Effects of silver nanowire concentration on resistivity and flexibility in hybrid conducting films

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Silver nanowires (AgNWs) are attracting much attention for their potential use in flexible or stretchable conducting film applications and in printed and wearable electronics devices. In this study, we fabricated flexible hybrid conducting films using different concentrations of composite silver ink prepared by mixing AgNW and silver nanoparticle (AgNP) materials, which we synthesized, for flexible interconnects and electrodes. These films had low resistivities at low sintering temperatures. Furthermore, they were also stable to tensile bending in comparison with a pure AgNP film. We found that there is an optimum concentration of AgNWs in the composite silver ink for the hybrid conducting film to have a lower resistivity even with sintering below 100 °C. We also found that the reason why hybrid conducting films are stable to repeated tensile bending is that AgNWs maintain functional conducting paths by making bridges that compensate for cracks between AgNPs during film bending.

1. Introduction

Recently, printed electronics or flexible electronics technologies have been attracting interest for use in electronic devices with organic transistors, which can be used to create novel products such as bendable, rollable or wearable devices via printing techniques at near-room temperature. In these technologies, regardless of whether organic or inorganic functional material (such as semiconductors or metals) is used, it is very important that functional materials can express their function after printing and sintering, as well as after repeated bending or stretching, and exhibit film adhesion without peeling or cracking. Therefore, flexible or stretchable conductive materials have been developed because metal materials are not stable and cracks or peeling appear after bending or stretching. For use as flexible or stretchable conductive materials, metal mesh, conductive rubber, or reduced graphene oxide materials have been studied. Accordingly, various flexible and stretchable devices have been fabricated using these materials.

Among such prior studies, silver nanowires (AgNWs) have received significant attention for use in printed electronics as a potentially flexible and stretchable material. AgNWs can be dispersed in water and mix readily with other materials to produce a composite material that leverages its advantages and minimizes its disadvantages. In this study, we focused on a composite material with AgNWs and silver nanoparticles (AgNPs) as a flexible conductive material for fabricating wearable devices, because hybrid conducting films made with the composite silver ink are expected to improve the stability to bending owing to the flexibility of AgNWs.

We synthesized AgNWs and AgNPs by the polyol synthesis method and made composite silver ink of different concentrations by mixing the two. A notable feature is that they are synthesized by the same method and can easily be mixed in the same solvent. We fabricated flexible hybrid conducting films on poly(ethylene naphthalate) (PEN) substrates using the composite silver ink.

As a result, we were able to fabricate hybrid conducting films that had low resistivity by thermal sintering at a low temperature and were stable to tensile bending. The resistivity of the hybrid conducting films was lower than that obtained in previous studies in which metal films were fabricated by the same synthesis methods. We have also assessed the mechanisms of how AgNWs minimize the change in resistivity depending on the bending radius. These results are expected to facilitate the design of hybrid conducting films through the use of composite ink of mixed AgNPs and AgNWs for printed flexible electronic applications.

2. Materials and methods

2.1 Synthesis of composite ink and fabrication of hybrid conducting films

AgNW and AgNP materials were synthesized by polyol synthesis. AgNWs were about 100 nm in diameter and 30 ± 10 µm in length, and AgNPs were about 80 nm in diameter. Composite ink of different concentrations was prepared by mixing AgNWs and AgNPs in 2-propanol (IPA). AgNWs were dispersed uniformly within the AgNPs.

The concentration of AgNPs in the composite silver ink was fixed at 15 wt% and the composite ink was mixed at various AgNW concentrations corresponding to 0, 0.5, 1.0, and 1.5 wt%. Flexible hybrid conducting films were prepared by bar coating on a PEN substrate and sintered at 80, 100, 120, and 150 °C. Pure AgNP films (AgNW concentration of 0 wt%) and pure AgNW films were prepared by the same method for comparison. The AgNP films were sintered at 120, 130, 140, 150, and 200 °C and the AgNW films were sintered at 80, 100, 120, and 150 °C. All conducting films were sintered with a hot plate for 60 min.

In these methods, we measured the AgNW and AgNP concentrations in ink by thermogravimetric analysis (TA Instruments SDT Q600). We used a bar coater (Dai-ichi Rika Wire No. 9) to make conducting layers on PEN substrates. We can make wet layers of 20 µm thickness using this bar coater. All conducting layers were around 240 nm in thickness after sintering. The surfaces of all films had a silvery luster like a mirror. With increasing AgNW concentration, the surfaces of the films became slightly tarnished with white turbidity, like a fogged mirror.

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2.2 Hybrid conducting film resistivity measurements

We first measured the resistivities of pure AgNP films, AgNW films, and hybrid conducting films as a function of sintering temperature. We then measured the dependence of resistivity on the bending radius and the number of bending cycles for the hybrid conducting films and AgNP films, which had a low resistivity owing to sintering at 150 °C. The bending radius was changed from 15 to 3 mm and bending was performed for 100 cycles at a bending radius of 6 mm.

In these measurements, we measured the sheet resistance of conducting films by a four-point probe method with a resistivity processor (NPS Sigma-5+) under a flat condition. The sheet resistance of the films after bending was also measured in the flattened state. The thickness of the conducting layers on the PEN substrate was measured with a laser microscope (Olympus LEXT OLS4100). The resistivities of the conducting layers were obtained by calculating the sheet resistance and layer thickness.

Scanning electron microscope (SEM) images of the surface were taken for all conducting films at each sintering temperature. Furthermore, hybrid conducting films were observed by SEM (Hitachi High-Technologies SU8000) under flat and bending conditions (bending radii of 8 and 4 mm) after 1000 bending cycles.

3. Results and discussion

3.1 Resistivity dependence on sintering temperature and AgNW concentration

We measured the resistivities of pure AgNP films and AgNW films made with AgNP and AgNW ink, respectively. Figure 1 shows the resistivities of AgNP films [Fig. 1(a)] and AgNW films [Fig. 1(b)] as a function of sintering temperature.

Pure AgNP films exhibited extremely low resistivities with sintering temperatures of 150 °C or more (an even lower resistivity of 5.3 μΩ·cm was attained by sintering at 200 °C). All AgNP films required sintering at temperatures higher than 120 °C to be conductive. On the other hand, pure AgNW films exhibited low conductivity without sintering, but the resistivity of these films did not decrease notably even at higher sintering temperatures.

We next explored the effects of AgNW concentration in the hybrid conducting films. Figure 2 shows the change in resistivity as a function of sintering temperature for selected AgNW concentrations. For comparison, the resistivity of pure AgNP films (AgNW concentration of 0 wt%) is shown in the same figure.

The pure AgNP films exhibited conductivity with sintering at 120 °C or higher, but the hybrid conducting films exhibited conductivity without sintering, even with a low AgNW concentration of 0.5 wt%. For higher AgNW concentrations (1.0 and 1.5 wt%), the resistivities were lower near room temperature. However, an optimal AgNW concentration close to 1.5 wt% was observed near room temperature, and the hybrid conducting films with various AgNW concentrations exhibited the same resistivity with sintering at 100 °C or more. Notably, the resistivity obtained by sintering at 150 °C (12.8 μΩ·cm) is lower than that of pure AgNP films sintered at 150 °C (42.8 μΩ·cm). This value is the lowest resistivity obtained in comparison with the reported resistivities for various metal conducting films synthesized by the polyol method.19,24-27)

These results indicate that AgNWs constitute primary conduction paths in the hybrid conducting films, as shown Fig. 3. In conducting films, the cause of resistance is the presence of various defects,30) which, in this case, form a metallic contact area. In pure AgNP films, there are numerous contact areas of AgNPs [Fig. 3(a)]. In hybrid conducting films, if electrons flow mainly through AgNWs, the number of contact areas, as well as resistivity, decreases [Fig. 3(b)].

Fig. 1. (Color online) (a) Resistivities for pure AgNP films as a function of sintering temperature. (b) Resistivities for pure AgNW films as a function of sintering temperature.

Fig. 2. (Color online) Resistivities for hybrid conducting films as a function of sintering temperature.
3.2 Resistivity dependence of bending radius and bending cycles

Next, we explored the effects of bending the hybrid conducting films. Figure 4(a) shows the change in resistivity ratio as a function of bending radius for selected AgNW concentrations. All films were sintered at 150 °C. In Fig. 4, the vertical axis shows the normalized resistivity ratio, since each conducting film had different conductivity values before bending. The resistivity ratio is defined as \( \frac{R_S - R_{S0}}{R_{S0}} \), where \( R_{S0} \) is the initial resistivity before bending and \( R_S \) is the resistivity after bending.

The bending radius was decreased from 15 to 3 mm, and we found that there was little increase in resistivity for radii ranging from 15 to 6 mm. However, the resistivity increased notably for bending radii of around 6 mm or less, regardless of AgNW concentration. In this study, we assumed that the bending radius of 6 mm is the “bending radius limit”.

Figure 4(b) shows the changes in resistivity ratio as a function of the number of bending cycles with the bending radius limit of 6 mm. The resistivity ratios for the hybrid conducting films showed almost no change after 1000 bending cycles, but the resistivity ratio of the pure AgNP film increased gradually.

Figure 5 shows the SEM images of a hybrid conducting film after 1000 bending cycles under a flat condition. No cracks, peeling or other defects could be seen. These results were the same for all conducting films with all selected AgNW concentrations (0–1.5 wt %).

Figure 6 shows the SEM images for the hybrid conducting films under two bending conditions. The bending radii were 8 mm more than the bending radius limit [Fig. 6(a)] and 4 mm less than the bending radius limit [Fig. 6(b)]. In these images, cracks are observed in AgNP films for both conditions. When the bending radius was 8 mm, the AgNWs made bridges over the cracks, as if to compensate for the cracks. However, when the bending radius was 4 mm, the cracks spread further and AgNWs were broken and disconnected. We measured the ratio of disconnected AgNWs over cracks in the SEM images and found that they were 76 and 24% under the bending conditions below and over the bending radius limit, respectively. This result indicates that the resistivity of the hybrid conducting film is increased by repeated bending owing to the decreased number of primary conduction paths made by AgNWs in the film.

4. Conclusions

We fabricated hybrid conducting films with different concentrations of composite silver ink by mixing AgNPs and AgNWs. Pure AgNP films required thermal sintering at temperatures higher than 120 °C, but AgNW films exhibited conductivity without such sintering.

We found that the resistivities of hybrid conducting films became lower with AgNW mixing, because AgNWs made primary conduction paths in the films. Furthermore, there is a...
limit to the concentration of AgNWs that results in a decrease in resistivity.

The hybrid conducting films exhibited improved stability to bending, because the AgNWs made bridges over the cracks to compensate for the cracks. However, when the bending radii are smaller than the bending radius limit, AgNWs are broken off. The resistivity of the films then increases, because the number of primary conduction paths made by AgNWs in the film decreases. If the diameter of AgNWs is larger than 100 nm (which is the diameter of AgNWs synthesized in this study), it is impossible to further reduce the bending radius limit. These results are expected to facilitate the design of hybrid conducting ink for printed flexible electronics device applications.

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1) H. Klauk, Chem. Soc. Rev. 39, 2643 (2010).
2) K. Fukuda, Y. Takada, Y. Yoshimura, R. Shiwaku, L. T. Tran, T. Sekine, M. Murakami, D. Kumaki, and S. Tokito, Nat. Commun. 5, 4147 (2014).
3) W. J. Hyun, S. Lim, B. Y. Ahn, J. A. Lewis, C. D. Frisbie, and L. F. Francis, ACS Appl. Mater. Interfaces 7, 12619 (2015).
4) C.-N. Chen, T.-Y. Dong, T.-C. Chang, M.-C. Chen, H.-L. Tsai, and W.-S. Hwang, J. Mater. Chem. C 1, 5161 (2013).
5) W. Henri, L. Vonna, and H. Haidara, Nano Lett. 15, 442 (2015).
6) J. A. Rogers, T. Someya, and Y. Huang, Science 327, 1603 (2010).
7) C. F. Guo, T. Sun, Q. Liu, Z. Suo, and Z. Ren, Nat. Commun. 5, 3121 (2014).
8) T. Sekitani, Y. Noguchi, K. Hata, T. Fukushima, T. Aida, and T. Someya, Science 321, 1468 (2008).
9) L. Hu, H. S. Kim, J.-Y. Lee, P. Peumans, and Y. Cui, ACS Nano 4, 2955 (2010).
10) G. Eda, G. Fanchini, and M. Chhowalla, Nat. Nanotechnol. 3, 270 (2008).
11) J. Kim, J. Park, U. Jeong, and J.-W. Park, J. Appl. Polym. Sci. 133, 43830 (2016).
12) L. Mo, J. Ran, L. Yang, Y. Fung, Q. Zhai, and L. Li, Nanotechnology 27, 065202 (2016).
13) P. Mahala, A. Kumar, S. Nayak, S. Belurra, C. Dhanavantni, and O. Jani, Superlattices Microstruct. 92, 366 (2016).
14) S. K. Lee, B. J. Kim, H. Jang, S. C. Yoon, C. Lee, B. H. Hong, J. A. Rogers, J. H. Cho, and J. H. Ahn, Nano Lett. 11, 4642 (2011).
15) F. Li, J. Chen, X. Wang, M. Xue, and G. F. Chen, Adv. Funct. Mater. 25, 4601 (2015).
16) T. Someya, T. Sekitani, S. Iba, Y. Kato, H. Kawaguchi, and T. Sakurai, Proc. Natl. Acad. Sci. U.S.A. 101, 9966 (2004).
17) D. Kuang, J. Brillet, P. Chen, M. Takata, S. Uchida, H. Miura, K. Sumioka, S. M. Zakeeruddin, and M. Grätzel, ACS Nano 2, 1113 (2008).
18) T. Araki, J. Jiu, M. Nogi, H. Koja, S. Nagao, T. Sugahara, and K. Suganuma, Nano Res. 7, 236 (2014).
19) D. Kim and J. Moon, Electrochem. Solid-State Lett. 8, 330 (2005).
20) Y. Sun, B. Meyers, T. Herricks, and Y. Xia, Nano Lett. 3, 955 (2003).
21) H. Moon, P. Won, J. Lee, and S. H. Ko, Nanotechnology 27, 295201 (2016).
22) D. Doganay, S. Coskun, C. Kuyruk, and H. E. Unal, Composites, Part B 99, 285 (2016).
23) S. Ji, W. He, K. Wang, Y. Ran, and C. Ye, Small 10, 4951 (2014).
24) M. A. H. Khondoker, S. C. Mun, and J. Kim, Appl. Phys. A 112, 411 (2013).
25) K. Woo, D. Kim, J. S. Kim, S. Lim, and J. Moon, Langmuir 25, 429 (2009).
26) Y.-C. Lu and K.-S. Chou, J. Chin. Inst. Chem. Eng. 39, 673 (2008).
27) W. Yiu, D. H. Lee, J. Choi, C. Park, and S. M. Cho, Korean J. Chem. Eng. 25, 1358 (2008).
28) D. Kim, S. Jeong, and J. Moon, Nanotechnology 17, 4019 (2006).
29) K. Izumi, Y. Ochiai, D. Shikawata, Y. Yoshida, D. Kumaki, and S. Tokito, Int. Conf. Flexible and Printed Electronics (ICFPE2016), 2016, P10-2.
30) K.-H. Ok, C.-J. Lee, M.-G. Kwak, D.-K. Choi, K.-S. Kim, S.-B. Jung, and J.-W. Kim, J. Nanosci. Nanotechnol. 14, 8808 (2014).