Physical Properties of Metal Coated Polymer Particles for Anisotropic Conductive Adhesive

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ABSTRACT

Metalized and monodisperse polymer particles in micron size are increasingly used in developing new electrical packaging technology. In this application, the large deformation is applied to the particles for increasing the contact area and hence achieving a reliable and low resistance connection. Therefore mechanical response of metal coated particles is very important during the bonding process. In this study, a nanoindentation-based flat punch method has been employed to compress individual Ni/Au coated polymer particles. Deformation and fracture of particles have been investigated with a wide range of test conditions. The effect of nanoscale Ni/Au coating on the deformation capacity and fracture process of particles has been analyzed. By compressing particles to different maximum loads, the cracking and delamination of the Ni/Au coating have been followed by SEM. The results provide crucial knowledge for the design of metal coated polymer particles to different applications.

Keywords: deformation, fracture, Ni/Au coated polymer particles, nanoindentation, flat punch.

1. INTRODUCTION

Monodisperse polymer particles with diameter ranging from 0.5 to 30 μm are increasingly used in new electrical packaging technologies, such as Anisotropic Conductive Adhesives (ACA), Ball Grid Array (BGA) and Chip Scale Packaging (CSP) in Flat Panel Displays (FPDs) [1]. Usually the particles used in these applications have a polymer core — double metal layer structure that consists of a polymer core for improving contact compliance, Ni inner layer for electrical conductivity and Au outer layer for protecting inner layer from the oxidation and increasing the reliability of electrical performance. The use of metal coated polymer particles in electrical packaging technologies is of high interest due to its advantages in terms of lead-free, reducing package size and achieving high-density interconnections. Some of unique properties for the polymer particles, such as chemical compositions, size distribution and mechanical performance, are critical for achieving a reliable and low resistance connection. Using Ugelstad multi-step swelling method, a extremely narrow size distribution and a wide variety of possible chemical compositions of polymer particles have been successfully obtained [2]. Due to the inherent complexity of spherical geometry, mechanical characterization of polymer particles possesses great challenges. However, the electrical characteristics as well as the reliability of the interconnection are mainly determined by the mechanical properties of metal coated polymer particles. Thus the detailed knowledge of mechanical properties of individual particles is essential for the design of electrical assemblies.

The contact load-displacement relationship, large deformation behaviour and size effect of individual polymer particles have been investigated by authors [3]-[5]. However, the particles suffer a large deformation during the bonding process, which may result in the fracture of metal coated particles. This can bring a significant impact on the electrical performance of the interconnection. The aim of the present work is to study deformation and fracture of Ni/Au coated polymer particles.

2. EXPERIMENTAL

2.1 Apparatus

A nanoindentation device (TriboIndenter® Hysitron Inc., MN., USA) has been employed to perform the mechanical testing. The resolutions of load and displacement are theoretically 1nN and 0.004nm, and actually 100nN and 1nm in the current conditions which are obtained through the indentation in air. The nanoindentation-based flat punch method with a diamond flat-end tip of 100μm in diameter, instead of a sharp tip commonly used for nanohardness measurement, has been used to compress individual particles, shown in Figure 1. The flat punch is required to be well calibrated, which are significant to the test precision. A polished indium which is soft and fully plastic has been used for the flat punch calibration. A well impressed indent on the indium surface is acceptable for the planarity and the parallelism of the flat punch as well as the in-situ system between integrated microscope and the flat punch.

2.2 Materials

The commercially available Ni/Au coated polymer particles (ConcoreTM, Conpart AS, NO) consists of a

acrylic copolymer core coated with Ni and Au layers, as shown in Figure 2. The core polymer particles are 3.8μm in diameter and strongly crosslinked by 40% acrylic with 60% diacrylic. The polymer core is amorphous and has been synthesized by using the Ugelstad method with a multi-step activated swelling process [2]. The CV (coefficient of variance) of particle size distribution is 1.7%, where CV is defined as the ratio of the standard deviation to the mean of particle diameter. The Ni/Au coating has been chemically plated on the polymer particle surface with a Ni inner layer of about 50nm in thickness and a Au outer layer of about 25nm. For comparison, uncoated particles with the same polymer chemistry and same size have been also prepared and tested.

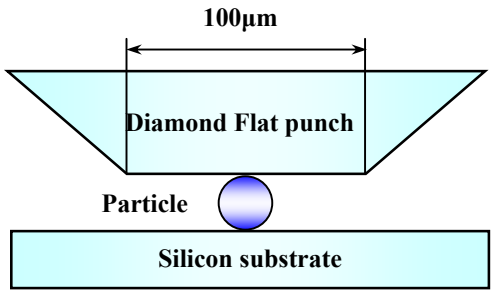

Figure 1: Schematic plot of nanoindentation-based flat punch test with a flat tip of 100 μm in diameter.

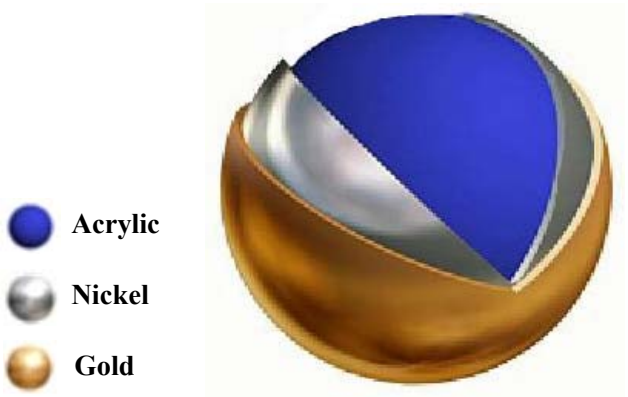

Figure 2: The Ni/Au coated polymer particles with 3.8μm in diameter.

2.3 Method

Due to a small volume and thus a large surface area of particles, dry particles usually occur in a state of clusters. The good dispersion of particles is important for mechanical characterization of individual particles. Therefore an efficient process of the sample preparation has been determined. First a tiny amount of dry particles have been dispersed into 95% industrial ethanol, after shaking in an ultrasonic vibration cleaner, a small suspension has been dropped onto a silicon wafer of the size 10×10×0.5mm. Then the specimen has been left in a clean environment for a certain time to ensure that there is no any ethanol left on the particles. Using the integrated optical microscope of Triboindenter, individual particles with more than 75μm distance to the closest neighbors have been easily identified for compression. The 2000μN linear loading/unloading rate with different maximum loads has been used to compress to particles. For each set of experiments, at least five individual particles have been tested in order to check the repeatability of the results. The morphology of tested particles has been observed using a scanning electron microscope (SEM) Zeiss Ultra 55 LE FESEM.

During compression, the applied force and displacement on particles have been monitored continuously. The force and displacement relationship have been obtained after compression. During compression, the volume and Poisson's ratio of polymer particles might change continuously with the large deformation because of the polymer nature and the sphere geometry. It is impossible to obtain the true stress-strain behaviours of particles from the current experiment. Therefore the nominal compression stress-strain relationships of the particles are calculated based on the diameter and the cross sectional area of the undeformed particle:

$$\sigma_N = \frac{P}{\pi R^2} \tag{1}$$

$$\varepsilon_N = \frac{D}{R} \tag{2}$$

where P is the applied force, D is the half displacement and R is the initial particle radius. In the following section, the nominal stress-strain relationships of particles which are calculated by Eq. (1) and (2) have been presented.

RESULTS AND DISCUSSION

Typical compression stress-strain curves for a Ni/Au coated polymer particle (filled square) and an uncoated polymer particle (unfilled square) are shown in Figure 3. At the beginning of loading, the stiffness of the coated particle is prominently higher than the uncoated one and increase monotonously until deformation up to around 18%. A displacement burst at 18% deformation indicates that a very significant change happens to the Ni/Au coating, probably including both cracking and delamination from the polymer core. Within the 20ms timeframe of the displacement burst, given by the measurement frequency, the deformation rapidly increases from 18% to 23%. However, the coated particle is still stiffer than the uncoated one, indicating that there are some mechanical integrity in the metal layer and adhesion to the polymer core left. Once the deformation surpasses around 43%, the loading curves of the coated and uncoated particles seem to overlap each other and the metal coating does not influence the particle behaviour any more.

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Even in unloading segment, two particles behave exactly identical, without any metal coating effect.

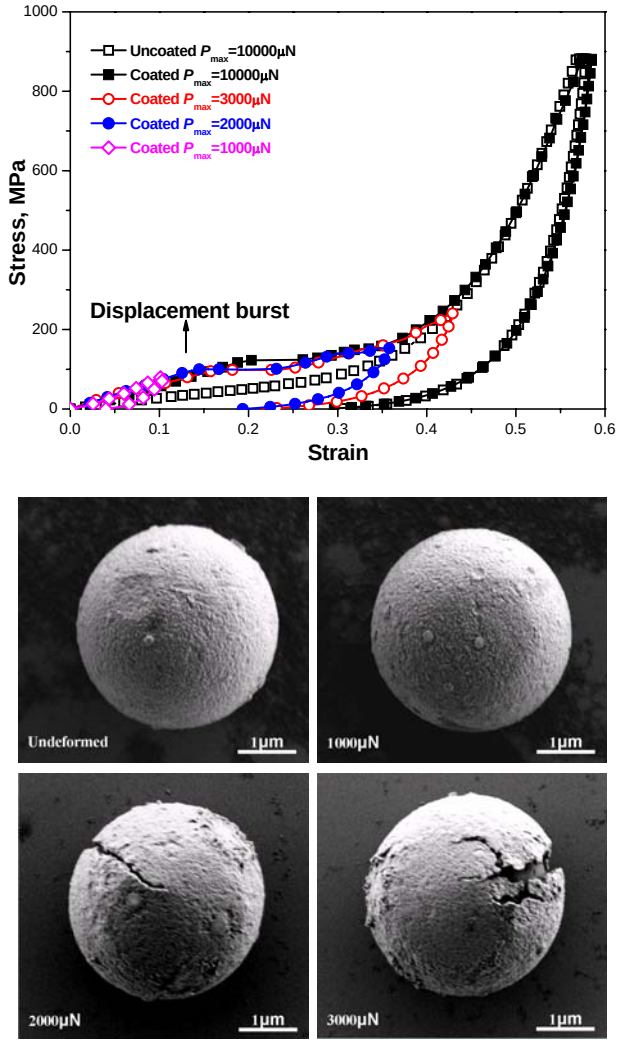

Figure 3: Compression stress-strain curves and SEM images of the metal coated polymer particles with peak loads 0, 1000, 2000 and 3000μN.

Figure 3 also shows the compression stress-strain curves of Ni/Au coated particles compressed to applied peak loads 1000, 2000, 3000 and 10000μN and the characteristic SEM images of coated particles under peak load 0, 1000, 2000 and 3000μN. All images are taken from top view in the direction of the compression. The loading segments of four curves, and even the displacement burst points at approximately 18% deformation, are remarkably coincident. The SEM image of the undeformed particle shows that the metal coating is well plated on the core polymer particles. When the peak load is 1000μN, the particle has maximum deformation about 11% which is less than the displacement burst deformation 18%. After unloading the particle mostly recovers and has a very small residual deformation. In the corresponding SEM image the microcracks can not be observed within what has been the contact area between the flat punch and the particle. Whilst there is a small flattened area which corresponds with the expected contact area under maximum deformation and indicates residual deformation. This can be considered as the local response to the initial deformation. Increasing the peak load to 2000 and 3000μN, the stress-strain curves pass through the displacement burst point. The particles partly recover and have a residual deformation after unloading. In the corresponding micrographs, the cracking and delamination of the Ni/Au coating are clearly shown and aggravated with increasing peak loads. Under 2000μN peak load the cracking of the Ni/Au coating is observed while both cracking and delamination are shown in the image corresponding to the particle compressed to 3000μN. The crack propagation is along the longitudinal direction of the particles, and the delamination usually occurs underneath the cracks or by the warping of the Ni/Au coating.

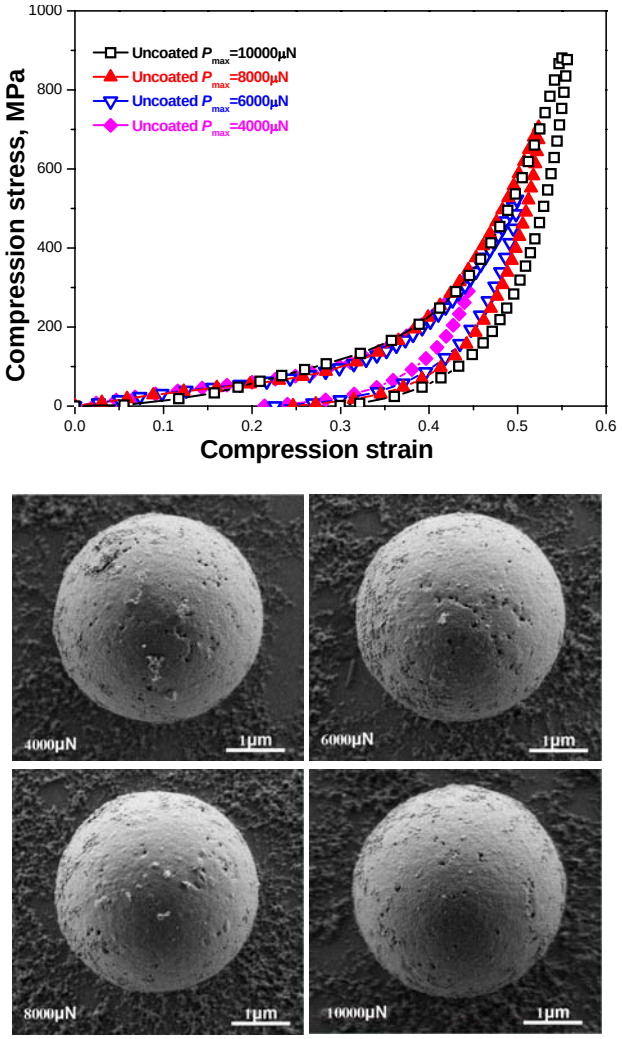

Figure 4: Compression stress-strain curves and SEM images of the core polymer particles with peak loads 4000, 6000, 8000 and 10000μN.

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The compression stress-strain curves and the corresponding SEM images of uncoated particles at different peak loads are shown in Figure 4. Four peak loads up to 10000μN have been applied to the uncoated particles. The loading behaviours of particles are very consistent and all particles show partly recovery after unloading. In the corresponding SEM images, there is no any cracking or failure observed on the polymer particles, even there is no a flattened area on the particle surface. The particle size shows identical after compression under different peak loads. It seems that the uncoated particle behaves viscoelastic and finally recovers completely within some time after unloading.

Through comparing the stress-strain relationships of Ni/Au coated particles and uncoated polymer particles, the effect of the Ni/Au coating has been revealed. According to this coating effect, three stages could be identified in the deformation process of metal coated particles. Initially, the Ni/Au coating has a remarkable strengthening effect thus the coated particle is harder than the uncoated one. Secondly, with the increasing deformation, the effect of the metal coating is significantly reduced when the cracking and the delamination of the Ni/Au coating occur. The critical deformation for the failure of the metal coating is found to be around 18%. Finally, the effect of the Ni/Au coating disappears completely and the coated particle shows nearly identical behaviour as the uncoated one when the deformation is over about 43%. There is no the effect of the metal coating during unloading.

The particle fragments induced by the cracking and delamination have been measured in SEM. The thickness of fragments is located in a range of 70 to 80nm, which agrees with the coating parameter during coating plating. That indicates that the delamination happens at the metal-polymer interface but not Ni-Au interface. There is a weaker cohesion at the metal-polymer interface than that at Ni-Au interface in metal coated particle structure.

Finally it should be mentioned that the assumption that the mechanical contact is frictionless has been made in this work. The friction forces at the polymer-diamond interface and the metal-diamond interface have been neglected.

Conclusions

The deformation and fracture of the Ni/Au coated polymer particles has been studied by the nanoindentation-based flat punch method. The effect of the Ni/Au coating on particle deformation behaviours has been analyzed, and its cracking and delamination have been investigated. A three stage deformation process has been defined through comparing the stress-strain relationship of metal coated particle to that of uncoated one. The threshold deformation for the failure of the Ni/Au coating has been determined to be around 18%. The results are integrated effects of particles geometry and material. The findings have important implications in the design of the metal coated polymer particles for electrical packaging applications.

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