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Fabrication of Core-Shell Structure of Ni/Au Layer on PMMA Micro-Ball for Flexible Electronics

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ABSTRACT: In this paper, core-shell structure of nickel/gold (Ni/Au) conductive layer on poly-methyl-methacrylate (PMMA) micro-ball was fabricated and its conduction property was investigated. Firstly, PMMA micro-ball was synthesized by using dispersion polymerization method. Size of the ball was 2.8 μm within ±7% deviation, and appropriate elastic deformation of the PMMA micro-ball ranging from 31 to 39% was achieved under 3 kg pressure. Also, 200 nm thick Ni/Au conductive layer was fabricated on the PMMA micro-ball by uniformly depositing with electroless-plating. Adhesion of the conductive layer was optimized with help of surface pre-treatment, and the layer adhered without peeling-off despite of thermal expansion by collision with accelerated electrons. Composite paste containing core-shell structured particles well cured at low temperature of 130°C while pressing the test chip onto the substrate to make electrical contact, and electrical resistance of the conductive layer showed stable behavior of about 6.0 Ω. Thus, it was known that core-shell structured particle of the Ni/Au conductive layer on PMMA micro-ball was feasible to flexible electronics.

Key words: Core-shell, PMMA Micro-ball, Conductive layer, Electroless-plating, Low temperature curing, Flexible electronics

1. Introduction

Recently, flexible electronics are expected to apply for various devices such as smart phone, smart pad, tablet PC, and other displays, etc. Moreover, the demand of flexible electronics is continuously increasing in home, industry, and mobile applications[1)]. One of promising application is photovoltaics (PVs)[2,3)]. The flexible devices must be adaptable to fine pith interconnection for high density circuits as well as flexibility[4)]. For the fine pitch interconnection, anisotropic conductive type materials are being paid attention[5)]. The material contains micron-sized conductive particles which are uniformly dispersed in adhesive resin, and the conductive particles interconnect chip bump to substrate electrodes by flip chip bonding. For flexible electronics, electrical conduction must be formed by the bonding at low temperature under 150°C. As well, to prevent the horizontal conduction that results in failure, electrical insulation to the horizontal direction should be ensured. Accordingly, the micro-ball of which size is less than 3 μm is increasingly demanded to prevent the lateral contact. In addition, most of the conductive particles are consistent of electrically conductive layers coated on polymeric core balls because elastic deformation of the particle is demanded for stable contact between them. The physical and electrical properties of the layers determine the quality of the particles, and the coating of the conductive layers is very important as well as polymeric core particles.

In this paper, as a first step, we fabricated core-shell structure of electrically conductive layer of nickel/gold (Ni/Au) on poly-methyl-methacrylate (PMMA) micro-ball having properties of elastic deformation for bonding at low temperature acceptable to flexible substrates that is thermally weak. Then, physical and electrical properties of the core-shell structured particle were investigated to determine feasibility as conductive particles for flexible electronics.

2. Experimentals

PMMA micro-balls were synthesized by using dispersion polymerization method which is commonly used for synthesis of polymers[6)]. Monomer, initiator, stabilizer, and emulsifier were put into an alcoholic solvent. As a monomer, methyl-methacrylate (MMA) was used. The monomer was dissolved into alcohol, and micro-sized balls were precipitated after its molecule was grown over solubility limit at 60°C. As a stabilizer,

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small amount of poly-vinyl-pyrrolidone (PVP) was added to prevent the agglomeration of the balls. Then, Ni/Au conductive layers were deposited onto the surface of micro-balls by electroless-plating. For electroless-plating, surfaces of the PMMA were degreased with alkaline chemical. Then, the surfaces were etched by diluted acidic solution followed by electrical activation of the surfaces by doping Pd catalyst onto the surfaces. After activation, Ni/Au layers were deposited onto the surfaces. The plating rates of the Ni and Au were optimized as 0.25 and 0.4 nm/sec, respectively. The morphology, size, and composition of the PMMA micro-balls were analyzed with environmental scanning electron microscope (ESEM), particle size analyzer, and FT-IR. The deformation behavior of the particle was investigated with ESEM after fixing the ball pressed by flip chip bonder on a glass substrate. Thickness of the conductive layer was measured by observing cross-sections of the conductive particles with transmission electron microscope (TEM). Adhesion of the conductive layer on the surface of PMMA micro-ball was evaluated by generating heat energy by collision the layers with accelerated electrons. Also, electrical properties of the layer were investigated using test chip and pattern. Au bump was formed on the electrode of the test chip, and ITO electrode of which pitch size is 20 μm is formed on the glass substrate in Fig. 1.

To fix the conductive particles on the substrate, the conductive particles were dispersed into thermosetting adhesive resin for low temperature curing of 130°C. The composite paste containing conductive particles was dispensed on the test pattern followed by curing at 130°C while pressing the test chip onto the substrate to make electrical contact. The electrical contact was fixed by hardening the resin while pressing the chip. After contact, resistance was calculated from the slope of I-V characteristic curve that was measured using KEITHLEY 2400.

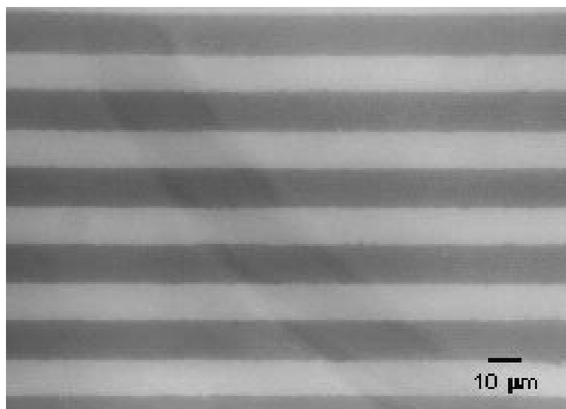

Fig. 1. ITO Test pattern

3. Results and Discussion

In Fig. 2, size of the synthesized PMMA micro-ball was linearly proportional to the reaction time. In addition, size distribution of the synthesized particles is very uniform. It is known that the polymerization rate has a significant effect on the particle size[7]. Dispersion polymerization is a relatively complex process that involves several factors including composition of the polymerization medium, the type and molecular weight (MW) of steric stabilizer, and concentrations of monomer, initiator, and stabilizer[7]. Also, ball size of PMMA is known to increase with increasing polymerization temperature, increasing initiator concentration, decreasing MW of stabilizer, and decreasing stabilizer concentration[8]. In contrary, the size decreases with decreasing polymerization temperature, decreasing concentration of initiator, and increasing MW and concentration of the stabilizer. These changes reduce the extent of coalescence, and thus, reduce ball size[9,10].

In this study, conditions of polymerization were optimized by lowering the concentration of initiator, temperature, and increasing concentration of PVP as stabilizer. As a result, PMMA micro-balls were uniformly synthesized. In Fig. 3, average size of the balls

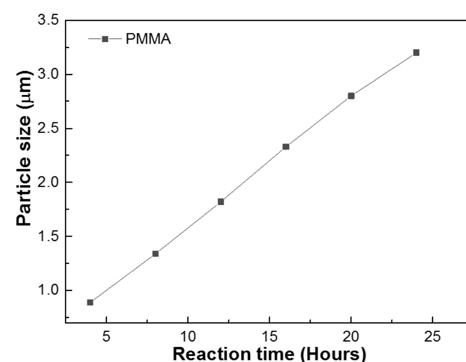

Fig. 2. Size of PMMA ball dependent upon reaction time

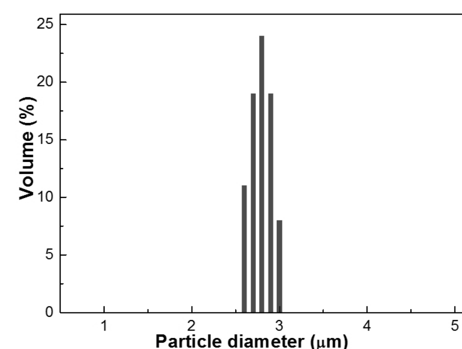

Fig. 3. Size distribution of PMMA micro-balls after synthesis for 20 hours

is about 2.8 μm, and the deviation is small within ±7%. It is guessed that the dispersing agent prevented the agglomeration. That is, stable surface state of the synthesized micro-balls is owing to depression of interface migration by adding the dispersing agent onto the surface of balls[11).

In Fig. 4, FT-IR analysis reveals that the synthesized polymeric ball is composed of PMMA. From the FT-IR spectra, C=O (1735 cm^{-1} stretching), C-O (1192 cm^{-1} anti-symmetric stretching), C-O (1149 cm^{-1} symmetric stretching), and C-O (753 cm^{-1} bending) absorption bands are observed. As those spectra are coincident with those of the reference PMMA, it is certified that the synthesized polymeric balls are formed as PMMA structure[12).

In the case of deformation of ball, in Fig. 5, the degree of deformation is linearly proportional to the loading pressure. The control of the deformation is very important because it ensures the stable contact, and the appropriate deformation is reported as ranging from 30 to 40%[13). In this paper, the elastic deformation behavior of the PMMA micro-ball is observed ranging from 31 to 39% when 3 kg pressure is applied. Comparing with the literature, the deformation is optimal value for the electrical contact, and stable connection is guaranteed with the PMMA balls. Thus, the control of the deformation was established.

Then, Ni/Au conductive layer was deposited on the surface of PMMA micro-ball by using electroless-plating. To observe adhesion properties between conductive layer and surface of PMMA micro-ball, two samples were prepared by differing time of degrease with alkaline chemical; one is degreased for 0.5 min. and the other is for 10 min. at 65°C, respectively. As a result, the difference in adhesion of the conductive layer to the surface of the PMMA micro-ball was found as shown in Fig. 6. In the case of a sample degreased for 0.5 min., the conductive layer was swelled to be pelt off from the PMMA micro-ball in Fig. 6(a). However, in the case of another sample degreased for 10 min., in Fig. 6(b), the conductive layer kept good adhesion despite of expansion generated by thermal energy. Those phenomena are attributed to the difference in bonding state between conductive layer and surface of PMMA micro-ball. In the case of sample which had been degreased for 0.5 min., the deposited layer was pelt off easily owing to poor adhesion arisen from weaker bonding strength that could not endure against the thermal expansion. In contrary, the deposited layer of sample which had been degreased for 10 min. endures against the severe expansion owing to good adhesion arisen from strong attachment between deposited layer and surface of the PMMA micro-ball. It is reported that the pre-treatments modify the surfaces of PMMA micro-ball physically and chemically[14). In general, pre-treatment of the polymeric surface affect adhesion between the substrate and the deposited layer as well as inserting an adhesion layer between the substrate and the seed layer[15,16). Especially, metallic layer on the polymer substrate by using electroless-plating cannot certify sufficient adhesion between them and, therefore, sufficient pre-treatment of the surface must be applied to improve the adhesion between the electroless-plated metal and the PMMA substrate. Thus, it is assumed that adhesion of the

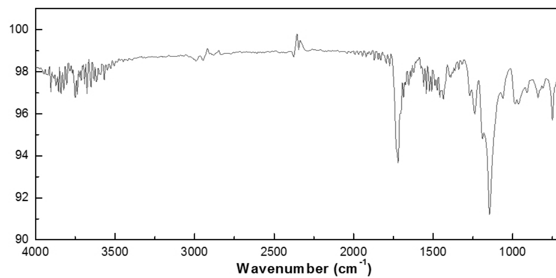

Fig. 4. FT-IR analysis of PMMA micro-ball

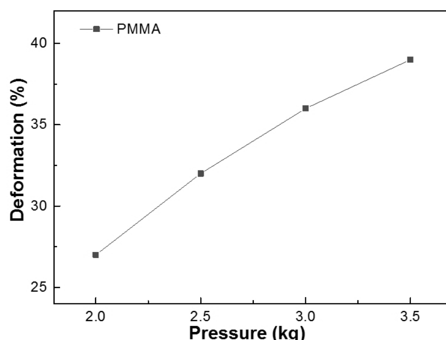

Fig. 5. Deformation behavior of PMMA micro-ball

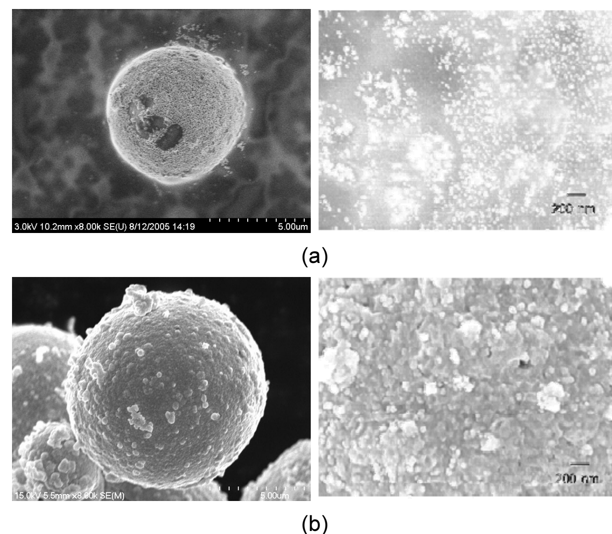

Fig. 6. Adhesive properties of Ni/Au conductive layers on PMMA micro-ball (a) poor adhesion (b) good adhesion

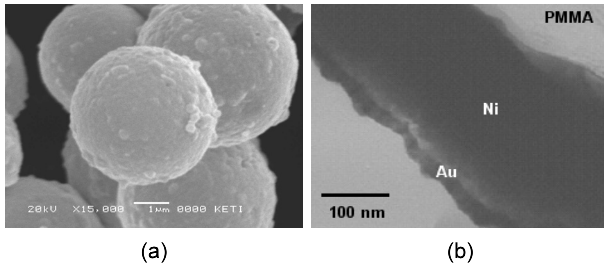

Fig. 7. Core-shell structured particles (Ni/Au conductive layer on PMMA core-particle) (a) overview (b) cross-sectional view

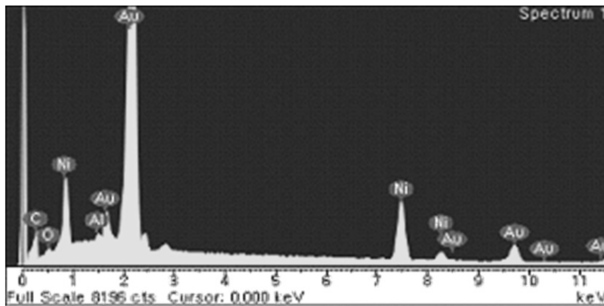

Fig. 8. Analysis of composition of the conductive particle with EDX

conductive layer on the surface of PMMA micro-ball was enhanced with help of improved pre-treatment condition of the surface.

Using the improved pre-treatment conditions, the core-shell structured particles were fabricated by depositing Ni/Au conductive layer. In Fig. 7(a), the core-shell structured particles were well fabricated with uniform size. Also, in Fig. 7(b), thickness of Ni/Au plated layer was measured to about 200 nm. The thickness of Au and Ni were easily controlled with plating time under the constant plating rate that was mentioned in experimental section. In Fig. 9, EDX analysis certifies that the conductive layer is composed of Ni/Au based on detected peaks indicating Ni and Au. In general, eletroless-plating is a method for the deposition of metals such as Ni and Au onto an insulating substrate, for example, PMMA, via catalyzed chemical reduction of solution-phase metal ions at the surface of the substrate[17)]. In contrast to electroplating where an applied current is needed to reduce a high-oxidation-state metal precursor, the basis of electroless-plating is an autocatalytic redox reaction[17)]. In the case of electroplating, thickness of deposited layer is not uniform because distribution of current density is not uniform dependent upon voltage reaction[18)]. However, in the case of electroless-plating, metallic ions are anchored in the solution so that local electro-chemical reactions occur near the catalytic sites on the PMMA

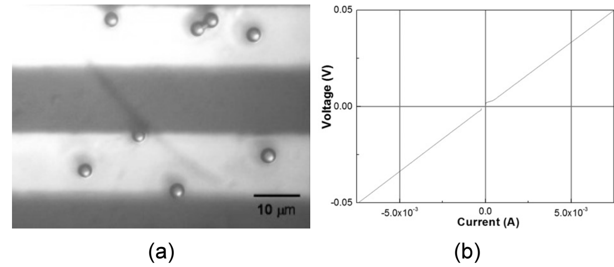

Fig. 9. (a) Dispensed core-shell particles on test pattern and (b) its I-V characteristic curve

surface when the metal crystallites were reduced from the ionic state in the aqueous bath with the presence of reducing agent[19)]. Accordingly, the uniform thickness of the conductive layers is owing to uniform distribution of catalytic sites on the surface of PMMA.

The core-shell structured particles were mixed with adhesive resin to investigate the electrical properties, and the mixed resin was dispensed on the test pattern substrate. In Fig. 9(a), the particles were uniformly dispersed on the pattern of which pitch is 20 μm. From the dispersion, it was certified that the core-shell structured particles were compatible to 20 μm pitch pattern. Test chip was bonded on the test pattern dispensed with the composite to form electrical contact, and the epoxy was hardened at 130°C to fix the electrical contact stably. In Fig. 9(b), I-V characteristic curve showed that current was linearly proportional applied voltage. The resistance is about 6.0 Ω compatible to the fine pitch interconnection[20)]. It is assumed that the linearity is owing to the stability of the conductive layer. That is, the stable state of the layer gives rise to the enhanced electrical properties. In general, electrical resistance is lowered as the thickness of the conductive layer is raised[21)]. In this study, thickness of the Ni/Au conductive layer with stable state was optimized to be suitable for applying to electrical interconnection of flexible electronics. Accordingly, electrical properties could be enhanced owing to the stable state of Ni/Au conductive layers, and the core-shell structured particles with good properties could be fabricated.

4. Conclusions

In this study, core-shell structure of Ni/Au conductive layer on PMMA micro-ball was well fabricated. 200 nm thick Ni/Au conductive layer was stably fabricated on 2.8 μm sized PMMA micro-ball by uniformly depositing the layer with electroless-plating. Adhesion of the conductive layer was optimized with

help of surface pre-treatment, and the layer endured without peeling-off despite of thermal expansion. Also, electrical resistance of the core-shell structure showed stable behavior of about 6.0 Ω after bonding and curing at low temperature of 130°C applicable to flexible substrate. Thus, it was known that the core-shell structure of Ni/Au conductive layer with PMMA micro-ball was feasible to flexible electronics such as flexible PVs.

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