

# **Electrical and Thermal Properties of Conducting Microbead Prepared by Green Electroless Plating Method Using Gold Nanoparticles**

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We developed a green electroless plating method that enables saving of resources and reduction in emissions to the environment because it uses a self-assembling reaction between gold nanoparticles (AuNPs) and a nontoxic thiol binder. In this method, a uniform surface coating and thickness reflected by the diameter of AuNPs were obtained on micrometer-sized core plastic beads. Thermal analysis has revealed that AuNP adsorption is based on the chemical reaction and interaction among the AuNP, binder, and bead. Further, the AuNP-plated microbead has high physical, electrical, and thermal stabilities, which would enable its practical applications.

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Rapid progress and developments have been made in information technology (IT) and its related fields; this has made it necessary to miniaturize compact electronic devices as well as consumer electronic products, such as mobile phones, personal digital assistants (PDAs), and laptops through high-density packaging and wiring technologies. Consequently, this has led to accelerated development in the metallic thin film technologies over the last few decades. Conventional electroless plating methods, which are well known and are commonly employed to obtain such metal thin films, are cost efficient but they involve environmentally-unfriendly processes and controlling these multistep processes to achieve the best coating result poses inherent difficulties. These methods utilize nongreen chemicals such as cyanide, chromic acid, strong alkalis, and acids, which are conflicting with the demand for lower emissions to the environment.<sup>1-3</sup> Despite the fact that as technological innovations have brought about convenience and comfort to society, environmental degradation problems have accelerated in recent years owing to the release of enormous amounts of harmful resources and energies. Therefore, it is important for researchers to consider environmental friendliness during research and development of technologies.

Recently, inorganic nanoparticles (NPs) and their arrays have been attracting the attention of researchers as important materials for nanoelectronics owing to their unique physical and chemical properties.<sup>4-7</sup> Self-assembly technology can be effectively used to assemble wellorganized one- to three-dimensional structures, and interparticle connections can be devised at a controllable single-particle level.<sup>8-10</sup> Metal NPs are one of the most frequently studied inorganic materials for application to various nanotechnology-oriented devices;<sup>11-13</sup> their distinct shapes and combinations, such as nanobarcodes, nanorods, and nanowires, can impart unique functions to the devices.<sup>14,15</sup> We previously reported the electroconductivity of gold NP (AuNP) array films, which consisted of AuNPs and thiol molecules as a binder.<sup>16-20</sup> The films were prepared by a single-step procedure that uses a selfassembly method for the deposition of a NP on a plastic substrate; we showed that this method can dramatically reduce the release of waste chemicals to the environment.

Recently, we reported a green electroless plating method for preparing conducting microbeads using AuNPs, and successfully applied it to anisotropic conductive films (ACFs), which are adhesive insulator films in which conductive particles are dispersed.<sup>21,22</sup> The ACFs have been used to construct many local connections between the input/output connections of a liquid crystal display (LCD) panel and the external circuit in a single installation procedure. This film can be used with conducting microbeads to establish reliable electrical connections. The beads have to be elastic to establish a reliable contact between the bump of an active component, such as LCD and large-scale integration, and an external bus line. Such beads have been commercially available since 1980s and they can generally be metallized with either one or more different layers, for example, a nickel base layer with a gold layer on top. However, an increase in the metallic layer thickness leads to decrease in the flexibility of the plated layer and causes mechanical and electrical fractures. Apparently, the crack formed on the metal layer often causes problems in the electronic conductions at the compressed ACF. Therefore, the thickness of the metal layer on the beads is a key factor for the practical use. Our plating technique to make efficient use of AuNPs has successfully reduced the thickness of the plated layer roughly in halves comparing with that of commercially available one, and given us good electrical property of the bead for a practical use.

In this study, we conducted the heat-cycle and cyclic loadingunloading tests to determine the electrical, thermal, and mechanical stabilities of the developed beads, which are considered to be very important for the practical use. Moreover, thermogravimetric analysis has been carried out to clarify the formation mechanism of the AuNP plated beads.

#### Experimental

Chemicals.— All the chemicals used were of reagent grade. Milli-Q grade water (>18 M $\Omega$  cm), after ultraviolet sterilization, was used throughout the experiment. Chloroauric acid and sodium citrate, which were used to prepare the AuNPs, and decanethiol, which was used as the binder, were purchased from Wako Pure Chemical Industries, Ltd., Japan. Polyvinyl alcohol (grade MW 500), used as a dispersing agent of AuNP-deposited beads, was obtained from Wako Pure Chemical Industries Ltd., Japan. Acrylic resin beads with a mean diameter *ca*. 6  $\mu$ m were used as a substrate (M-11N, Hayakawa Rubber Co., Ltd., Japan).

*Preparation of AuNPs.*— The AuNPs used here were prepared by the reduction of aqueous HAuCl<sub>4</sub> with sodium citrate, as follows. A 24 mL aliquot of 1 wt% HAuCl<sub>4</sub> was added to 179 mL of 0.26 wt% sodium citrate and stirred at 80°C for 20 min. The AuNPs (0.57 gL<sup>-1</sup>) produced were stored at 5°C. Characterization using a zeta-potential & particle size analyzer (ELSZ-2Plus, Otsuka Electronics Co., Ltd., Japan) revealed that the AuNPs produced had a mean diameter of 28 ± 4.0 nm.

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**Scheme 1.** Model illustration of the preparation procedure of a conducting microbead. SEM images along with cross-sectional TEM images of an uncoated microbead (a), a AuNP-deposited microbead (b), and a AuNP-plated microbead (c).

*Procedure for AuNP plating of microbeads.*— Our plating method consisted of two processes —-AuNP deposition and AuNP growth on plastic beads, as shown in Scheme  $1.^{21,22}$  The –SH group of the binder molecules adsorbed onto the AuNP surface through chemical adsorption, whereas the alkyl chains bound with the plastic surface through a hydrophobic-hydrophobic interaction (a and b). The NPs deposited on the beads as follows: Microbeads (34 mg) and decanethiol (3 µg) were added to 22.5 mL of the colloidal gold dispersion, and then the mixture was stirred at room temperature for 1 day.<sup>21</sup> After the beads were filtered, they were washed with an ample amount of water and then dried in a vacuum.

The AuNP-deposited beads were dispersed and stirred in an aqueous mixture comprising chloroauric acid and a reducing agent to enlarge the AuNPs adsorbed on the beads by infilling the airspace (grain boundary) and improving the electrical properties in the following manner (AuNP-growth process). AuNP-deposited beads (10 mg) were added to a 25 mL aqueous solution containing 50% ethanol, 18 nM polyvinyl alcohol, 0.18 mM sodium ascorbate as a reducing agent, and 0.19 mM chloroauric acid. The mixture was stirred at 50°C for 1 h. The beads were then filtered, thoroughly washed with water, and dried in a vacuum (c). The surfaces of the microbeads were imaged by field-emission scanning electron microscopy (FE-SEM S-4700, Hitachi, Japan) at an applied voltage of 10 kV.

Thermal properties of Au-plated microbeads.— Thermogravimetric analyses (TGA) were performed using a Bruker AXS 9600 series thermogravimetry-differential thermal analysis/mass spectrometry (TG-DTA/MS) system under 99.9999% helium atmosphere. The temperature was raised from 25°C to 700°C at a programmed heating rate of 5°C min<sup>-1</sup>. Samples dried in a vacuum overnight were transferred to a platinum (Pt) sample holder to measure the TG/MS spectra.<sup>18,23–26</sup>

Electrical evaluation of Au-plated microbeads.— The electrical resistance of a single conducting microbead was measured using a digital multimeter (model 34970A, Agilent Technologies) in a constant current mode (1 mA) using a laboratory-prepared probe setup in an air-conditioned room  $(25^{\circ}C \pm 1^{\circ}C)^{.21,22}$  The setup consisted of a Pt plate (1 × 1 cm) that served as the common ground, and an electrochemically polished tungsten (W) tip (5 µm in diameter) that served as the movable electrode. During the measurements, a single microbead was sandwiched between the probe tip and the Pt plate at a compression rate of 20%. The resistance was measured for at least 10 plated beads to obtain an average value.

## **Results and Discussion**

Electrical stability of Au-plated Microbeads.— Figure 1 shows the time course of the electrical resistance of the AuNP-plated (a) and commercially available electroless-plated (b) microbeads, which were kept in an incubator controlled at 85°C (A) and  $-50^{\circ}$ C (B). The AuNPplated microbeads had an average electric resistance of approximately 0.8  $\Omega$  (with a variation of  $<\pm5\%$ ), which remained constant over 300 h at both higher and lower temperatures as shown in Figs. 1Aa and Ba. In contrast, the electrical resistance of the conventional electrolessplated microbeads was initially approximately 1.7  $\Omega$  with a variation of  $\pm0.2 \Omega$  ( $\pm12\%$ ), and the readings were scattered over 30% during the monitoring for 300 h (Figs. 1Ab and Bb).

A heat-cycle test was carried out in detail to investigate the electrical properties as well as environmental stability of the AuNP-plated microbeads. The temperature profile of the test is shown in Fig. 1. The AuNP-plated microbeads had an average electrical resistance of approximately 0.8  $\Omega$ , which remained constant over 300 cycles (Fig. 1Ca). In contrast, the electrical resistance of the conventional electroless-plated microbeads was initially 1.7  $\Omega$  with a variation of  $\pm 0.2 \Omega$  and fluctuated over 0.5  $\Omega$  during the monitoring for 300 cycles (Fig. 1Cb). The AuNP-plated microbeads were found to have higher thermal stability in the electrical property than the conventional electroless-plated microbeads.

The mechanical properties of the AuNP-plated microbeads were also investigated, as shown in Fig. 2. During the 10 load-unload tests, a single bead was sandwiched at a compression rate of 40% between the W tip and Pt plate. The resistance of the AuNP-plated microbeads was 0.8  $\Omega$  at the first measurement, and it showed no change during the repeated measurements. In contrast, the electrical resistance of the conventional electroless-plated microbeads was 1.5  $\Omega$  at the first measurement, and it increased with each subsequent measurement; finally, the resistance was unmeasurable (over  $100 \text{ M}\Omega$ ) during the 10th repeated measurement. As already mentioned, the AuNPplated microbeads were plated with a thin gold layer (ca. 50 nm), (Scheme 1).<sup>21,22</sup> The commercially available microbeads used for the measurements obtained by the conventional electroless plating, had a 100-nm thick conducting layer that consisted of a double metallic layer, a 50-nm nickel (Ni) base layer and 50-nm gold (Au) top layer.<sup>27-30</sup> Commercially available conductive microbeads have Au/Ni plated layers of approximately 100 nm thickness, whereas microbeads subjected to AuNP plating can have a thinner plated layer (ca. 50 nm). The increase in thickness of the metallic layer decreased the flexibility of the plated layer on the commercial microbeads leading to a subsidiary fracture and a corresponding broken conducting pathway. The fracture occurs for two reasons: (1) the increase in the thickness of the metallic layer and (2) the elastic modulus of nickel (1.8  $\times$  10<sup>-10</sup> Pa) being lower than that of gold ( $2.2 \times 10^{-10}$  Pa). Therefore, the electrical conductivity of the conventional electroless Au/Ni-plated microbeads decreased owing to the subsidiary fracture of the plated



**Figure 1.** Results of heat test at  $85^{\circ}C$  (A) and  $-50^{\circ}C$  (B), and heat-cycle test (C) to determine the electrical resistance of the conducting beads; AuNP-plated microbead (a) and commercially available conducting microbead (b). The inset shows the temperature profile of the heat-cycle test.

layer and disappeared during the measurements. These indicate that the flexible AuNP-plated layer on the microbeads has high physical and electrical stabilities than the conventionally plated ones.

TG curves of the uncoated (a), AuNP-deposited (b), and AuNPgrowth (c) microbeads exposed previously to the helium atmosphere are shown in Fig. 3A. The total weight loss observed at 700°C was





Figure 3. TG/MS spectra (A) of the uncoated (a), AuNP-deposited (b), and AuNP-plated (c) microbeads. Temperature was raised from  $25^{\circ}$ C to  $700^{\circ}$ C at a programmed heating rate of  $5^{\circ}$ C min<sup>-1</sup>. MS spectra (B) of the AuNP-deposited microbead were measured at four different temperatures:  $70^{\circ}$ C,  $217^{\circ}$ C,  $450^{\circ}$ C, and  $500^{\circ}$ C.

Figure 2. Results of cyclic loading-unloading tests to measure the electrical resistance of the conducting beads at  $25^{\circ}$ C: AuNP-plated microbead (a) and commercially available conducting microbead (b).



**Figure 4.** TG/MS spectra (A) of decanethiol (a), uncoated microbead (b), and AuNP (c). Temperature was raised from  $25^{\circ}$ C to  $700^{\circ}$ C at programmed heating rate of  $5^{\circ}$ C min<sup>-1</sup>. MS spectra (B) were measured at different temperatures:  $70^{\circ}$ C (a),  $450^{\circ}$ C (b), and  $450^{\circ}$ C (c).

92.7% for (a), 62.6% for (b), and 41.3% for (c). The slight weight loss at 70°C is attributed to the desorption of atmospheric gases,  $H_2O(m/z)$ 18), N<sub>2</sub> (m/z 28), and O<sub>2</sub> (m/z 32) as shown in Fig. 3B,<sup>18,23–26</sup> these gases are also included as a background for the entire temperature region. Some fragment peaks of organic components (m/z 41) have been observed at 217°C in the TG curve (c). A large weight loss was observed at about 450°C, and many fragment peaks of the main chain of organic polymers were observed owing to the degradation of the bead core in all the microbeads. Residual components, accounting for 7.3% of the total components in the Pt holder after the TG analysis are cold ashes of the uncoated microbeads in Fig. 3Aa. Therefore, 30.1% and 51.4% of gold as the metal component were estimated as being the residues of the AuNP-deposited (b), and AuNP-growth (c) microbeads, respectively. The TG measurements have been also carried out for each constituent, i.e., decanethiol (a), uncoated microbead (b), and AuNP (c), as shown in Fig. 4. The weight loss of decanethiol was approximately 100% at less than 100°C as shown in the TG curve (a). Many fragment peaks attributed to the degradation of the core of the microbead at 450°C were observed in curve (b), corresponding to those observed in Fig. 3. In contrast, slight weight loss was observed in the case of AuNP (c). The degradation of the passivation layer consisting of an organic citrate covering the AuNPs is negligible owing to its small weight. Therefore, the weight loss at 217°C is caused by decanethiol, which is confirmed by the appearance of the peak at m/z 41 and some other fragments peaks (at m/z 55, 70, and 83) in Fig. 3B. The weight loss was found to be due to only desorption of decanethiol as a binder, because the microbead (b) and AuNP (c) did not undergo any weight loss in the TG curves at the temperatures below 300°C, ex-



**Figure 5.** MS fragment intensity for the peak at m/z 41. Decanethiol (a), decanethiol modified AuNP (b), AuNP-deposited microbead (c), uncoated microbead (d), and decanethiol modified microbead (e). Temperature was raised from  $25^{\circ}$ C to  $300^{\circ}$ C at a programmed heating rate of  $5^{\circ}$ C min<sup>-1</sup>.

cept for the slight weight loss caused by the desorption of atmospheric gases.

To investigate the composition of the AuNP-plated microbeads, the intensity of the fragment peak at m/z 41, which is attributable to the desorption of decanethiol, was plotted as a function of temperature (see Fig. 5).<sup>23,31</sup> A strong peak intensity was observed at 78°C in the curve of simple decanethiol (a). The decanethiol-modified AuNP (b) and AuNP-deposited microbead (c) show a peak intensity at 217°C, whereas the decanethiol-modified microbead (e) has a broad peak at 160°C. The peak intensities are attributed to the desorption of the binder molecules from the surfaces of the AuNPs (217°C) and the microbead (160°C) has been observed at a higher temperature than that of simple decanethiol (78°C). This means that decanethiol forms a chemical bond and/or undergoes an interaction with the other components, as shown in Scheme 2. The AuNP-plating is based on the binding of the thiol group (-SH) of binder to the surface of AuNP (a) and the hydrophobic-hydrophobic chemical interaction between the alkyl chains of the binder and the surface of the microbead (b).  $^{22,\,32-34}$  It is well known that the Au-S binding proceeded spontaneously.<sup>33,34</sup> On the other hand, we have reported that an increase in the surface roughness of plastic substrate by adsorption of alkylthiol was confirmed in the AFM observation.<sup>32</sup> This implies that the alkyl chain of binder adsorbs to the surface of substrate with the hydrophobic-hydrophobic interaction, because binder and substrate have no functional group for binding site with each other. In fact, it is hard to conclude the reaction rates of the binder to Au and microbead, however, the binding force of Au-S (a) is stronger than that of hydrophobic-hydrophobic interaction (b), according to the results by TG/MS analysis. The presence of a binder between the AuNP and the microbead results in a strong adhesion between the microbead and the AuNP-plated layer (c). Such a strong adhesion lends excellent properties such as flexibility, conductivity, and environmental stability to the AuNP-plated layer on the microbead. Therefore, this method leads to the formation of a superior



**Scheme 2.** Model illustrations of the adsorption mechanism of alkylthiol on the surface of AuNP (a) and microbead (b) in the AuNP-deposited layer (c).

metallic thin layer on the microbead to that formed by conventional electroless plating methods.

#### Conclusion

The AuNP-plated microbead shows not only good electrical properties, but also high thermal and physical stabilities. These are attributed to the adhesion between the AuNPs and the microbead via the binder, which is based on the Au–S bond between the thiol group of the binder and the AuNPs, and the chemical interaction between the alkyl chain of the binder and the microbead. Therefore, the presence of the binder leads to the formation of a superior metallic thin layer on the microbead with a high flexibility compared to that formed by conventional methods. This AuNP-plating method facilitates the realization of low environmental emissions since nongreen chemicals such as cyanide, chromic acid, and strong alkalis and acids, which are usually used in conventional electroless plating, are not required in the process; further, lesser amount of Au is required because of the use of AuNPs, leading to a low-cost manufacturing.

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