

Effects of Electroplating Current Density and Duty Cycle on Nanocrystal Size and Film Hardness

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Abstract

Pulse electroplating was studied to form nanocrystal structure effectively by changing plating current density and duty cycle. When both of plating current density and duty cycle were decreased from 100 mA/cm² and 70% to 50 mA/cm² and 30%, the P content in the Ni matrix was increased almost up to the composition of Ni₃P compound and the grain growth after annealing was retarded as well. The as-plated hardness values ranging from 660 to 753 HV are mainly based on the formation of nanocrystal structure. On the other hand, the post-anneal hardness values ranging from 898 to 1045 HV, which are comparable to the hardness of hard Cr, are coming from how competition worked between the precipitation of Ni₃P and the grain coarsening. According to the ANOVA and regression analysis, the plating current density showed more strong effect on nanocrystal size and film hardness than the duty cycle.

Key Words : nanocrystal, pulsed electroplating, over-potential, duty cycle, Ni-P alloy

1. Introduction

Nanocrystal electroplating has been widely acknowledged in producing nano structured materials [1]. In Ni-P system, when P concentration falls between 4 and 16 atomic percent, the matrix results in nanocrystal structure [2]. Nanocrystal electroplating of Ni-P was evaluated to see the possibility as a substitute for the conventional hard Cr electroplating, which is applied to the surface of transfer mold die to improve wear resistance against to silica-filler abrasion in the auto molding process [3].

In general, two methods have been utilized to produce nanocrystal: one is adding grain refiners, the other is using over-potential with pulsed mode [4]. The role of grain refiners is inhibition to adatoms to diffuse around on the growing surface by adsorption of grain refiners as a foreign species. The over-potential, which makes high current density, plays a role of promoting massive nucleation to result in low

surface diffusion rates and consequentially reduced grain growth rates. It is even more intensified by adding pulse mode. In the pulse mode, the charging effect should be considered in selecting proper plating conditions because of the following reason. During off-duty cycle in pulse plating, negative charges are discharged from the diffusion layer and fresh adions are supplied to the diffusion layer in front of the cathode. With increasing duty cycle and frequency, the discharge and supply described above are getting retarded, which is so-called charging effect [5]. Therefore the duty cycle and frequency should be confined in certain ranges. The charging effect was negligible when the on-duty cycle was much longer than the critical time periods, which were 35 μ s for 100 mA/cm² and 75 μ s for 1,000mA/cm² [6]. In this article, electroplating with over-potentials at pulse mode, without using grain refiners, was examined.

In the Ni-P alloy, the nanocrystal electrodeposited as a supersaturated solid solution undergoes precipitation of Ni₃P as a second phase and grain growth of the nanocrystals by annealing above 553 K [7]. The onset and peak temperatures for precipitation of Ni₃P and

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grain growth of nanocrystals were dependent on heating rates. They were obtained from the analysis of DSC curves. At the heating rate of 10°C/min, the onset and peak temperatures were 620.4K and 643.7 for the Ni₃P precipitation and 664.0K and 688.4K for the nanocrystal grain growth, respectively [8]. In Ni-1 wt% P alloy, the size of the nanocrystal right after electroplating was about 10nm and its hardness values after annealing were almost doubled [4].

The ANOVA (analysis of variance) is useful to see the significance of main effects and their interactions to the experimental results. And regression analysis is also useful to see the correlation between measured data. The MS Excel supports ANOVA and regression analysis as well [10].

2. Experimental Procedure

Titanium and nickel of 100nm thick for each were sequentially sputtered on silicon wafer after oxidation. The Si substrate was tape masked to expose the electroplating area of 1 × 1 cm². Nickel-phosphorus alloy was electrodeposited from a Watts Bath containing NiSO₄·6H₂O 15 g, NiCl₂·6H₂O 5g, H₃PO₄ 5 ml, and H₃PO₃ 0.5 g in 100 ml. Among plating parameters, the plating current density and duty cycle were changed. The current densities were set at 100 mA/cm², 75 mA/cm², and 50 mA/cm². The duty cycles were set at 70%, 50%, and 30%. In order to get electroplated film of about 2 μm thick, plating times were linearly estimated from the reference time, which was 4minutes applied for the electroplating condition of 100 mA/cm² current density and 50% duty cycle. The plating current was controlled by the Keithley 220 programmable current source. The pulse frequency was set at 10Hz. Bath temperature was maintained at 333K and the solution was stirred by magnet bar rotation. In order to see the annealing effects, the electrodeposited film was heat treated at 400°C for 20 minutes in N₂ atmosphere. The heating rate was 7°C/min. After 20 min. dwell time, samples were furnace cooled.

Film thickness was measured by the KLA-Tencor alpha-step stylus surface profiler. The phosphorus contents was analysed by EDX at the Oxford Instrument Model 7557 Inca X-sight attached to the

JSM 6500F. The grain size of nano crystallites was estimated by using the grazing incidence x-ray diffraction (GID) method at the PANalytical B.V. X'Pert PRO [9]. The angle of incidence was set at 1 degree. The hardness values in the depth of 1.0 μm were measured by nano-indenter at 20gf. All the measured data was treated with two-way ANOVA (analysis of variance) with balanced data in Excel to compare the significance of main effects and their interactions. And regression analysis was also done to see the correlation between the measured data.

3. Results and Discussion

3.1. Film thickness and composition

As shown in Table 1, the average film thickness was 2.15 μm with a standard deviation of 0.33 μm. Although the standard deviation is over 10% of the average, the film thicknesses were in safe criterion to evaluate the following tests.

As shown in Table 1, Phosphorus contents in the Ni matrix fall in the region of nano crystal composition at the plating conditions of 100 mA/cm²-70% and 100 mA/cm²-50%. The rest of the conditions belongs to the amorphous region, according to the reference [2]. The increasing tendency of P contents with simultaneous decreasing both of PCD (plating current den-

Table 1. Measured film thickness and composition

No.	current density (mA/cm ²)	duty cycle (%)	plating time (sec)	film thickness (μm)	P content (%)
1	100	70	160	2.07	13.9
2		50	240	2.16	15.8
3		30	300	2.32	17.3
4	75	70	215	1.62	17.2
5		50	320	2.49	17.4
6		30	530	2.64	18
7	50	70	320	2.06	20.8
8		50	480	2.23	22.9
9		30	800	1.72	24.3
average				2.15	17.9
standard deviation				0.33	3.4

sity) and DC (duty cycle) may be related to the charging effect. Based on the ANOVA, PCD is more influential than DC in order to increase the P contents in the electroplated film, but no interaction of main effects of PCD and DC is noticeable.

3.2. Grain size and hardness before annealing

As shown in Table 2, as-plated grain sizes from all conditions are in the nm range. It is obvious that the combination of the solution and the plating parameters were sufficient to produce nano crystallites or amorphous phase in the film.

The effects of both nano crystallites and P contents are combined to result in the elevated hardness in as-plated samples. The elevated hardness value moves along with P content and also with grain size, as shown in Table 2. The correlations of P content and grain size are coming from solute dispersion strengthening and internal stress strengthening, respectively. Based on the ANOVA, PCD is more influential than DC in order to increase the hardness value in the electroplated film, but no interaction of main effects of PCD and DC is noticeable.

3.3. Grain size and hardness after annealing

As shown in Table 3, grain sizes are changed from several nano meters before anneal to ranges of hun-

dreds of nano meters in higher PCD and tens of nano meters in lower PCD after anneal. Since the higher PCD with higher DC provides preferable conditions to adions of Ni to be absorbed to the surface compared to the adions of P, and provides not enough time to adatoms to diffuse to low energy sites on the surface, P contents are lowered and internal stress is increased compared to the lower PCD with lower DC. Grain growth is a competitive process between annihilation of internal stress and prohibition of grain ripening by dispersed solvent atoms. Therefore, since internal stress is evidently more accumulated with increasing PCD, the degree of grain growth is aggravated with increasing PCD in every duty cycle. It is well known that high degree of internal stress results in fast recrystallization and grain growth upon annealing above a certain critical temperature. As for the prohibition of grain ripening, since more dispersed atoms of P and precipitated nickel phosphide disrupt diffusion of Ni atoms to make grain ripening delayed, grain size in the lower PCD with lower DC is smaller than that in higher PCD with higher DC. As studied in the reference [8], the onset for the Ni₃P precipitation precedes the onset of the Ni grain growth. According to the ANOVA, PCD is the major factor to distinguish the size differences between conditions, but duty cycle also relatively affects the difference in

Table 2. Grain size and hardness before annealing

no.	current density (mA/cm ²)	duty cycle (%)	P content (%)	grain size (nm)	hardness (HV)
1	100	70	13.9	6.7	689.8
2		50	15.8	5.2	659.7
3		30	17.3	5.4	683.8
4	75	70	17.2	7.7	719.1
5		50	17.4	3.9	674.7
6		30	18	5.0	723.3
7	50	70	20.8	2.9	723.7
8		50	22.9	1.9	714.4
9		30	24.3	8.5	752.7
average			17.9	4.8	698.6
standard deviation			3.4	2.2	29.4

Table 3. Grain size and hardness after annealing

no.	current density (mA/cm ²)	duty cycle (%)	P content (%)	grain size (nm)	hardness (HV)
1	100	70	13.9	213	961.1
2		50	15.8	226	898.2
3		30	17.3	167	931.4
4	75	70	17.2	164	904.6
5		50	17.4	125	907.1
6		30	18.0	120	951.5
7	50	70	20.8	149	913.8
8		50	22.9	47	1014.2
9		30	24.3	81	1045
average			17.9	151.4	935.2
standard deviation			3.4	57.8	51.8

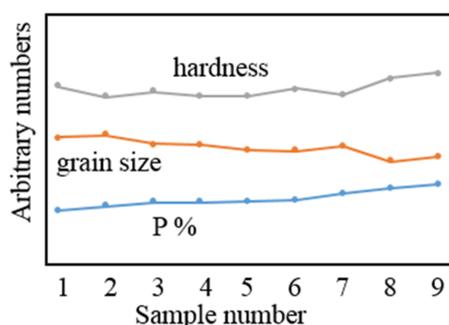


Fig. 1. Comparison of the normalized data among P contents, grain sizes and hardness values.

grain size.

Hardness values listed in Table 3 are well aligned with p contents and reversely aligned with grain sizes as shown in Fig. 1, except the sample #1. The sample #1 was deposited at the condition of one extreme end, 100 mA/cm²-70%. This condition generated low P % with high internal stress. High internal stress was not totally exhausted at the adopted annealing temperature and time. The residual stress possibly invoked the twin formation to increase the hardness even at low P %. The hardness-up in the sample #1 is a product of the interaction of the main effects of PCD and DC indicated by the ANOVA. Post-anneal hardness values are comparable to hardness of the conventional hard chromium coating.

3.4. Ni₃P precipitation and grain growth by annealing: regression analysis

In order to figure out the correlation among the measured data as compared in Fig. 2, regression analysis is carried out among P contents, post-anneal grain size, pre-anneal hardness, and post-anneal hardness. When the p-values in regression analysis are less than 5%, there is a correlation with the reliability level of 95%. As listed in Table 4, the P content has correlation with post-anneal grain size, pre-anneal hardness and post-anneal hardness, but the post-anneal grain size is only correlated with post-anneal hardness.

The explanation about the correlation is as follows. Since the plating temperature of 333K is far below the onset temperature of Ni₃P precipitation, it is obvi-

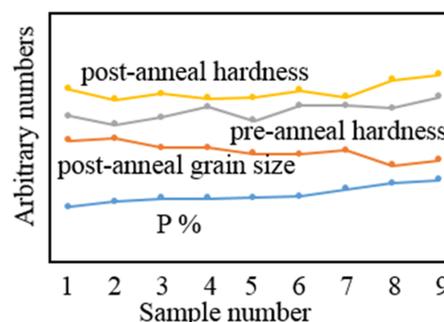


Fig. 2. Comparison of the normalized data among P contents, post-anneal grain sizes and pre- and post-hardness values.

Table 4. p-values by regression analysis

p-value	grain size (post-ann.)	Hardness (pre-ann.)	Hardness (post-ann.)
P content	0.00316	0.02324	0.0375
post-anneal g.s.	-	0.06483	0.04114

ous that pre-anneal (*i.e.* as-plated) hardness is dependent solely on solid solution hardening and formation of nano crystallites which are caused by the excess P content and over-potential. Referring to the growth of Ni₃P phase prior to the Ni phase upon annealing with a heating rate of 10K/min [8], the post-anneal hardness increase is mainly governed by increment of P content. But the high hardness value even at low P content in sample #1 may be explained by the twin formation. At the same current density, medium duty cycle showed a tendency of lower hardness compared to other duty cycles ought to be studied in the future.

4. Conclusion

Pulsed current electrodeposition enables to form the supersaturated Ni-P nano crystal phase. It was possible to make the P contents reach almost up to the composition of Ni₃P, which played a major role to produce nano crystal phase. In order to increase the P contents in the film, changing PCD was more influential than Changing DC. The as-plated hardness values ranging from 660 to 753 HV result from the formation of nano crystallites. The post-anneal hardness

values ranging from 898 to 1045 HV result from the precipitation of Ni₃P, which is quite comparable to the hardness of the conventional hard Cr coating. ANOVA and regression analysis are quite useful to classify the significance of the parameters and to evaluate the correlation among measured data.

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