO6	0.75 ~ 1.625	0.125
FeCl3	0.00625 ~ 0.05	0.00625
NiCl2	0 ~ 0.25	0.025



F ig. 3. Optical microscopic Picture for Variation of zincate morphology with ZnO concentration (g/l) while keeping the other components at fixed levels (1000X): a: 0.05, b: 0.20, c: 0.25, d: 0.40, e: 0.50, f: 0.70

Table 5 Optimum bath Composition

Composition	contents (g/l)			
ZnO	0.20			
NaNO3	0.025			
C4H4KNaO6	0.6			
FeCl3	0.015	or	NiCl2	0.075
NaOH	40			



F ig. 4. Optical microscopic Picture of Zincate morphology produced with the optimum bath (1000 X).