

# FABRICITON OF HIGH STRENGTH NICO ALLOY AND RH COATING USING ELECTROPLATING METHOD

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## ABSTRACT

NiCo alloys are electroplated in sulfate bath. The concentration of cobalt sulfate and current density were varied to optimize the surface hardness. The properties of NiCo deposits were analyzed using field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The surface hardness of the NiCo alloy was increased up to 500Hv at 24 w% Co in the deposits due to the grain refinement. The size of grain was reduced to 12 nm. The residual stress of the deposits was varied from tensile to compressive as the saccharine concentration increased. The zero residual stress was achieved at 0.05 g/L saccharine addition. The electrodeposition of rhodium (Rh) on silicon substrate at different current conditions were investigated. The cracks were found at high current density during the direct current (DC) plating. The pulse current (PC) plating were applied to avoid the formation of cracks on the deposits. Off time in the pulse plating relieved the residual stress of the Rh deposits and consequently the current conditions for the crack-free Rh deposits were obtained. Optimum pulse current (PC) condition is 5:5 (on:off) for the crack-free Rh electroplating.

Key words: Electroplating, NiCo alloy, Pd pulse current plating, saccharin, grain refinement

## INTRODUCTION

Probe card is component of semiconductor inspection equipment. Probe tip in the card are directly touched on the device to find the defects. More than million touch downs are made and then tip should be very durable. NiCo alloy has superior mechanical properties and then its suitable for the probe tip material<sup>1-3</sup>. The high surface hardness is important however the low residual stress is also required due to the high aspect ratio of probe tip. The study of electroplated NiCo alloy have shown that their mechanical properties and microstructure were found to depend on the Co contents<sup>4-6</sup>. Co contents in NiCo alloy can be controlled by bath composition, temperature, pH and current density. In this study, NiCo alloy were electroplated for the high surface hardness with low residual stress and zero residual stress NiCo alloys were fabricated.

For the extension of the NiCo probe tip life time, Pd coatings on the NiCo were investigated<sup>7-10</sup>. Pd is the very hard material as well as wear resistant material. Pd coating over NiCo can increase the life time of MEMS probe tip,

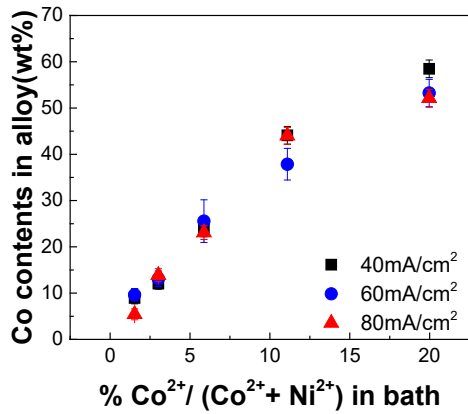
however to obtain thick Pd coating is very difficult due to low current density and high residual stress. In this study electroplating of Pd was investigated to optimize the crack free Pd coating conditions.

## EXPERIMENTAL PROCEDURES

NiCo alloy were electroplated from Watts-type bath, containing nickel sulfate(250g/L), nickel chloride(45g/L), boric acid(30g/L), cobalt sulfate(0-80g/L) and saccharin(0-1g/L). NiCo alloy were plated on Cu substrate. The current density was varied from 20 to 80 mA/cm<sup>2</sup>. The pH of the bath was fixed at 4. The temperature of bath was kept at 60 °C. The DSA was used as inert anode. Pd was electroplated using commercial electroplating solution. The concentration of Pd was maintained at 2 g/L in sulfuric solution. The pH of the bath was fixed at 0.6. The temperature of bath was kept at 50 °C. The DSA was used as inert anode. The surface morphologies of electrodeposits were analyzed using FESEM and the compositions were determined with EDS. The grain size was calculated using Scherrer formula based on the data from XRD analysis. The residual stress were measured using a deposit stress analyzer.

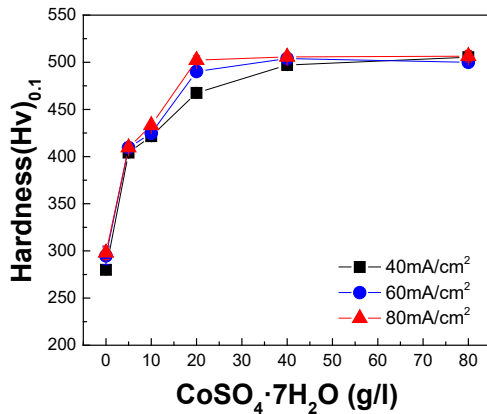
## RESULTS AND DISCUSSION

The correlation of Co contents in the NiCo alloy and proportion of Co<sup>2+</sup> ion in electrolyte at each current density are shown in Fig. 1. It is observed that Co contents in alloy increased with Co<sup>2+</sup> ion concentration in the bath. The percentage of Co in the alloys was much higher than in the proportion of Co<sup>2+</sup> ion in electrolyte and it is evidence of the anomalous codeposition<sup>11</sup>. The effect of Co concentration and Co contents in the alloy on the surface hardness is shown in Fig. 2(a) and (b) respectively. The surface hardness of the NiCo alloy was increased as the Co concentration in the bath increased. However the surface hardness reached to the 500 Hv and maintained the same even though the Co contents in the NiCo alloy increased. It reached to the maximum at 24 wt% Co contents in NiCo alloy.

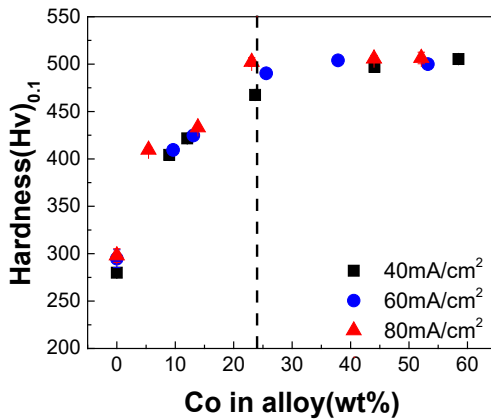


**Fig. 1.** Effect of Co concentration in the bath on the alloy composition

It is noticeable that the effects of current densities on the surface hardness and Co content in the alloy is very little. It is due to the mechanism of anomalous deposition is not diffusion controlled.



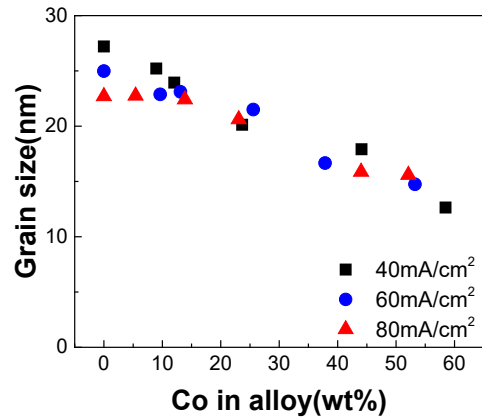
(a)



(b)

**Fig. 2.** Effect of Co on the surface hardness (a) Co in the bath (b) Co in the alloy

The grain size was calculated using Scherrer formula from XRD analysis. The grain size of NiCo alloy at different Co contents are shown in Fig. 3. The grain size of NiCo alloy were steadily decreased as Co contents increased, however it reached to 12 nm and was not changed. The correlation of the grain size and the surface hardness are shown in Fig. 4. Generally, grain size refinement effect is explained the Hall-Petch relation.

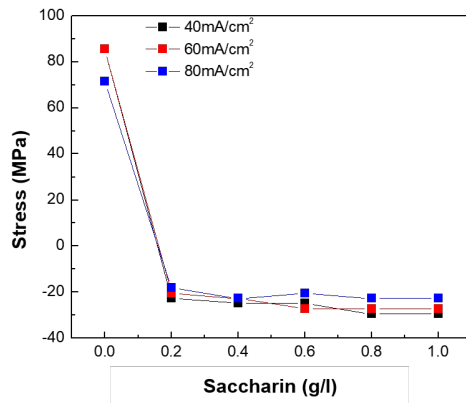


**Fig. 3.** The correlations of Co contents in the alloy and grain size

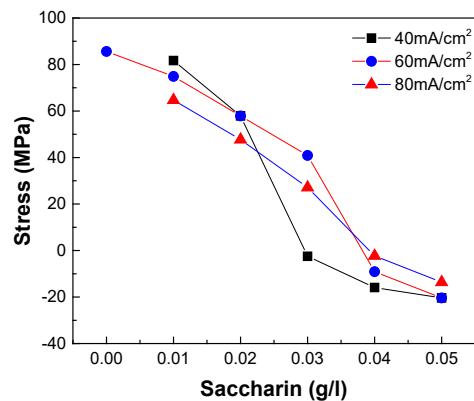
$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

The square root of grain size and hardness has a reverse linear relationship<sup>12,13</sup>. And the hardening mechanism of NiCo alloys is the grain size refinement.

For the low residual stressed NiCo alloy, the effect of saccharin on the residual stress were investigated and shown in Fig. 4. The residual stress of the alloy was changed from tensile to compressive as saccharin was added in the bath. The change of residual stress is over 100 MPa even addition of 0.2 g/l of saccharin.



(a)

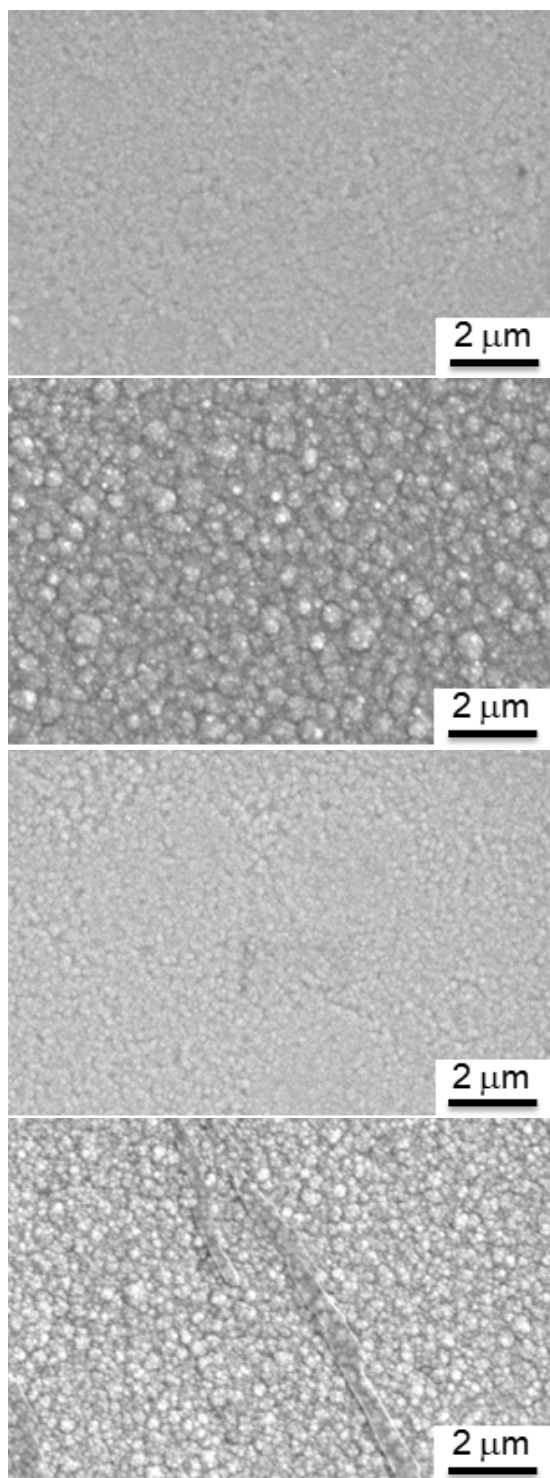


(b)

**Fig. 4.** Effect of saccharin concentration on the residual stress of NiCo alloy (a) high concentration (b) low concentration

The change of residual stress from tensile to compressive occurred at 0.05 g/l of saccharin. Finally, the zero residual stressed NiCo alloy was electroplated from 0.2M cobalt sulfate bath with addition of 0.05 g/l saccharin at 40 mA/cm<sup>2</sup>.

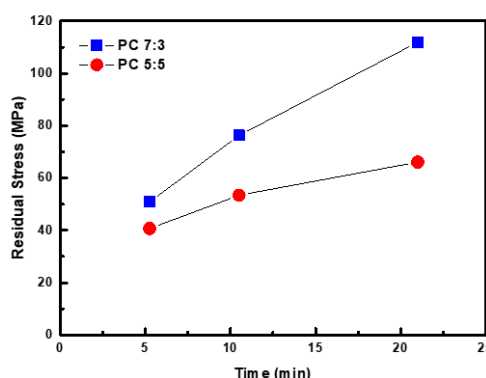
The electroplating of Pd was investigated at different current densities at DC. The current densities were varied from 1 to 15 mA/cm<sup>2</sup>. The cracks on the coating surface were found over 3 mA/cm<sup>2</sup>.



**Fig. 5.** Surface morphology at different pulse durations and times. Current density was 2 mA/cm<sup>2</sup> (a) PC 7:3 and 14 min, (b) PC 7:3 and 140 min, (c) PC 5:5 and 14 min, (d) PC 5:5

and 140 min

To avoid the cracks on the coating surface, the pulse current electroplating method was applied to coat Pd. The pulse current electroplating can lower the residual stress to avoid the surface cracks<sup>14</sup>. The on/off time of pulse current were varied. After the preliminary test, the on:off ratio 7:3 and 5:5 were applied. The surface morphologies of Pd surface at different conditions are shown in Fig. 5. The crack free surfaces were observed even at long time electroplating for thick coating, Fig. 5(b) and (d). The pulse current electroplating can reduce the residual stress and then the crack free surface were obtained. The surface hardness of electroplated Pd at 3μm thickness was measured as 800 Hv after applying pulse current electroplating at 2mA/cm<sup>2</sup>. The residual stress was reduced as the off time increased. Fig. 6 shows the effect of off time to relieve the residual stress of Pd coating. As the results, the pulse current electroplating of Pd can provide the high strength surface as well as the crack free surface.



**Fig. 6.** Residual stress of Pd electrodeposits at different pulse conditions

## CONCLUSION

The Co contents in alloy was increased linearly with Co<sup>2+</sup> ion proportion in the bath. Surface hardness of NiCo alloy reached to maximum 500 Hv at 24 wt% Co contents in the alloy. The size of grain was decreased as Co contents in alloy increased, however it reached to 12 nm, even though Co contents in the alloy was increased. The residual stress of the NiCo alloy was lowered by addition of saccharin. It was changed from tensile to compressive and zero residual stress was achieved at 0.05 g/l of saccharin. Zero residual stressed NiCo alloy was electroplated from 0.2M cobalt sulfate bath with addition of 0.05 g/l saccharin at 40 mA/cm<sup>2</sup>.

Pulse current plating of Pd can give the high surface hardness up to 800 Hv without heat treatment. The longer off time relieved the internal stress of the coating. And consequently, the residual stress of the Pd coating was reduced after applying pulse current electroplating method.

## ACKNOWLEDGEMENTS

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## REFERENCE

- [1] B.H. Kim and J.B. Kim, *J. Micromech. Microeng.*, **18**, 8 (2008)
- [2] F. Wang, R. Cheong, and X. Li, *J. Microelectromech. Sys.*, **18**, 933 (2009)
- [3] B.H. Kim, H.C. Kim, S.D. Choi, K. Chun, J.B. Kim, and J.H. Kim, *J. Micromech. Microeng.*, **17**, 1350 (2007)
- [4] Y. Li, H. Jiang, D. Wang, H. Ge, *Surf. Coat. Tech.*, **202**, 4952 (2008)
- [5] L. Wang, Y. Gao, Q. Xue, and H. Li, *Appl. Surf. Sci.* **242**, 326 (2005)
- [6] M. Zamani, A. Amadeh, and S.M. Laribaghali, *T. Nonferr. Metal. Soc.*, **26**, 484 (2016)
- [7] D. Pletcher, and R. Urbina, *J. Electroanal. Chem.*, **421**, 137 (1997).
- [8] D. Pletcher, and R. Urbina, *J. Electroanal. Chem.*, **421**, 145 (1997).
- [9] M. Arbib, B. Zhang, V. Lazarov, D. Stoychev, A. Milchev, and C. Buess-Herman, *J. Electroanal. Chem.*, **510**, 67 (2001)
- [10] R.T.S. Oliveira, M.C. Santos, L.O.S. Bulhoes, and E.C. Pereira, *J. Electroanal. Chem.*, **569**, 233 (2004).
- [11] R. Orinakova, R., A. Turonova, D. Kladekova, M. Galova, and R.M. Smith, *J. Appl. Electrochem.*, **36**, 957 (2005)
- [12] M. Zhao, Z.C. Li, and Q. Jiang, *J. Alloy Compd.*, **361**, 160 (2003)
- [13] C.A. Schuh, C.A., T.G. Nieh, and T. Yamasaki, *Scripta Mater.*, **46**, 735 (2002)
- [14] J.C. Puipe, F. Leaman Eds., *Theory and Practice of Pulse Plating, AESFS, Ch. 1*, Orlando (1986)