J Mater Sci (2007) 42:2121–2125
DOI 10.1007/s10853-006-1225-y

Deposition of electroless Ni on micro-sized acrylic spheres

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Received: 13 October 2005 / Accepted: 30 January 2006 / Published online: 15 December 2006

Abstract In this work a thin film of electroless Ni was deposited on the surface of commercial acrylic spheres about 4 μm in size. After the acrylic spheres were cleaned, sensitized and activated successively, they were put into an acid plating bath containing sodium hypophosphite as reducing agent for the electroless Ni deposition. The acrylic spheres with a film of Ni deposit were molded into a cold set resin and ground and polished to form a cross section for observation. The thickness of the Ni film was measured and the state of the adhesion of Ni film to the surface of the acrylic sphere was observed by a scanning electron microscope. The results showed that the Ni film deposited in a plating bath with pH 4.2 can tightly adhere on the surface of the acrylic sphere due to the compressive stress of the Ni film. The thickness of the Ni film on the acrylic sphere can reach about 0.35 μm in 3 min of deposition time at 50–70 °C of plating temperature. The activation energy of electroless Ni deposition in plating bath with pH 4.2 is about 28.50 kJ/mole. The acrylic spheres with a layer of electroless Ni film deposited by the method proposed in this work can be further applied to anisotropic conductive adhesives in flip chip package.

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Introduction

It is more and more important and wide-spreading for the anisotropic conductive adhesive (ACA) to be used for electrical connection in the electronic package. Because the ACA can conduct electricity along only one direction vertical to the chip and cannot do along the other two directions parallel to the chip, it can be spread on the whole surface of a chip in the packaging process. Therefore, the ACA greatly improves the packaging work due to the lower working temperature, shorter working time and smaller pitch [1, 2].

The ACA consists of electrically conductive particles and an insulating binder. Metal particles and polymer spheres coated with a metal film are the most important conductive particles [3]. Under a better condition electrically conductive particles should have equal size and their quantity in the binder should be optimized so that they cannot touch each other but can touch the bondpads of the substrate and the chip for the electrical conduction in one direction under an appropriate pressure. After the insulating binder hardened at an appropriate temperature the electrical connection between the particles and the bondpads of the substrate and the chip can be kept a long time [4, 5].

If polymer spheres coated with a metal film are used as the electrically conductive particles of ACA, the cost of ACA can be lowered and the contact area between particles and bondpads can be increased due to the plasticity of the polymer particles. The metal film coated on the surface of the polymer spheres in general consists of an inner layer of Ni and an outer layer of Au. Au has better electrical conductivity and anti-corrosiveness and Ni is used to improve the combination between Au and polymer [6]. If the size of the electrically conductive particles is too large, the pitch cannot be greatly shortened and if too small, it is difficult for the particles to uniformly disperse in the binder. Therefore, the size of the particles is in general between 3 and 8 μm [6].

For improving the adhesion of the electroless metal film to the polymer, the surface of the polymer frequently modified before deposition by various methods, such as chemical treatment, ion beam treatment, plasma treatment, ozone treatment and graft copolymerization [7–12]. After surface modification the surface of the polymer is sensitized and activated by a two-step process [13] in $SnCl_2$ solution and $PdCl_2$ solution successively or by a one-step process [14] in a mixed $SnCl_2/PdCl_2$ solution. The surface of the polymer is then deposited a metal film in an electroless plating bath.

The electroless Ni deposit may have an intrinsic stress due to hydrogen, phosphors and defects in itself and an extrinsic stress due to the difference of thermal expansion coefficient between deposit and substrate. The intrinsic stress of the electroless Ni deposit is primarily determined by the content of phosphor in deposit [15–20]. The intrinsic stress can be changed from tensile to compressive state as the phosphor content increases [20].

Up to now the deposition of electroless Ni on micro-sized acrylic spheres is seldom studied. In this work, a thin film of electroless Ni was deposited on the surface of commercial acrylic spheres about 4μm in size in an acid plating bath containing sodium hypophosphite as reducing agent. The phosphor content in Ni deposit was controlled by the pH value of the plating bath in such a manner that an electroless Ni film with compressive stress could be obtained and tightly adhered to the surface of the acrylic spheres. Therefore, the acrylic spheres coated with a film of electroless Ni with a compressive stress can be well applied to the ACA for the flip chip package.

Experimental procedure

The commercial acrylic spheres about 4 μm in size were first cleaned up in deionized water with ultrasonic oscillation for 20 min. They were then sensitized by dipping in $SnCl_2 + HCl$ solution (40 g/l $SnCl_2$ + 3 ml/l HCl) for 2 min, and activated by dipping in $PdCl_2 + HCl$ solution (0.15 g/l $PdCl_2$ + 3 ml/l HCl) for 30 s. The spheres were rinsed with deionized water after each step. Then the electroless Ni plating process was immediately carried out. The plating bath composition and operation condition of electroless Ni deposition were listed in Table 1. The plating bath contains nickel sulfate as nickel ion source, sodium hypophosphite as reducing agent, sodium succinate as complexing agent, and lead nitrite as stabilizer. The pH of the plating bath was adjusted with sodium hydroxide aqueous solution.

In order to measure the thickness of the electroless Ni film on the surface of the acrylic spheres and estimate the adhesion of the film to the sphere, the acrylic spheres coated with a Ni film were molded into a cold set resin and then ground and polished to form a cross section for observation by a scanning election microscope (SEM) (JEOL Ltd, JSM-T330A). The measurement for the thickness of Ni film was carried out in an image analyzer (LVM 100). The diffraction pattern of the electroless Ni film were made by a transmission election microscope (TEM) (JEOL Ltd, JSM-2010) and the elements contained in the electroless Ni film were analyzed by the energy dispersive X-ray spectrum (EDS) equipped in TEM.

Results and discussions

Figure 1 shows the SEM image of commercial acrylic spheres of which sizes are about 4 μm. Shown in Fig. 2 are the acrylic spheres coated with a film of electroless Ni that was deposited in a plating bath at 70 °C and pH 4.2 for 15 min. The acrylic spheres coated with a Ni film look quite spherical and relatively large. But there are some bumps of Ni deposits on their surface. Figure 3 shows the cross-sectional SEM image of acrylic spheres coated with a Ni film that was deposited in an electroless plating bath at 70 °C and pH 5.2 for 10 min. It is clearly seen that there are gaps with arc shape between the surface of acrylic sphere and the electroless Ni film. This means that the electroless Ni film deposited in the bath of pH 5.2 cannot well adhere to the surface of acrylic sphere. The reason for the bad adhesion between acrylic sphere and electroless Ni deposit made in the bath of pH 5.2 is very probably due to the tensile stress in the electroless Ni deposit.

Table 1 The composition of electroless Ni–P plating bath and the plating parameters

Composition of bath and plating parameters	Specifications
$NiSO_4·6H_2O$	35(g/l)
$NaH_2PO_2·H_2O$	40(g/l)
$Na_2C_4H_4O_4·6H_2O$	16(g/l)
$Pb(NO_3)_2$	1 ppm
pH	5.2, 4.2
Temperature (°C)	50, 55, 60, 65, 70
Time (min)	1, 2, 3, 6, 9, 12

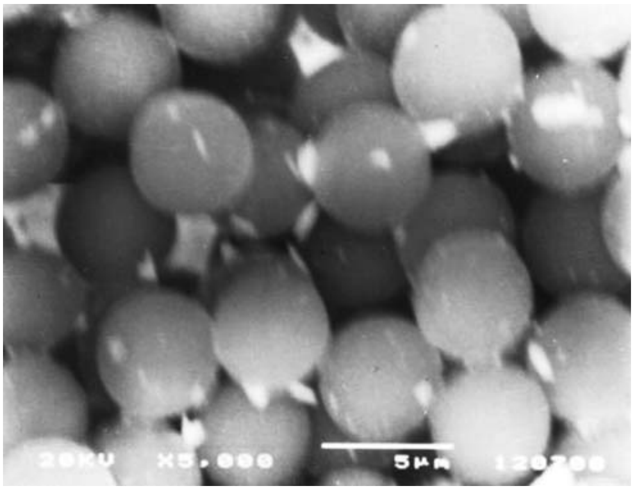

Fig. 1 SEM image of commercial acrylic spheres

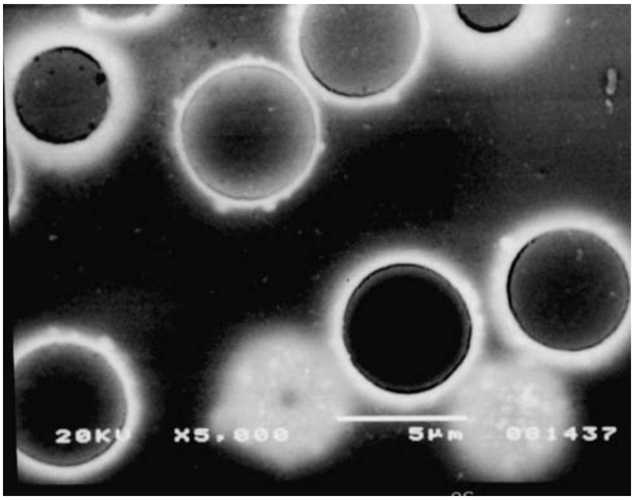

Fig. 3 SEM cross-sectional image of acrylic spheres with a Ni film deposited in an electroless plating bath at 70 °C and pH 5.2 for 10 min

Figure 4 shows the cross-sectional SEM image of acrylic spheres coated with a Ni film that was deposited in an electroless plating bath at 70 °C and pH 4.2 for 10 min. No any gap can be seen between the electroless Ni film and the surface of the sphere. Therefore, a well adhesion between the surface of acrylic sphere and the electroless Ni film made in bath of pH 4.2 can be obtained due to the compressive stress in the electroless Ni film. Figure 5 shows the TEM bright field view of acrylic spheres coated with a Ni film that was deposited in an electroless plating bath at 70 °C and pH 5.2 for 30 min. The surface of the Ni film is quite uneven. The diffraction pattern of the electroless Ni deposit in Fig. 5 is shown in Fig. 6, which confirms the film on the surface of acrylic sphere is Ni metal with crystallite structure. The compositions of electroless Ni films made in bath of pH 5.2 and pH 4.2 are 89.3 at.% Ni, 10.7 at.% P and 79.7 at.% Ni, 20.3 at.% P, respectively.

Because the electroless Ni film made in bath of pH 4.2 could tightly adhere to the acrylic sphere, it was then studied in more detail. In order to precisely measure the variation of the thickness of the electroless Ni film made in the bath of pH 4.2 at various temperatures and for various times, every thickness was determined in such a manner that every cross section was measured thrice along three different directions with 120° of cross angle each other and ten different cross sections were measured to get the average. The results were listed in Table 2. Because there were 0.545 g of acrylic spheres added in 1 liter of

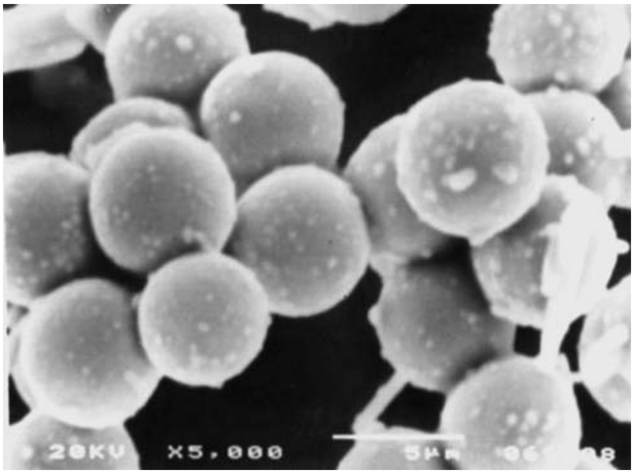

Fig. 2 SEM image of acrylic spheres with a film of electroless Ni deposited in a plating bath at 70 °C and pH 4.2 for 15 min

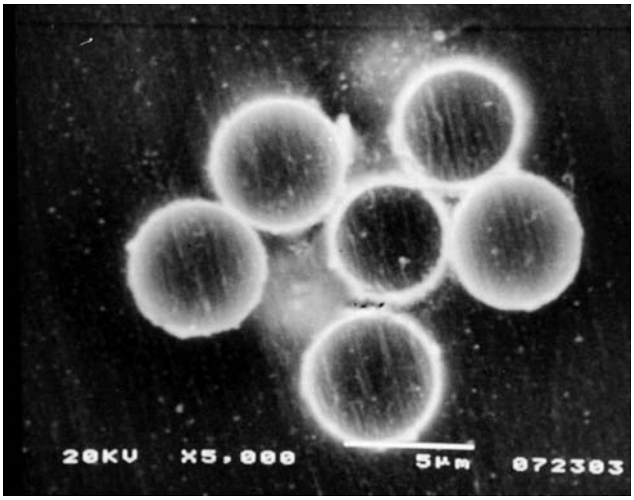

Fig. 4 SEM cross-sectional image of acrylic spheres with a Ni film deposited in an electroless plating bath at 70 °C and pH 4.2 for 10 min

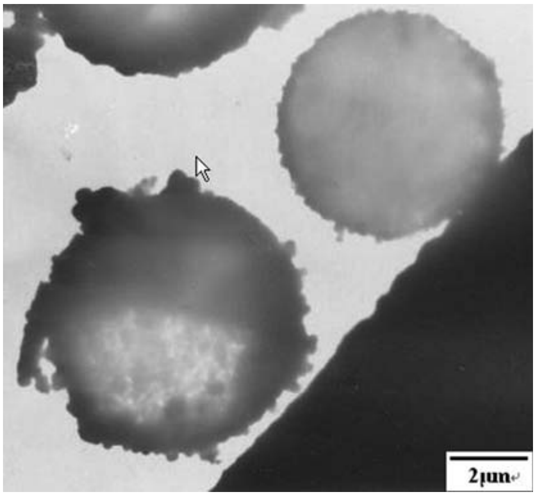

Fig. 5 TEM bright field view of acrylic spheres with a Ni film deposited in an electroless plating bath at 70 °C and pH 5.2 for 30 min

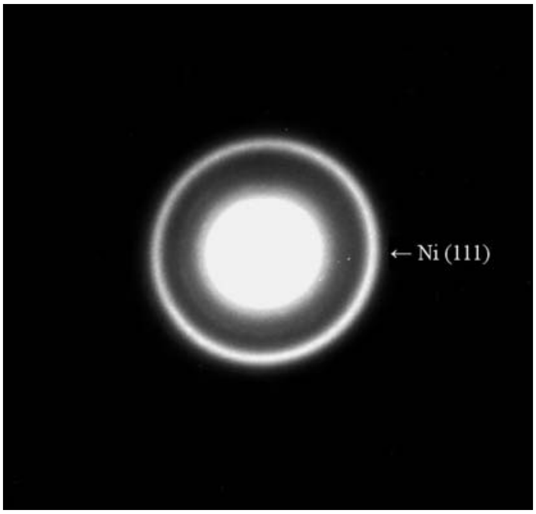

Fig. 6 Diffraction pattern of the electroless Ni film in Fig. 5

Table 2 The thickness variation of electroless Ni films on the surface of acrylic spheres deposited in a plating bath of pH 4.2 for various plating temperatures and times

Temperature (°C) Time (min)	50	55	60	65	70
1	0.101	0.075	0.157	0.106	0.203
2	0.153	0.216	0.253	0.208	0.359
3	0.256	0.269	0.303	0.353	0.467
6	0.257	0.272	0.380	0.383	0.467
9	0.257	0.268	0.378	0.431	0.493
12	0.282	0.343	0.381	0.460	0.454

plating bath, and the spheres have about 4 μm in size and 0.89 in specific gravity, the number of spheres is 1.83×10^{10} and the total surface area of spheres is 9,185 cm^2. This is a very large area for deposition in 1 liter bath, so the concentration of composition in plating bath will be rapidly lowered and the deposition rate of electroless Ni film also becomes very small in the same time. This is the case in Table 2 where the thickness of the Ni films deposited at various temperatures is almost unchanged after 3 min.

The growth rate of electroless Ni film deposited on the surface of acrylic spheres can be defined as the volume increment on unit area per time, that is, growth rate = $\mathrm{d}V/A\mathrm{d}t = d(4/3\pi r^3)/4\pi r^2\mathrm{d}t = \mathrm{d}r/\mathrm{d}t$, where V, A and r are the volume, surface area and radius of the sphere, respectively. Therefore, the growth rate is independent of the size of acrylic sphere. It can be determined by only measuring the variation of the sphere radius with the plating time.

In order to find the growth rate and the activation energy of the electroless Ni film deposited on the surface of the acrylic spheres, it is reasonable that only these data before 3 min in Table 2 are used for calculation. Figure 7 shows the growth rates of electroless Ni films deposited in a bath of pH 4.2 at various temperatures and the activation energy, Q = 28.50 kJ/mole, derived from the slope of the regress line.

Conclusion

After the commercial acrylic spheres about 4 μm in size were cleaned up in deionized water with ultrasonic oscillation, sensitized in $SnCl_2 + HCl_2$ solution and activated in $PdCl_2 + HCl$ solution successively, a film of electroless Ni could be deposited on their surface in

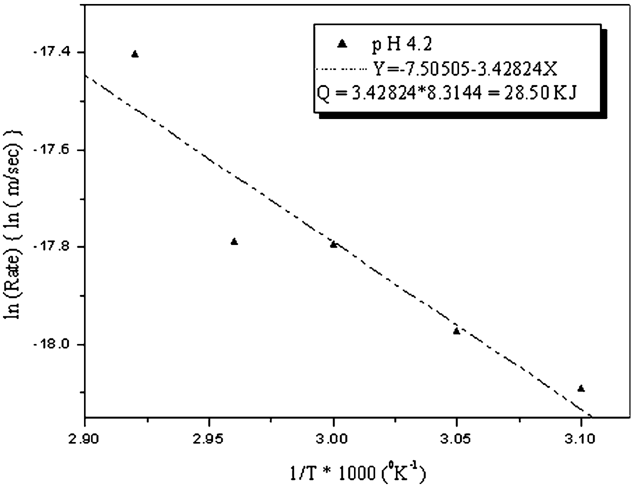

Fig. 7 The growth rates of electroless Ni films deposited in a bath of pH 4.2 at various temperatures and the activation energy derived from the slope of the regress line

an acid plating bath containing sodium hypophosphite as reducing agent. When the pH value of plating bath is 5.2, between the surface of the spheres and the Ni films there exist gaps, occurred due to the tensile stress in Ni film. When pH is 4.2, the Ni film can tightly adhere to the surface of the sphere due to the compressive stress in Ni film. An electroless Ni film about 0.35 μm in thickness could be got in 3 min plating time in a bath at 50–70 °C and the activation energy for plating this film is 28.50 kJ/mole. The commercial acrylic spheres coated an electroless Ni film with a compressive stress can be further applied to anisotropic conductive adhesives for flip-chip package.

References

1. Chang DD, Crawford PA, Fulton JA, McBride R, Schmidt MB, Sinitski RE, Wong CP (1993) In: Proceedings of the 43rd Electron Compon Technol Conf, 1–4 June, 1993, Orlando, FL, USA, p320
2. Tong H-M (1995) Mater Chem Phys 40:147
3. Seppälä A, Ristolainen E (2004) Microelectron Reliabil 44:639
4. Briegel R, Ashauer M, Ashauer H, Sandmaier H, Lang W (2002) Sens Actuators A 97–98:323
5. Chan YC, Luk DY (2002) Microelectron Reliabil 42:1185
6. Sarkar G, Mridha S, Chong TT, Tuck WY, Kwan SC (1999) J Mater Process Technol 89–90:484
7. Yang GH, Lim C, Tan YP, Zhang Y, Kang ET, Neoh KG (2002) Eur Polym J 38:2153
8. Kang ET, Zhang Y (2000) Adv Mater 12:1481
9. Sacher E (1994) Prog Surf Sci 47:273
10. Mathieson I, Brewis DM, Sutherland I, Cayless RA (1994) J Adhes 46:49
11. Ponter AB, Jones WR, Jansen RH (1994) Polym Eng Sci 34:1233
12. Wu SY, Kang ET, Neoh KG, Han HS, Tan KL (1999) Macromolecules 32:186
13. Muller G, Baudrand DW (1971) Plating on plastics, 2nd edn. Robert Draper Ltd, Teddington, p88
14. Meek RL (1975) J Electrochem Soc 122:1478
15. Chen Z, Xu X, Wong Chee C, Subodh M (2003) Surf Coatings Technol 166:170
16. Deckert CA, Andrus J (1978) Plating Surf Finish 65:43
17. Yu J, Song JY (2002) Thin Solid Films 402:167
18. Doo JY, Paik KW (2002) IEEE Trans Compon Packaging Technol 25:169
19. Farr JPG, Abbas Noshani A (1996) Transactions of the Institute of Metal Finishing 74:221
20. Parker K, Shah H (1971) Plating 58:230