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Nano-Welding of Ag Nanowires Using Rapid Thermal Annealing for Transparent Conductive Films

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Ag nanowire (NW) films obtained by the spraying the Ag NWs on the substrates were nano-welded by rapid thermal annealing (RTA) process and the effect of RTA process on the change of sheet resistance and optical transmittance of the Ag NW films was investigated. The increased number of Ag NW sprays on the substrate decreased the sheet resistance but also decreased the optical transmittance. By the annealing for 60 sec in a nitrogen environment to 225~250 °C, the sheet resistance of Ag NW film could be decreased to about 50%, even though it was accompanied by the slight decrease of optical transmittance less than 5%. The decrease of sheet resistance was related to the nano-welding of the Ag NW junctions and the slight decrease of optical transmittance was related local melting of the Ag NWs and spreading on the substrate surface. Through the nano-welding by RTA process, the Ag NW film with the sheet resistance of ~20 Ω/sq. and the optical transmittance of 93% could be obtained.

Keywords: Rapid Thermal Annealing, Ag Nanowire, Transparent Conductive Film, Nano-Welding.

1. INTRODUCTION

Transparent conductive films (TCFs) are investigated due to various application to electronic devices such as touch screen, displays, flexible photovoltaics, etc. Currently, the most commonly used transparent conductive material in the manufacturing of TCFs is indium tin oxide (ITO).[1–6] However, ITO is very expensive due to the indium price in the ITO film and, when the ITO films are applied to flexible and stretchable electronics, some major problems encountered due to its brittleness, requirements of high processing temperature, etc.[7–9]

For this reason, several alternatives to ITO have been investigated extensively. These materials include carbon nanotubes (CNTs)[10], graphene,[11] conducting polymers,[12] metal (Ag, Cu, etc.) nanowires,[8] metal meshes,[13] etc. Among these alternative materials, silver nanowires (Ag NWs) currently show the best properties such as mechanical flexibility, electrical, and optical performance, chemical stability, etc. which can be comparable to ITO. One of the easiest methods to form an Ag NW film on the substate is to spray an Ag NW solution on the substrate. However, when the Ag NW films formed by spraying the Ag NWs are applied as the electrodes for various electronic devices such as organic light emitting diodes (OLEDs), photovoltaics, etc., other serious problems such as lack of long-term stability, difficulty in current spreading due to the presence of uncoated area between nanowires which cannot exchange electrons for an active layer are observed. Moreover, they have inherent roughness and are easily detached from the substrate due to weak adhesive forces with substrates/between NWs and that causes weak bendability.

Some of these problems can be solved if the Ag NWs sprayed on the substrates are welded each other on the substrate. To weld the Ag NWs sprayed on the substrate, chemical treatment,[14] long-term mechanical bending[15] have been investigated. In this study, rapid thermal annealing (RTA) which is widely used[16] for annealing of the semiconducting materials has been used to weld the Ag NWs sprayed on the substrate, and the effects of RTA processing on the optical properties and electrical properties of the RTA treated Ag NWs were investigated.

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It was found that the RTA process facilitated the local nano-welding among the NWs junctions in the network structure. During the RTA process, the electrical connection and strength of the contacts among AgNWs were increased, thereby significantly decreased the sheet resistance of the electrode while not significantly changing the optical transmittance.

2. EXPERIMENT SETUPS

A commercially available Ag NWs (NANOPYXIS) solution with the length of 22 ± 5 um and the diameter of 27 ± 5 nm was used in this experiment. This solution was then diluted with 10 ml isopropyl alcohol (IPA) to 0.05 wt%. Glass substrates of 25 mm × 25 mm were used to spray Ag NWs and, before spraying the Ag NW solution, the substrates were cleaned by sonication in acetone, alcohol, and de-ionized (DI) water for each 15 minutes in sequence. Spray coating was performed using a spray coating equipment (SPARMAX GP-35) which can coat the nanowires uniformly over the 30 cm × 30 cm scale by using X–Y stage. The substrate was attached on the X–Y stage of the spray coating equipment and the Ag NW solution was sprayed with 15 psi of N_2 gas while heating the X–Y stage to about 50 °C in order to remove the solvent easily. The number of Ag NW solution spays was varied from 7 to 15 times to control the density of Ag NW random networks on the glass substrate.

The Ag NW network formed on the glass substrates was annealed using a rapid thermal annealing (RTA) equipment and the RTA process was carried out in a nitrogen atmosphere to prevent oxidation of Ag NWs. The RTA process temperature was varied from 150 from 300 °C to observe the change of resistance variation of Ag NWs. The annealed Ag NW networks were observed by field emission scanning electron microscopy (FE-SEM; Hitachi S-4700). The optical transmittance of the Ag NW network on the glass substrates was measured using ultraviolet visible (UV-Vis) spectroscopy (UV-3600; Shimadzu). The sheet resistance of the Ag NW network on the glass substrate was measured using a 4-point measurement method (Keithley 2000; Keithley).

3. RESULTS AND DISCUSSION

Figure 1 shows a schematic diagram on the Ag NW spray process and the following RTA nano-welding process used in the experiment. Ag NWs were sprayed on the glass substrate for 7, 10, 13, and 15 times to increase the density of NWs and to reduce the resistance. Figure 2 shows the SEM images of Ag NWs sprayed on the glass substrate after spraying for (a) 7, (b) 10, (c) 13, and (d) 15 times. As shown in the figure, with increasing the number of sprays, the density of Ag NWs was increased and the number of Ag NW junction was also increased. When the electrical resistances of Ag NW coated glass substrates were measured, the resistances were decreased as approximately 60.05, 38.7, 27.9, and 9.0 Ω/sq. for 7, 10, 13, and 15 times of spraying, respectively.

Using the RTA, the Ag NWs were annealed and the effect of RTA process conditions on the welding of the junctions was investigated. Figure 3 shows the SEM images of Ag NWs after the annealing with RTA at the temperature of (a) 150, (b) 175, (c) 200, (d) 225, (e) 250, (f) 275, (g) 300 (×200), and (h) 300 °C (×50) for 60 sec in a nitrogen environment. The number of Ag NW sprays used in this experiment was 7 to 15 times. The melting point of bulk Ag is about 962 °C. However, the melting point of Ag NWs can be decreased significantly due to the increased surface mobility. As shown in Figure 3, even though the shapes of Ag NWs were not changed noticeably when the Ag NWs were annealed at 150 °C, partial welding of Ag NW junctions was observed at the temperature equal to and higher than 175 °C. At 250 °C, almost all of the Ag NW junctions were observed to be welded. However, when the annealing temperature was increased further to 275 °C, partial melting of Ag NWs was observed and, after the annealing at 300 °C, as shown in Figure 3(g) and (h), almost all of the Ag NW junctions were disconnected and the Ag NWs were broken.

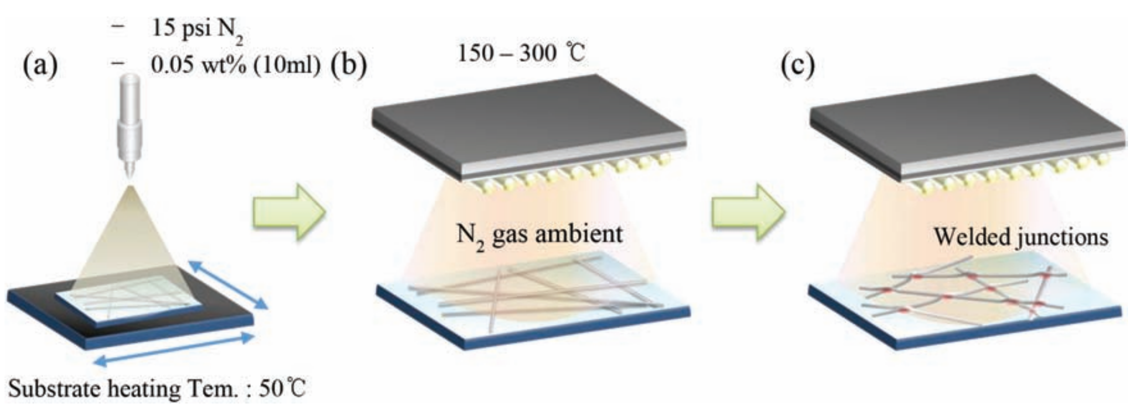

Figure 1. The processes forming AgNWs on glass substrate by spraying an Ag NW solution and nano-welding by RTA process. (a) Ag NW spraying, (b) and (c) show the welding of Ag NWs by RTA process.

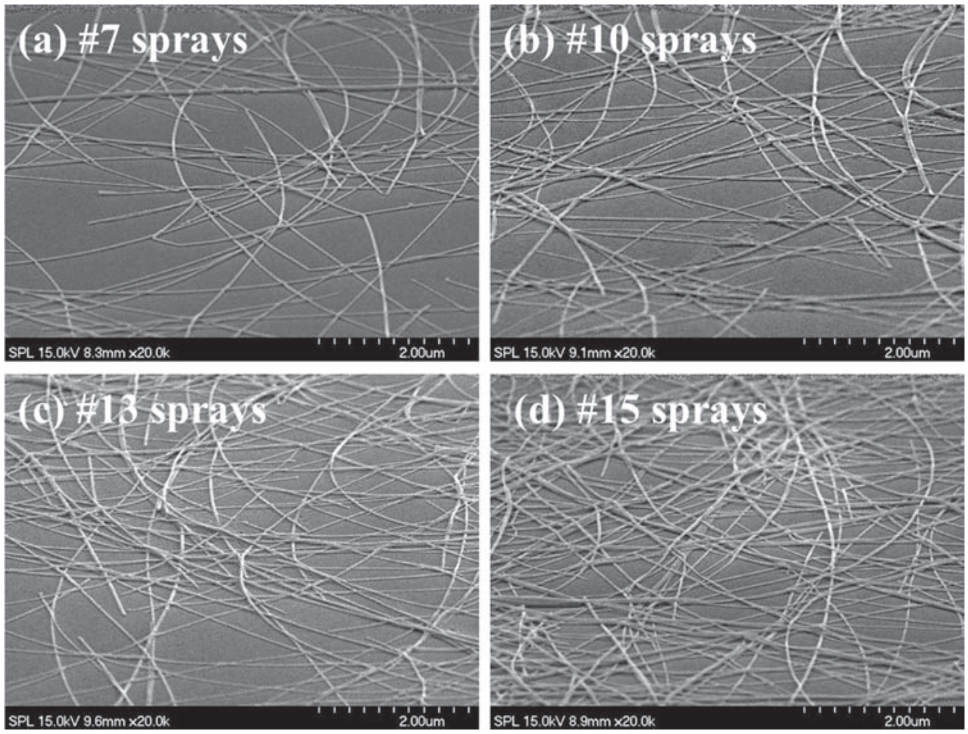

Figure 2. SEM images of Ag NW distribution observed for different number of Ag NW sprays. (a) 7, (b) 10, (c) 13, and (d) 15 times.

Optical transmittances of the annealed Ag NWs at different temperatures were measured using UV-Vis spectroscopy and the results are shown in Figure 4(a) for 7 sprays and (b) for 15 sprays. The annealing conditions are the same as those in Figure 3. As shown in Figure 4(a) and (b), the optical transmittance curve of Ag NWs was nearly flat for the wavelength from 400 to 800 nm and the increase of number of sprays decreased the optical transmittance due to the decrease of opening area of the Ag NW film on the glass substrate. In addition, the increase of RTA temperature decreased the optical transmittance slightly possibly due to the local melting of the Ag NWs and spreading on the substrate surface.

The change of optical transmittance at 550 nm of wavelength with annealing temperature for different Ag NW sprays in Figure 4 was measured and the results are shown in Figure 5. As shown in the figure, before the annealing, the optical transmittances of the Ag NWs for the number of sprays of 7, 10, 13, and 15 were 96.9, 94.3, 91.4, and 87.4%, respectively, therefore, the optical transmittance was decreased significantly with increasing the number of sprays. When the annealing temperature was increased to

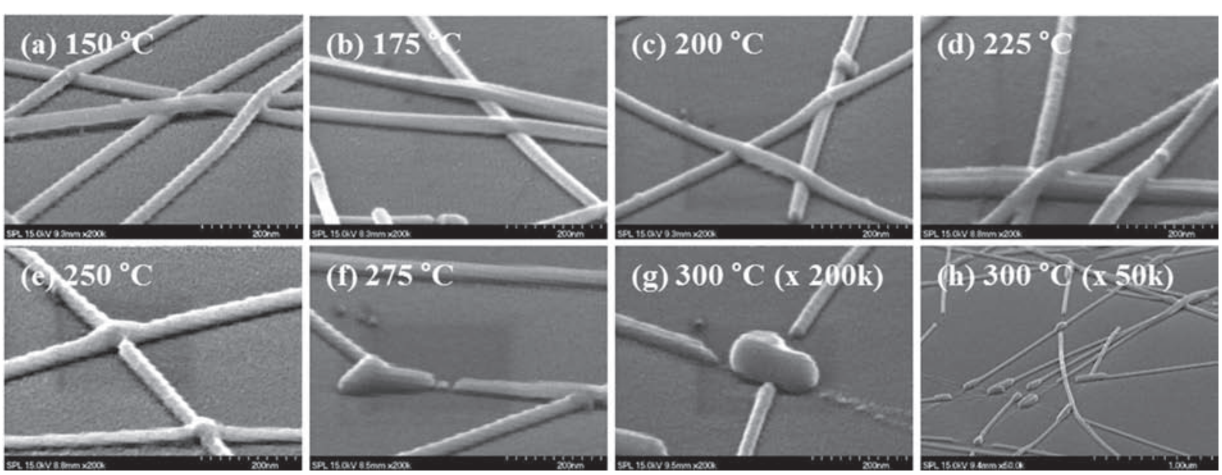

Figure 3. SEM images of Ag NW junctions observed after the annealing with RTA at the temperature of (a) 150, (b) 175, (c) 200, (d) 225, (e) 250, (f) 275, (g) 300 (×200), and (h) 300°C (×50) for 60 sec in an nitrogen environment.

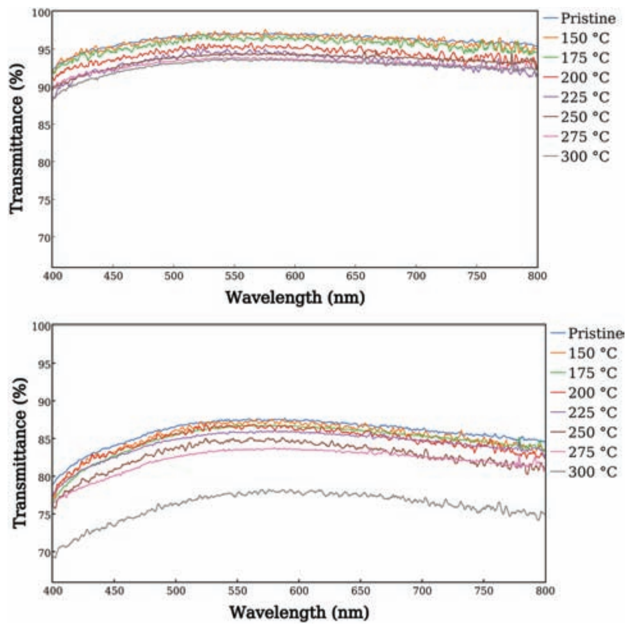

Figure 4. Optical transmittances of the annealed Ag NWs at different temperatures measured using UV-Vis spectroscopy. (a) 7 sprays and (b) 15 sprays.

150 °C, possibly due to no significant change in the Ag NW structure in the films, the optical transmittance was not changed noticeably. However, at the annealing temperature equal to and higher than 175 °C, the optical transmittance was slightly decreased with increasing the annealing temperature and, at the temperature of 250 °C, the optical transmittance was decreased to 94.3, 92.8, 87.8 and 84.7% for the number of sprays of 7, 10, 13, and 15, respectively.

The nano-welding of Ag NWs by the RTA process can decrease the sheet resistance. Figure 6 shows the sheet resistance of Ag NWs measured as a function of annealing

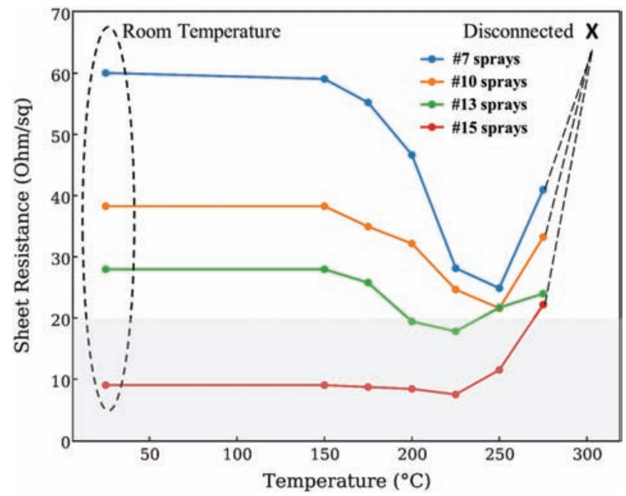

Figure 6. Sheet resistance of Ag NWs measured as a function of annealing temperature using a 4-point probe system for different Ag NW sprays.

temperature using a 4-point probe system for different Ag NW sprays. As shown in the figure, the increase of annealing temperature to 150 °C did not change the sheet resistance. However, the annealing at higher temperature showed the decrease of sheet resistance and, at the temperature of 225∼250 °C, the sheet resistances were the lowest possibly due to the sufficient nano-welding of the junctions at the temperatures. Especially, in the case of the Ag NWs with 7 and 10 sprays, after the annealing at 250 °C, the sheet resistances decreased to about 50%. However, the further increase of annealing temperature increased the sheet resistances rapidly and, at 300 °C, the sheet resistance was infinite due to the disconnection of the nanowire junctions as shown in Figure 3.

Using the data in Figures 5 and 6, the sheet resistances of the Ag NW film were redrawn as a function of

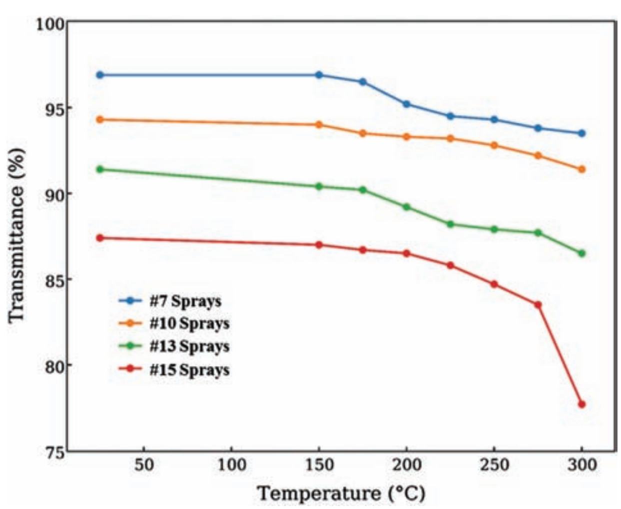

Figure 5. Change of optical transmittance at 550 nm of wavelength with annealing temperature for different Ag NW sprays. The process conditions are the same as those in Figure 4.

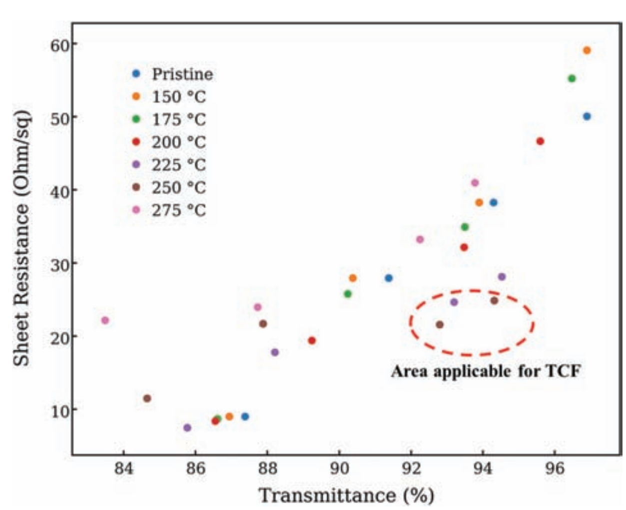

Figure 7. Sheet resistances of the Ag NW film redrawn as a function of optical transmittance for all of the NW films before and after annealing at various temperatures using the data in Figure 5 and 6.

optical transmittance for all of the NW films before and after annealing at various temperatures. As shown in the Figure 7, a linear relationship between the sheet resistance and the optical transmittance was observed when the Ag NWs were not welded. However, as shown in red dotted circle area, by the nano-welding of the Ag NWs using the RTA process, the sheet resistance versus the same optical transmittance was located out of the linear relationship. By the nano-welding, the lower sheet resistance of ~20 Ω/sq. while maintaining the optical transmittance higher than 93% which can be applicable as TCFs for flexible displays, flexible solar cell, etc. could be obtained.

4. CONCLUSIONS

The substrates spray coated with Ag NWs were annealed with RTA and the effect of RTA on the change of sheet resistance and optical transmittance of Ag NW film was investigated.

The increase of number of spray coating on the substrate decreased the sheet resistance but, due to the decrease of opening area, the optical transmittance was also decreased. Even though the melting point of bulk Ag is about 962 °C, by the annealing using RTA, Ag NW junctions were welded at the temperature higher than 150 °C for 60 sec in a nitrogen environment due to the increased surface mobility. The annealing at the higher temperature decreased the sheet resistance of Ag NWs due to the nano-welding of the Ag NW junctions and the lowest sheet resistance which was decreased to about 50% could be obtained at 225~250 °C due to the sufficient nano-welding of the Ag NW junctions. But it was accompanied by the slight decrease of optical transmittance of less than 5% due to the local melting of the Ag NWs and spreading on the substrate surface. The increase of the annealing temperature higher than 250 °C not only increased sheet resistance but also decreased the optical transmittance due to the disconnection of Ag NW junctions and further spreading on the substrate.

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