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Improvement of the Conductivity of Silver Nanowire Film by Adding Silver Nano-Particles

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The change of conductivity and transparency of silver nanowire (AgNW) films by adding silver nano-particles (AgNPs) onto their surface is studied. The results show that the conductivity of the AgNW film is greatly improved with its sheet resistance reduced about 78.7% to 51.9 Ω/sq, and there is no obvious reduction of the transmittance. Further studies show that there is a self-assembling process pushing the AgNPs to concentrate at the intersecting points between AgNWs to weld them, which would reduce the intersection resistance between the AgNWs. This self-assembling behavior is led by the surface interactivities among the dispersing liquid of AgNPs, the surface of the substrate and AgNWs when the dispersing liquid is drying.

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Transparent conductive films are important for optoelectronic devices such as solar cells, liquid crystal displays (LCDs) and organic light emitting displays (OLEDs).[1−3] The doped metal oxide thin films such as indium-tin-oxide films (ITO) were traditionally used.[4−6] However, such a film requires high temperature curing during its fabrication processes. It is fragile in texture and prone to cracking on flexible substrates, which makes the film very difficult to use in the next generation optoelectronic devices, especially for the flexible optoelectronic devices, such as flexible OLEDs and solar cells. In the meantime, some studies showed that transparent conductive thin films based on silver nanowires (AgNWs) have high conductivity and transparency and are thought to be one of the most promising candidates which would replace the ITO film.[7−10]

AgNW films are a kind of two-dimensional conductive net with AgNWs scattered on the surface, in which AgNWs ensure the film to be conductive while the spaces among AgNWs ensure the films to be transparent. In the present studies, the AgNW film employed performs with good flexibility, low sheet resistance of about 13 Ω/sq, and high transmittance of about 85%.[8] Hu *et al.* reported that the sheet resistance of the AgNW film results mainly from the intersection resistance between the AgNWs, and reducing the resistance would be an important way to improve the conductivity of the film.[11]

Recently, there have been some reports on the self-assembling behavior of silver nano-particles (AgNPs).[12,13] In this Letter, we report that adding AgNPs onto the AgNW film under some special conditions can also trigger a self-assembling process and can make the intersection resistances between AgNWs decrease to improve the conductivity of the AgNW film.

In the experiments, AgNWs with diameters of 70–120 nm and length of 14–25 μm dispersed in the isopropyl alcohol suspension with concentration of 25 mg/ml were selected and diluted by distilled water to 0.25 mg/ml as a dispersing liquid. The 0.05% sodium dodecyl benzene sulfonate (SDBS) was added as the surface active agent. Then the dispersing liquid was subjected to 0.5 h ultrasonic treatment in a sonic bath. The substrates to fix the AgNWs were $2 \times 2\,\mathrm{cm}^2$ soda-lime glass plates with a transparent hydrophobicity acrylic resin layer, which was formed by spin-coating methods with 0.5 μm thickness, drying under 85℃ for 10 min, and then coated by a very thin teflon film (about 10 nm) by the vapor depositing method. Then the AgNWs dispersing liquid was dripped onto the substrates with an amount of 0.01–$0.025\,\mathrm{ml/cm}^2$ and dried under 85℃ for 10 min after self-leveling. After this, the substrates were baked under 100℃ to make the acrylic resin layer soften and the AgNWs were fixed by pressing methods with a silica gel plate. Lastly, the surface active agent was rinsed off by distilled water and stayed for 24 h. The original AgNW film with different densities of AgNWs were made and marked as samples A.

AgNPs with diameters of 100–180 nm were added into the distilled water and subjected to 0.5 h ultrasonic in a sonic bath as a AgNPs dispersing liquid with the concentration of 0.05 mg/ml. Samples B were achieved by dripping this dispersing liquid onto the surfaces of sample A with the amount of $0.01\,\mathrm{ml/cm}^2$, which were dried under the temperature of 25℃ and humidity of 62% RH, which will make the drying speed slow enough for an interacting process.

The 0.05% SDBS was added into the AgNPs dispersing liquid as a surface active agent. Then the dispersing liquid was dripped onto the surface of samples

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A and dried by the same way, which were marked as sample C.

The transmittances were tested by a transmittance tester (LS103A); the sheet resistances were measured by a four-probe tester (DMR-1C); the contact angles were measured by a contact angle tester (KRUSS DSA30); and the surfaces of samples were observed by an SEM (JEOL JSM 6360LA).

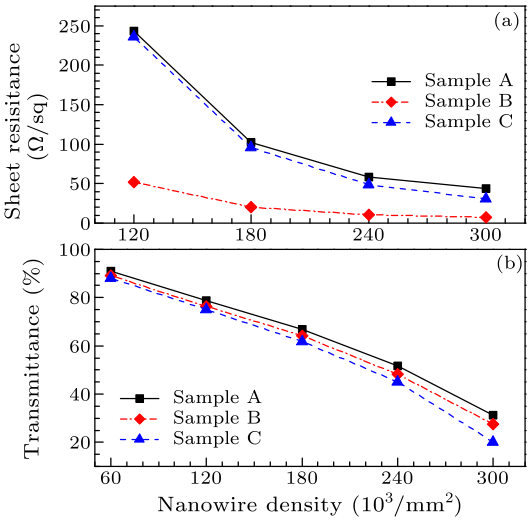

Fig. 1. Sheet resistance (a) and transmittance (b) of samples.

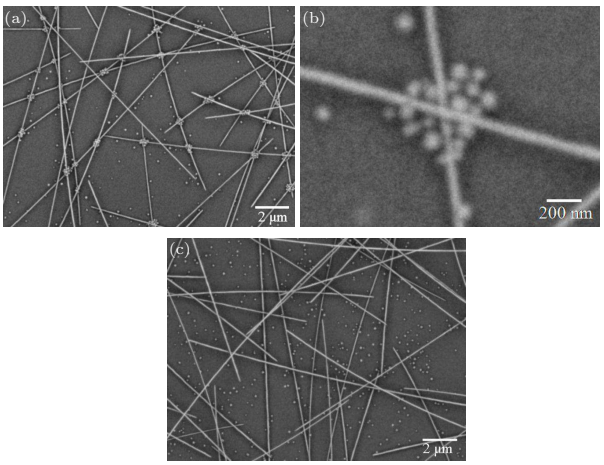

Fig. 2. SEM images of samples B and C. (a) SEM images of a sample B. (b) A detail with enlarged scale of (a). (c) SEM images of sample C.

Figure 1 shows that for sample B, after adding the AgNPs the sheet resistances fell obviously while the transmittances have just a small drop. For the sample of the AgNW density of 120×10^3/mm^2, the transmittance just decreases from 78.8% to 76.4%, while its sheet resistance decreases from 243 Ω/sq to 51.9 Ω/sq, which is calculated as −78.7% of changing rate. However, such a change cannot be seen in sample C, its sheet resistance just decreases from 243 Ω/sq to 236.0 Ω/sq, which is calculated as −2.9% of changing rate.

Figures 2(a) and 2(b) show on the surface of sample B the AgNPs concentrates at the intersecting points between some AgNWs and made AgNPs 'welded' each other. However, Fig. 2(c) shows the AgNPs scattered randomly on the surface of sample C. There are almost no AgNPs concentrated at the intersecting point of the AgNWs.

Thus we guess the sheet resistances of sample B were reduced by this principle. When two AgNWs are welded, the intersection resistance between them will be reduced, and due to the fact that the resistance of the AgNW film originates mainly from the intersection resistance between the AgNWs,[12] the drop of intersection resistance would reduce the film's sheet resistance significantly. However, due to the fact that just very few AgNPs were needed to make the 'welding', the transmittance would be changed scarcely.

In sample B, since the AgNPs concentrate at the intersecting points of AgNWs orderly, this process can be thought of as a kind of self-assembly behavior.

In sample C, there are no AgNPs concentrated to the intersecting points of the AgNWs, thus the sheet resistance does not change obviously.

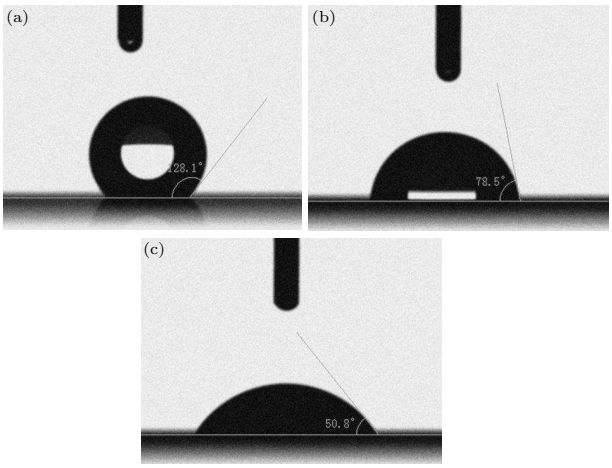

Fig. 3. The contact angles of the substrate with original dispersing liquid (a), the AgNW fixed substrate with original dispersing liquid (b), and (c) the AgNW fixed substrate with dispersing liquid of SDBS.

Figure 3 shows the contact angles of the samples. Figures 3(b) and 3(c) correspond to samples B and C, respectively. Figure 3(a) shows the blank glass plates as the substrate with just a hydrophobicity acrylic resin layer being hydrophobic. Figure 3(b) shows that the fixed AgNWs on the substrate can make the contact angle decrease, implying that compared with the substrate, the AgNWs are hydrophilic, which makes it capable of guiding the flow of the dispersing liquid when it is almost dry; while in Fig. 3(c), after adding SDBS into the dispersing liquid, the contact angle reduces greatly, meaning that the difference of the hydrophilicity between the substrate and the AgNWs is eliminated, and the AgNWs are not capable

of guiding the flow of the drying dispersing liquid any more. Based on this, as shown in Fig. 4, a mechanism can help to explain the self-assembly process of sample B. Due to the surface interaction of dispersing liquid, when the dispersing liquid's surface energy with the AgNWs is smaller than the substrate, in the process of drying the dispersing liquid keeps shrinking and at the end it just coats the intersecting points between AgNWs. Therefore, the AgNPs are restricted by the dispersing liquid, guided and pushed to the intersecting points, and finally are located at the intersecting points to form the 'welding' of AgNWs.

However, in sample C the above-mentioned mechanism is destroyed by SDBS, and no 'welding' is formed.

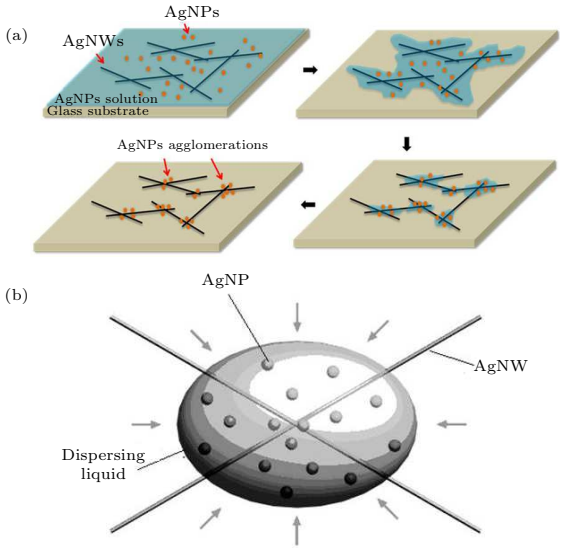

Fig. 4. Mechanism of the self-assembly behavior. (a) The process of drying, and (b) form of the welding.

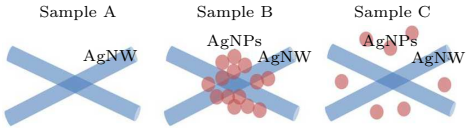

Fig. 5. Comparison conductive path of different samples.

Another mechanism of how AgNPs improve the conductivity of the AgNW film should also be largely considered. A conductive path model was proposed as shown in Fig. 5. Since AgNWs in the AgNW film connect to each other, they form a continuous conductive network. Depending on the intersections density and contact conditions (e.g., contact area and contact tightness) at the intersections, AgNW films exhibit different sheet resistances. As shown in Fig. 5, two AgNWs in sample A join together via the intersection. Different intersections have different contact levels. There is certain probability that AgNWs could not contact well with one another. In the whole film, the existence of numerous loose contacts would lead to poor conductivity. However, as sample B shows in Fig. 5, the large numbers of AgNPs wrapped around the intersection could effectively prevent such a problem. In the case of loose contact, AgNPs offer complementary paths to the charge transport. As a result, AgNPs significantly increase the conductivity of the AgNW film. To further confirm the conductive path model and single out the function of agglomerations of AgNPs, sample C as mentioned above is taken into comparison. It is clear that AgNPs separately distribute away from AgNWs, resulting in no additional conductive path to the AgNW network (as sample C shows in Fig. 2(c)). Sheet resistance measurement result shown in Fig. 1(A) also corresponds with the speculation. Sample C shows an ignorable improvement on sheet resistance, which is different from sample B.

In summary, AgNW films with different transmittance and sheet resistance have been made and tested by adding AgNPs. The results show that adding AgNPs is able to improve the conductivity of AgNW films greatly without an obvious drop of their transmittance. The change of the conductivity of AgNWs was based on a self-assembling process caused by the AgNPs concentrating to the intersecting points between AgNWs, and such self-assembling behavior appears by the surface interaction among the dispersing liquid, the surface of the substrate and the surface of the AgNWs when the dispersing liquid is evaporating.

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