Individually Dispersed Nanoparticles formed by Gas Evaporation Method and their Applications

Masaaki Oda, Masato Ohsawa, Kyuukou Tei, Shigeo Hayashi, Yoshiaki Hayashi

Ulvac Corporate Center, 516 Yokota, Sanbu-city, Chiba-pref. 289-1297, Japan

Abstract

Individually dispersed Au, Ag, Cu and ITO nanoparticle ink are formed by using the industrial scale modified gas evaporation method where formed particles are covered with an organic surfactant just after their formation. The average diameters of these particles are less than 10 nm. These nanoparticle inks are called Nanometalink and suitable for ink-jet printing. Ink-jet printing using Nanometalinks are expected to substitute a patterning process using sputtering and photolithography. The inner structures of the cured films are much dependent on curing conditions such as a curing temperature, a temperature profile and a curing atmosphere which affect the resistivities and the mechanical strengths of the films. An Ag Nanometalink film low temperature curing type which is heat treated at 150℃ and 180℃, 200℃ for 60min with a thickness of 1 μm has a resistivity of 15μΩ･cm, 4 μΩ･cm, and 3μΩ･cm respectively. The adhesion strengths are improved by adding Cu nanoparticles to Ag Nanometalink in the case of high temperature (over 350 C) curing process and by coating resins on a substrate in the case of low temperature curing process.

The ITO film which is heat treated at 230℃ for 60 min with a thickness of 240 nm has a specific electric resistance of 0.0055Ω･cm and transparency of 95% at 550nm.Other inks properties and application examples are also going to be presented.

Introduction

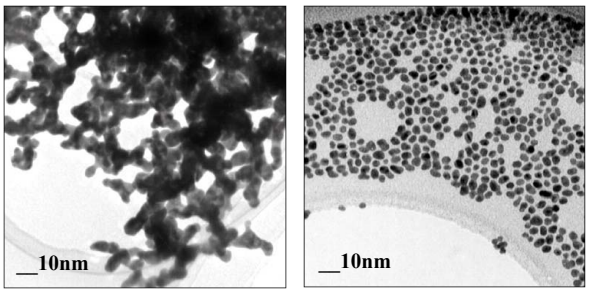
In response to the trend toward miniaturized and highly functionalized electrical equipment, nano-particles sized less than 100 nm in diameter for; wirings, electrode formations for electrical equipment and other applications are being discussed as candidate materials and are clearly anticipated. It is widely known that the sintering of nanoparticles occurs below 200℃, much lower than the melting points of metals [1,2]. Nano-particles however often sinter together, forming aggregations, due to the active nature of their surface. This has presented a barrier to the development of materials required in applications for electrical components such as the forming of fine wirings and the filling of fine holes. If it is possible to disperse highly pure nanoparticles without aggregation, in a high concentration, films with a thickness of less than submicron to over one micron thickness can be produced in a low temperature curing process.In this paper, formations and properties of individually dispersed metal inks will be presented. These inks are expected to be use for forming wirings and electrodes of electrical equipment with existing printing technologies such as ink-jet printing.

Individually Dispersed Metal Nanoparticles

Formation of Dispersed Metal Nanoparticles

Individually dispersed nanoparticles are formed in the modified gas evaporation method [3,4,5] using resistive heating or induction heating as an evaporation source. Metal atoms are evaporated from a crucible in an evaporation chamber causing collisions with gas molecules in the atmosphere. The particles are cooled down and condensed into nanoparticles. Near the crucible, particles are in an isolated state. Far from the crucible, particles repeatedly collide and form agglomerates. Several vaporized surfactants are introduced into the chamber where it sticks to the particles and covers their surfaces; so even though the particles collide, they do not aggregate. In this state, the covered particles are brought by gas flow to a cooling substrate. The particles are then collected and put into a dispersion solvent. Into this dispersion solvent, a polar solvent like alcohol is added where the particles precipitate and are washed in alcohol. The process; precipitation, solvent removal, and alcohol addition is repeated three or more times to complete the washing. Another non-polar or weakly polarized solvent such as Toluene, Cyclododecen, Cyclohexylbenzene, Dodecane and Tetradecane are then added to redisperse the nanoparticles. Figure 1 shows TEM image of individually dispersed Au nanoparticles compared with ordinary aggregated Au nanoparticles. The average particle size of individually dispersed Au nanoparticles is 5 nm. Ag, Cu and ITO nanoparticles are also individually dispersed.

This ink can be condensed, for example up to 70 wt% for Au, 60 wt% for Ag and Cu, 40 wt% for ITO



(a) Conventional nanoparticles Particles sinter at room temperature due to surface activeness.

(b) Individually dispersed nanoparticles Individually dispersed due to surface covering

Fig.1 TEM image of Au nanoparticles.

respectively. The viscosities of these inks are kept at around 10 mPa・s even if condensed to this level. Tetradecane or Cyclododecen is a suitable solvent for ink-jet ink because the boiling point is around 250℃. Thus inks located on a nozzle plate dose not dry quickly.

Formation of Films using Ag and Au Nanometalink

Films are formed by the spin coating method using Ag Nanometalink, where nanoparticles are dispersed uniformly without aggregations as the particles have a special covering. Film thickness is controlled by the coating thickness and content of metal in the ink. The metal nanoparticles are grown in conditions with oxygen. Particle size is affected by amounts of oxygen introduced to the atmosphere during processing, because decomposed organic materials are eliminated by reacting with the oxygen. Films are cured in air atmosphere.

There are two types of Ag Nanometalink, one is standard Ag Nanometalink (S-Ag), another is a low curing temperature type Ag Nanometalink (L-Ag). The covering surfactant of S-Ag Nanometalink particles is replaced by another low molecule weight material and L-Ag Nanometalink is formed. Resistivities of S-Ag Nanometalink films are shown in Figure 2. The films cured at 220-250℃ for 60 min with a thickness of 1 μm have a resistivity of 2.8 μΩ・cm. The resistivities of the films cured at below 200℃ are over 10 μΩ・cm level because sinterings of the particles are insufficient. The resistivities of the films cured at over 250℃ are also over 10 μΩ・cm level. This is due to the fact that the profile of the film becomes discontinuous by excessive grain growth of the Ag particles.

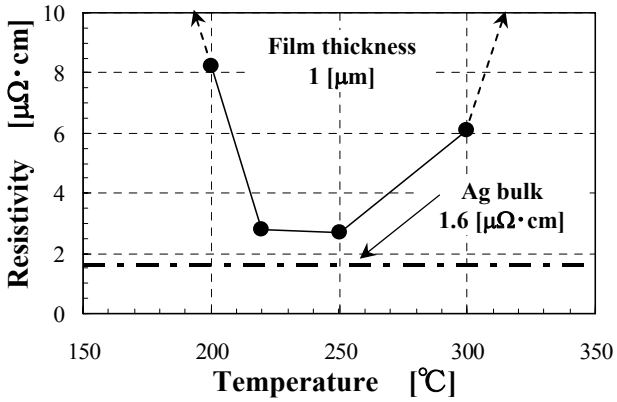


Fig. 2 Resistivity of S-Ag Nanometalink films, cured for 60min.

Resistivities of L-Ag Nanometalink films are shown in Figure 3. Resistivity becomes low with increasing curing temperature. The film cured at 150℃ for 60 min with a thickness of 1 μm have a resistivity of 15 μΩ・cm. Resistivities of films cured at over 180℃ reach down to less than 5 μΩ・cm.

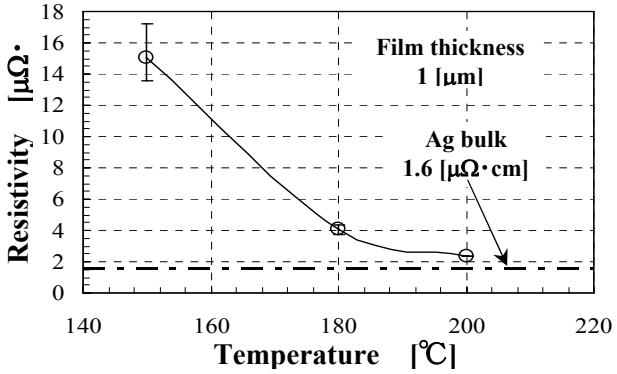


Fig. 3 Resistivity of L-Ag Nanometalink films, cured for 60min.

Resistivities of Au Nanometalink films are shown in Figure 4. Resistivity becomes low with increasing curing temperature. The film cured at 250℃ for 60 min with a thickness of 0.4 μm have a resistivity of 11 μΩ・cm. Resistivities of films cured at 300℃ reach down to less than 7 μΩ・cm.

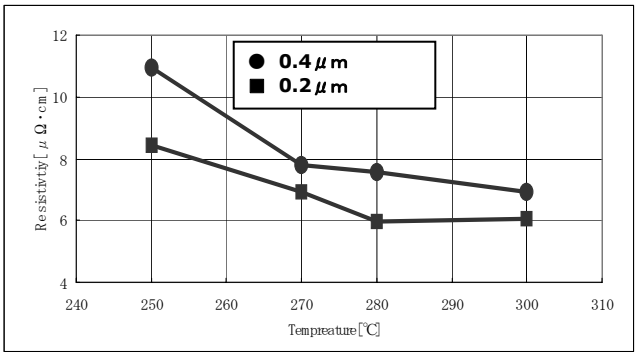


Fig.4 Resistivity of Au Nanometalink film, cured for 60min. Film thickness is 0.4 μm and 0.2 μm respectively.

Formation of Films using ITO Nanometalink

Viscosity of ITO nanmetalink can be controlled from 5 to 300 mPa.s by adjusting it's concentrations and selecting a dispersing organic solvent among a-Terpineol, Cyclododecene and Cyclohexylbenzene shown in Fig.5.

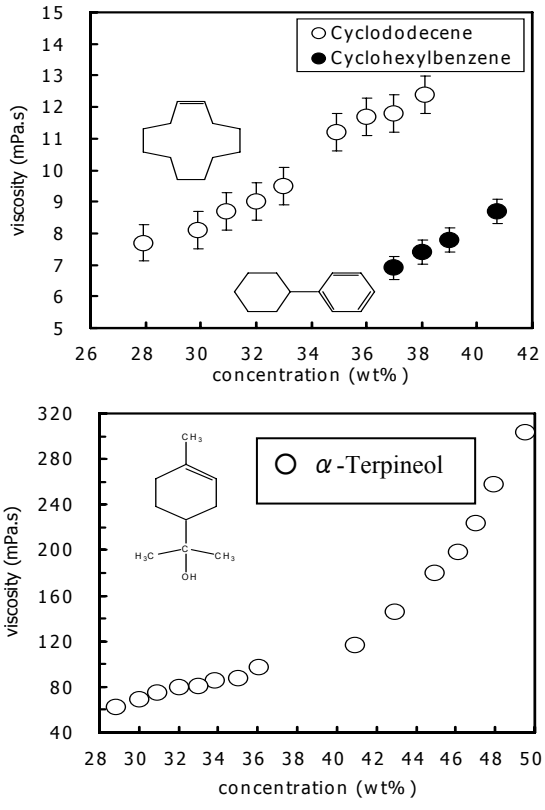


Fig. 5 Viscosity of ITO Nanometalink.

ITO Nanometalink with a viscosity of 10mPa.s is spin coated on a glass plate and cured in an atmosphere of 8Pa at a temperature between 200℃ and 270℃ for 10min followed with curing in air at for 60min. The ITO films formed on a glass plate do not peel off in a tape test. Specific electric resistances of ITO films are shown in Fig.6. The resistance is sharply reduced at 220℃.The specific electric resistance reaches 0.0055Ωcm at 230℃.

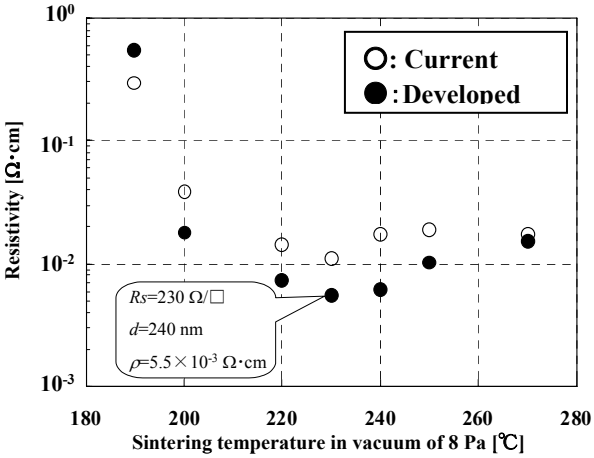


Fig. 6 Resistivity of ITO Nanometalink films.

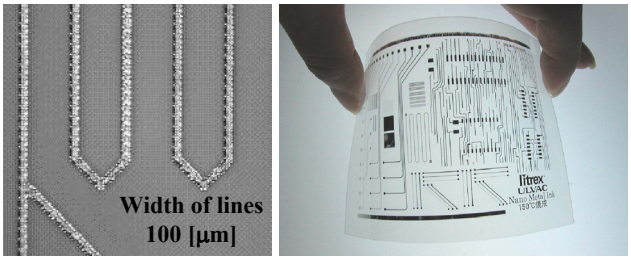
Adhesion

It was reported that the adhesion strengths were improved by adding Cu nanoparticles to Ag Nanometalink in the case of high temperature (over 350℃) curing process and by coating resins on a substrate in the case of low temperature curing process (below 300℃) by M.Oda *et al* [6]. There are other procedures to improve adhesion strengths depending on substrate materials. For example, a Mn oxide layer formed with Mn ink can improve the adhesion of Ag Nanometalinks on a glass substrate [7].

Ink-jet Printing

Figure 7 shows two Ag patterns formed by ink-jet printing. The pattern shown in Figure 7a is formed using S-Ag Nanometalink to which Cu nanoparticles has been added. The pattern film is formed on a glass substrate and cured at 550℃ for 60 min. The resistivity of the film with a thickness 2.3 μm has a 2.8 μΩ·cm. The pattern film passes the tape peeling test and the pencil Scratch test. The adhesion strengths were improved by Cu nano-particles added to S-Ag Nanometalink. The

pattern shown in Figure 7b is formed by L-Ag Nanometalink. The pattern film is formed on a PET film which is cured at 150℃ for 30 min. The resistivity of the film has 10 μΩ･cm. Conventional metal film pattern forming processes such as photolithography of sputtering deposition film are expected to be replaced by Nanometalink ink-jet printing.



a) Ag pattern is formed on glass substrate using S-Ag Nano-metalink and cured at 550℃ for 60 min.

b) Ag pattern is formed on PET film using L-Ag Nanometalink and cured at 150℃ for 30 min.

Fig.7 Ag patterns are formed by ink-jet using Nanometalinks.

Conclusion

This paper has concluded the followings:

1) S-Ag Nanometalink films which are heat treated at 220-250℃ for 60 min with a thickness of 1 μm have a resistivity of 3 μΩ･cm.
2) L-Ag Nanometalink films which are heat treated at 150℃, 180℃ and 200℃ for 60min with a thickness of 1 μm has a resistivity of 15 μΩ･cm, 4 μΩ･cm and 3 μΩ･cm respectively.
3) Au Nanometalink films which are heat treated at 250℃ for 60 min with a thickness of 0.4 μm have a resistivity of 11 μΩ･cm. and a resistivity of less than 7 μΩ･cm at 300℃.
4) ITO Nanometalink films which are heat treated in an atmosphere of 8Pa for 10 min followed with a treatment in air for 60min at 230℃ with a thickness of 240 nm have a resistivity of 0.0055Ωcm.
5) Wiring patterns are formed by ink-jet using Ag Nanometalink added with Cu nanoparticles. The pattern cured at 550℃ for 60 min with a thickness of 2.3 μm has a resistivity of 2.8 μΩ･cm. The adhesion strength is improved by adding Cu nanoparticles to S-Ag Nanometalink. L-Ag pattern cured at 150℃ for 30 min has a resistivity of 10 μΩ･cm.

References

1. C.R.M.Wronski, “The size dependence of the Melting Point of Small Particles of Tin”, Brit.J.appl.Phys., 18, 1731 (1967).
2. R.P.Berman and A.E.Curzon, “The Size Dependence of the Melting Point of Small Particles of Indium”, Can.J.Phys., 52, 923 (1974).
3. R.Uyeda, “Studies of ultra fine particles in Japan”, Progress in Material Science, 35, No.1 (1991).
4. T.Suzuki and M.Oda, Proc. of the 9th International Microelectronics Conference, pg. 37 (1996).
5. G.Kutluk *et al*, Proc. of Advanced Metallization Conference 2000, pg. 199 (2001).
6. M.Oda *et al*, Proc. of Digital Fabrication 2005, pg. 186 (2005).
7. M.Furusawa *et al*, “Inkjet-Printed Bus and Address Electrodes for Plasma Display”, Tech. Digest of SID02, pg. 753 (2002).

Author Biography

Masaaki Oda received his BS(1971), MS(1973) and PhD (1986) in applied physics from Nagoya University. Since then he has worked in the nanoparticle development department at ULVAC. He was dispatched to government ERATO project (1981-1986). He has focused on the development of nanoparticle formations by the gas evaporation method. He is the general manager of Nanoparticle Application Department of ULVAC Corporate Center.