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ELECTROLESS PLATING OF NICKEL FOR MICRO-STRUCTURE FABRICATION

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Abstract

Electroless plating nickel has superior mechanical property to electroplated nickel. Furthermore nickel can be coated on nonconducting substrate. In this research, electroless plating of nickel were conducted in different bath condition to find optimum conditions of electroless nickel plating for MEMS applications. The selectivity of activation method on several substrates was investigated. The effects of nickel concentration, reducing agent concentration and inhibitor on deposition rate were investigated. The effect of pH on deposition rate and content of phosphorous in deposited nickel was also investigated.

Key words : *Electroless nickel, Sodium hypophosphite, MEMS, Thiourea,*

1. INTRODUCTION

Microstructure for MEMS application is usually fabricated by electroplating[1,2]. Electroless nickel plating proceeded only on catalytic surface selectively and electrodeposit have properties of higher corrosion resistance, hardness and wear resistance than electrodeposit by electroplating[3,4]. And deposit films are more uniform than those by electroplating. Thus, it is expected that microstructure fabricated by electroless nickel plating have a good quality. However, it is difficult to control the conditions of electroless nickel plating solution and also there are problems of high operating temperature and low deposition rate[5]. In this research, electroless nickel plating were conducted with varying bath composition and concentration to obtain optimum electroless plating solution with low operating temperature and high deposition rate.

2. EXPERIMENTAL PROCEDURE

Nickel sulfate ($NiSO_4$) $\cdot 6H_2O$ was used as nickel source and sodium hypophosphite ($NaPH_2O_2 \cdot H_2O$) was used as a reducing agent. Titanium, copper, alumina, PCB, glass were prepared as substrate and selectivity of electroless plating with plating solution, pretreatment, operating temperature and pH was investigated in re-

spective substrate. Sodium pyrophosphite ($Na_4P_2O_7$), sodium acetate ($NaC_2H_3O_2 \cdot H_2O$), sodium citrate ($Na_3C_6H_5O_7$) and potassium sodium tartrate ($C_4H_4O_6KNa \cdot 4H_2O$) were used as complexing reagents and the effect of complexing ligand was investigated. Thiourea was used as stabilizer. Table 1 shows the composition of plating bath. Substrate was alkaline soak-cleaned, etched and activated and then it was immersed in plating solution. The temperature was controlled and maintained with vacuum oven. The adhesion of film was evaluated by tape test method. Hardness of nickel deposit was measured and structure of deposit was observed with XRD, Optical micrographs and SEM.

3. RESULTS AND DISCUSSION

3. 1 Effects of activation methods on selectivity

The selectivity of electroless plating bath and activation on various substrates were investigated. Table 2 shows the results of selectivity test on various substrates for the different solutions. From the results of Table 2, the selectivity were varied with activating method. And then if activating method were properly chosen, nickel can be selectively coated on catalyzed surface only.

3. 2 Effects of solution composition on deposition rate

The effects of solution composition on deposition rate were observed. The concentration of nickel was varied from 5 to 45gpl in a mean while the other conditions were fixed. Fig. 1 shows the effect of nickel concentration on deposition rate. From Fig. 1 the deposition rate was linearly increased with concentration upto 15gpl, however the deposition rate were hardly influenced by nickel concentration over 15gpl. This is due to that the excess amounts of nickel is not affected on deposition rate when the con-

Table 1. Electroless nickel plating bath composition

	Solution I		Solution II	
Nickel source	$NiSO_4 \cdot 6H_2O$	25g/1	$NiSO_4 \cdot 6H_2O$	25g/1
Reducing agent	$NaPH_2O_2 \cdot H_2O$	25g/1	$NaPH_2O_2 \cdot H_2O$	25g/1
Complexing agent	$Na_4P_2O_7 \cdot 10H_2O$	50g/1	$Na_4P_2O_7 \cdot 10H_2O$	50g/1
Stabilizer	H_2NCSNH_2	0-4ppm	H_2NCSNH_2	0-4ppm
pH adjuster	NH_4OH		NH_4OH	

Table 2. Selectivity of elecetroless nickel plating

Solution	Method \ Substrate	Cu	Ti	Alumina	Glass	PCB
I	Activation	○	○	×	×	×
	Catalyst & Accelerator	△	○	○	△	△
	Activation & Sensitization	△	○	○	△	×
II	Activation	○	○	×	×	×
	Catalyst & Accelerator	△	○	○	△	△
	Activation & Sensitization	△	○	○	△	×

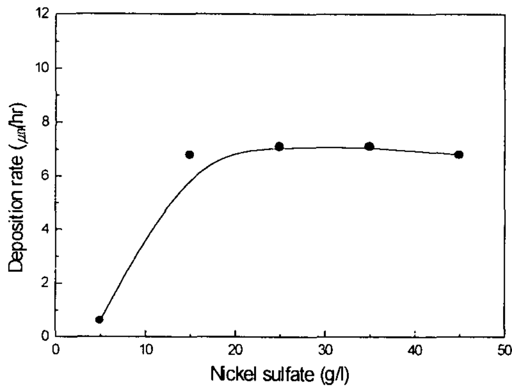


Fig. 1. Deposition rate with nickel sulfate concentration.

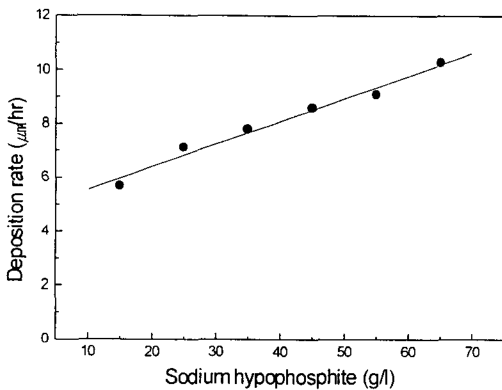


Fig. 2 Deposition rate with sodium hypophosphite concentration.

centration of reducing agent was fixed.

The concentration of reducing agent, sodium hypophosphite, was varied from 25 to 75gpl with 10gpl increment. Fig. 2 shows the effect of reducing agent concentration on deposition rate. On the contrary to the results of nickel concentration, the deposition rate was linearly increased with concentration of reducing agent. When the concentration of reducing agent was over 75gpl, the electroless plating bath was unstable and the homogeneous decomposition of solution was observed.

3. 3 Effect of temperature

The deposition rate was observed at different temperature. Fig. 3 shows the effect of temperature on deposition rate. The deposition rate was increased exponentially with temperature. And then to improve the deposition rate, the higher temperature was recommended. However considering other factors in MEMS, such as PR toleration, surface selectivity and etc., the optimum temperature is lower than 70℃. The activation energy on deposition was calculated as 34KJ/mole from the Arrhenius plot.

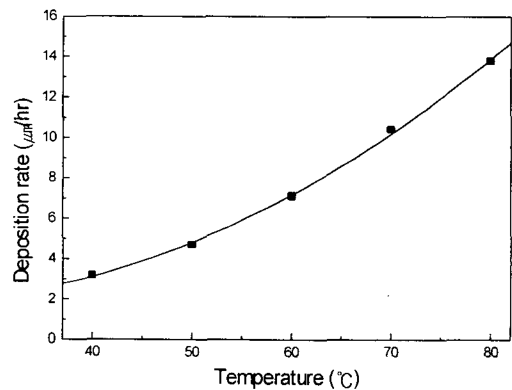


Fig. 3 Nickel deposition rate with temperature at pH 10.

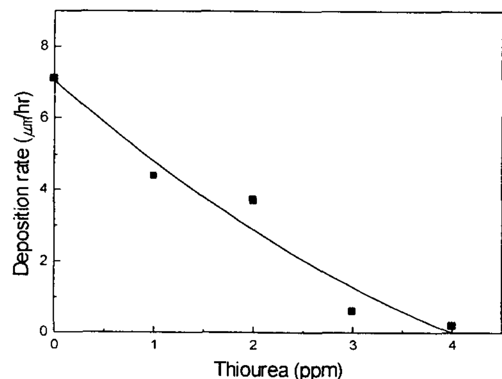
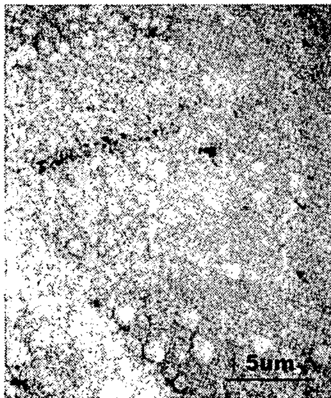


Fig. 4 Nickel deposition rate with thiourea concentration.

3. 4 Effect of stabilizer

The deposition rate was observed with varying the concentration of stabilizer, thiourea, from 1 to 4ppm. Fig. 4 shows the effect of the concentration of stabilizer on deposition rate. The deposition rate was linearly decreased with thiourea concentration and the deposition was completely inhibited at 4ppm. With addition of stabilizer, the surface morphology was improved. Fig. 5 shows the SEM images of nickel deposits with an without stabilizer.



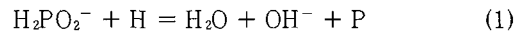
(a)

(b)

Fig. 5 SEM images of deposited nickel with an addition of thiourea.
(a) no addition, (b) 1ppm

3. 5 Effect of pH

The deposition rate was observed with varying pH of the solution from 9 to 11. Fig. 6 shows the effect of pH of solution on deposition rate. The deposition rate was linearly decreased with pH. The contents of phosphorous in deposit were changed with pH. Fig. 7 shows the phosphorous contents with pH. The content of phosphorous was decreased with pH. This is due to high pH inhibits formation of phosphorous. Equation I shows the decomposition of hypoyhosphite to form phosphorous.



$$H_2PO_2^- + H = H_2O + OH^- + P \quad (1)$$

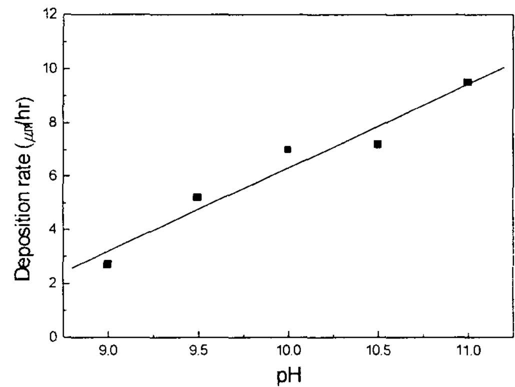


Fig. 6. Deposition rate of nickel with pH at 60℃.

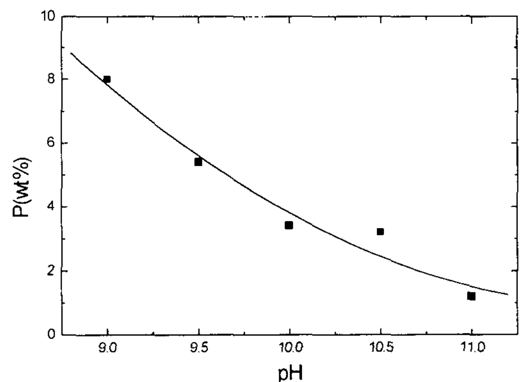


Fig. 7. Phosphorous content in nickel deposit with pH at 60℃

3. 6 XRD patterns of deposit

The crystallization of deposit was investigated with XRD patterns. Fig. 8 shows the XRD patterns of deposit with pH. At low pH, the content of phosphorous was high and then the deposit was amorphous. However, at high pH, the content of phosphorous was low and then the deposit was crystallized.

4. CONCLUSION

1) The selectivity was sensitively changed with activating method on different substrates.

2) The deposition rate was linearly increased with sodium hypophosphite concentration and was not affected by concentration of nickel sulfate over 15gpl. The deposition rate was exponentially increased with temperature. The activation energy of deposition was 34KJ/mole. The deposition rate was decreased with thiourea concentration and completely inhibited at 4ppm thiourea. The deposition rate was increased with pH and the content of phosphorous was decreased with pH.

3) The deposit was amorphous at pH 9 due to high content of phosphorous and became crystallized with increasing pH due to low content of phosphorous.

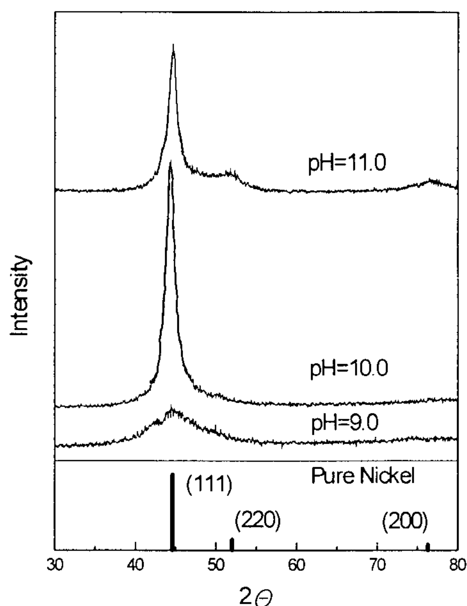


Fig. 8. XRD patterns of deposited nickel with pH.

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