The printed circuit manufacturing using the nano metal ink and fabrication of transparent fine electrodes by gravure offset printing

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We introduce silver nanoparticle ink, namely nanometal ink, which is essential for printed electronics. In recent, flexibility is required in the field of transparent electrodes for future flexible devices. Although indium tin oxide (ITO) is the most widespread material as transparent electrode, its lack of adequate flexibility and poor conductivity restrain from further development for future devices.

We have attempted to make patterns of invisible and high conductive fine silver electrodes by a gravure offset printing method to meet both of transparency and flexibility. Here, silver nanoparticle ink was developed and applied to fabricate fine invisible silver electrodes with the line width of 5 μm. The fabricated electrode pattern of which the line/space is 5 μm / 300 μm has excellent electric conductivity and transparency. The patterned electrode has sheet resistance of sub-10 $\Omega/\square$, while its transparency is higher than 90 .

1. Introduction

In recent years, there has been demand for further reduction of both the cost and number of processes in device manufacturing. For example, patterning, one of the conventional technologies in device manufacturing, is carried out by first forming a functional thin film by sputtering and then shaping it into the desired shape through photolithography. Despite the advantage of the extremely high precision of the pattern formation, this method (involving the removal of unnecessary parts of a thin film) is inherently inefficient in the use of materials. Also, due to the higher costs and the many processes involved, this process is suitable for small item large scale production. In contrast, printed electronics directly produces the desired pattern only where necessary, instead of removing the unnecessary parts of a thin film. Due to the highly efficient use of materials and the few processes involved, this printing method is suitable for large item small scale production at a low cost.

The performance of devices produced by printed electronics depends greatly on the properties of the inks, pastes, and other printing materials. Take a metal nanoparticle ink dispersed in a solvent as an example. A metal circuit pattern printed with such an ink demonstrates excellent performance comparable to bulk conductivity even with sintered at a low temperature. This article describes nano metal inks made of metal nanoparticle ink suitable for printed electronics and the characteristics of a transparent microgrid electrode printed with the ink.

2. Nano metal inks

2.1 Metal nanoparticles and dispersant for forming conductive films

Metals are known to experience a dramatic drop in their melting points as they become ultrafine particles. This phenomenon owes to the increase in the surface area per unit volume and surface energy corresponding to the decrease in the diameter of a metal particle. Such an effect makes it possible to sinter particles at low temperatures. Thus, metal films produced by metal nanoparticle inks achieve excellent conductivity[1, 2]. As a matter of fact, "naked" nanoparticles with a clean surface clump together and sinter by themselves even at room temperature (Figure 1). Therefore, it is essential to adsorb a dispersant on the surface of nanoparticles to keep them from clumping together and stably disperse them in inks and pastes at room temperature.

Meanwhile, nanoparticles must be sintered together after removing the dispersant adsorbed on their surfaces to impart conductivity to the ink film. The firing temperature of an ink film for removing a dispersant and sintering nanoparticles together greatly depends on the desorption temperature of the dispersant on the surface of the particles. Dispersants with greater molecular weights require a higher firing temperature for desorption. For this reason, the right dispersant must be chosen for the intended purpose. Take flexible devices for example, with which a dispersant adsorbed on the particle surface must have a low molecular weight and be easily desorbed at a low temperature in order to print a circuit on a film substrate with low heat resistance[3].

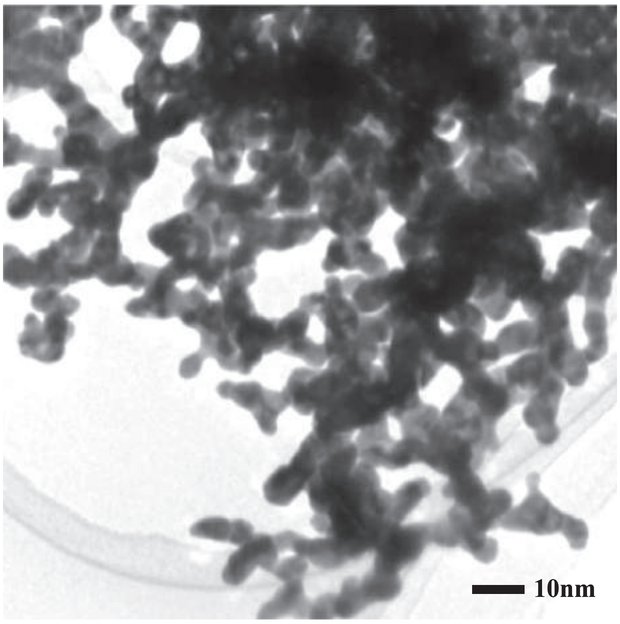

Figure 1 TEM image of typical Au nanoparticles.

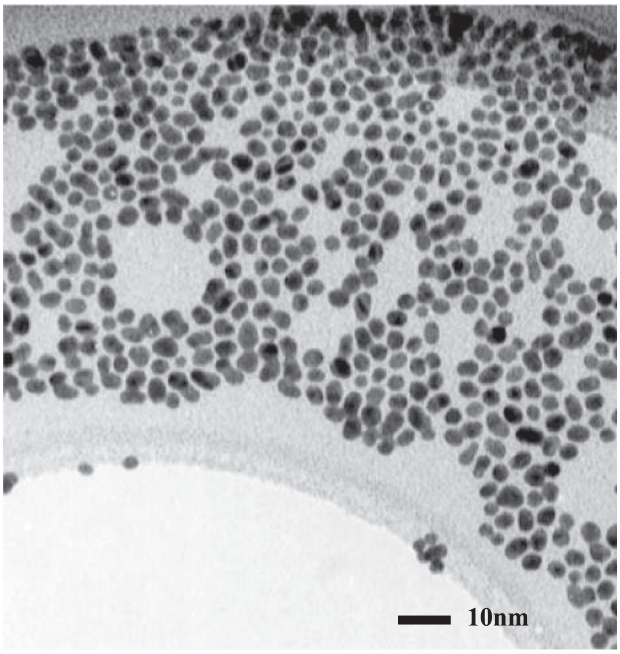

Figure 2 TEM image of Au nanoparticles in Au nano metal ink.

2.2 Preparation of metal nanoparticles

Methods for preparing metal nanoparticles are roughly divided into methods involving metal evaporation under reduced pressure or in inert gases, and those involving chemical reaction in the liquid or gas phase. As explained earlier, nanoparticles tend to clump together immediately after they are produced, which is why a dispersant must be adsorbed on their surfaces.

One of the methods for preparing nanoparticles by metal evaporation is the gas evaporation method. Normally in this method, metal atoms that have evaporated from a crucible in an evaporation chamber collide with the gas atmosphere before being cooled down and condensed into nanoparticles. Isolated particles near the crucible experience secondary cohesion as they repeatedly collide with one another at a greater distance from the crucible. As an improvement to such gas evaporation method, an additional function was provided to supply an organic substance as a dispersant for isolated particles[4, 5]. This modified method can be used to prepare independently dispersed nanoparticles by completely avoiding their cohesion thanks to the adsorption of the supplied organic dispersant on the surface of the metal nanoparticles produced by evaporation in a gas[6]. Nano metal ink is the name of an ink product made of metal nanoparticles produced via this method and dispersed in an organic solvent.

The hydrophobic groups (lipophilic groups) of dispersants adsorbed on the surface of metal nanoparticles dispersed in the nano metal inks is directed outward. Hence, these metal nanoparticles stably disperse in toluene, tetradecane, cyclododecene, cyclohexylbenzene, and other hydrocarbon organic solvents with low polarity. As an example, Figure 2 shows an image of Au nanoparticles dispersed in Au nano metal ink as captured by a transmission electron microscope (TEM).

2.3 Sintering mechanism of nano metal ink

The sintering mechanism of nano metal ink is schematically illustrated in Figure 3. Desorption of a dispersant by heating exposes the surface of metal particles and "naked" metal particles are brought into contact with one another. While physical contact between particles alone does not impart excellent conductivity, once a dispersant is desorbed and nanoparticles with a large surface energy touch one another, these particles migrate to smaller surface areas to reduce the surface energy. The sintering of particles advances in this manner. The resulting conductive paths for electrons between particles achieve excellent conductivity that rivals bulk conductivity. As such, the firing temperature of nano metal ink is essentially the same as the temperature at which a dispersant is desorbed from the particle surface.

2.4 L-Ag nano metal ink made with low temperature sintering

Substrates must be resistant to heat above the firing temperature of nano metal ink to gain conductivity by the heating and firing process. The firing temperature is es-

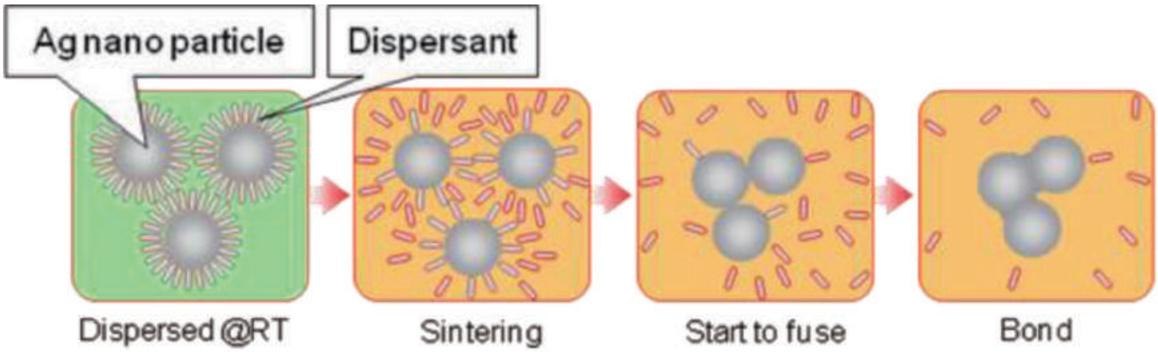

Figure 3 Sintering mechanism of the nano metal ink.

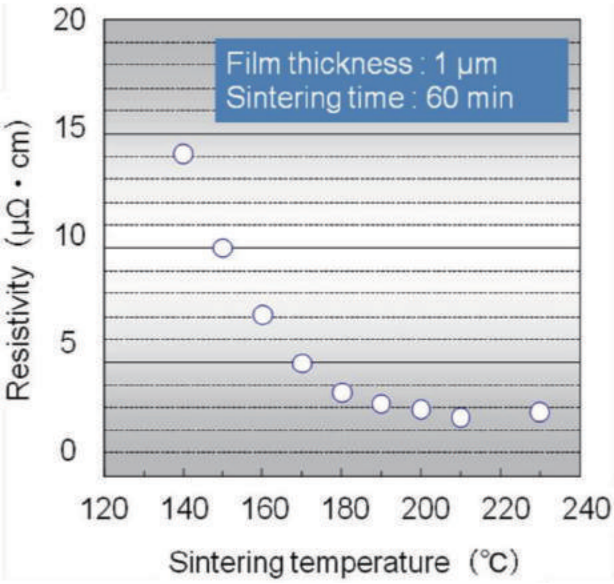

Figure 4 Electric resistivities depending on sintering temperature of L-Ag nano metal ink.

sentially the same as the temperature at which an adsorbed dispersant is desorbed from nanoparticles. If a highly transparent film or a versatile film with low heat resistance is used, a dispersant adsorbed on the surface of the nanoparticles must be desorbed at a temperature of no greater than 180℃. In general, a dispersant with a small molecular weight adsorbed to the surface of metal nanoparticles enables desorption of the dispersant at a low firing temperature to impart conductivity to an ink film. However, the small molecular weight may compromise the dispersion stability of particles. ULVAC discovered a dispersant with a low desorption temperature that maintains the dispersion stability of particles. The dispersant was adsorbed to the surface of Ag nanoparticles to successfully develop Ag nano metal ink made by means of low temperature firing. The ink can be calcined on a versatile film substrate with low heat resistance to impart excellent conductivity.

Figure 4 presents the relationships between the firing temperature and specific resistance of Ag nano metal ink (L-Ag nano metal ink) with a low firing temperature. The specific resistance of an Ag film obtained by calcination at a temperature no less than 150℃ for 60 minutes is no greater than 10 μΩ・cm, a great conductivity at such a low firing temperature.

3. Wiring formation by printing method

Figure 5 compares conventional photolithography and the wiring formation by printing method. Circuit printing is expected to bring about innovations in electronic device manufacturing due to its advantages over photolithography, including: (1) no masking required for lithographic exposure; (2) excellent efficiency in material use as patterns can be drawn only where necessary; (3) ease in application to a large substrate; and (4) low device cost.

Generally, deposition on a substrate by printing involves the three processes of pretreatment of the substrate surface, printing, and heat treatment[7].

Printing methods are roughly divided into those using printing plates and those that do not. This article describes gravure offset printing as a versatile printing process using a printing plate.

With reference to the processes shown in Figure 6, gravure offset printing embodies the characteristics of gravure (intaglio) printing and offset (transfer) printing. A plate engraved with the desired printing pattern is filled with ink by using a doctor blade. The ink is transferred to a substrate after passing through a blanket roll. The thickness of a printed pattern is determined by the depth of the plate (depressed portion) and ink concentration. Unlike planography and flexography, this method suffers less unevenness in film thickness associated with the line width. Printing through the blanket roll restrains the fluidity of ink-coated films transferred to the substrate so the printed pattern is less prone to bleeding. Because of these ad-

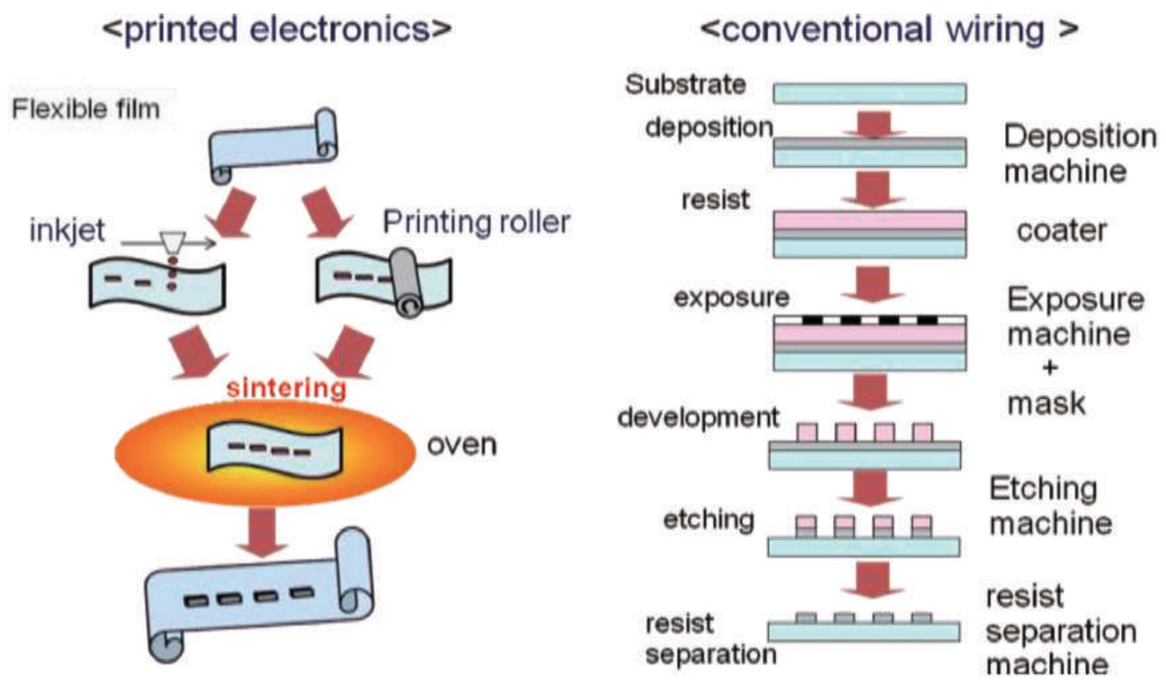

Figure 5 Comparison with conventional method and printing method.

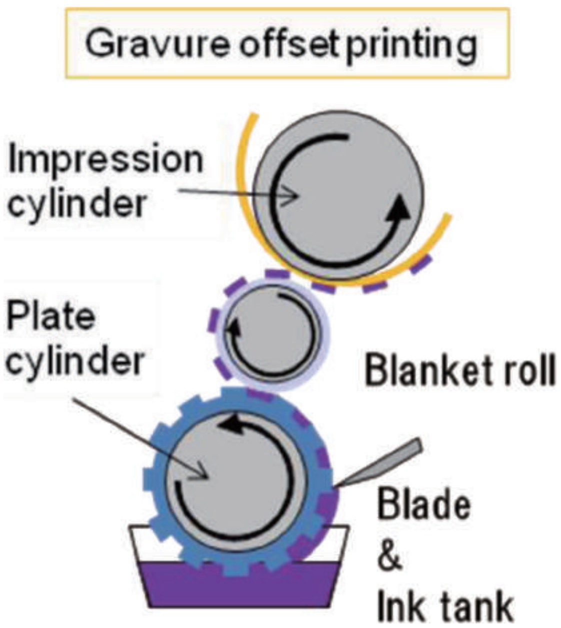

Figure 6 Schematic illustration of the gravure offset printing process.

vantages, gravure offset printing is suitable for micro-wiring. In terms of the processing precision of the printing plate, recent advancements in plate-making technology have brought the wiring width down to the level of a few micrometers. However, suitable inks for gravure offset printing of micro-wiring with a width of few micrometers have yet to be developed.

4. Requirements for transparent electrodes

In recent years, demand for greater transmittance, lower resistance, and flexibility has arisen for transparent electrodes for their application in touch panels and the like. Unfortunately, ITO and other commonly used oxide materials cannot ensure sufficient flexibility. Conductive polymers such as poly(3,4-ethylenedioxythiophene) and polystyrene sulfonate (PEDOT/PSS) demonstrate enough flexibility but lack the necessary conductivity.

Flexible grid electrodes with a low resistance are gathering attention as a solution to address this problem, as the transmittance can be enhanced by printing circuit patterns with a width of less than 10 μm, barely visible to the human eye. The gap in the grid needs to be widened to gain a high transmittance. For instance, over 95 percent of the surface will be empty when the width of the wiring is 5 μm and the gap in the grid is 300 μm. Conventional photolithography would need to remove over 95 percent of the deposited materials by etching to fabricate such a grid electrode. Such a use of material is inefficient. The following section reports the outcome of gravure offset printing with nano metal ink to form transparent microgrid electrodes only where necessary. The width of wiring (L) and the gap in the grid (S) were chosen so that L/S is 5 μm/300 μm.

5. Printing grid electrodes

5.1 Development of ink for gravure offset printing

As mentioned earlier, processing technology has advanced to the point where engraved plates can be made with grooves as narrow as 5 μm. But, circuit printing has been difficult because micron- and submicron-sized particles often contained in conventional inks for gravure offset printing could not be properly poured onto an engraved plate with grooves as narrow as 5 μm. Ag nano metal ink makes it possible to evenly fill such grooves thanks to stably dispersed Ag nanoparticles with a diameter no greater than 10 nm. In general, gravure offset printing is performed with an ink with a high viscosity of around 3,000 mPa･s. In the Ag nano metal ink used in this printing experiment, the ink composition was optimized to maintain the stable dispersion of Ag nanoparticles even when the ink is made highly viscous. In addition, good ink transfer performance was imparted by providing adequate solvent-absorption properties to the blanket while using a solvent mixture mainly composed of hydrocarbons as the ink solvent. In order to form a grid electrode on a versatile transparent film with low heat resistance, Ag nano metal ink in this printing experiment was developed based on L-Ag nano metal ink for low-temperature firing as mentioned earlier.

5.2 Properties of the grid electrode

A grid electrode pattern was printed with a width (L) of 5, 8, and 10 μm, and grid interspace (S) of 150 and 300 μm by using the abovementioned L-Ag nano metal ink developed for gravure offset printing. A polyethylene naphthalate (PEN) film with a thickness of 125 μm was used as a substrate. The firing conditions for the ink film after the printing was either 150℃ for 60 minutes, or 180℃ for 60 minutes.

Figures 7 and 8 show the printed circuit pattern.

As shown in Figure 9, with the use of an engraved plate designed to make wiring with a width of 5 μm, the wiring obtained by printing and calcination had an actual width of 6 μm and a film thickness of 0.6 μm. Among other printed grid electrode patterns, the pattern with an L/S of 5 μm/300 μm achieved good conductivity with a sheet resistance of 15 $\Omega/\square$ by firing at 150℃ and 6 $\Omega/\square$ by firing at 180℃. As shown in Figure 10, the transmittance was 80 percent when combined with the substrate film and 94 percent when the film was excluded. Considering the interrelation between the transmittance and the circuit density, the pattern can be adjusted according to the desired transmittance.

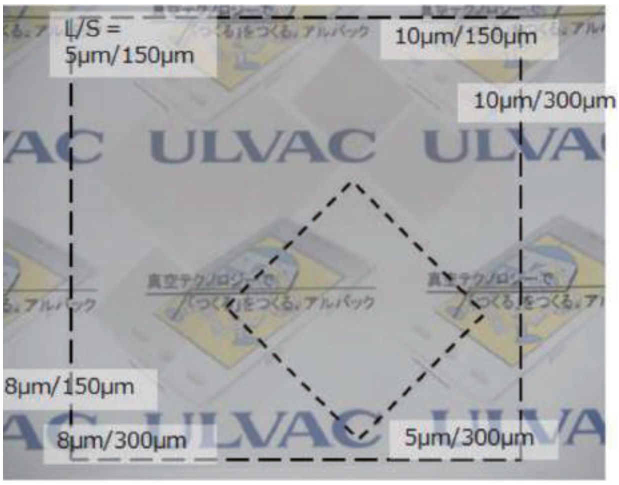

Figure 7 Image of the printed grid electrode.

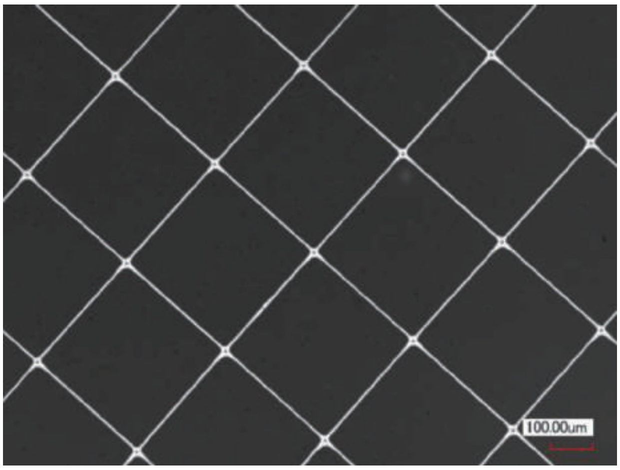

Figure 8 Optical microscope image of the printed grid electrode.

6. Conclusion

Ag nano metal ink for gravure offset printing was developed to print a transparent Ag microgrid electrode to provide an alternative to ITO electrodes. After the printing process, the transparent Ag grid electrode was calcined at a temperature of 180℃ for 60 minutes, which achieved excellent conductivity with a sheet resistance of 6 $\Omega/\square$ and a high transmittance of 94 percent.

The use of nano metal ink featured in this article opens the way for the patterning of transparent metal grid electrodes by a widely used means of gravure offset printing. Conductivity can only be imparted to printed ink films by calcination. Instead of inserting a prefabricated transparent conductive film, the right grid electrode pattern for each device can be directly printed on the desired func-

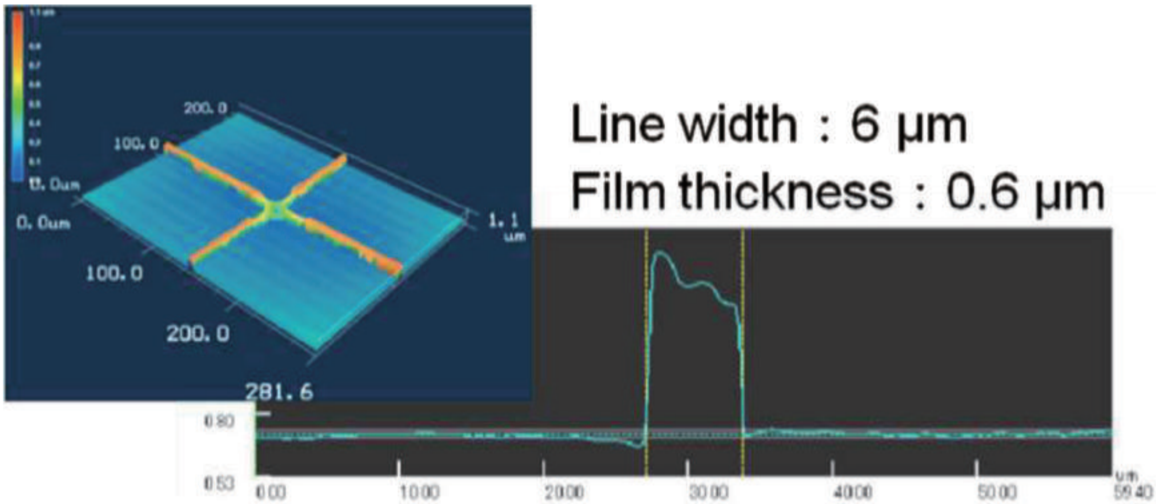

Figure 9　Wiring profile of the printed grid electrode.

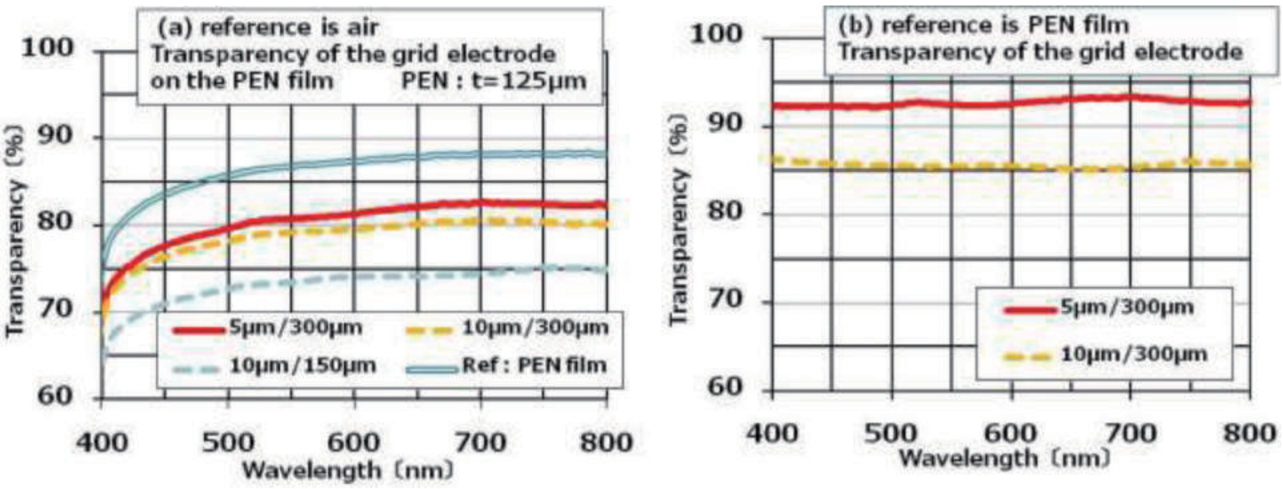

Figure 10　Optical transparencies of the printed grid electrodes on PEN film. (a) reference is air (b) reference is PEN film.

tional thin film. Thus, the technology provides more freedom in device design. Direct patterning of grid electrodes can achieve even higher transmittance by eliminating the need for supporting film layers for electrodes. Such low-cost transparent electrodes hold promise for application to flexible devices.

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