

Fabrication of Oxide Nanocrystals Dispersed in a Polyimide Film

Young-Ho Kim*

Division of Materials Science and Engineering, College of Engineering, Hanyang University,
17 Haengdang-dong, Seongdong-Ku, Seoul 133-791, Korea

A simple and economical method to fabricate metal-oxide nanocrystals in the polyimide film was developed from a reaction of polyamic acid with metal films and subsequent curing. This paper reviews the formation of nanocrystals and describes the effects of curing conditions. Curing time, curing temperature, curing atmosphere, and polyimide type all influenced the size, density, and distribution of nanocrystals.

Keywords: nanoparticles, Cu₂O, ZnO, polyimide, Imidization, curing, nanocrystals

1. INTRODUCTION

Recently, nanoparticles dispersed in dielectric films have attracted much attention because their novel electrical and optical properties could be the basis for applications in photonic and electronic devices^[1,2]. Many studies on the synthesis of nanoparticles have been conducted by using precursors from a liquid, solid, or gas phase and by employing chemical or physical deposition approaches^[3]. Gas-aerosol reactive electrostatic deposition has been applied to produce nanoparticles embedded in a polyvinyl alcohol film^[4]. In addition, colloid solution methods have been reported, and the obtained nanoparticles can be uniformly dispersed in solution with a relatively narrow size distribution. However, there are some problems involving the difficulty of mass production and the removal of by-products (metal ions or residual organic solvent or both)^[5,6]. In contrast, vapor synthesis methods, the majority of which utilize the condensation of atomic metal vapor into an inert gas, have an advantage in that they can produce stable particle dispersions without employing stabilizing agents, such as ions, polymers, or surfactants, which are usually used with a liquid phase reduction method^[7]. However, this process is comparatively complex and is sometimes difficult to control.

Previously, ultra-small Cu₂O particles were observed at the polyimide (PI)/Cu interface during fabrication of thin film multichip modules for electronic packaging^[8]. These Cu₂O particles were formed in the PI layer while polyamic acid (PAA) that was spin-coated on the Cu layer was cured to create a PI insulation layer on top of Cu. Recently, it has been observed that this phenomenon could be applied to syn-

thesize well-crystallized Cu oxide nanoparticles dispersed in the PI film^[9]. Accordingly, Cu₂O particles were formed from the reaction of PAA with metal films and subsequent curing. This is a simple and economical method of fabricating metal-oxide. In this paper, the formation of nanoparticles in polyimide films is reviewed and the factors that influenced the nanoparticle formation are also discussed.

2. FABRICATION METHOD

The substrates used in this study were bare Si, oxidized Si, glass, and fused quartz substrates. Cu or Zn thin films were deposited on the various substrates by thermal evaporation or DC magnetron sputtering. The PAA in N-methyl-2-pyrrolidone (NMP) was spin-coated onto Cu or Zn films. The final thickness of the PI layer was controlled by adjusting the concentration of the polyamic acid in the solvent. The PI precursor was subsequently treated at 135 °C for 30 min to evaporate the solvent. The PAA/thin film metal stacks were cured at 200 °C -400 °C in various environments. The curing temperature depended on the PI types. A schematic diagram of nanoparticle formation is given in Fig. 1.

3. NANOPARTICLE FORMATION MECHANISM AND THE IDENTIFICATION OF NANOPARTICLES

During curing, PAA will dehydrate and imidize, forming PI. Figure 2(a) shows the imidization process, in which biphenyltetracarboxylic dianhydride-p-phenylenediamine (BPDA-PDA) type PAA was transformed to PI during curing. When the PAA is in contact with metal films, PAA easily reacts with Cu to form a Cu complex, since PAA is a strong acid^[8]. Reaction with NMP demonstrated that the sol-

*Corresponding author: kimyh@hanyang.ac.kr

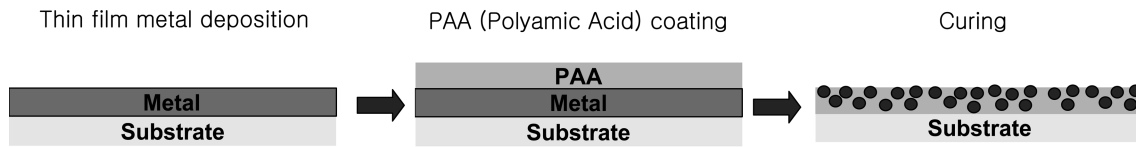


Fig. 1. Schematic diagram showing nanoparticle formation.

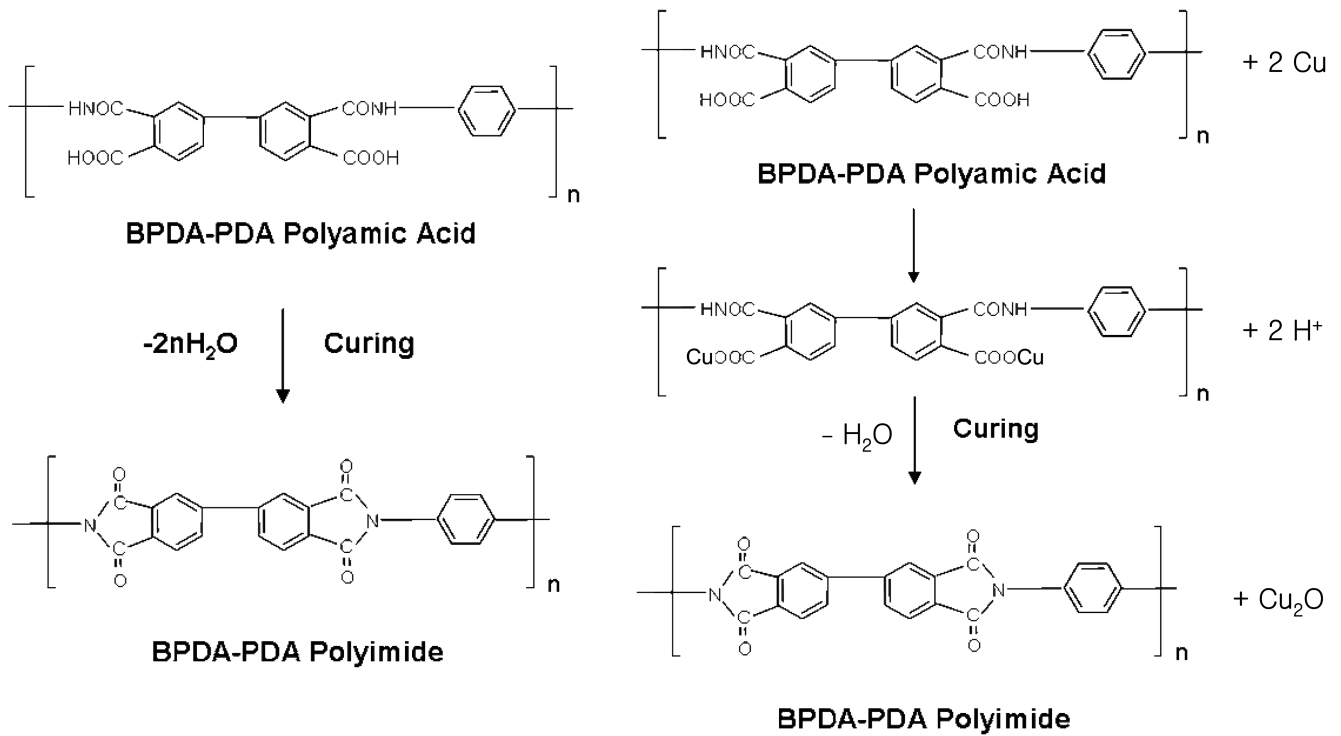


Fig. 2. Chemical structure showing transformation of a BPDA-PDA type PAA to a PI. (a) pure PAA (b) PAA reacted with Cu.

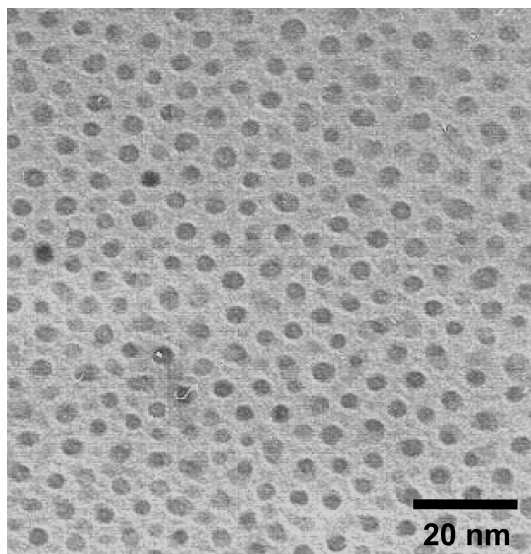


Fig. 3. Plane-view TEM image of nanoparticles in the PI. Nanoparticles were fabricated by curing a PAA/Cu(10 nm)/SiO₂/Si stack at 350 °C for 2 hours.

vent provided the mobility for the copper oxide particles to diffuse and aggregate^[10]. As shown in Fig. 2(b), during the curing process of the PAA containing the Cu complex, the PAA-Cu salt will dehydrate and imidize, forming PI, accompanied by precipitation of Cu₂O particles^[8,9]. Figure 3 shows a typical example of nanoparticles in a PI film where the PI film was fabricated by curing a PAA/Cu(10 nm)/SiO₂/Si stack at 350 °C for 2 hours. The curing was carried out in a flowing nitrogen atmosphere. These nanoparticles were identified as cubic Cu₂O. The synthesized Cu₂O particles had the relatively narrow distribution and high density. Their average particle size was 4.3 nm in diameter.

4. THE EFFECTS OF CURING TIME AND TEMPERATURE

As the PAA was cured at higher temperatures and longer times, the degree of imidization increased. Since Cu₂O nanoparticles precipitate as the imidization proceeds, more nanoparticles will form with increasing curing times and

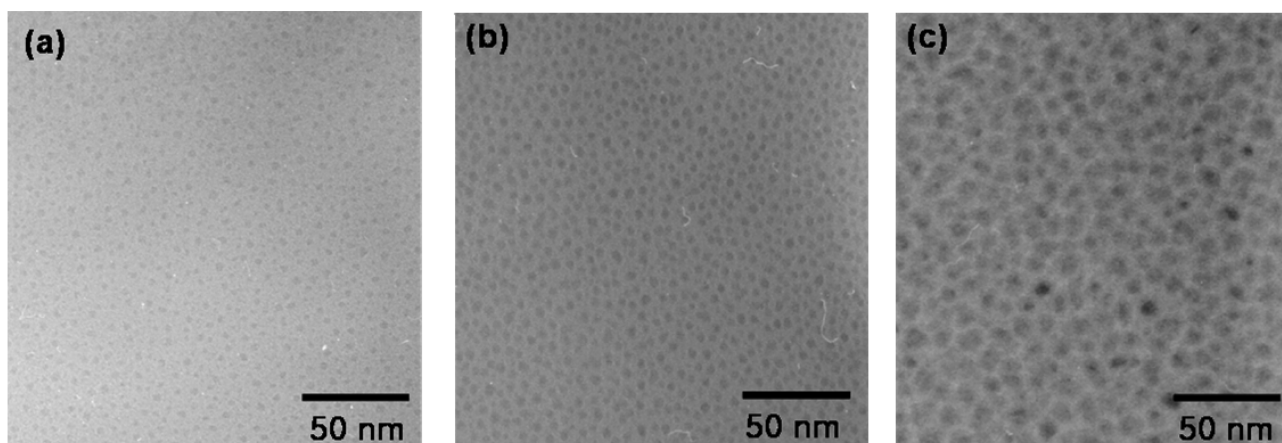


Fig. 4. Plane-view TEM images of Cu_2O nanoparticles in BPDA-PDA type PI films cured at $350\text{ }^\circ\text{C}$ with different curing times in a nitrogen atmosphere: (a) 1 hour, (b) 2 hours, and (c) 4 hours.

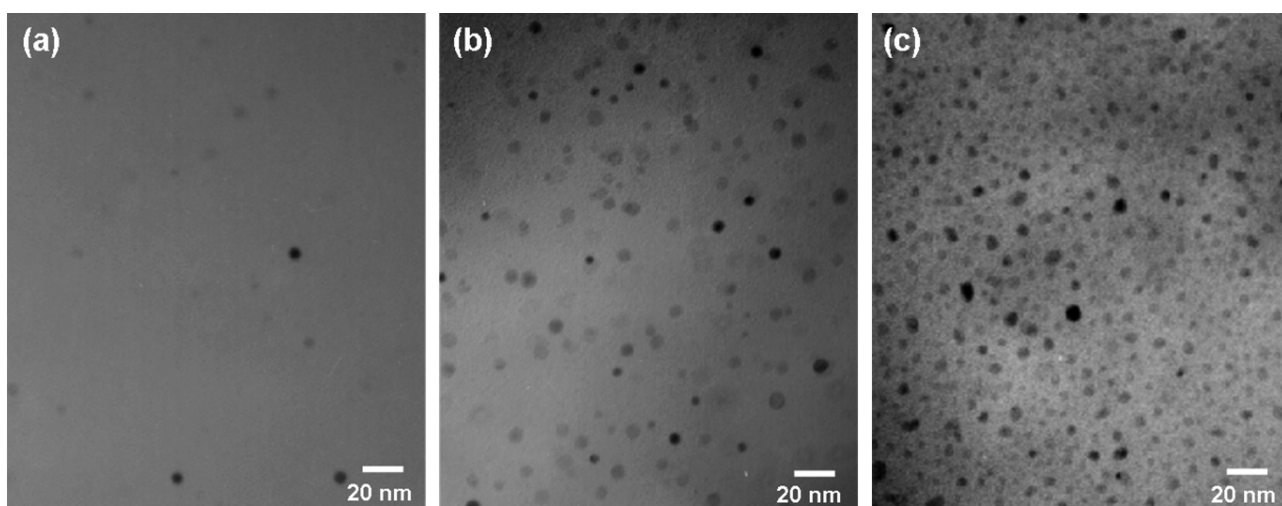


Fig. 5. Plane-view TEM images of ZnO nanoparticles in BPDA-PDA type PI films cured at $350\text{ }^\circ\text{C}$ with different curing times in a nitrogen atmosphere: (a) 1 hour, (b) 2 hours, and (c) 4 hours.

temperatures. Figures 4 and 5 show the effects of the holding time during the curing of BPDA-PDA type PAA^[11]. Figure 4 shows bright field TEM images of the nanoparticles formed by curing PAA/Cu stacks for 1 to 4 hours in a nitrogen atmosphere. The nanoparticles in all specimens were characterized to be cubic Cu_2O via selected electron diffraction pattern analysis. The size of the Cu oxide nanoparticles was about 3.4 nm, 4.1 nm, and 9 nm in the specimens cured at $350\text{ }^\circ\text{C}$ for 1 hour, 2 hours, and 4 hours, respectively. Figure 5 shows bright field TEM images of nanoparticles dispersed in BPDA-PDA type PI after curing PAA/Zn stacks at $350\text{ }^\circ\text{C}$ for 1, 2, and 4 hours in a nitrogen atmosphere^[12]. A selected-area electron diffraction pattern analysis indicated the ZnO nanoparticles had a hexagonal crystal structure in all specimens. Nano-sized particles were formed and were randomly distributed in the PI film. When the specimen was cured at $350\text{ }^\circ\text{C}$ for 1 hour, particles were rarely observed; however,

particle size and density increased as curing time increased from 1 hour. The Zn oxide nanoparticles cured at $350\text{ }^\circ\text{C}$ for 1, 2, and 4 hours were about 4 nm, 4.3 nm, and 5.6 nm in diameter, respectively. Nanoparticles, as seen in Fig. 4(c) and Fig. 5(c) formed with very high density in the PI. When the curing time increased, a coalescence of particles also occurred reducing the surface energy. A similar effect was observed when the curing temperature was increased; more nanoparticles formed and the nanoparticles became larger at the higher curing temperatures^[13,14].

Meanwhile, it was possible to limit the particle size to a nanometer scale because formation of the oxide particles proceeded essentially at a molecular level. Another contributing factor for obtaining the fine particles was that the surrounding polymer material, which retarded the migration of materials, suppressed the ripening of the oxide particles.

Temperature-increasing processes, for example, dimpling

and ion-milling are necessary for TEM specimen preparation. Such TEM sample preparation methods may affect the particle formation. Therefore, a Si_3N_4 TEM mask was used

to characterize the particle formation since particles formed in the PI on a Si_3N_4 TEM mask can be directly observed without further treatments. However, the results of the parti-

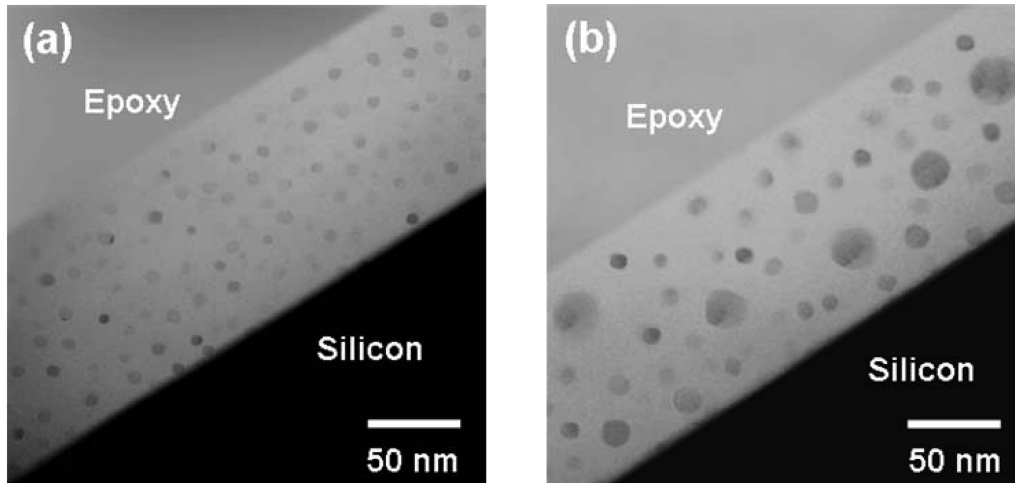


Fig. 6. Cross-sectional TEM images of ZnO nanoparticles in BPDA-PDA type PI films with cured at 350 °C for 4 hours in (a) a nitrogen atmosphere and in (b) a vacuum atmosphere.

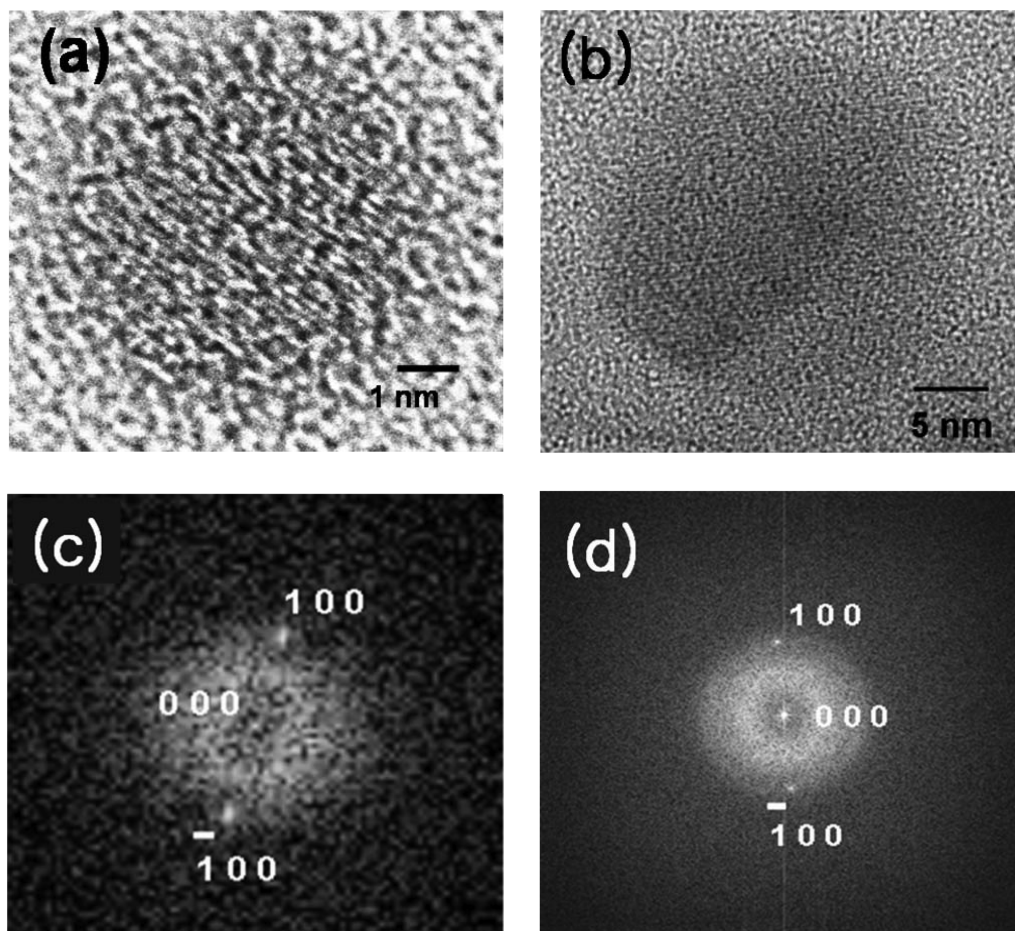


Fig. 7. High-resolution TEM images and corresponding Fourier transformation images of ZnO nanoparticles in BPDA-PDA type PI films cured at 350 °C for 4 hours in a nitrogen atmosphere [(a) and (c)] and in a vacuum [(b) and (d)].

cle formation on the TEM mask were similar to those of specimens prepared by using Si substrates^[15].

5. THE EFFECT OF CURING ATMOSPHERE

The curing atmosphere also influenced particle formation. Figure 6 shows cross-sectional TEM images of BPDA-PDA/Zn stacked films that were cured at 350 °C for 4 hours (a) in a nitrogen atmosphere and (b) in a vacuum^[12]. ZnO nanoparticles were randomly distributed in the 110 nm thick PI layer in both cases. However, the size and distribution of the nanoparticles cured in a vacuum were different from those cured in a nitrogen atmosphere. The particle size was relatively uniform in the specimens that were cured in a nitrogen atmosphere. In contrast, with the vacuum-cured specimens, a bimodal distribution of particles, with relatively large and fine particles, was observed. The average size of the particles in the specimen cured in vacuum was larger than that of the particles cured in N₂. The imidization degree was affected by the curing environment^[16,17]. The evaporation rate of solvent and the reaction by-product, water vapor can be changed with a change in curing conditions. These effects will subsequently influence the particle formation. The size and the density of particles shown in the cross-sectional image in Fig. 6(a) were similar to those of the plane-view results in Fig. 5(c).

High-resolution lattice images of the ZnO nanoparticles obtained in the specimens cured at 350 °C for 4 hours in a nitrogen atmosphere and in a vacuum are presented in Fig. 7. Lattice fringes attest that the particles were well crystallized. Single patterns of lattice image in a single particle (Fig. 7(a) and (c)) and the corresponding Fourier transformation results (Fig. 7(b) and (d)) prove that the particles are indeed single crystals (nanocrystals) containing no other secondary structures or grain boundaries.

6. NANOPARTICLE FORMATION IN DIFFERENT PI FILMS

Figure 8 shows a TEM image of nanoparticles formed inside the oxydiphthalic dianhydride 3-sulfur dianhydride (ODPA-3SDA) type PI film^[12]. The nanoparticles formed by curing a PAA/Zn stack at 250 °C for 1 hour in a nitrogen atmosphere. It was observed that relatively small ZnO nanoparticles were formed and that the average size of particles was about 4.8 nm. The crystal structures of particles were also identified as hexagonal ZnO. Our mechanism for the formation of nanoparticles in a BPDA-PDA type PI seems to have operated in this PI.

7. SUMMARY

We have shown that nanocrystals can be easily fabricated

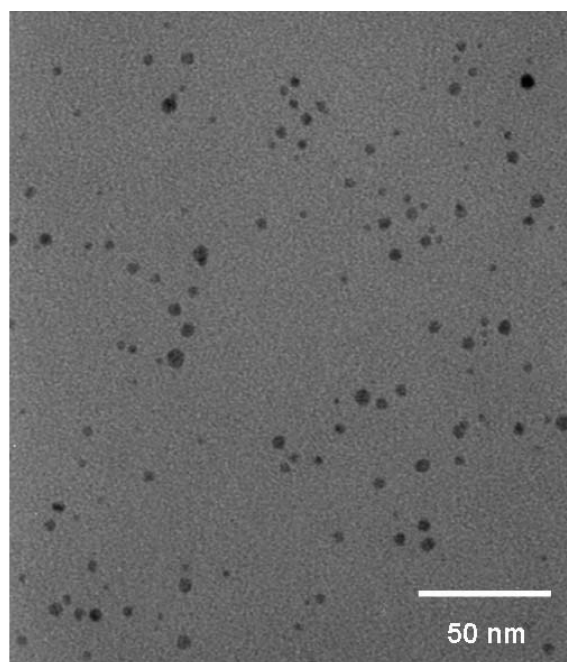


Fig. 8. A plane-view TEM image of Zn oxides in ODPA-3SDA type PI films cured at 250 °C for 1 hour.

from a reaction of a PAA with thin film metals and a subsequent curing process. We observed that oxide particle formation was sensitive to curing conditions. Increasing the curing time and the temperature increased the particle size and decreased the particle density. The curing atmosphere and polyimide type also influenced the particle formation. The final particle size and volume fraction of the particles are strongly related to curing conditions.

ACKNOWLEDGEMENTS

This research was supported by a grant (code #: 05K1501-02510) from the Center for Nanostructured Materials Technology under the 21st Century Frontier R&D Programs of the Ministry of Science and Technology, Korea. The author would also like to thank the graduate students in the electronic packaging Laboratory at Hanyang University for their contributions to this research.

REFERENCES

1. W. J. Parak, L. Manna, F. C. Simmel, D. Gerion, and P. Alivisatos, *Nanoparticles* (ed. G. Schmid), p. 4-49, Wiley-VCH, Weinheim (2004).
2. K. Akamatsu and S. Deki, *Scripta Mater.* **44**, 2149 (2001).
3. M. Tanaka, S. Sawai, M. Sengoku, M. Kato, and Y. Masumoto, *J. Appl. Phys.* **87**, 8535 (2000).
4. O.V. Salata, P. J. Dopson, P. J. Hull, and J. L. Hutchison, *Thin Solid Film*, **251**, 1 (1994).

5. Thierry Cassagneau and Janos H. Fendler, *J. Phys. Chem. B.*, **103**, 1789 (1999).
6. S. Banerjee and D. Chakaravorty, *J. Appl. Phys.* **87**, 8541 (2000).
7. P. Taneja, R. Chandra, R. Banerjee, and P. Ayyuub, *Scripta mater.* **44**, 1915 (2001).
8. Y.-H. Kim, G. F. Walker, J. Kim, and J. Park, *J. Adhesion Sci. Tech.* **1**, 331 (1987).
9. Y. Chung, H. P. Park, H. J. Jeon, C. S. Yoon, S. K. Lim, and Y. -H. Kim, *J. Vac. Sci. Technol. B* **21**, L9-L11 (2003).
10. S. P. Kowalczyk, Y.-H. Kim, G. F. Walker, and J. Kim, *Appl. Phys. Lett.* **52**, 375 (1988).
11. M. S. Song, C. S. Yoon, and Y.-H. Kim, *Mater. Sci. Forum*, **475-479**, 3335 (2005).
12. H. G. Roh, G. H. Kim, and Y. -H. Kim, *High performance polymers* (submitted).
13. H. P. Park, C. Yoon, C. S. Yoon, S. S. Jo, and Y. -H. Kim, *Mater. Sci. Forum*, **449**, 1237 (2004).
14. H. J. Jeon, Y. Chung, C. S. Yoon, and Y.-H. Kim, *Mater. Sci. Forum.* **449**, 1145 (2004).
15. M. S. Song, *Ms. Thesis*, Hanyang University, Seoul (2005).
16. S. K. Lim, C. S. Yoon, C. K. Kim, and Y. H. Kim, *J. Phys. Chem.* **108**, 18179 (2004).
17. S. K. Lim, Ik S. Chun, Ki S. Ban, Chong S. Yoon, Chang K. Kim, and Young H. Kim, *J. Colloid and Interface Sci.* **295**, 108 (2006).