Method to Synthesize Silver Nano-particles for Inkjet Inks to Reduce Environmental Load

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Abstract

We have been studying the method to prepare metal nano-particles in aqueous solution. We presented the role of low molecular compounds as a dispersing agent in aqueous solutions to synthesize silver particles at NIP27, last year. At NIP28 of this year, we would like to present the effect of PVA and polyacrylic acid compounds on the growth of silver particles. The PVA used in this experiment are as follows: Saponification ratio is 78.5-99.4 mol% and polymerization degree is 500-2600, where the saponification ratio is defined as the ratio of the number of OH group to total number of OH and $COOCH_3$ groups. The above both factors have affected the growth of silver particles and we have found in a series of our experiments that the PVA with the polymerization degree of 500 and the saponification ratio of 99.4 mol% has produced mono-dispersed silver particles of 10nm in average diameter. Furthermore, we have found that polyacrylic acid compounds as a dispersing agent have resulted in around 5nm in average diameter. Since this method to synthesized silver nano-particles does not use any organic solvents, we can avoid the problem regarding environmental pollution caused by organic fluids.

Introduction

Inkjet printing technology has been used widely in order to manufacture flexible printed circuits (FPC) of several electronics devices. Applying this technology for manufacturing conductive thick films has three major advantages. The first is the non-contact pattern formation. It enables to print on some media regardless of the shape, material and size. The second is a method without press plates to print. Printing patterns are variable and suitable for high-variety and low-quantity manufacturing. The third is that processes of removing impurities can be omitted. Since inkjet printing method can put an ink droplet on a precise place, the probability that material comes into effect is relatively high. Therefore, in comparison with the other method for printing circuits, inkjet printing method is capable of manufacturing with low environmental load. Printing electronic circuit with inkjet printing technology has the advantage as mentioned above [1-3].

To apply inkjet printing technology to manufacture of FPC, it is important to prepare metallic particles used as electronic conductive substance [4-6]. Generally, silver nano-particles have been used for the purpose. The conventional method to prepare silver nano-particles has the following problems [7-13]: (1) A lot of organic solvent is used. (2) Reduction rate is slow and consequently reaction time is consumed. (3) Keeping high temperature is required to accelerate chemical reaction.

We have been proposing new methods to prepare silver nano-particles [14-15]. As we reported at NIP 27, we examined the role of low molecular compounds as a dispersing agent in aqueous solutions to synthesize silver particles and found that the silver nano-particles prepared there could be sintered at low-temperature [16].

In this paper, we would like to present the effect of PVA and other several polymers on the growth of silver particles. Polyvinyl pyrrolidone (PVP), polyacrylic acid (PAA), sodium polyacrylate and polyethylene imine (PEI) have been used. We have sintered the silver nano-particles at 150 to 300℃ and then measured the volume resistivity. We have not used any organic solvent in a series of process to synthesize silver nano-particles this time. This fact is considered to profit us from the viewpoint of preventing environmental pollution caused by organic fluids.

Experimental

Materials

Silver nitrate ($AgNO_3$), polyacrylic acid (PAA, Mw = 5,000), sodium polyacrylate (polymerization degree is 2,700-7,500), polyethylene imine (PEI, M_w = 600), triethylamine and gallic acid monohydrate were purchased from Wako Pure Chemical Industries, Ltd. Polyvinyl pyrrolidone (PVP, M_w = 10,000) was purchased from Tokyo Chemical industry Co., Ltd. Four kinds of polyvinylalchol (PVA) were obtained from The Nippon Synthetic Chemical Industry Co., Ltd. PVA are a series of GOHSENOL®. Saponification ratio is 78.5-99.4 mol% and polymerization degree is 500-2600, where the saponification ratio is defined as the ratio of the number of OH group to total number of OH and $COOCH_3$ groups.

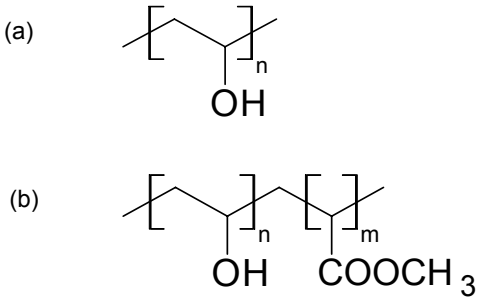

Figure 1. *The structure of PVA: The value of n/(m+n) is number of saponification ratio.*

Preparation of Silver nano-particles with PVA

Silver nano-particles of 10nm in average diameter were prepared by reduction method at room temperature. The preparation procedure is as follows: PVA (1g) dissolved in de-

ionized water (20 ml) was stirred for 10 min at room temperature. Into this solution, $AgNO_3$ (0.50 g) was added and the solution was kept stirring for 10 min in order to dissolve completely the $AgNO_3$, then triethylamine (0.298 g) was added drop-wise using a micro pipette. After all of the solution was added, an aqueous solution of gallic acid monohydrate (0.25 g) dissolved in de-ionized water (0.30 ml) was added to the reaction mixture drop by drop using a peristaltic pump. Then the mixture was kept stirring for 1 hour at room temperature. After the reaction was finished, the silver particles were separated from the solution by centrifugation (5000 rpm), and then dispersed again into de-ionized water (10 ml). The same reaction procedure as described above was used to prepare other silver particles with varying the kinds of polymers.

Measurement the volume resistivity of silver nano-particles

To measure the volume resistivity, silver nano-particle dispersions were coated on polyimide films. Then the silver nano-particle samples were dried at 100℃ for 20 min, and then sintered in an electric oven for 1 hour at 150, 200, 250, or 300℃.

Characterization

A drop of the silver suspension was placed on a carbon-coated formvar film on copper grids, dried at room temperature, and then pictures of silver nano-particles by transmission electron microscope (TEM) were taken with a JEOL JEM2010 operating at 200 kV.

Volume resistivity was measured with Loresta-GP MCP-T610 resistivity meter (Mitsubishi Chemical Analytech Co., Ltd). A four-probe method was used for measuring the volume resistivity. The diameter distribution of silver particles was measured with Zetasizer Nano Series (Malvern Instruments). Energy Dispersive X-ray Spectroscopy measurement (EDS) was made with the emission scanning electron microscope (SEM, Hitachi S-5000) equipped with an EDS instrument. X-ray diffraction (XRD) experiment was carried out with Rigaku D/MAX-IIIV X-ray Diffractometer using Cu-Kα radiation. UV-Visible spectra of silver suspensions were obtained with a Hitachi U-4100 UV-VIS spectro-photometer.

Result and Discussion

Silver nano-particles prepared with four kinds of PVA

Characteristics of four kinds of PVA used in this study are as follows. NH-26 has saponification ratio of 99.4 or more and polymerization degree of 2600, NL-05 saponification ratio 98.5 or more and polymerization degree 500, KH-20 saponification ratio 78.5 to 81.5 and polymerization degree 2500, and KL-05 saponification ratio 78.5 to 81.5 and polymerization degree 500.

The size of silver particle prepared with the PVA is listed in table 1, where particle size is calculated as the average diameter of particles randomly selected from TEM picture. TEM picture of silver nano-particles with NL-05 is shown in Fig. 2.

Table 1. The characteristics of PVA and silver particle size.

Dispersing Agent	Saponification ratio [mol%]	Polymerization degree	particle size [nm]
NH-26	99.4 or more	2600	20
NL-05	98.5 or more	500	10
KH-20	78.5 to 81.5	2500	25
KL-05	78.5 to 81.5	500	15

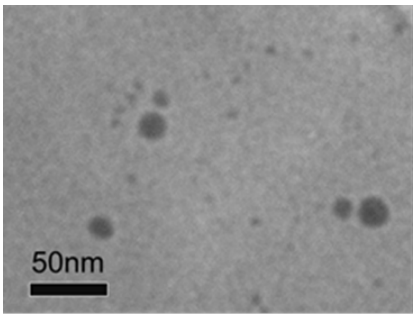

Figure 2. *TEM picture of silver nano-particles prepared with PVA (NL-05).*

When compared NH-26 to KH-20, both have similar value of polymerization degree, but NH-26 shows higher saponification value than KH-20. Regarding particle size, NH-26 has led smaller than KH-20. The same relation has been observed between NL-05 and KL-05, but in this case the particle diameters have been smaller than the case of NH-26 and KH-20. These facts suggest strongly that higher saponification ratio and lower polymerization degree have led smaller diameter. As a result, NL-05 has produced the smallest silver particles in a series of the present experiments. The effect of these kinds of compounds is expected to be based on the capability to prevent agglomeration of silver particles.

We have also examined volume resistivity of silver nano-particles. Figure 3 shows the result, where silver nano-particles have been dried at 100 ℃ for 20min and then sintered at 150, 200, 250, or 300℃ for 1 hour each. As seen in Fig. 3, silver particles with PVA of low polymerization degree (NL-05 and KL-05) have lowered the volume resistivity of 8 to $9\times10^{-4}\Omega$ cm by sintering at 200 ℃. However, for the case of high polymerization degree PVA (NH-26 and KH-20), the reached level of volume resistivity has been 2.6 to $2.8\times10^{-3}\Omega$ cm. The polymers added as dispersing agents have to be burned to get high electric conductivity.

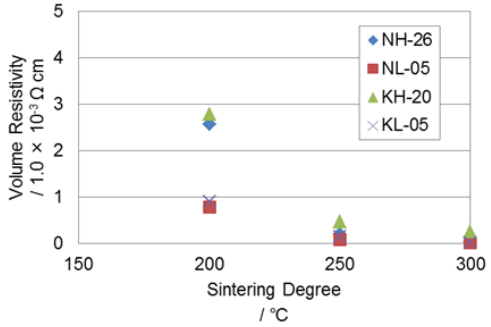

Figure 3. *Change in volume resistivity of silver nano-particles with each PVA sintered for 1 hour at 150℃, 200℃, 250℃, or 300℃.*

Silver nano-particles prepared with other polymers

We have prepared silver nano-particles with PVP, PAA, sodium polyacrylate and PEI to examine the effect of these polymers on particle size and volume resistivity. Each of the polymers is expected to play an important role as a dispersant. The experimental methods have been the same as mentioned above. The size of synthesized silver particles is listed in table 2. The experiment procedure is the same as with PVA in Table 1.

Table 2. Particle size.

Dispersing Agent	Particle Size [nm]
PVP	8
PAA	8
Sodium Polyacrylate	5
PEI	10

Compared with the results described in the preceding section, the particle size has been relatively small in these experiments. Above all, sodium polyacrylate has brought the smallest particle size. TEM picture of silver nano-particles prepared with sodium polyacrylate is shown in Fig. 4 and the diameter distribution in Fig. 5. Sodium polyacrylate would have been a good dispersing agent and consequently resulted in narrow distribution of mono-dispersing type.

Not only sodium polyacrylate, but also PVP and PAA have led small size of particles. These results are expected to have been based on the strong capability of pyrrolidone group to make coordinate bond to PVP [17] and carboxy group to polyacrylic acid compounds [18]. On the other hand, since PEI has a branch structure, silver particles may not approach to each other, resulting in such the particle size.

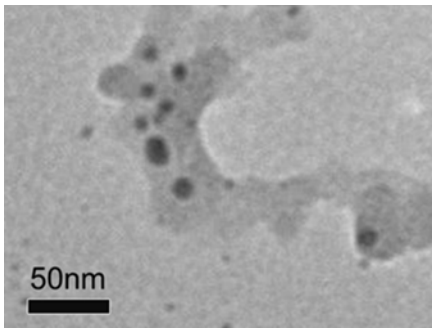

Figure 4. *TEM picture of silver nano-particles prepared with sodium polyacrylate.*

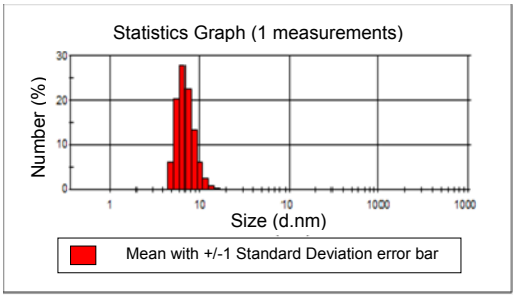

Figure 5. *Diameter distribution of silver nano-particles prepared with sodium polyacrylate.*

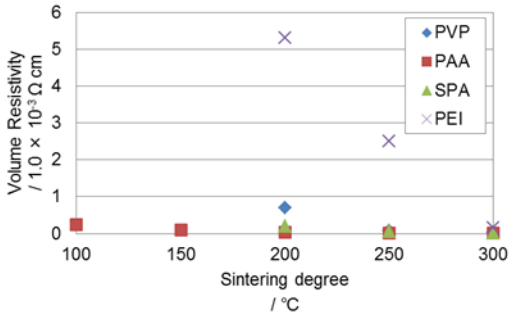

Figure 6. *Change in volume resistivity when sintered for 1 hour at 150℃, 200℃, 250℃, or 300℃. Silver nano-particles were prepared with PVP, PAA, SPA, or PEI.*

Figure 6 shows volume resistivity with PVP, PAA sodium polyacrylate and PEI, respectively. In this case, sufficient electric conductivity has been obtained by sintering at 100℃, whereas it has needed to sinter at 200℃ or higher for the silver nano-particles mentioned above (Fig. 3).

It is notable that silver nano-particles with PAA have shown electric conductivity of $2.4\times10^{-4}\,\Omega$ cm with only treatment of drying at 100℃ for 20min. When we sintered these particles at 150℃ for 1 hour, the volume resistivity decreased to near level of silver inkjet inks on the market today (sintered at 150℃ for 1 hour.: $4.4\times10^{-5}\,\Omega$ cm). On the other hand, sodium polyacrylate which has the same substituent group ($-COO^-$) has not resulted in such the high electric conductivity through sintering even at 200℃. The fact that sodium polyacrylate did not lead high electric conductivity might be based on the existence of metal atoms other than silver, namely, sodium.

Every sample of this study has shown a certain level of electric conductivity by sintering at 150℃ for 1hour. We have supposed the role of the two compounds, that is, triethylamine and gallic acid monohydrate as reduction agent in bringing electric conductivity. However, when only triethylamine was used, silver particles of nano-size was synthesized but sufficient electric conductivity was not obtained. When only gallic acid was used, reduction of silver ions did not proceed enough and consequently silver particles were not obtained. These facts suggest that the combination of triethylamine and gallic acid monohydrate is important to reduce particle diameters and lower sintering temperature.

Identification

The composition of particles has been examined analytically. The results of Energy Dispersive X-ray Spectroscopy (EDS) and X-ray diffraction (XRD) are shown in Figs. 7 and 8, respectively. Figure 9 shows UV-VIS spectrum, where plasmon absorption appears clearly. These results indicate that the particles are pure silver metal.

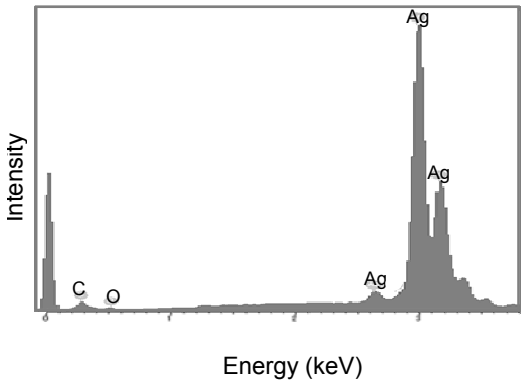

Figure 7. EDS Pattern of silver nano-particles prepared with PAA.

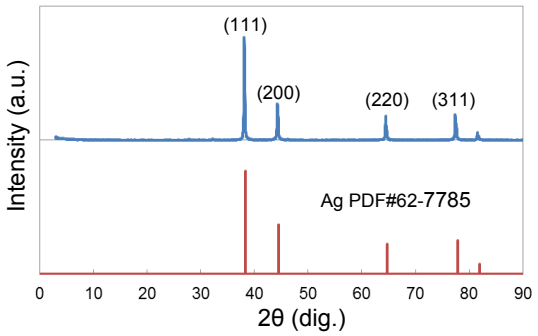

Figure 8. X-ray diffraction pattern of silver nano-particles prepared with PAA.

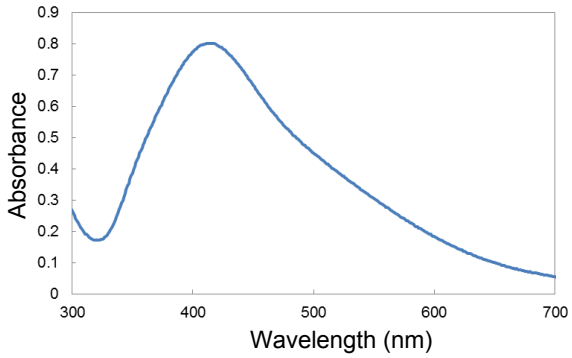

Figure 9. UV-Vis absorption spectrum of a suspension of silver nano-particles.

Conclusion

Polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), polyacrylic acid (PAA), sodium polyacrylate and polyethylene imine (PEI) have been used to examine the effect of dispersing agents on the growth of silver particles. We have found the following matters:

(1) We prepared silver nano-particles with four kinds of PVA with varying saponification ratio and polymerization degree. We have found that higher saponification ratio and lower polymerization degree have led smaller diameter.

Silver particles prepared with PVA of high polymerization degree (NH-26 and KH-20) have higher volume resistivity than that of silver nano-particles prepared with PVA of low polymerization degree (NL-05 and KL-05). This fact is based on that more heat quantity is needed to remove polymers of higher polymerization degree.

(2) We prepared silver nano-particles with the following polymers: PVP (M_w=10,000), PAA (Mw=5,000), sodium polyacrylate (polymerization degree 2,700 to 7,500), and PEI (M_w = 600). Compared with the case described in the above (1), the particle size has been relatively small. In terms of controlling the silver particle size, we have discussed on the basis of the strong capability of pyrrolidone group to make coordinate bond to PVP and carboxy group to polyacrylic acid compounds. In the case of PEI, its branch structure has been considered to prevent the growth of silver particles.

(3) Sodium polyacrylate would have been a good dispersing agent and consequently resulted in narrow distribution of mono-dispersing type.

(4) Silver nano-particles with PAA have shown electric conductivity of $2.4\times10^{-4}\Omega$ cm with only treatment of drying at 100℃ for 20min. When we sintered these particles at 150℃ for 1 hour, the volume resistivity decreased to near level of silver inkjet inks on the market today (sintered at 150℃ for 1 hour.: $4.4\times10^{-5}\Omega$ cm).

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