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Preparation of Silver Nanoparticle with Different Particle Sizes for Low-Temperature Sintering

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***Abstract*—In this study, silver nanoparticles were synthesized by chemical reduction from silver nitrate using different organic compounds as the protecting agent and organic bases as the reaction promoter. The average sizes of the resulting silver nanoparticles were between 3 to 15 nm depending on the type of the protecting agent, which allowed low-temperature sintering of the metal. These suspensions of silver nanoparticles prepared by this method are free from any metal ion contamination and are suitable for use in semiconductor industry. The suspensions will be used to make micro-interconnects in integrated circuits (IC) devices by inkjet printing.**

Keywords-Silver; Nanoparticles; Suspensions

I. INTRODUCTION

In recent years, metallic nanoparticles have drawn a lot of attention due to their unusual physical and chemical properties, which largely differ from their bulk properties [1, 2]. They shows unique properties such as excellent conductivity, chemical stability, and catalytic activity, etc. which are dependent on the particle size, size distribution and shape [3-5]. Among all metals, silver has the highest electrical and thermal conductivity. Silver materials with zero-, one-, or two-dimensional nanostructures such as nanoparticles, nanowires, and nanocubes are believed to have great potential for applications in optics, catalysis, and other fields [6-9]. In the characteristic of silver material, the low sintering temperature of silver nanoparticles is important in flexible electronic applications [10,11].

In previous literature, to prepare silver nanoparticles suspensions by the chemical reduction method, a protecting agent needs to be added, such as long-chain thiol, long-chain amines, carboxylic compounds, poly(vinyl pyrrolidone) [12-14], etc. In addition, reagents such as formaldehyde, glycol ethylene, NaBH4 etc., are usually needed to be the reducing agent [15-17]. In this research, we use different organic compounds as the protecting agent and organic bases as the reaction promoter to prepare contamination-free suspensions of silver nanoparticles with different particle sizes for ink jet printing application.

II. EXPERIMENTAL

A. Materials

Silver nitrate ($AgNO_3$) was obtained from Showa Chemical Co. Triethylamine (TEA) were purchased from Tedia Company Inc. Alpha-Terpineol was obtained from J. T. Baker. Formaldehyde (HCHO, 37 wt. % in water) was purchased from Tedia Company Inc. Thiosalicylic acid (TSA) was obtained from Acros Organic. Poly(N-vinyl-2-pyrrolidone (PVP) (molecular weight ~10,000) was obtained frrom ICN Biomedical Inc.

B. Preparation of silver nanoparticles suspensions

The $AgNO_3$ was dissolved in de-ionized water in a beaker. To this solution, a protecting agent〔poly(N-vinyl-2-pyrrolidone or thiosalicylic acid or triethylamine〕was added. After being stirred, HCHO solution was then added to the solution. Subsequently, a promoter (triethylamine or pyridine) was added drop wise. The color of the solution turned from clear to black. After being stirred for 200 min at room temperature, the precipitates were washed several times with ethanol, followed by centrifugation (6000 rpm, 10 min), to remove unbounded TEA. The particles were then dried at room temperature under vacuum for 24 h. The silver nanoparticles suspensions were prepared from the dried silver nanoparticles by re-dispersing them into alpha-terpineol.

C. Characterization

The transmission electron microscopy (TEM) images of silver nanoparticles were obtained with a JEOL JEM-1200EX transmission electron microscope operating at 120 KV with an Energy Dispersive Spectrometer (EDS). The X-ray diffraction (XRD) experiment was conducted on a Rigaku D/MAX-IIIV X-ray Diffractometer using Ni-filtered Cu-Kα radiation with a scanning rate of 4° min−1 at 30 kV and 20 mA. The weight loss of the silver films was analyzed using a TA Instrument Thermogravimetric Analyzer (TGA) 2050 at a heating rate of 10 ^{o}C/min under air. The UV-visible spectra of the silver nanoparticle suspensions were obtained on a Hitachi U-2001 UV-VIS spectrophotometer.

III. RESULTS AND DISCUSSION

A. *Poly(N-vinyl-2-pyrrolidone) stabilized silver nanoparticles*

According to literature, the reduction reaction of $AgNO_3$ by formaldehyde is slow without the addition of basic catalysts. A higher pH is favored for higher reducing power. In order to avoid the use of inorganic bases as the reaction promoter, which usually contains other unwanted metal ions, we chose organic bases, triethylamine or pyridine as the reaction promoter. These bases are easy to be washed out after reaction and will not contaminate the resulting silver nanoparticles. In our process, all reagents are organic materials except the $AgNO_3$ precursor. The final product is only pure silver nanoparticles without other metal ion impurities, so the silver nanoparticles product is suitable to use in IC devices. As shown in Fig. 1(a) shows the silver nanoparticles prepared from pyridine. The viscosity of the dispersion was 1.25 cps and the particles sizes were around 10-20 nm. Fig. 1(b) is the EDS pattern of the silver particles. Fig. 1(c) show the UV-Vis absorption spectra of silver nanoparticles prepared from pyridine with different concentrations of $AgNO_3$. They have the characteristic absorption bands with maxima at 420-430 nm. That could be due to the increase of polydispersity of particle sizes in higher concentration of the reagents. The X-ray diffraction patterns of the silver nanoparticles, presented in Fig. 1(d), show the peak characteristics of metallic silver. The reflection peaks are indexed as the fcc (111), (200), (220), and (311) planes, indicating that the silver is well crystallized.

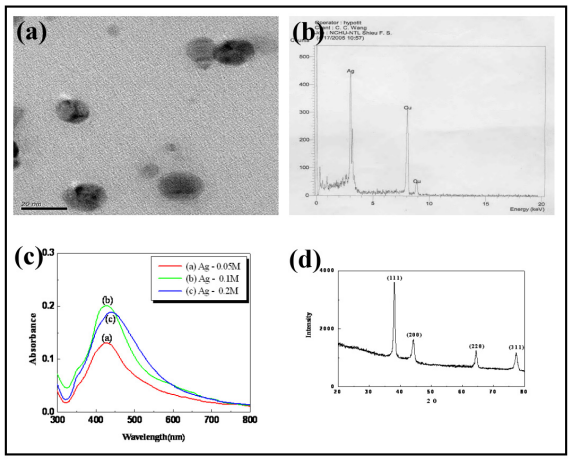

Figure 1. (a) TEM micrographs of silver nanoparticles prepared from PVP (b) EDS pattern (c) UV pattern (d) XRD pattern.

B. *Thiosalicylic acid stabilized silver nanoparticles*

The low molecular weight organic compound, thiosalicylic acid (TSA), was also used as a protecting agent to prepare the nanoparticles in order to reduce the sintering temperature. As shown in Figure 2(a), when we used triethylamine as the reaction promoter and TSA as the protecting agent, the silver nanoparticles were successfully reduced from the $AgNO_3$ precursor. The EDS analysis shown in Figure 2(b) confirms that the particles are silver. Figure 2(c) presents the particle size distribution of silver nanoparticles. The average size of the particles is 7.99 nm with a standard deviation of 2.24 nm, which was calculated by Matrox Inspector 4.1 software from Figure 2 (a).

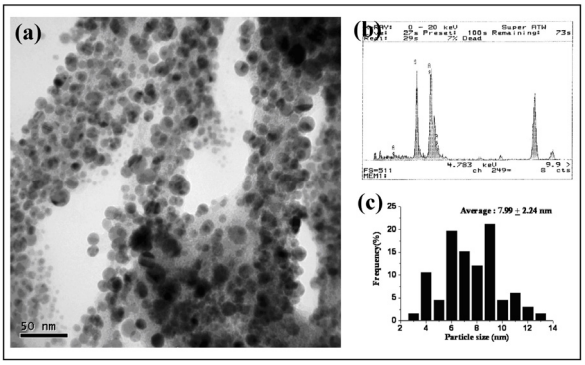

Figure 2. (a) TEM micrographs of silver nanoparticles prepared from TSA (b) EDS pattern (c) Particle size distribution of silver nanoparticles

Fig. 3 shows the thermograms of pure TSA, TSA protected silver nanoparticles and PVP protected silver nanoparticles. From the TGA thermogram, we can see the decomposition temperature of pure TSA is at 150 ^oC. When the TSA is bounded to silver nanoparticles, its decomposition temperature increased to 280 ^oC. Although its decomposition temperature increases, it is much lower than PVP (at 450 ^oC), which was used in our previous experiment. We anticipated that TSA-protected silver nanoparticles could be sintered at lower temperatures than PVP-protected silver nanoparticles.

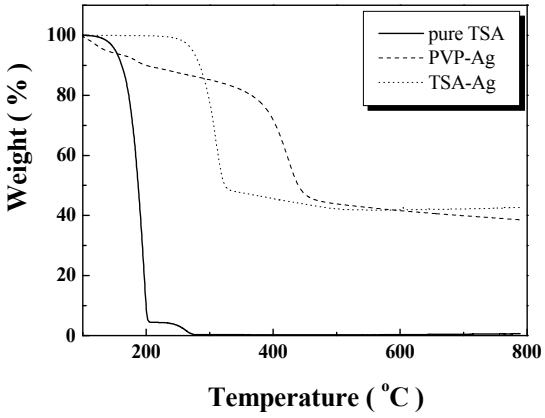

Figure 3. TGA thermograms of pure TSA, silver nanoparticles prepared from TSA , and silver nanoparticles prepared from PVP .

C. *triethylamine stabilized silver nanoparticles*

During the preparation of Ag nanoparticle suspensions, the individual particles had a tendency to form large agglomerates through the van der Waals force or Coulomb's

force. In order to prevent the agglomeration of small particles, we added TEA to the suspensions as the stabilizer. The amine group can form a protective monolayer on the particle's surface through the Ag-N bonding. The TEA has a dual function in the experiment. It can be served as a protecting agent and also a reducing agent.When we used the TEA as the reducing and protecting agent, the silver nanoparticles were successfully reduced from the $AgNO_3$ precursor. For TEA-protected silver nanoparticles, the agglomeration of small particles increased with the increasing TEA concentrations.

Fig. 4 shows a typical TEM image of the silver nanoparticles, the histogram of diameters, and EDS. The silver diffraction pattern is shown at right corner in Fig. 4(a). The EDS analysis (in Fig. 4(c)) confirms that the nanoparticles are silver. We were able to control the particle size and the size distribution of silver nanoparticles from the $AgNO_3$/TEA molar ratio, and produce silver nanoparticles less than 5 nm in diameter.

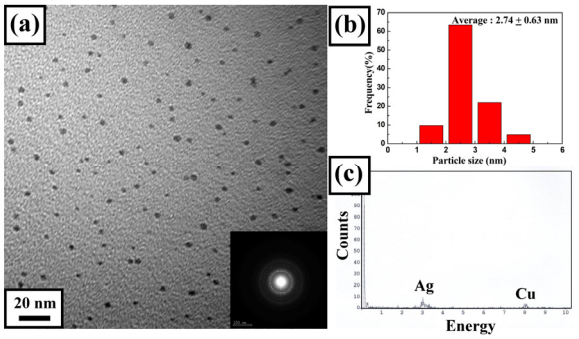

Figure 4. (a) TEM micrographs of silver nanoparticles prepared from TEA (b) Particle size distribution of silver nanoparticles (c) EDS pattern .

The UV–Vis absorption spectra of silver nanoparticles prepared from TEA with different molar ratios are shown in Fig. 5. For Fig. 5(a), the absorption peak with the maxima at 402 nm is due to the presence of silver nanoparticles. The X-ray diffraction patterns of the silver films, presented in Fig. 5(b), show the peak characteristics of metallic silver. The reflection peaks are indexed as the fcc (111), (200), (220), and (311) planes, indicating that the silver is well crystallized. From the TGA thermogram, we can see that the decomposition temperature of the TEA-protected silver nanoparticles is at 150 ^{o}C (as shown in Fig. 5(c)). In addition, TGA was used to analyze the amount of TEA bounded on the particles. The as-made silver nanoparticles contain about 10 % TEA. From the result, we are sure that the silver nanoparticles can be sintered and converted to the silver film at a low processing temperature and low protecting agent content.

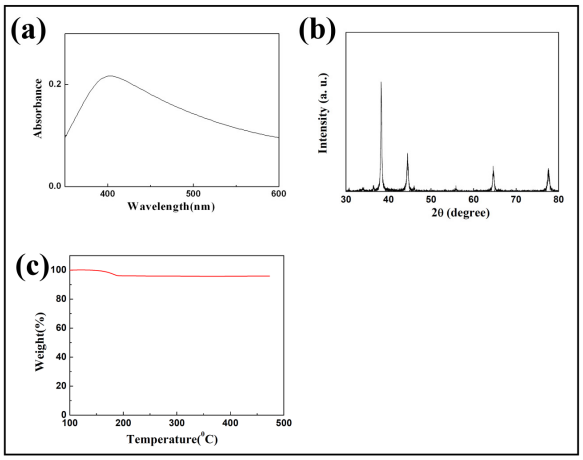

Figure 5. (a)UV-Vis absorption spectra of silver nanoparticles suspension prepared from different AgNO3/TEA ratios (b) XRD (c) TGA

IV. Conclusions

Using PVP, TSA and TEA as the protecting agents, we successfully prepared stable silver nanoparticles suspensions. The average diameters of the nanoparticles were 15 nm, 7.99 nm, and 2.74 nm, when the protect agents were PVP, TSA and TEA, respectively. The resulting silver nanoparticles showed high crystallinity. The silver nanoparticle can be used to fabricate flexible electronics by ink-jet printing, because they have relatively low sintering temperatures.

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References

[1] J. M.Kohlera, L. Abahmanea, J. Wagnera, J. Albertb and G. Mayerb, "Preparation of metal nanoparticles with varied composition for catalytical applications in microreactors"Chemical Engineering Science vol. 63, 2008, pp. 5048-5055.

[2] J. Perelaer, A. W. M. de Laat, C. E. Hendriks and U. S. Schubert, "Inkjet-printed silver tracks: low temperature curing and thermal stability investigation" J. Mater. Chem. Vol 18, 2008, pp. 3209-3215.

[3] D. Kim, S. Jeong and J. Moon, "Synthesis of silver nanoparticles using the polyol process and the influence of precursor injection" Nanotechnology vol 17, 2006, pp.4019-4024.

[4] R. Zhang, K. S. Moon, W. Lin and C. P. Wong, "Preparation of highly conductive polymer nanocomposites by low temperature sintering of silver nanoparticles" J. Mater. Chem. vol 20, 2010, pp.2018-2023.

[5] Y. Xiong, A. R. Siekkinen, J. Wang, Y. Yin, M. J. Kimb and Y. Xia, "Synthesis of silver nanoplates at high yields by slowing down the polyol reduction of silver nitrate with polyacrylamide" J. Mater. Chem. vol 17, 2007, pp.2600-2602.

[6] D. G. Thompson, R. J. Stokes, R. W. Martin, P. J. Lundahl, K. Faulds and D. Graham, "Synthesis of Unique Nanostructures with Novel Optical Properties Using Oligonucleotide Mixed–Metal Nanoparticle Conjugates" small vol 4, 2008, pp. 1054-1057.

[7] N. Pradhan, A. Pal and T. Pal, “Silver nanoparticle catalyzed reduction of aromatic nitro compounds” Colloids and Surfaces A: Physicochemical and Engineering Aspects vol 196, 2002, pp.247-257.

[8] B. Y. Ahn, E. B. Duoss, M. J. Motala, X. Guo,S. I. Park, Y. Xiong, J. Yoon, R. G. Nuzzo, J. A. Rogers and J. A. Lewis “3Omnidirectional Printing of Flexible, Stretchable, and Spanning Silver Microelectrodes” Science vol 23, 2009, pp.1590-1593.

[9] T. Takenobu, N. Miura, S. Y. Lu, H. Okimoto, T. Asano, M. Shiraishi and Y. Iwasa, “Ink-Jet Printing of Carbon Nanotube Thin-Film Transistors on Flexible Plastic Substrates” Applied Physics Express vol 2, 2009, pp.0250051-.0250053.

[10] J. Perelaer, C. E. Hendriks, A. W. M. de Laat and U. S. Schubert, “One-step inkjet printing of conductive silver tracks on polymer substrates” Nanotechnology vol 20, 2009, 1653031-1653035.

[11] T. H. J. van Osch, J. Perelaer, A. W. M. de Laat and U. S. Schubert, “Inkjet Printing of Narrow Conductive Tracks on Untreated Polymeric Substrates”Adv. Mater. vol 20, 2008, pp.343-345.

[12] C. Jiang, D. J. Cardin and S. C. Tsang, “Conductive Three-Dimensional Material Assembled from Silver Nanoparticles Using a Conjugated Dithiol Linker” Chem. Mater. vol 20, 2008, pp.14-16.

[13] I. K. Shim, Y. I. Lee, K. J. Lee and J. Joung, “An organometallic route to highly monodispersed silver nanoparticles and their application to ink-jet printing” Materials Chemistry and Physics vol 110, 2008, pp.316-321.

[14] X. Wang, S. Zhang and Z. Zhang, “Synthesis of hexagonal nanosized silver sulfide at room temperature” Materials Chemistry and Physics vol 107, 2008, pp.9-12.

[15] A. Wang, H. Yin, M. Ren, Y. Liu and T. Jiang, “Synergistic effect of silver seeds and organic modifiers on the morphology evolution mechanism of silver nanoparticles” Applied Surface Science vol 254, 2008, pp.6527-6536.

[16] M. Tsuji, P. Jiang, S. Hikino, S. Lima, R. Yano, S. M. Jang, S. H. Yoon, N. Ishigami, X. Tang and K. S. Nor Kamarudin, “Toward to branched platinum nanoparticles by polyol reduction: A role of poly(vinylpyrrolidone) molecules” Colloids and Surfaces A: Physicochem. Eng. Aspects vol 317, 2008, pp.23-31.

[17] L. Li, Y. J. Zhu, Journal of Colloid and Interface Science vol 303, 2006, pp.415-418.