Individually Dispersed Nanoparticle Ink for Film Formation using Ink-jet

Masaaki Oda, Hiroshi Yamaguchi, Noriyuki Abe, Tsutomu Atsuki, Kyuukou Tei, and Masaki Kitazaki, Ulvac Corporation, Sanbu-gun, Chiba-pref, Japan; Sadayuki Ukishima, Hideo Takei, and Satoru Ishibashi, ISM Ulvac Japan, Sanbu-gun, Chiba-pref., Japan; Toshiharu Hayashi, Shinya Shiraishi, and Reiko Kiyoshima, JEMCO Inc. Kashima-gun, Ibaraki-pref., Japan

Abstract

Individually dispersed Au, Ag, Cu, Pd and ITO nanoparticle inks are formed by using the modified gas evaporation method (gas condensation) where formed particles are covered with an organic surfactant just after their formation. The particles formed by the gas evaporation method are alkaline and sulfur impurity free and have a narrow size distribution. The average diameters of these particles are less than 10 nm and the particles are stably dispersed in Toluene or Tetradecane or Decalin with a solid content of 70wt% for Au, 60wt% for Ag and Cu, 50wt% for Pd and 40wt% for ITO respectively. These nanoparticle inks are suitable for ink-jet printing. Ink-jet printing using nanoparticle ink is expected to substitute patterning processes using sputtering and photolithography. An Ag nanoparticle ink film (low temp.curing type) which is heat treated at 150C for 2hr with a thickness of 300nm has a specific electric resistance of 6μΩcm. An ITO nanoparticle ink film which is heat treated at 230C for 70 min with a thickness of 160 nm has a specific electric resistance of 0.02 Ωcm and transparency of 95% at 550nm.

Introduction

In response to the trend toward miniaturized and highly functionalized electrical equipment, nano-particles sized less than 100 nanometers 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 degrees C, 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 and ITO nanoparticles 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.

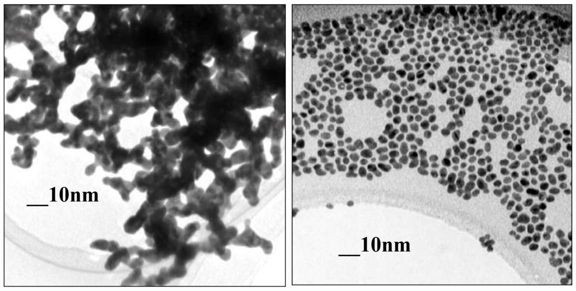
Individually Dispersed Metal Nanoparticles

Formation of Dispersed Metal Nanoparticles

Individually dispersed nanoparticles are formed in the modified gas evaporation method,[3-5] 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 solvent such as Toluene, Decalin and alcane, which is like a straight chain hydrocarbon, are then added to re-disperse the nanoparticles. At this point the nanoparticles are ready to produce film formations in the form of Nanometalink. Industrial scale production equipment (1000kg ink/month) has been built so far.

Formation of Films using Nanometalink

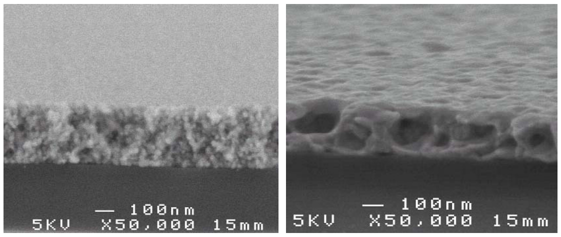
Nanoparticles in Nanometalink disperse uniformly and without aggregations as the particles have special covering. This ink can be condensed, for example up to 70wt% for Au, 60w%t for Ag and Cu, 50wt% for Pd respectively. The viscosities of these inks are around 10 mPa.s which is suitable for ink-jet printing. It is also possible to make viscosity higher, up to 20000 mPa.s without losing dispersion uniformity by adding a type of organic material. TEM image of ordinary aggregated Au nanoparticles and individually dispersed Au nano-particles are shown in Fig. 1. The average particle size of individually dispersed Au nanoparticles is 5nm. Ag, Cu and Pd also show individual dispersion in the TEM picture. Cross sections of Ag nanoparticle thin film coated on glass and cured and formed under two different conditions are presented in Fig. 2. Particles 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. Film thickness is controlled by the coating thickness and content of metal in the dispersion liquid.



(a) Conventional n-particles
Particles sinter at room temp.
due to surface activeness

(b) Individually dispersed n-particles
Individually dispersed
due to surface covering

Figure 1. TEM image of Au nanoparticles.



Curing condition
(a) 220°C × 30 min in N_2 gas
(b) 220°C × 30 min in $N_2 + O_2$ gas

Figure 2. SEM image of films formed from Ag dispersed nanoparticles.

Table 1: Specific electric resistance of films formed using Nanometalink. Inks are coated by spin coating. Curing condition: S-Ag 220C in air for 30 min, L-Ag 150C in air for 30 min, Au 350C in air for 30 min, Cu 350C in 10Pa air for 2 min + 10^{-4}Pa for 10 min.

	Stand. Ag	Low Temp. Ag	Au	Cu
Bulk (μΩ cm)	1.6		2.2	1.7
Nanometal -ink Film (μΩ cm)	2	13	10	2.2
Thickness (μm)	0.5	0.4	1	0.5

Properties of Films

The specific electric resistances of films formed using Tetradecane dispersed Ag, Au and Cu Nanometalink are summarized in Table 1. Specific electric resistances of s-Ag and Cu are within 1.3 times that of single crystals, thus the films are essentially perfect metal films.

The covering surfactant of particles of standard Ag (S-Ag) Nanometalink is replaced by another low molecule weight material and low curing temperature type Ag (L-Ag) Nanometalink is formed. The particles are dispersed in Toluene and Tetradecane with a solid content of 50 wt%. Tetradecane type ink is suitable for ink-jet printing. The specific electric resistance dependence against curing temperatures is shown in Fig. 3. Films cured at 150C for 30min with a thickness of 400 nm and 700 nm have a specific resistance of 10 to 15 μΩcm and 30 to 35 μΩcm respectively. Specific electric resistances of films cured at over 180C reaches down to less than 5 μΩcm. Films cured at 150C for times as long as 120min with a thickness 300 nm have a specific resistance of 6 μΩcm.

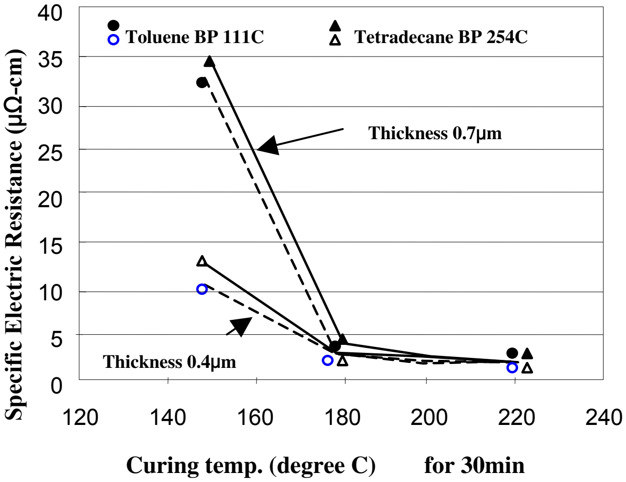


Figure 3. Specific electric resistance of films formed using L-Ag Nanometalink dispersed in Toluene and Tetradecane.

Adhesion strengths of films on a glass substrate measured by the Sebastian method which were formed by mixing Cu in various forms into Ag Nanometalink are summarized in Table 2. The adhesion strength of film formed from standard Ag Nanometalink without any additional elements is shown in sample type 1. The adhesion strength of the ink with the addition of Cu metallo organic compound is shown in sample type 2. The adhesion strength with the addition of Cu nano particle is shown in sample type 3. The adhesion strengths of types 2 and 3 are over 3kgf/mm.

There are other procedures to improve adhesion strengths depending on substrate materials used in the applications. For example, a Mn oxide layer formed from Mn ink can improve the adhesion on a glass substrate.[6] Adhesion improvement with anchor effect can be applied to a substrate with pores. An organic primer coating can improve the adhesion on an organic material substrate whose heat resistant temperature is lower than 200C.

Conventional vacuum processes such as vacuum deposition and sputtering deposition are expected to be replaced by the process of spin coating, dipping and ink-jet methods of Nanometalink which produce thin films under a few micrometers in thickness. An example of Ag wiring pattern formed on PET film by ink-jet using L-Ag Nanometalink is shown in Fig. 4.

Table 2: Adhesion strength on a slide glass of films formed using standard Ag Nanometalink mixed with Cu organic compound and Cu Nanometalink. Curing condition: 350C in air for 60min.

	Adhesion Strength (kgf/mm2)			Sebastian Test Break at
	1	2	3	
Ag Type1	0.96	0.66	0.46	Between Film and Glass
Ag Type2 Cu 10wt%	5.91	6.65	4.72	Between Glue and Film
Ag Type3 Cu 5wt%	4.86	4.96	3.87	Between Glue and Film
Ag Type3 Cu 10wt%	6.25	6.44	4.72	Between Glue and Film

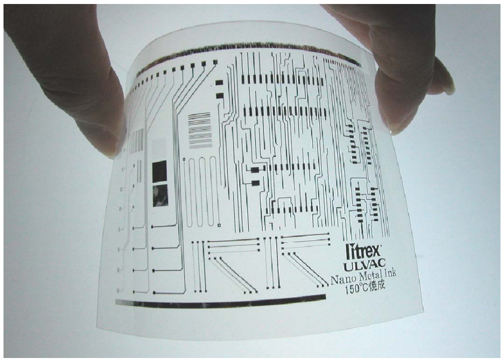


Figure 4. Ag pattern is formed on PET film by ink-jet using Tetradecane dispersed L-Ag Nanometalink and cured at 150C for 30min.

Individually Dispersed ITO Nanoparticles

Formation of ITO Nanoparticles

In the ITO gas evaporation method, metal vapors of In and Sn are evaporated from molten metal in an evaporation source where the content of Sn in In is controlled and collided with inert gas atoms and condensed into nanoparticles whose Tin content is about 7 atm%. Several vaporized surfactants are introduced to the surface of the particles while they are at an isolated stage and cover their surfaces. The particles are collected in an organic solvent and are stably dispersed. The same process as in the metal nanoparticle are proceeded, then d-ITO nanoparticles are re-dispersed in a non-polar or weak polarized organic solvent such as Toluene or Decalin (Decahydronaphthalene) with the content of up to 40wt%. The viscosity of d-ITO nanoparticle ink is around 10 mPa.s which is suitable for ink-jet printing.

A transmission electron microscope (TEM) image of d- ITO nanoparticles is shown in Fig. 5. Particles are well separated with each other because of the surfactants covering the surfaces of particles. The average particle size of d-ITO is about 4 nm.

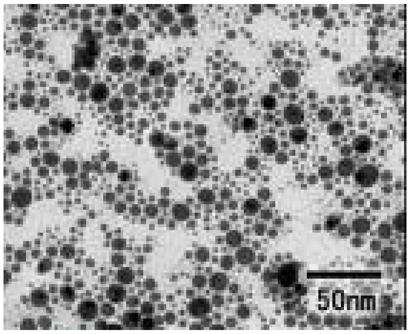


Figure 5. TEM image of dispersed ITO nanoparticles.

Formation of Film using D-ITO Nanoparticle Ink

D-ITO nanoparticle ink is spin coated on a glass plate and cured in an atmosphere of several Pa at 230C for 10 min followed with curing in air at 230C for 60 min. The ITO films formed on a glass plate do not peel off in a tape test. A SEM image of the ITO cured film on a glass plate is shown in Fig. 6. It is shown that the particles have grown to about 0.05 μm in size and are closely attached and sintered to each other resulting in the formation of a film with nanograins.

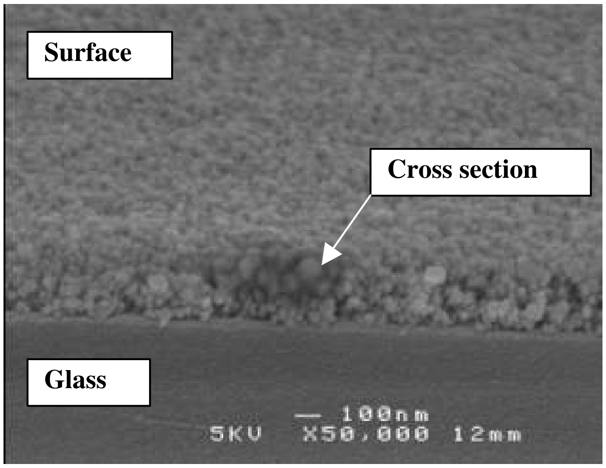


Figure 6. SEM image of ITO film on glass formed using d-ITO nanoparticle ink.

Electric Resistance of ITO Film

Specific electric resistances of ITO films which are cured at a temperature between 200C and 270C are shown in Fig. 7. The specific electric resistance reaches 0.02Ωcm at 230C. The films are heat treated in an atmosphere of 8 Pa for 10 min followed with a treatment in air for 60 min. The resistance is sharply reduced at 220C.

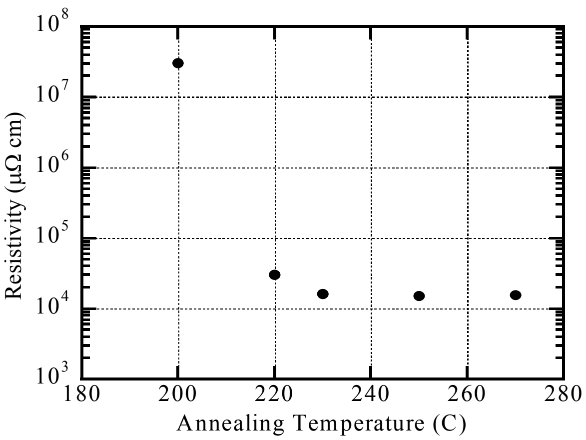


Figure 7. Specific electric resistance of ITO films. The Resistance is Sharply Reduced at 220C.

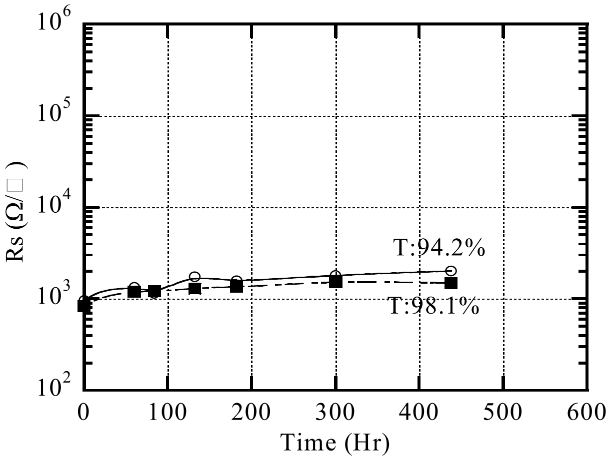


Figure 8. Change of electric sheet resist. of d-ITO film kept at 60C and 90%RH. Transparencies at 550nm of the films are 94.2% and 98.1% respectively.

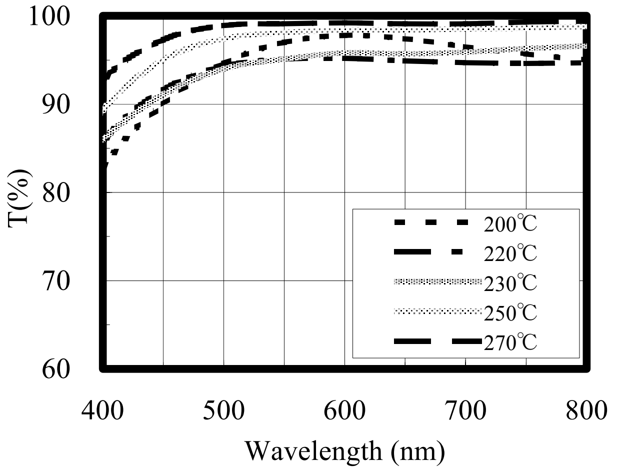


Figure 9. Optical transparent properties of d-ITO film cured at temperatures from 200C to 270C. Film thickness is 160 nm.

Changes of electric resistance of d-ITO film which were placed in 60C and 90%RH conditions are shown in Fig. 8. The resistance increased only by 1.5 times after being kept for 400 hrs.

Optical Transparent Property

Transparency of the ITO film is shown in Fig. 9. The film thickness is 160 nm. The film heat treated at 230C with specific electric resistance of 0.02 ohm cm has a transparency of 95% at 550 nm The film heat treated at a temperature higher than 250C has the transparency of 95% even at 450 nm.

Sputtered ITO films usually have an optical transparent property indicated by a convex curve, shown in Fig. 10. However d-ITO film does not show such a property, seen in Fig. 10. Generally an interference of incident light and reflected light results in the penetration of more light with a wave length 4 times of the film thickness than others. In the d-ITO film however, it is supposed that the density of the film is less than the bulk ITO because of existing pores and thus reflection does not occur at the boundary of the glass.

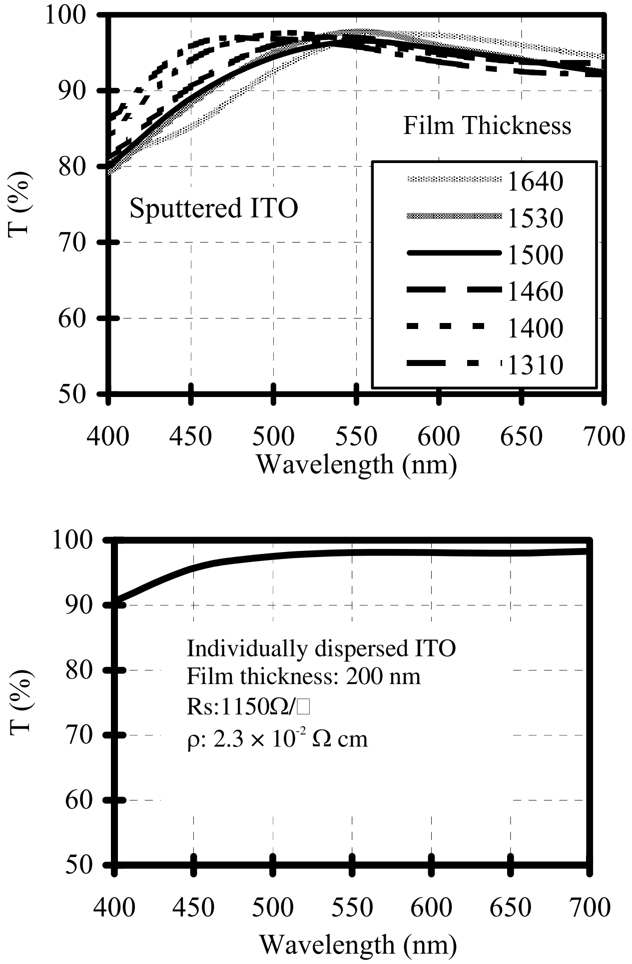


Figure 10. Comparison of optical transparent properties of sputtered ITO film and d-ITO film.

Conclusion

In this paper, it is reported that individually dispersed metal and ITO nanoparticles are produced by the modified gas evaporation method which is already at a large scale production stage up to 1000kg ink / month. The modified gas evaporation method can also be applied to other materials besides ones reported in this paper. These inks have dispersion stability and meet properties which ink-jet printing process requires. By comparing the ink-jet process with the photolithography process, a number of advantages become apparent. 1) The ink-jet process is a maskless process. 2) Materials are used efficiently as they are applied only where necessary. 3) The ink-jet method is an atmospheric method and therefore easily applied to large sized boards. 4) The cost of equipment is relatively low. 5) Bumpy or irregular surface plates can be drawn on. 6) With the growing use of CAD, on demand printing will be possible, making rapid production and accurate delivery dates more easily achievable and should speed the reformation of display production. Thus it is expected that these inks are going to be used for applications targeting display fields where substrate size is becoming increasingly large and packaging field where high density packaging is required.

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. 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 Corporation.