Direct patterning by NanoPaste® and its application

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Abstract

Direct patterning of NanoPaste® is a smart process for environment compared with conventional method like photography. Total process is simplified and the waste stemming from etching and cleansing steps is eliminated. The fine conductive pattern was demonstrated on various substrates. The thermal behavior of silver nanoparticles was investigated. Nanoparticle of 5nm in diameter can be sintered at temperature much lower than silver melting point to form a bulk metallic structure. Patterns with 70µm L/S were obtained by piezo type ink-jet printer. The sintering process has newly developed for copper NanoPaste® and copper circuit patterning was achieved by ink-jet printing. The fabrication of SiP is described. Super ink-jet technology provides the ultra-fine patterning with several micrometer rules and produces micro-bumps that are three dimensional structures. NanoPaste® is demonstrated to be a promising candidate for alternative material to the conventional plated silver. Sintered layer of silver NanoPaste® shows high bonding strength equivalent to the value for the silver plated surface in the ultrasonic bonding.

Introduction

In recent years, direct fabrication technology is the novel approaches of forming conductive pattern on substrate with ink-jet equipment. The ink-jet printing technology provides conductive pattern with silver nanoparticle [1]. This technology offers numerous advantages including environmental friendliness such as etching solution, fewer processing step, reduction of process time and low cost. No contact with substrate eliminates the preparation of masks.

Ink-jet printing is usually used in the graphic arts and page printing. Besides these applications, there is a tendency to produce the electronic devices using metallic nanoparticles [2, 3, 4]. Print head equipped with piezoelectric ink-jet nozzle mainly used. This head is controlled by computer. The uniform ejection of the droplets of ink from print head enables to deliver accurate amount of the ink to specified position on a substrate. The ink with high amount of nanoparticles should be ejected by piezoelectric ink-jet nozzle to obtain the metal trace. The ink should satisfy physical and rheological property of liquid

Metallic nanoparticles have a large amount of the atoms in the surface in the nanoparticle. Melting point behavior is subject to the property known as quantum size effect. The large depression of melting point occurs in the case of less than 5nm of gold nanoparticle in diameter [5]. Low sintering temperature ensures the use of organic substrate. Metallic nanoparticles printed by ink-jet on organic substrate should be converted into bulk metal after heat-treatment.

Silver nanoparticles are synthesized by various methods. Xianhao et al. obtained 7nm of silver nanoparticle in diameter from thermal decomposition from silver behenate [6]. Also, the silver nanoparticle is produced by laser ablation, microwave-assisted preparation and gas evaporation process [7, 8, 9].

Conductive metal trace is usually obtained by heat treatment. Laser sintering is a smart process [10]. The silver NanoPaste® was applied by ink-jet on substrate. Subsequently laser was irradiated on the pattern in order to remove protective compound to give a bulk metal structure [11].

In this paper, ink-jet printing technology is demonstrated by application to the circuit formation with the novel conductive inks such as NanoPaste®.

Metallic nanoparticles

NanoPaste® is based on metallic nanoparticles that have narrow size distribution. Figure 1 shows TEM images of gold and silver nanoparticles used in NanoPaste®. The nanoparticle covered by protective compound, that is special dispersants, is very stable. The TEM images reveal that the sizes of nanoparticles are quite uniform with an average diameter of 5nm.Figure 2(a) shows the particle size distribution of gold nanoparticles.

Silver NanoPaste® did not show any aggregation and precipitation for long time. Its viscosity is very low around 10mPa･s even if the metal content is up to 60wt% and is suitable for ink-jet printing. NanoPaste® acts as like liquid in Figure 2(b).

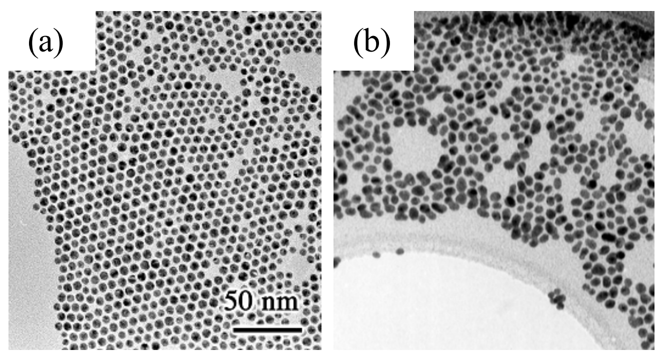

***Figure 1**. TEM image (a) gold nano particles, (b) silver nanoparticles*

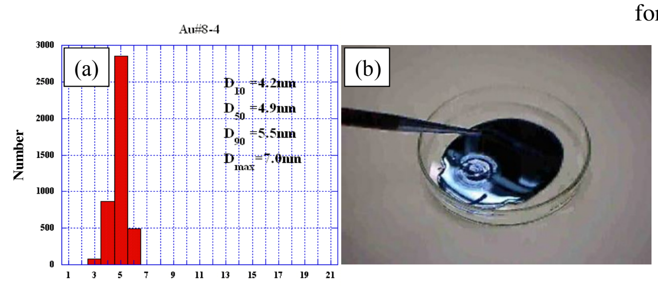

***Figure 2**. (a)Particle size distribution of gold nano particles, (b) Silver NanoPaste®*

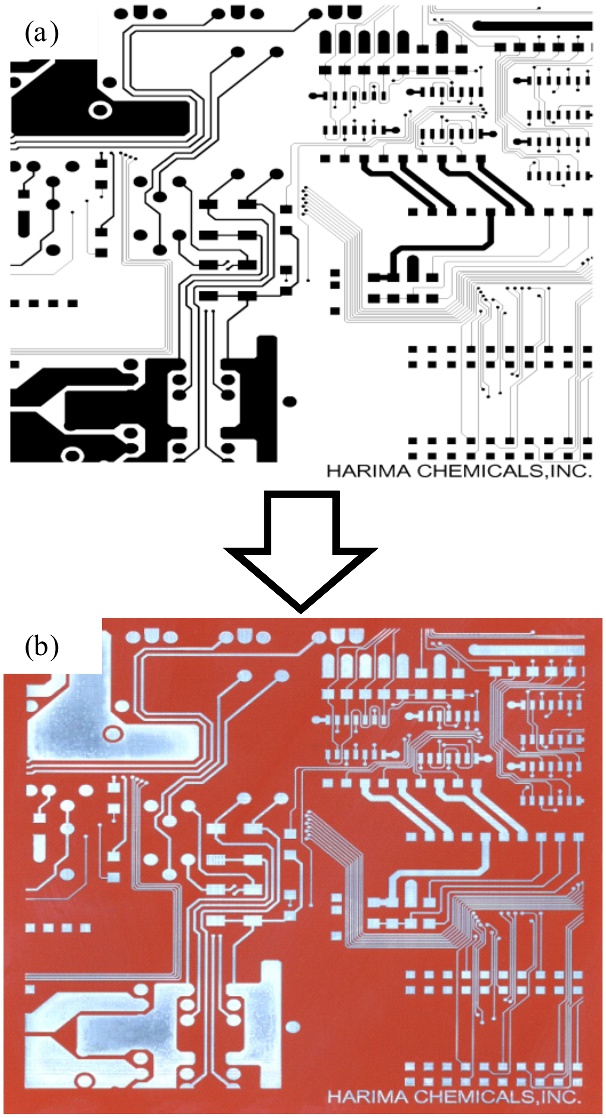

Figure 3. *Printed pattern on polyimide film; (a) CAD data, (b) silver NanoPaste®*

Ink-jet printing of silver NanoPaste®

The silver NanoPaste® was fabricated onto polyimide film in Figure 3(b). The uniform ejection of droplets was performed by piezo-type ink-jet printer that was commercially available. The printed pattern whose line is with 70μm at minimum line width precisely reflects on the bit-map data transformed from CAD data (Figure 3(a)). Silver NanoPaste® was so stable that clogging in the nozzle did not occur during ink-jet printing. Conductive pattern can be obtained by thermal treatment in the range of 200-300℃. The organic compounds of silver NanoPaste® were decomposed during sintering process and removed from silver conductive pattern. The sintering temperature is reduced down to 230℃ in the case of silver NanoPaste®. When sintering temperature is 230℃, volume resistivity is constant after 1hr for sintering as shown in Figure 4. However, in the case of 220℃, volume resistivity is gradually decreasing. The volume resistivity of sintered silver

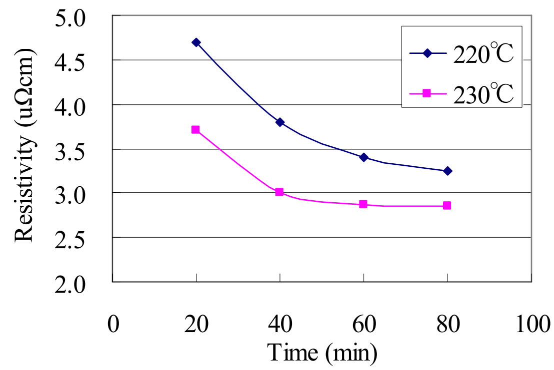

Figure 4. *Relationship between sintering time and resistivity*

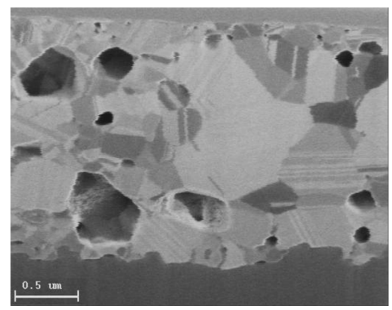

Figure 5. *Cross-sectional SIM image of sintered silver NanoPaste®*

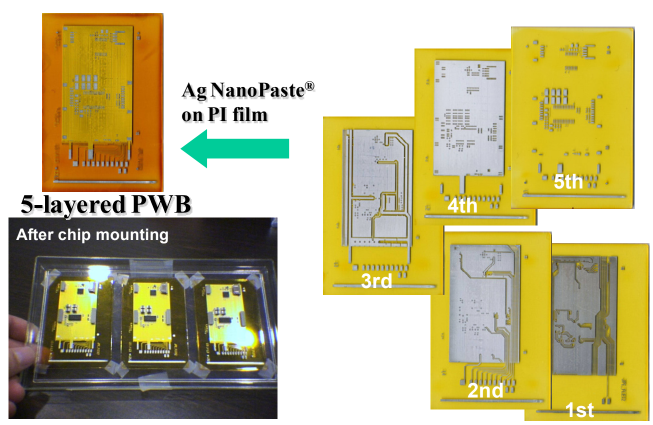

Figure 6. *Trial for the 5 layered printed wiring circuit by NanoPaste®*

layer is very low and close to silver value (1.6μ cm). The cross-sectional SIM image of the silver NanoPaste® sintered at 230℃ was as shown in Figure 5. Metallic inner structure was observed by FIB. Several voids exist in the silver layer.

The commercially available piezo piezoelectric ink-jet printer was used for the micro fabrication of NanoPaste® onto the substrate. This substrate was treated by surface treatment to prevent droplets from spreading on substrate. Insulating layer of polyimide was spin-coated on the sintered silver NanoPaste®. The connection between layers was achieved by laser drilling process and filling of silver NanoPaste®. Each circuit patterns and 5-layered PWB are shown in Figure 6.

Trial production of SiP

We challenged trial production of SiP for mobile terminal. This trial was achieved by ink-jet printing. SiP has 4 conductive layers and 4 insulation layers. Nokia designed SiP for mobile terminal. Harima provide silver Nanopaste® and build up silver conductive layer and insulation layer using ink-jet. Bump creation and pattern formation by ink-jet was achieved. Figure7 shows the conductive third layer. Finally this module mounted in mobile terminal.

Ink-jet printing of copper NanoPaste®

In Figure 8, conductive patterns of copper NanoPaste® were printed on polyimide whose surface was treated. For ink-jet printing, clogging in the nozzle did not occur similar to silver NanoPaste®. The sintering process is key step to obtain the conductive patterns. The critical issue is the oxidation of copper in the surface of nanoparticles. The oxidized copper needs to be converted into copper. The unique sintering process that was newly developed provided conductive patterns with high conductivity. The sintering process of copper NanoPaste® is at more than 250℃for 15 minutes. The special reductive gas was used. The resistivity of 5μ cm was obtained at the sintering temperature of 300℃ in figure 9.

Bonding pad formation by silver NanoPaste®

The silver plating is much conventional method for the formation of bonding pad in lead frame. The gold wire was bonded

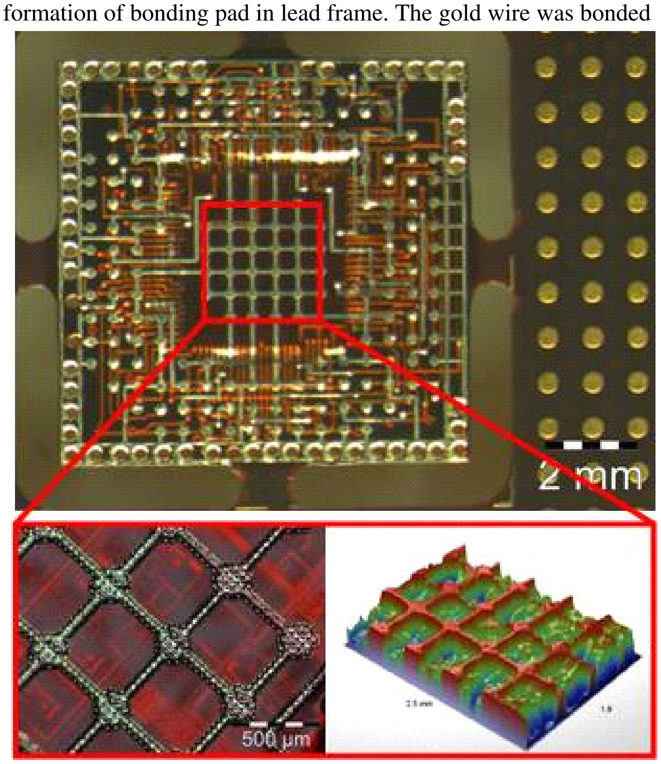

***Figure 7**. Trial for the SiP for mobile terminal*

on this silver pad. The bonding pad pitch in lead frame is getting fine in recent years. The conventional pad formation could not

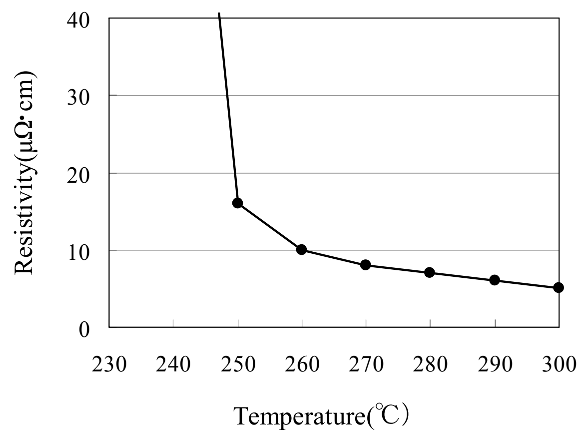

***Figure 9**. Relationship between sintering time and resistivity*

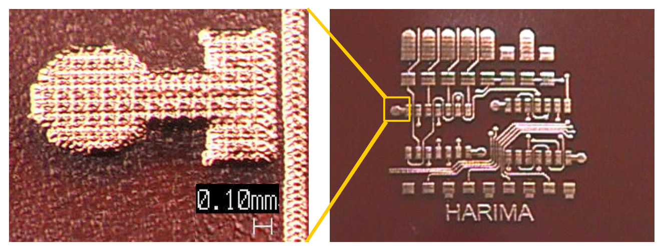

***Figure 8**. Pattern formation of copper NanoPaste® by ink-jet*

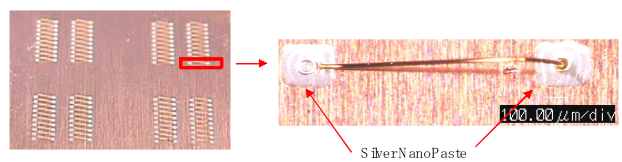

***Figure 10**. Gold wire bonded on silver pad by NanoPaste®*

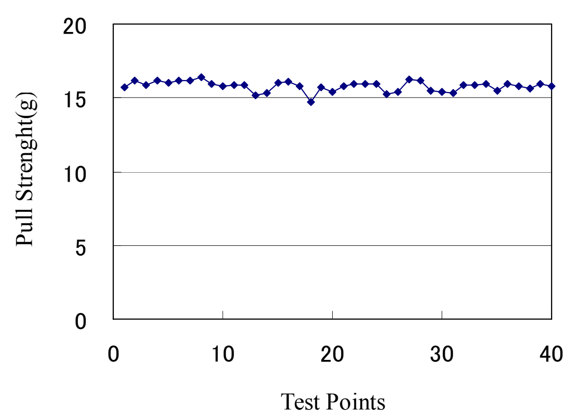

***Figure 11**.Gold wire bonded on silver pad by NanoPaste®*

satisfy this requirement. Direct pad formation by ink-jet using silver NanoPaste® has numerous advantages. The amount of silver consumption is less compared with plating method. Fine pitch pad formation is also great feature. Figure 9 shows wire-bonding using 30 μ m gold wire on silver pad (200 μ m in square) formed by NanoPaste®

At each test point, the pull strength more than 14gf was obtained.

Super Ink-jet Technology

The conventional photolithographic process directed on wafer level rerouting pattern formation requests sub micron rules. On the other hand, printing circuit board generally manufactures conductive line pattern in the range of 30 to 100μm. Super ink-jet technology provides the possibility to produce the line pattern with 1μm to 30μm. Super ink-jet technology developed by AIST (National Institute of Advanced Industrial Science and Technology) will be expected to build the next generation of printable electronics. NanoPaste® was investigated as the ink for this technology.

Figure 12(a) shows the fine patterning with 3μm on silicon substrate without stage heating and surface treatment of substrates. The volume of a droplet is sub femto liters less than 1/1000 in comparison with commercially available ink-jet printer. The droplet diameter is 0.5μm. Solvent evaporation from droplets prior to impact increases the viscosity and produce micro-bumps with high aspect ratio in Figure 12(b) [12].

Conclusions

The silver nanoparticles from NanoPaste® were converted into bulk metal when it heat-treated over 230℃. The pattern was highly conductive. The technology to obtain the patterns with 70μ cm L/S by using piezo-type industrial head and machine was applied to fabricate 5-layered PWB. SiP for mobile terminal was created by ink-jet technology using silver NanoPaste® and insulation materials. Super ink jet technology provided the ultra-fine patterning with several micrometer rules and micro-bumps without stage heating and surface treatment on substrates. The sintering process to reduce the oxidized layer of copper NanoPaste® was newly developed and copper circuit patterning was attained by ink-jet printing. Silver NanoPaste® is applied for lead frame and is the promissing material for the replacement of silver plating.

Acknowledgements

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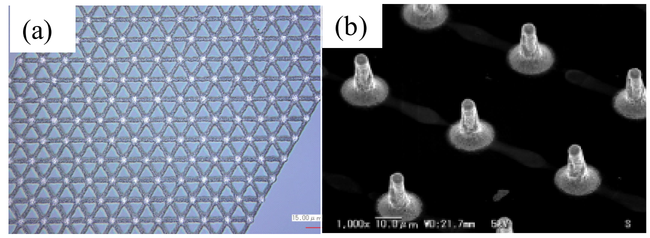

***Figure 12**. a) Fine patterning with several micrometer rules, (b) Micro-bumps with high aspect ratio*

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Author Biography

Nobuto Terada received his BS in physical chemistry from Nagoya institute of Technology (1983). He has worked in Tsukuba Research Laboratory at Harima Chemicals Inc He produced printing inks and underfill materials. He is developing Nanopaste using metallic nanoparticle and conductive paste mixed with polymer.