Synthesis of Concentrated Cu-Ag Nano Sol for Ink-Jet Method

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Abstract

The Cu-Ag nanoparticles have been synthesized in aqueous medium using a hydrazine reduction method. The assisted role of polymeric dispersant on synthesis of highly concentrated Cu-Ag nanoparticles was studied. The 30wt% of Cu-Ag nanoparticles with the range of 10 nm in diameter was prepared.

1. Introduction

Recently, a lot of research efforts were devoted to develop ink-jet printing as a patterning method substituting screen printing and/or photolithography methods for making micron-sized patterns. [1-4]

Cu, Ag and their alloys are major materials used for interconnects in ultra-large-scale integration(ULSI), printed circuit board (PCB), flexible printed circuit board (FPCB) and electrode of plasma display panel (PDP) due to their good conductivities. The typical preparation methods of Cu, Ag and their alloys nanoparticles for conductive ink or material are well known, such as γ-radiation [5], inert gas condensation [6], ion beam [7] and electrochemical reaction [8]. Although the conductive material has been prepared by many methods already, it needs expensive equipment; therefore, it would be more favorable to develop direct chemical preparation method for conductive ink or material.

In order to develop novel conductive ink for fabricating several tens of micrometer width ordered lines on various substrates, it is necessary to meet strict physicochemical properties of conductive-inks, such as surface tension, viscosity, particles size distribution, dispersion stability, and adhesion to a substrate and etc.

The synthesis of highly concentrated Cu-Ag nano sol assisted by polyelectrolytes was carried out in this study. The highly concentrated Cu-Ag nano sol for ink-jet method could be prepared with varying of polyelectrolytes and control of initial nucleation and growth of Cu-Ag nanoparticles. We can achieve the stable Cu-Ag nano sol with control the size of Cu-Ag nanoparticles.

2. Results

The role of polyelectrolytes on the synthesis of Cu-Ag nano sol was studied by varying the molar ratios (R=[COO^-]/[Ag^+ and Cu^{2+}]) of them. The 10 wt% of silver nano sol was synthesized by reduction the cation (Ag^+ and Cu^{2+}) and anionic polyelectrolytes (COO^-) complex. To investigate the effect of complex on the synthesis of Cu-Ag nano sol, the molar ratio was changed in the range of 0 ~ 2. The particle size and shape, and particle size distribution of the Cu-Ag nano sol was shown in Figs. 1 and 2, respectively.

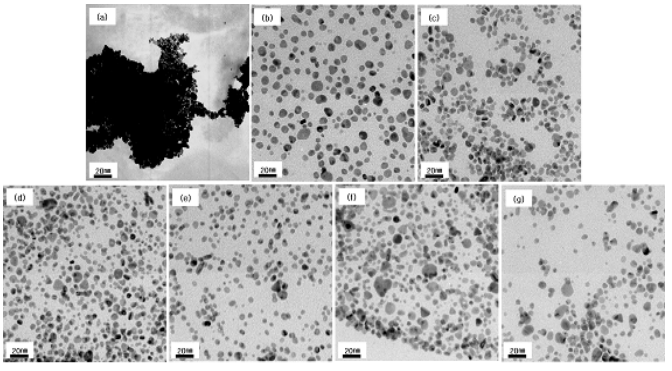

Fig. 1. TEM image of 10wt% Cu-Ag nano sol assisted by various concentrations of polyelectrolyte; R=[COO^-]/[Ag^+ and Cu^{2+}] (R=0~2), (a) 0eq, (b) 0.1eq, (c) 0.25eq, (d) 0.5eq, (e) 1eq, (f) 1.5eq, (g) 2eq

The particle size of Cu-Ag nano sol assisted by the polyelectrolytes (Mw=15,000) was typically kept below 5~20 nm as shown in Fig. 2.

In this study, highly concentrated silver nano sol was prepared from $Cu(NO_3)_2$ (reagent; <99%, Aldrich) as copper source materials and $AgNO_3$ (reagent; <99%, Aldrich) as silver source materials with $NaBH_4$ and/or hydrazine monohydrate (reagent; 97%, $H_2NNH_2 \cdot H_2O$, hydrazine, Aldrich) as reducing agent. The polyelectrolyte (polyacrylic acid ammonium salt; Mw=15,000, Aldrich) was used as

the best assisting material to prepare Cu-Ag nanoparticles. Ice cold solution of $Cu(NO_3)_2$ or $AgNO_3$ (10–30 wt% of Cu-Ag) that contains various polyelectrolyte was reduced by adding hydrazine monohydrate and/or $NaBH_4$ slowly. The formation of $Cu\text{-}Ag^{(0)}$ nanoparticles was confirmed by FE-TEM. The particle size and zeta potential of Cu-Ag nano sol were measured by the Zeta sizer (ELS-800, Otsuka, Japan) after diluting them by 10,000 times.

In preliminary experiment, we could obtain the Cu-Ag nanoparticles smaller than 10 nm with the adding speed of 0.5–1.0 mL/min of 0.5mM $NaBH_4$ solution and/or 0.5mM hydrazine monohydrate.

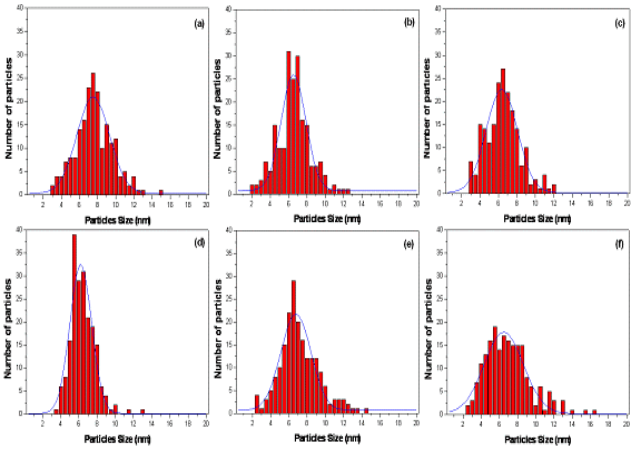

Fig. 2. Particle size distribution of 10 wt% Cu-Ag nano sol assisted by various concentrations of polyelectrolytes; $R=[COO^-]/[Ag^+$ and $Cu^{2+}]$ (R=0.1~2), (a) 0.1eq, (b) 0.25eq, (c) 0.5eq, (d) 1eq, (e) 1.5eq, (f) 2eq

The chemistry of borohydride reduction is complex and the nature of the product depends on the experimental conditions. Depending upon the concentration of reactants, the borohydride reduction generally follows one of the following chemical paths [9-11]:

$$4Cu^{2+}+(BH_4)^-+8(OH)^-\rightarrow 4Cu+(BO_2)^-+6H_2O \quad (1)$$

$$4Cu^{2+}+2(BH_4)^-+6(OH)^-\rightarrow 2Cu_2B+6H_2O+H_2 \quad (2)$$

$$8Ag^++BH_4^-+8OH^- \rightarrow 8Ag+H_2BO_3^-+5H_2O \quad (3)$$

Since reduction potential of noble metal, such as Ag, Pt and Au, is very high, the noble metal nanoparticles are more stable than their ionic state. But reduction potential of Cu is relatively very low comparing to that of novel Ag metal. It means that the difference of reduction potential causes the difference of initial stage of nucleation of nanoparticles. Therefore, the control of reducing rate of these Cu-Ag metal ions could be very important to reproduce homogeneous particle size and shape [11–15]. For this reason, the polyelectrolytes will play an important role in synthesis of Cu-Ag metal nanoparticles. The success of highly concentrated Cu-Ag nano sol synthesis assisted by polyelectrolytes can be explained as follows: the complex effect of $[COO^-]$ group in polyelectrolytes with $[Cu^{2+}]$ and $[Ag^+]$ ion will help for preparing Cu-Ag nanoparticles, since the limited migration of $[Cu^{2+}]$ and $[Ag^+]$ ion for reduction results in a control of nanoparticle nucleation and growth. In case of R=0 (without polyelectrolytes), the particle size is very large and aggregate of particles, which is more than 10 times larger than that of Cu-Ag nanoparticles at R=0.1–1.0. Owing to complex effect of polyelectrolytes with Cu-Ag ions, we can prepare a narrow particle size distribution of Cu-Ag nano sol for ink-jet method.

Furthermore, the polyelectrolytes, in which every segment in polyelectrolytes has anionic functional group, are more efficient compared with simple surfactant. It was considered that the polyelectrolytes provided the proper nucleation rate at initial stage and sufficient charge density on Cu-Ag nanoparticles resulted in stabilizing Cu-Ag sol. Thus, the under 10 nm sized Cu-Ag nanoparticles can be produced easily by introducing reducing agent slowly.

To conclude, the ratio of $[COO^-]$ to $[Cu^{2+}]$ and $[Ag^+]$ is related with the degree of complex formation, which affects the particle size and size distribution. Another important role of polyelectrolyte is contribution to the dispersion of Cu-Ag nanoparticles after the synthesis. To control the particles size and distribution, the nucleation and crystal growth is very important [16-17], which is controlled by reducing power and reducing speed.

To investigate the effect of concentration of reducing agent on the synthesis of Cu-Ag nano sol, the particle size and shape, and particle size distribution of the Cu-Ag nano sol was investigated. The particle size of silver nanosol assisted by the reducing agent was typically kept below 6 nm.

Therefore, the size and dispersion stability of Cu-Ag nano sol have depended largely on concentration of polyelectrolyte and reducing agent that determines initial nucleation and growth of Cu-Ag nanoparticles. The highly concentrated Cu-Ag nano sol from 10 to

30 wt% was prepared at R=0.1 as the molar ratio of reducing agent to Cu and Ag ion was kept at 1eq. as shown in Figs. 3.

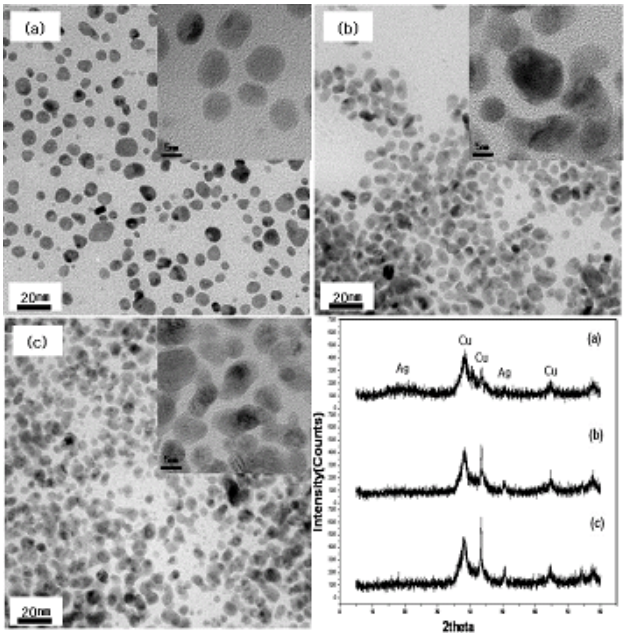

Fig. 3. TEM image and XRD pattern of high concentrated Cu-Ag nano sol.
(a) 10wt%, (b) 20wt%, (c) 30wt%

The particle size of all of them was below 10 nm, even though the particle size of them decreased with increasing concentration. Finally, the highest concentration of batch-synthesized Cu-Ag nano sol was achieved successfully to 30 wt%.

3. Conclusion

We have studied the synthesis of Cu-Ag nano sol application for Ink-Jet method. The size and dispersion stability of Cu-Ag nanoparticle has been depended largely on the concentration of polyelectrolyte and reducing agent. The synthesis of Cu-Ag nanoparticle assisted with polyelectroyte, which molecular weight is 15,000, was possible in the wide range of R=0.1–1.0. The 5–10 nm sized Cu-Ag nanopaticles were produced in case of the slow adding of reducing agent. The maximum concentration of batch-synthesized Cu-Ag nanoparticles was up to 30 wt%.

4. Acknowledgements

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5. References

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