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PREPARATION OF ANISOTROPIC CONDUCTIVE FINE PARTICLES BY ELECTROLESS NICKEL PLATING.

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ABSTRACT

Mechanical solderless chip packaging with small gold bumps or metal balls has increased in the electronic devices. The preparation of conductive particles ($5\sim7\mu m$ diamiter) by electroless nickel plating have been investigated. Generally, batch type electroless plating is applied to provide conductivity on the nonconductors. Since the surface areas of particles are much larger than the bulk substrate, accordingly the electroless plating bath becomes unstable. Thus, we applied the continuous dropping method for the preparation of conductive particles. The uniform coverage of deposited nickel on the particles was obtained by using ammonium acetate as a complexing agent, and surface coverage is further improved without coagulation of particles by the surface active agent treatment before enter the plating bath.

INTRODUCTION

Solder is widely applied as a mounting technology for electronic components. However, fine pitch connection becomes difficult with the progress of high density mounting. A leadless connection such as conductive pastes, anisotropic conductive films$^{1)}$ and other mechanical connection method has been examined. We have investigated production of the anisotropic conductive fine particles by electroless nickel plating$^{2)}$. Fig. 1 shows preparation process of anisotropic conductive particles. It is widely accepted as a connection material.

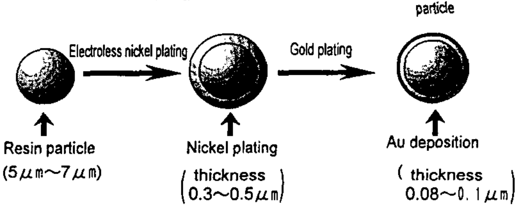


Fig. 1 Preparation processes of anisotropic conductive particles.

EXPERIMENTAL PROCEDURE

Selection of the catalyst processes

$5\sim7\mu m$ polystyrene resin particles were used as a sample. Fine particles were treated with various catalyst processes. A surface morphology of particles after plating observed with a Scanning Electron Microscope (SEM).

Plating bath and operating conditions

The deposition rate on the fine particles is accelerated because the specific surface area of fine particles is large. Therefore, decomposition reaction tend to occur when the batch process is applied. Accordingly, nickel is plated on the fine particles with a dropping process. The Plating reaction progresses properly because each chemicals is stored separately and mix into the reaction solution. The solution that is used for the dropping process is divided into the following three kinds of chemicals. 0.85M nickel sulfate hexahydrate with a 1.0M complexing agent as a metal salt, 2.0M sodium hypo-phosphite as a reducing agent, and 1.0M sodium hydroxide as a pH adjustment solution were used.

The deposition conditions of nickel were investigated.

X-ray diffraction measurement

Crystal structure of Ni films analyzed by using a X-ray diffraction (XRD). Phosphorus contents in Ni-P films was measured by an Electron probe X-ray microanalyzer (EPMA). Relationship between crystal structure and phosphorus contents of Ni films were investigated.

Flexibility of deposited films

The flexibility of Ni films were measured by a compression test device. Morphology of Ni films was evaluated based on the measured results of the flexibility deformation of the fine particles.

RESULT AND DISCUSSION

Selection of the catalyst processes

After adsorbing a catalyst[3)] on the fine particles with each catalyst process, deposited Ni surface was observed. The SEM micrographs of nickel deposits using different catalyst solutions are shown in Fig. 2. When the fine particles are catalyzed with palladium ions, palladium are tend to dissolved into the solution and the bath became unstable. Also, nodules were observed extensively on the Ni deposited particles using the colloidal catalyst[4, 5)] and the alkaline catalyst. On the contrary, uniformly deposition can be obtained by using the two step catalyst process.

Addition effects of the surfactant

The nodules occurred on the nickel films because the palladium catalyst did not adsorb uniformly when the particles were catalyzed with the colloidal catalyst or alkaline catalyst.

Therefore, a conditioning effect by surfactant was investigated to create the uniformly adsorption of the catalyst on the particles. Fig. 3 shows SEM micrographs of condition-

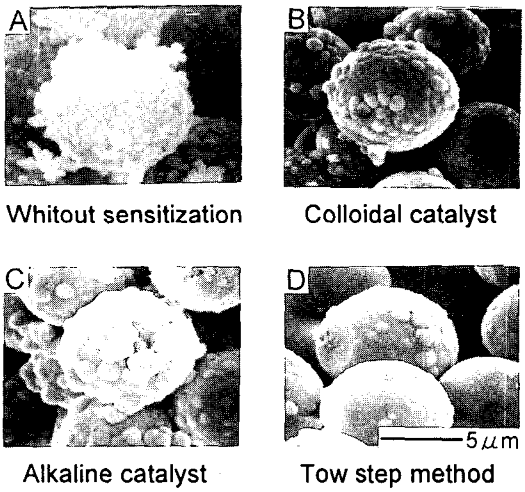
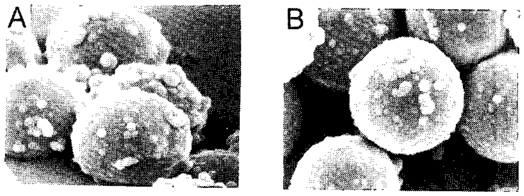
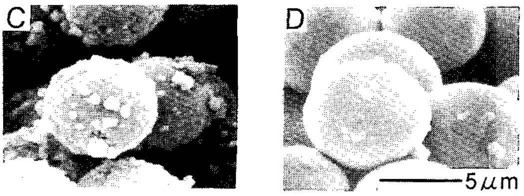


Fig. 2 SEM micrographs of nickel films treated with the different activation solutions. (A) Without sensitization; (B) Colloidal catalyst; (C) Alkaline catalyst; (D) Two step method



PEG1000 → Whitout sensitization　PEG1000 → Colloidal catalyst



PEG1000 → Alkaline catalyst　PEG1000 → Tow step method

Fig. 3 The effects of the surfactant treatment (Polyethylene glycol) before sensitization.

ing effects. Tin and palladium absorbed on the particles uniformly and extraneous deposition decreased.

Optimum stannous chloride and palladium chloride concentration

The surface morphology of the Ni films observed after changing the concentration of tin and palladium ions of the two step process. The extraneous depositions were observed on the Ni films with increase the tin and palladium concentrations. The results are shown in Table. I. Optimum stannous chloride and palladium chloride concentrations are 0.1g/L and 0.05g/L, respectively. On the contrary tin did not adsorb uniformly with a decrease in the stannous chloride concentrations.

Relationship between deposition rate and phosphorus contents at various pH

By changing the pH of the plating bath from 4 to 6, the deposition rate and phosphorus contents were measured. The phosphorus contents of nickel films and deposition rate at pH4-6 on fine particles are investigated. When the pH exceeds 6, nickel hydroxide colloids were easily formed. On the other hand, electroless nickel plating reaction did not initiated under pH4. Accordingly, pH of the plating solutions were adjusted between 4 and 6.

Table. 1 Effects of stannous chloride and palladium chloride concentrations of nickel films on the catalyzing process. (A) Uniform deposition; (B) Dimple deposition; (C) Extraneous deposition; (C) Extraneous deposition; (D) No deposition

$SnCl_2$ $PdCl_2$	0.1g/L	1.0g/L	5.0g/L
0.01g/L	D	D	D
0.05g/L	A	B	C
0.50g/L	B	C	C

Relationship between complexing agent and deposition rate

The deposition rate on various complexing agents at pH4～6 are shown in Fig. 4. The deposition rate increased along with raising the pH. The glycine bath showed the fastest deposition rate, followed by sodium tartrate, and the ammonium acetate bath.

Surface morphology of deposited nickel

By changing the pH, complexing agent, and bath temperature, surface morphologies were observed. Many extraneous deposits were observed on the particles at pH6, since deposition rate was increased with increasing the pH value. On the other hand, deposition rate and extraneous deposition decreased by decreasing the pH value. Among these

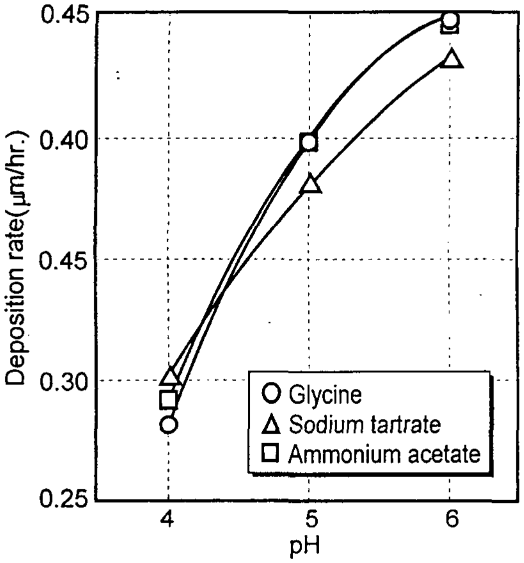


Fig. 4 Ni deposition rate from the various complexing agents at three different pH values.

complexing agent, the uniformly deposited nickel can be obtained in a range from pH 4 to 5 at 70℃by using ammonium acetate. Uniform films were also obtained without depending on the complexing agents at pH4 and 70℃.

Crystal structure analysis by X-ray diffraction

Fig. 5 shows the XRD analysis of nickel crystal structures at various phosphorus contents. Phosphorus contents of the nickel films that were 4.9wt% from glycine bath at pH6, result in sharp diffraction peaks derived from Ni(111) plane. As phosphorus content in the nickel films increased, peaks derived from Ni (111) plane gradually became broadend[6,7]. When phosphorus contents in the Ni films reached 6.1wt%, Ni (111) plane and Ni (200) plane became one broad peak. When phosphorus contents reached 8.6wt%, peaks based on the nickel became completely broadened.

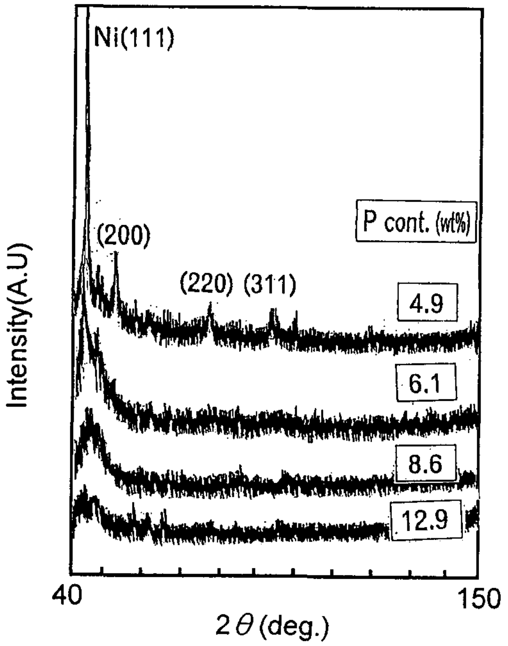


Fig. 5 X-rayiffractograms of various phosphorous contents of Ni-P alloys.

Flexibility of the nickel films

Anisotropic conductive particles should be compressively adhered with electrodes as the connection material. Accordingly the flexibility of the films was evaluated using the micro compression test device. The result are shown in Fig. 6. Cracks developed very fast on the nodular films. Especially, Ni deposited particles obtained at pH6 were fragile and cracks developed very rapidly. On the other hand, cracks were developed slowly on the uniform films.

CONCLUSIONS

Anisotropic conductive film particles by electroless nickel plating have been investi-

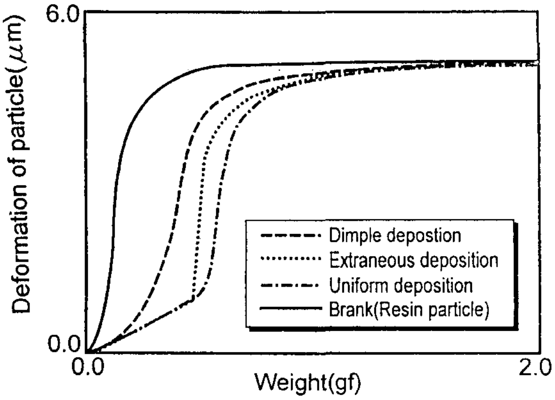


Fig. 6 Relationship between phosphorous contents in the Ni-P alloy and the deposition rate on the particles.

gated and the following conclusion were obtained.

1) It was confirmed that the palladium catalyst absorbed uniformly on the particles by the treatment with cationic surfactant before the catalyzation process.

2) The nodulous nickel deposits associated with a rise in the pH can be inhibited by lowering the bath temperature.

3) Uniform films were obtained at 70℃ and pH4.

4) The uniformly deposited nickel films were obtained in a range from pH4 to pH6 by using ammonium acetate as a complexing agent.

5) Uniformly deposited particles without coalescence can be obtained when phosphorus content was over 8.6 wt%.

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