Metal Coated Polymer Particles for Electronic Packaging

Ionel Halaciuga[1], Keith Redford[2], and Dan V. Goia[1,3]

[1] Center for Advanced Materials Processing, Clarkson University
8 Clarkson Avenue, Potsdam, NY 13699-5814, USA
[2]Conpart AS, Dragonveien 54, 2013 Skjetten, Norway
[3]goiadanv@clarkson.edu; Phone: +1-315-268-4411; Fax: +1-315-268-2139

Abstract

Anisotropic conductive adhesives (ACA) are widely used as interconnect materials in the manufacturing of LCD screens. To be integrated in a broader range of interconnect applications several technical and economic issues still need to be addressed. One significant challenge is to encapsulate polymer particles with well controlled modal diameter and size distribution into continuous, compact, and uniform conductive metallic shells. This presentation describes a method to deposit layers of nickel with different thickness (30 – 120 nm) onto monosized polymer particles ranging in size from 1 to 10 micrometers. The novelty of the approach consists in a pre-treatment of the epoxy functionalized polymer particles with linear polymeric amines. We show that by increasing amine chain length the distribution of the palladium catalyst, and consequently the adhesion and distribution of nickel metal deposited, can be improved dramatically. The effect of several plating parameters is discussed and illustrated.

Keywords: ACA, polymer, electroless plating, nickel

1. Introduction

Miniaturization and robustness are key factors in today's electronics industry when considering manufacturing complex devices. Anisotropic conductive adhesives (ACA) that pass electricity along only one axis provide electrical connection in many critical electronic systems. This approach can replace traditional methods, like soldering, and provides connectivity where conventional technologies fail. ACA also facilitate a more efficient use of the board 'real estate' as well as more flexible and reliable interconnects [1-3]. Typical ACA pastes contain electrically conductive metallic particles, ranging in size from 2 to 10 micrometers, incorporated in an insulating binder. When used as conductive filler, metal coated polymer spheres offer a lower consumption of metal and a larger bonding surface due to their deformability. The deposited metallic shell consists typically of an inner Ni layer and an outer Au layer. The former represents a cost effective electrical conductor while the latter enhances electrical conductivity and corrosion resistance [4-6].

The successful deposition of Ni on polymer substrates requires an effective surface activation [7,8]. Despite numerous attempts to develop viable alternatives [9,10], the Sn^{2+}/Pd^{2+} system remains the most widely used approach to activate polymeric surfaces [11,12]. After successful activation, the Ni coating is deposited typically through an electroless process. This step makes possible the deposition of continuous nickel layers onto polymer spheres of various sizes and surface composition. The uniformity, continuity, and compactness of the metallic shell are essential in preventing catastrophic mechanical failures [13,14] while the ability to tailor the composition of the polymer core/surface provides materials with a broader range of mechanical properties. Since most existing commercial electroless nickel baths contain chemicals that are either toxic or detrimental to the properties of the deposited nickel layer [4-11], extensive research is directed towards the development of alternative systems.

This study describes a plating process which provides Ni and NiAu polymer coated spheres suitable for ACA applications. The approach combines a novel method for activating the surface of polymer spheres of different size, composition, and surface functionality with a simple, cost effective, and relatively nontoxic Ni plating step.

2. Materials and characterization methods

2.1. Reagents and materials

The monodisperse polymer spheres supplied by Conpart AS (Oslo, Norway) with modal diameters

of 3.0 and 3.8 μm and different compositions were prepared according to ref. [15]. Ammonium tetrachloropalladate [$(NH_4)_2PdCl_4$], ethylenediamine [EDA], diethylenetriamine [DETA], triethylene-tetramine [TETA], tetraethylenepentamine [TEPA], ethyleneglycol [EG], dimethylaminoborane [DMAB], nickel chloride hexahydrate [$NiCl_2 \cdot 6H_2O$], and sodium pyrophosphate [$Na_4P_2O_7 \cdot 10H_2O$] were all purchased from Alfa Aesar (Ward Hill, MA) and used as received. Polyvinylpyrrolidone K30 [M.W. 40,000] was purchased from Fluka Analytical (Milwaukee, WI).

2.2. Characterization methods

The morphology of the particles and coatings was investigated by Field Emission Scanning Electron Microscopy (FESEM) with a Jeol JSM-7400F instrument and Scanning Transmission Electron Microscopy (STEM) using a Jeol JEM-2010 instrument (Jeol Ltd., Japan). The crystalline structure of the nickel phase was assessed by X-ray diffraction analysis (XRD) using a Bruker D8 Focus diffractometer (Newark, DE) with the Cu-$K\alpha_1$ radiation source (1.5406 Å). The crystallite size of Ni was estimated based on the Scherrer's equation 1 [16].

$$d = \frac{k \cdot \lambda}{\beta \cdot \cos\theta} \qquad (1)$$

where d is the crystallite size, k is a shape factor (0.9), λ is the wavelength of the incident radiation (1.5406 Å), β is the peak broadening at half of the intensity, and θ is the Bragg angle.

The size and size distribution of the uncoated and coated polymer particles was determined with a Malvern Mastersizer 2000s instrument (Westborough, MA).

2.3. Activation of the polymer spheres

The epoxy functionalized polymer particles (5 g) were dispersed in a mixture of 15 cm^3 deionized water (Di-H_2O)/30 cm^3 polyamine/50 cm^3 EG in a 4-neck round bottom flask and kept at 110±2 ^oC under mixing for controlled lengths of time (Table 1). After separation by filtration, the amine functionalized polymer spheres were activated using a previously published protocol [17]. For this purpose, the polymer beads were dispersed in 60 cm^3 of aqueous solution of $(NH_4)_2PdCl_4$ (10^{-4}M) and maintained at 85 ^oC for 30 minutes under continuous mixing. The particles were next washed with DI water and redispersed in 30 cm^3 DI water. The surface adsorbed Pd(II) species were next reduced at 60 ^oC by adding 10 cm^3 of reducing solution containing $13.5x10^{-3}$ moles of DMAB.

Table 1. Conditions used in the functionalization of the polymer surface.

Sample #	Polyamine	GMA content (wt.%)	Time (hours)
A1	--	20	--
A2	EDA	20	22
A3	DETA	20	22
A4	TETA	20	22
A5	TEPA	20	22
A6	TEPA	20	96
A7	TEPA	40	96

2.4. Deposition of the Nickel

The Ni coatings were deposited on the activated polymer beads using a modified version of the electroless plating bath described in ref. [17]. The experimental parameters used for the optimization of the plating process are given in Table 2.

Table 2. Experimental conditions used for the deposition of Ni coatings

Sample #	Polymer ($g \cdot dm^{-3}$)	Ni ($mol \cdot dm^{-3}$)	NH_3:Ni molar ratio	pH	Ni thickness (theoretical/nm)
1	10	$8.4x10^{-2}$	2:1	10.1	40
2	10	$8.4x10^{-2}$	2.5:1	10.2	40
3	10	$8.4x10^{-2}$	3.5:1	10.4	40
4	10	$8.4x10^{-2}$	6:1	10.9	40
5	10	$8.4x10^{-2}$	3:1	10.3	40
6	10	$16.8x10^{-2}$	3:1	10.5	80
7	10	$21.8x10^{-2}$	3:1	10.6	100
8	10	$26.6x10^{-2}$	3:1	10.7	120

3. Results and discussion

The electron micrographs of Ni coated polymer beads prepared according to the conditions given in Table 1 are shown in Figure 1.

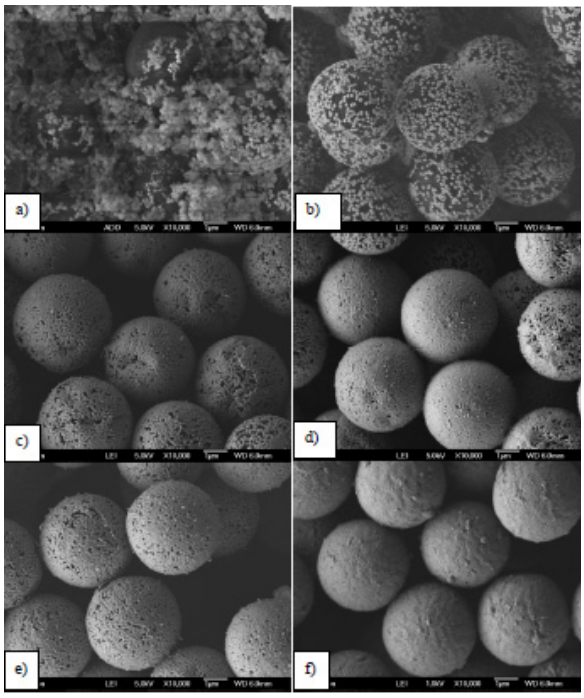

Figure 1. FESEM images of Nickel coated polymer particles not conditioned with amine (a) and conditioned for 22 hours with EDA (b), DETA (c), TETA (d) and TEPA (e), and for 96 hours with TEPA (f) (Note: the nominal diameter of the polymer spheres is 3.8 μm).

In the case of non-aminated polymer spheres, Ni precipitated as large (60 - 80 nm) nanoparticles of which only a small fraction were attached to the polymer surface (Figure 1a). When the polymer particles were conditioned with EDA for 22 hours, all nickel nanoparticles were deposited on the surface of the polymer spheres (Figure 1b). However, since their size was still large (~50 nm) the nickel shell was not completely closed. The gradual increase in the length of the linear polyamines chain (from DETA to TEPA) resulted in the decrease of the size of Ni nanoparticles and a smoother, more continuous Ni shell (Figure 1 c-e). In the case of TEPA, extending the contact time with the polymer beads with the amine from 22 to 96 hours further improved the compactness and smoothness of the metallic layer (Figure 1 f).

Intuitively, the efficiency of the activation process depends on the density of Pd clusters formed on the surface of the beads, which depends again on the ability of the latter to bind Pd(II) ions. Since in this regard amine groups are more effective than the functional groups in the epoxy surface, the EDA molecules imbedded in the surface during the amination process bind more Pd(II) ions on the surface. The formation of a larger number of smaller and better distributed Pd clusters facilitates the deposition of all Ni on the particle's surface. Linear polyamines with longer chain provide a higher density of amine groups per unit surface and stronger interactions with the epoxy groups of the polymer [18]. As a result, a larger number of smaller and better distributed Pd clusters form with an increased amine molecular weight. Thus, large (up to 50 nm) and polydisperse Pd clusters are formed in the case of EDA (Figure 2a), while in the case of the prolonged treatment with TEPA the Pd clusters are much smaller (~ 4 nm), more uniform and better distributed (Figure 2c). Since the Pd clusters act as nucleating sites for the reduction of the base metal, the size of the Ni crystallite and implicitly the structure of the coating differed significantly for the two amines. In the case of EDA, the shell consisted of much

larger Nickel primary particles (~100 nm) (Figure 2b), whereas in the case of TEPA their average size was only ~30 nm (Figure 2d). This difference was responsible for the improved continuity and smoothness of the Ni shell in the latter case.

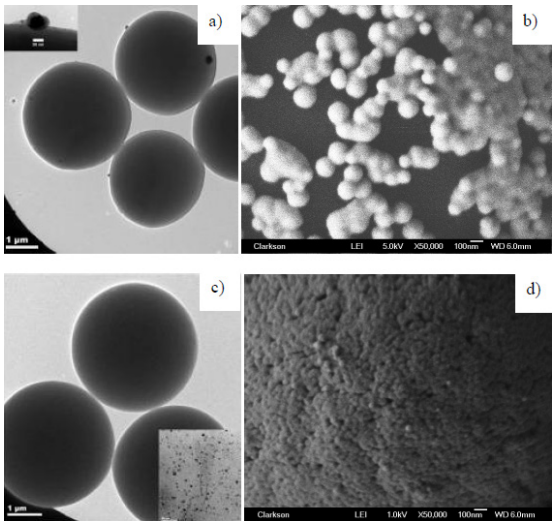

Figure 2. a) TEM image of Pd coated polymer particles conditioned in EDA for 22 hrs (the inset shows the image of a large Pd cluster), b) high magnification FESEM of the surface of a polymer particle shown in (a) coated with nickel, c) TEM image of a Pd coated polymer sphere conditioned in TEPA for 96 hours, and d) FESEM of a polymer particle shown in (c) coated with nickel. (Note: Nominal diameter of the polymer spheres is 3.8 µm).

The X-ray diffraction analysis of the coated polymer spheres revealed in all cases a pure crystalline fcc (face centered cubic) nickel phase (Figure 3). It is noteworthy that the primary particles revealed by FESEM appeared to be polycrystalline, the crystallite depending on the reaction conditions. It the case of the prolonged treatment with TEPA the crystallite size was ~2 nm.

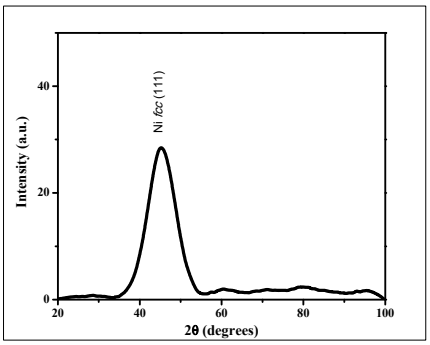

Figure 3. X-ray diffraction pattern obtained for the Nickel coated particles obtained with prolonged TEPA treatment (Experiment A6, Table 1).

The very small nanocrystallites were fused together forming a compact, mechanically strong, and adhering metallic shell, which required significant force to be fractured and dislocated (Figure 4).

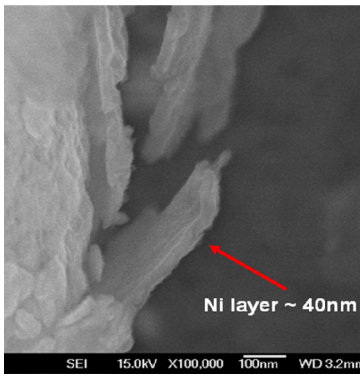

Figure 4. Scanning electron micrograph of a portion of the fractured dislocated Nickel shell. The nominal diameter of the polymer spheres is 3.8 µm, and the thickness of the nickel layer (~40 nm), is in agreement with the amount of Ni deposited (Sample 5, Table 2).

As suggested by the FESEM images in figures 1(f), the Ni deposition did not result in inter-particle bridging, the particles remaining fully dispersed and non-aggregated through the plating process. This was confirmed by the particle size distribution analysis, which did not exhibit a shift or a broadening for the coated beads when compared with the original polymer spheres (Figure 5).

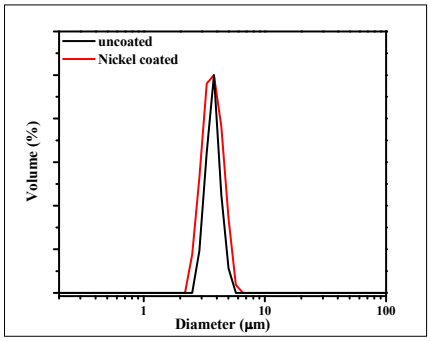

Figure 5. Particle size of input polymer particles (black line) and Ni coated particles (red line).

The plating technique developed was equally effective in providing a continuous,

adherent, smooth film on smaller polymer particles. As shown in Figure 6, the aspect of the coating did not change when decreasing the polymer sphere diameter to 3.0 micrometers from 3.8 micrometers.

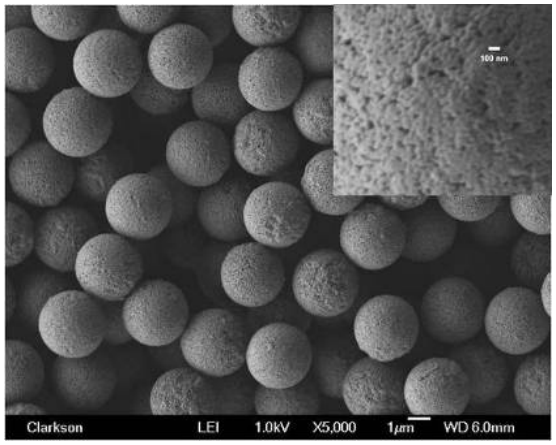

Figure 6. Scanning electron micrograph of Nickel coated polymer particles with a nominal diameter of 3.0 μm. Inset shows high magnification of the surface of a single coated particle.

It's worth mentioning that the same coating protocol was successfully applied to core particles having different internal composition (40% glycidyl methacrylate/GMA vs. 20%). The variation in surface functionality of the polymer spheres did not affect the quality of the final nickel shell as indicated by the FESEM images (low and high magnification) in Figure 7. In the case of higher GMA content, the successful implementation of the same protocol was somewhat expected since a larger number of the epoxy groups in the surface of the polymer particles likely favors an improved reactivity with the polyamine molecules [18].

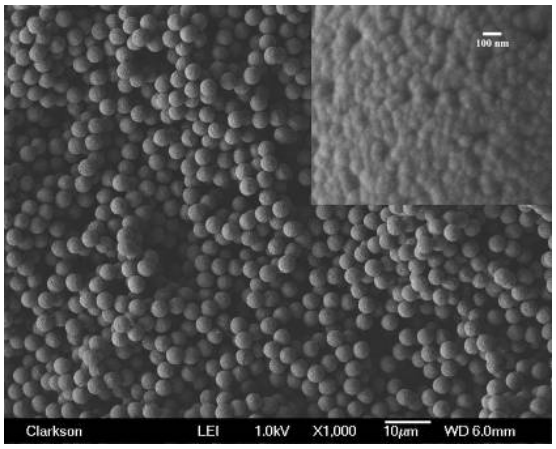

Figure 7. Electron micrograph of Nickel coated polymer particle with 40% GMA content. Inset shows high magnification of the surface of a single particle.

While the polymer surface treatment with polyamines was a critical factor in ensuring the formation of a continuous, compact and adherent Ni coating, other parameters of the plating baths were found to play also an important role. As expected, the amount of ammonia ligand used for the complexation of the Ni^{2+} ions affected strongly the kinetics of the reduction of the metal as well as the quality of the deposited Ni shell (Samples 1-4, Table 2). The value of the Ni^{2+}/ammonia molar ratio which ensured the best reaction kinetics, yield and coating continuity and structure was 2.5 (Figure 8).

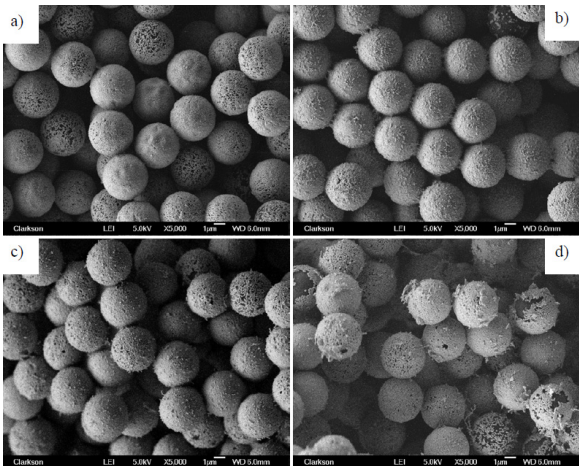

Figure 8. FE-SEM images obtained using different NH_3:Ni molar ratios: 2:1 (a), 2.5:1 (b), 3.5:1 (c), and 6:1 (d) (Samples 1-4, Table 2) (Note: the nominal diameter of the polymer spheres is 3.8 μm).

By adjusting the concentration of the Ni salt the plating bath described could be used to deposit successfully continuous smooth Ni shells of different thicknesses. Figure 9 illustrates the ability to control the thickness of the metal layer by gradually increasing the concentration of the Ni salt in the plating bath.

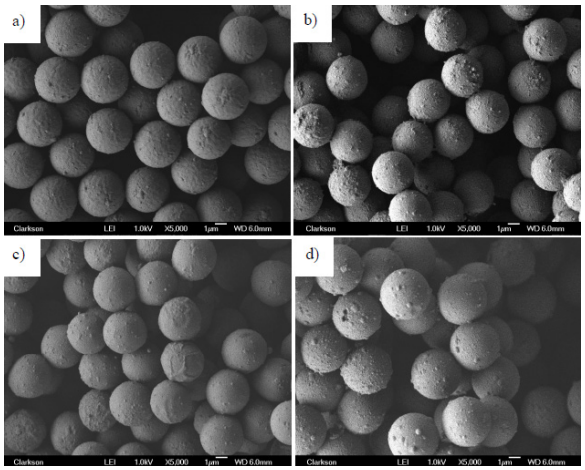

Figure 9. FE-SEM images of Nickel coated polymer particles with a varying Ni layer thickness: a) 40 nm, b) 80 nm c) 100 nm, and d) 120 nm (Samples 5-8, Table 2) (Note: the nominal diameter of the polymer spheres is 3.8 μm).

Conclusions

The paper/poster describes an effective method to deposit continuous, compact, and smooth Ni layers onto monodisperse polymer spheres. The resulting Ni shells are mechanically strong and have a good adherence to the polymer substrate, making the resulting metal/polymer composite particles excellent choices for ACA applications. The ability to control the thickness of the Ni shell offers the possibility to control the mechanical properties of the Ni coated polymer spheres and enhanced versatility in regard to the subsequent deposition of a gold shell.

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