반도체디스플레이기술학회지 제12권 제4호(2013년 12월)
Journal of the Semiconductor & Display Technology, Vol. 12, No. 4. December 2013.

Nano Crystalline Change by Heat Treatment

Yong-Bin Sun†

†Semiconductor-Display-Mechatronics Program, GS_CEI, Kyonggi University 154-42, Gwanggyosan-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, 443-760 Korea

Abstract

Mold die sticking arises from silica filler abrasion to the cavity surface. Ni-P electroplating was examined to substitute conventional hard Cr plating. More than 4% of Phosphorus in the electroplated film produces nano crystal structure and annealing makes Ni_3P precipitated to get hardness values equivalent to hard Cr.

Key Words : Nano crystal, Ni-P plating, Phosphorus acid, Ni_3P precipitation, Sticking

1. Introduction

When the hot hardness of epoxy molding compound (EMC) is not enough to endure the sticking force between package and mold die, the silicon die in a plastic molded package is going to break at the following ejection step. Waxing and cleaning work removes EMC residue to prevent sticking, but it is a desire to eradicate the root of sticking trouble.

Previously hydrogen bonding at the EMC-metal oxide interface was studied by plasma modification, but mechanical interlocking and large contact area is the major governing factor [1]. Hard Cr plating on die surface is the only countermeasure to withstand abrasion by the silica-filler. However, hard Cr plating uses highly toxic electrolytes.

As a substitute, Ni-P plating was studied. When P concentration exceeds 4% in the film, Ni-P plating forms nano crystalline. And subsequent annealing of the film at about 400°C results in Ni_3P precipitates at the grain boundaries of nano crystalline [2-4]. These make the film matrix hard comparable to the hard Cr, measuring between 860-1020 HV.

†E-mail : ybsun@kgu.ac.kr

2. Experimental Procedure

The sample composition of tool steel, SKD11, is 1.4-1.6% C, 0.15-0.35% Si, 0.3-0.6% Mn, 0.85% Ni, 0.25% Cr, 2.1% Mo, < 0.025% P and V, < 0.01% S and Cu, and the balance Fe. The sample dimensions are 20Φ*3t mm^2. The starting samples were quenched and polished.

The composition of the plating solution of 100 ml is $NiSO_4 \cdot 6H_2O$ 15g, $NiCl_2 \cdot 6H_2O$ 5g, H_3PO_4 5 ml, and H_3PO_3 in different amounts of either 0.5g or 1.0g. As noted, the amount of Phosphorus acid was varied. As an option, saccharin 0.5g was added to increase the P content in the film, but adverse effect due to severe outgassing made it ruled out.

Electroplating Teflon bath was specially designed to get an exposed area of 15 mm in diameter. The interface between sample and bath bottom hole was sealed with a rubber ring. The plating apparatus is schematically shown in Fig. 1.

The Autolab, PGSTAT302N, was used to stabilize the plating current at 100mA/177 mm^2. Total plating time was set at either 240 seconds or twice 120 seconds with a 20-seconds break, in order to produce the film thickness of about 1 μm. The experimental spilt conditions are summarized in Table 1. The bath temperature was held at 80°C.

In order to precipitate Ni_3P at the nano-size grain boundaries, electroplated samples were heat treated at

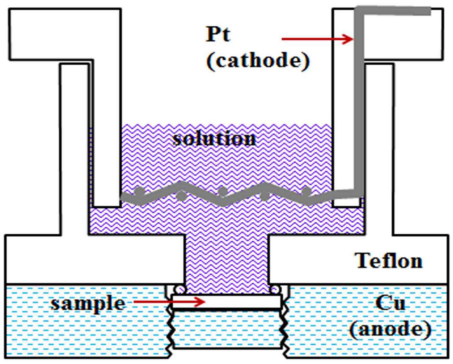

Fig. 1. Schematic diagram of Teflon bath.

Table 1. Experimental split conditions

samples	H_3PO_3 (g)	time (s)
Sample A	0.5	120*2
Sample B	0.5	240
Sample C	1.0	120*2
Sample D	1.0	240

400°C for 40 minutes in N_2 atmosphere. The heating rate was 20°C/min. Samples were furnace cooled and took out at 200°C.

Plated film thickness was measured by KLA-Tencor Alpha-Step. The film composition was EDX analysed by Oxford Instrument Model 7557 Inca X-sight at JSM 6500F. The film crystal structure was low-angle XRD analysed by PANalytical B.V. X'Pert PRO. The hardness was measured by nano indenter in the conditions of force 4.5 gf and depth 0.5 μm. The abrasion resistance was measured by a scratch tester, MSTX S/N 50-0217 of the CSM instrument.

3. Results and Discussion

3.1. Film thickness

Since the rim of sample surface was covered with a rubber ring, surface profile produced by the α-Step, made it possible to measure the film thickness along the radial direction.

As shown in Fig. 2, surface profile graphs provide in-situ data of plated film thickness. As an experimental result, 1.0 g of H_3PO_3 (samples C&D) retards plating rate compared to 0.5 g H_3PO_3 (samples A&B). The average film thicknesses are listed in Table 2. In 0.5 g of H_3PO_3, the 2-step plating shows thickness thinner than the 1-step plating since the 2-step provided the incubation time twice longer than the 1-step plating. But, in 1.0 g of H_3PO_3, higher concentration ruled the plating rate over the 2-step plating effect.

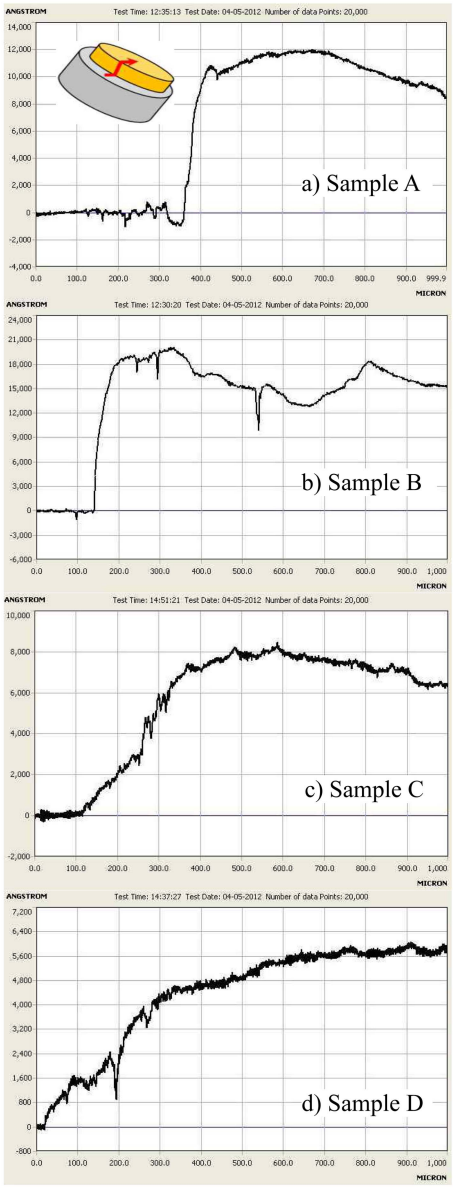

Fig. 2. Surface profiles by the α-Step: (from top to bottom) a) Sample A b) Sample B c) Sample C d) Sample D.

Table 2. Average film thickness

H_3PO_3	plating time	
	120x2 s	240 s
0.5 g	A: 1.0 μm	B: 1.5 μm
1.0 g	C: 0.7 μm	D: 0.6 μm

Table 3. EDX results of P% in the film

H_3PO_3	plating time	
	120 × 2 s	240 s
0.5 g	A: 95.4Ni-4.6P	B: 95.7Ni-4.3P
1.0 g	C: 85.4Ni-14.6P	D: 84.0Ni-16.0P

3.2. Film composition

EDX analysis shows that Phosphorus acid 1.0 g (samples C & D) results in more weight percentage of P in the film compared to 0.5 g (samples A&B). As listed in Table 3, the atomic percentage of Phosphorus ranges from 4 w/o to 16 w/o, the range of which produces nano crystalline in the film, according to the reference [3].

3.3. Ni_3P precipitation after annealing

According to the low-angle X-ray diffraction results as shown in Fig. 3, both Ni peaks and Ni_3P peaks appeared after anneal. Phosphorus acid 1.0g (samples C&D) in the plating solution shows more Ni_3P peaks compared to 0.5 g (samples A&B).

3.4. Hardness values after annealing

Hardness numbers measured by a nano indenter cover the ranges from HV 900 to HV 1000 as shown in Table 4. As expected, more Ni_3P precipitates exhibited little higher hardness value in 1.0 g of H_3PO_3 than 0.5 g of H_3PO_3. But the 2-step plating sample A shows highest hardness value since the 2-step plating provided fine nano crystallites during the incubation time, which is grain size strengthening. The hardness values attained in this experiment are very comparable to the conventional hard Cr plating, the measuring values of which are between 860-1020 HV.

3.5. Abrasion resistance

Scratch test generates several properties regarding friction, adhesion and abrasion.

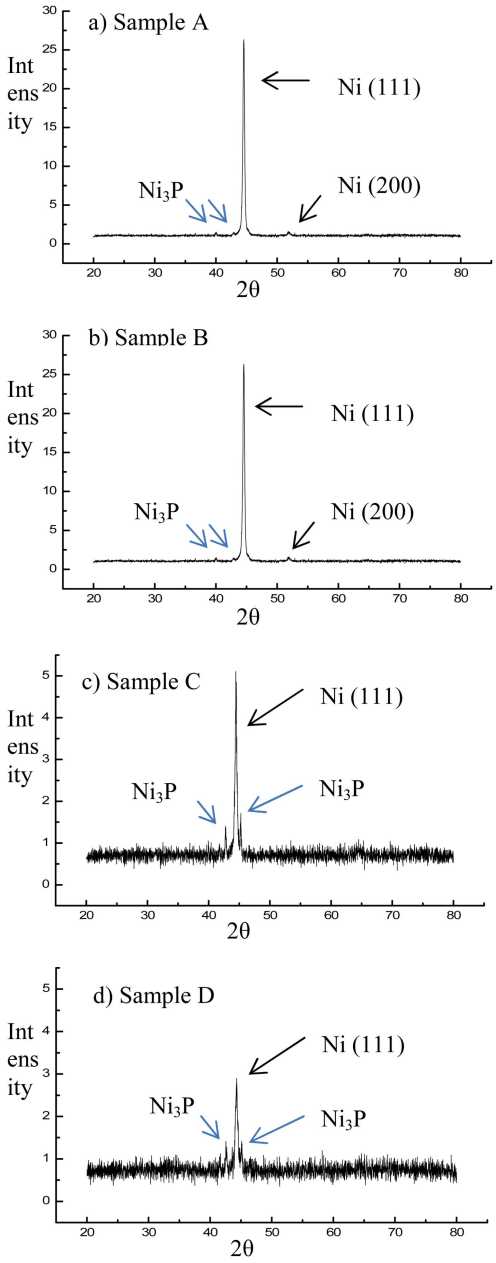

Fig. 3. Low-angle X-ray diffraction: (from top to bottom) a) Sample A b) Sample B c) Sample C d) Sample D.

As shown in Fig. 4, friction coefficients (FC) around 0.1 at the beginning stage means all samples provided same surface condition such as roughness for the scratch test.

Table 4. Hardness values after annealing

H_3PO_3	plating time	
	120 × 2 s	240 s
0.5 g	A: 1024±63	B: 893±52
1.0 g	C: 915±38	D: 914±87

As noticed from the abrupt changes at the acoustic emission (AE) curves, the critical loads (Lc) to break the film are 3.5 N in sample B and 2.0 N in sample A, respectively. It implies that plating without pause time produced better adhesion strength in thin film.

Under the condition of not breaking the film during scratching, *i.e.* below Lc, there is a direct correlation between penetration depth (PD) and abrasion resistance. Since the PD of sample B is longer and shallower than the PD of sample A, sample B is higher in abrasion resistance than sample A. It means the film plated without pause time (sample B) is more likely to withstand abrasion by silica during EMC moulding process.

Samples C&D showed no amplified emission since the thickness was less than 1 μm, which is mandatory requirement for the scratch test. However, the ratio of penetration depth (PD) to load (L) can be an index of abrasion resistance. At the end-load, 5N, the PD/L values are 0.3 (=1.5/5) in sample D and 1.3 (=8/5) in sample C. In other words, sample D ought to exhibit better abrasion resistance than sample C.

NF represents the normal force and FF represents the frictional force.

4. Summary

The designed electroplating bath was quite reliable to maintain the IDC at constant. More addition of Phosphorus acid in the plating solution resulted in more P% in the film, more Ni_3P precipitation after anneal, but adversely less deposition rate. In the aspect of plating pause, samples without a pause resulted in better abrasion resistance. As a conclusion, hard surface comparable to the hard Cr was obtained because of nano crystalline and Ni_3P precipitation.

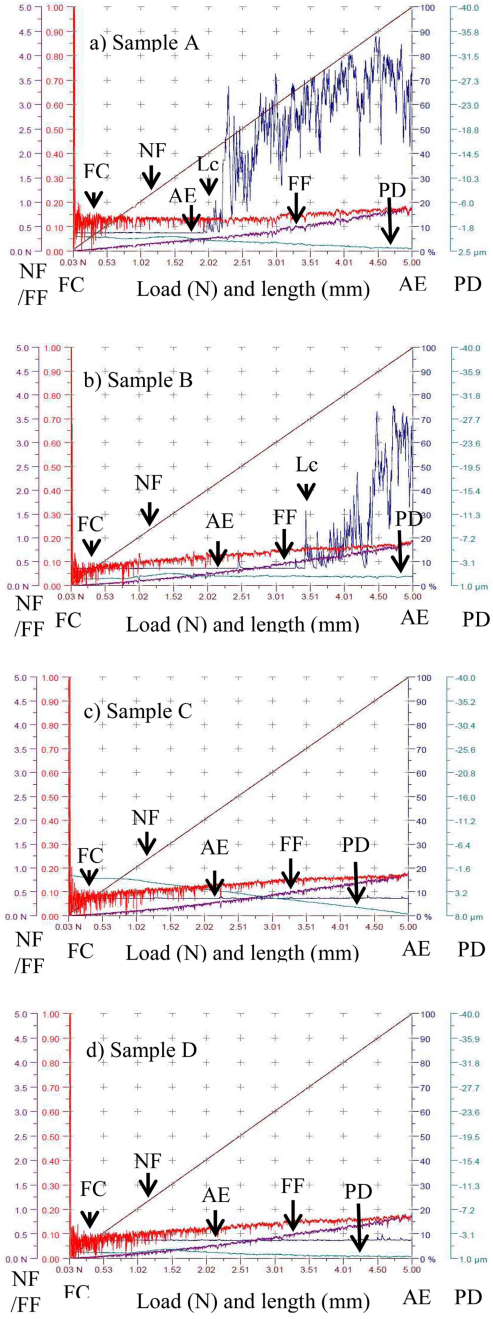

Fig. 4. Scratch test results: (from top to bottom) a) Sample A b) Sample B c) Sample C d) Sample D.

Acknowledgements

This work was supported by Kyonggi University Research Grant 2011. Also I owe thanks to Dr. C.Y.

Kim at the KICET and Prof. S.B. Jung at the SKKU.

References

Y.B. Sun, Adhesion Mechanism at Metal-Organic Interface Modified by Plasma, Materials Transactions, 44(2003), 1636-1639

Uwe Erb and Karl T. Aust, Electrodeposited Nanocrystalline Metals, Alloys, and Composites, Nanostructured Materials, Noyes Publications, Ch.5 (2002) 179-222

El-Sherik, J. Shirokoff, U. Erb, Stress measurements in nanocrystalline Ni electrodeposits, J. Allloys and Compounds, 389(2005) 140-143

N. Wang, Z. Wang, K. Aust, U. Erb, Isokinetic analysis of nanocrystalline Nickel electrodeposits upon annealing, Acta Mater., 45(1997) 1655-1669

접수일: 2013년 12월 3일, 심사일: 2013년 12월 10일, 게재확정일: 2013년 12월 16일