J. Microelectron. Packag. Soc., 28(1), 73-77 (2021)
Print ISSN 1226-9360 Online ISSN 2287-7525

https://doi.org/10.6117/kmeps.2021.28.1.073

Effect of Argon Plasma Treatment On Silver Nanowires

Vo Thi Bao Tran and Dooho Choi†
School of Advanced Materials Engineering, Dong-Eui University, 176 Eomgwangro, Busan 47340, Republic of Korea

(Received March 20, 2021: Corrected March 27, 2021: Accepted March 30, 2021)

Abstract: In this study, we report on the effects of argon plasma treatment on Ag nanowires by varying the power and duration. Sheet resistance was found to be significantly reduced to 10 ohm/sq. relative to the value of 21 ohm/sq. for the pristine sample. Such a reduction was found to be associated with welded junctions between Ag nanowires, which results in enhanced current flow. With the optimized plasma treatment conditions, the maximum and average transmittance were 76.8% and 71%, respectively. Finally, we fabricated transparent heating devices based on the methodology, which exhibited superior heating capability.

Keywords: Sputtering, Thin Films, Transparent Electrodes, Sheet Resistance, Transmittance

1. Introduction

In recent years, flexible transparent electrodes have been used as the core components of many optoelectronic devices, involving organic light-emitting diodes, electronic displays, photovoltaic devices, and wearable sensors. Although indium tin oxide (ITO) possesses a low sheet resistance, high optical transparency, good stability, and strong adhesion to the substrate, the shortcomings such as intrinsic brittleness, high processing temperature required for improved electrode properties, and the scarcity of resources have hindered its applications in the flexible transparent electrodes. Therefore, various types of alternative transparent conductive materials with high optical transparency,1) low sheet resistance,2) and compatible mechanical flexibility have been under intense research, which includes conducting polymers, graphene, carbon nanotubes, metal grids, and metal nanowire meshes.1)

Among the candidates, silver nanowires (AgNW)3) are considered a promising candidate to replace ITO,4,5,9,14-16) and research interests in improving AgNW properties have been actively studied. These include annealing at elevated temperatures,6) UV exposure, electrolyte solution, solvent washing, etc. In this work, the AgNW surfaces were modified via Ar plasma (ArP) exposure by varying the power and duration, and the optimized ArP treatment8) resulted in a significant reduction in sheet resistance to 10 Ω/sq., relative to 21.0 Ω/sq. for the pristine sample, while no distinct differences in the the optical transmittance were observed. The improved conductivity can be attribuited to welded junctions between AgNWs, formed by the ArP process. Finally, we fabricated transparent heating devices to examine the applicability of the methodology.

2. Experiment Details

The AgNWs (Novarials) have an average dimension of 30 nm × 30 μm. A mixture solution of 0.4 ml AgNWs and 1.6 ml Isopropyl Alcohol (IPA) was prepared in a bottle. 20 drops of AgNWs solution were dropped on the glass substrates by a syringe having a volume of 5 ml. The substrates were rotated at 8000 rotations per minute10) during the dropping process to improve spatial uniformity and sparing with AgNWs accumulation by a spin coater (ACE–200, Dong Ah Trade Corp, South Korea)11,12) for 60 seconds. The surface of the samples were then modified by an Ar plasma generator (Covance, Femto Science, South Korea). The chamber was evacuated to a base pressure of 5 × 10^{-6} Torr, and elevated to 5 × 10^{-2} Torr with the introduction of Ar gas at 20 standard cubic centimeters per minute. AgNWs were then treated at varying powers of 10, 20 and 30 W and durations of 1, 3, 5 and 7 minutes. Following the fabrication of the AgNWs heaters, 5 nm–wide, 100 nm–thick Ag electrodes along the opposite edges of the heating

---

†Corresponding author
E-mail: dhchoi@deu.ac.kr

elements were deposited by radio frequency sputtering.

The sheet resistance of the AgNWs layer and photon transmittance were measured using the four point probing method (CMT-100S, AIT, South Korea) and spectrophotometry (CARY-100, Agilent, U. S. A.), respectively. The surface morphologies of the AgNWs layer were observed using ultrahigh-resolution field emission scanning electron microscopy (SEM) (S-5500, Hitachi, Japan). A direct current power supply (EPS-3305, EZT, South Korea) was used to induce Joule heating and the temperature was measured by an infrared (IR) camera (PT1120, Fluke, the Netherlands).

3. Results and discussion

Fig. 1(a) shows the schematic structure of AgNWs on top of the glass substrate that were treated by Argon plasma treatment. Photographs of a bare glass substrate and a substrate with AgNWs (after surface treatment) are compared in Fig. 1(b), the visual comparison shows a decrease in transmittance when the sample was covered by AgNWs. The average visible light transmittance decreased by approximately 22.6% as shown in Fig. 4.

In Fig. 2(a), SEM micrographs show the morphology of the AgNWs before plasma treatment, and Fig. 2(b) and 2(c) represent enlarged images for the AgNWs in the circle and square in Fig. 2(a), respectively. Fig. 2(d) shows the AgNWs after the plasma modification, and Fig. 2(e) and Fig. 2(f) represent enlarged images in Fig. 2(d), respectively. After plasma modification, the junctions of AgNWs were found to be tightly contacted as shown in Fig. 2(e) and Fig. 2(f). This phenomenon may be enhanced with the removal of polyvinylpyrrolidone (PVP) residual surfactants that originally covered AgNWs.[4)]

Fig. 3 illustrates a comparison of sheet resistance of

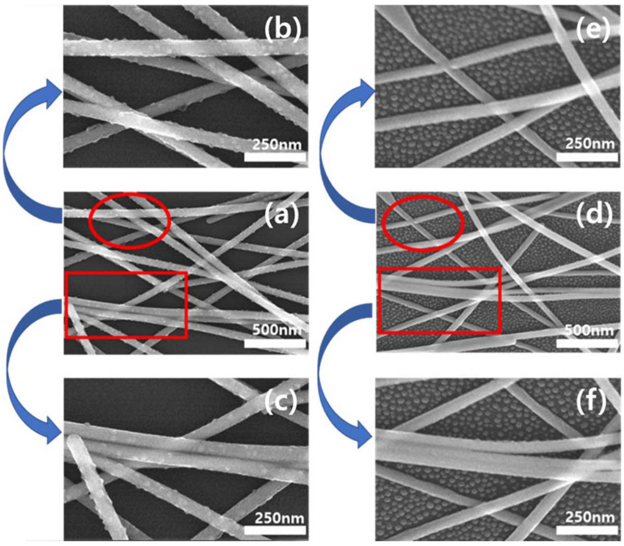


Fig. 2. SEM micrographs showing the morphologies of AgNWs layer with the inclination angle of 25^{o} (a) before plasma treatment, (c) and (e) represent enlarged images before plasma treatment in the circle and square on Fig. (a), respectively; (b) after plasma treatment, (d) and (f) represent enlarged images after plasma treatment in the circle and square in Fig. (b), respectively.

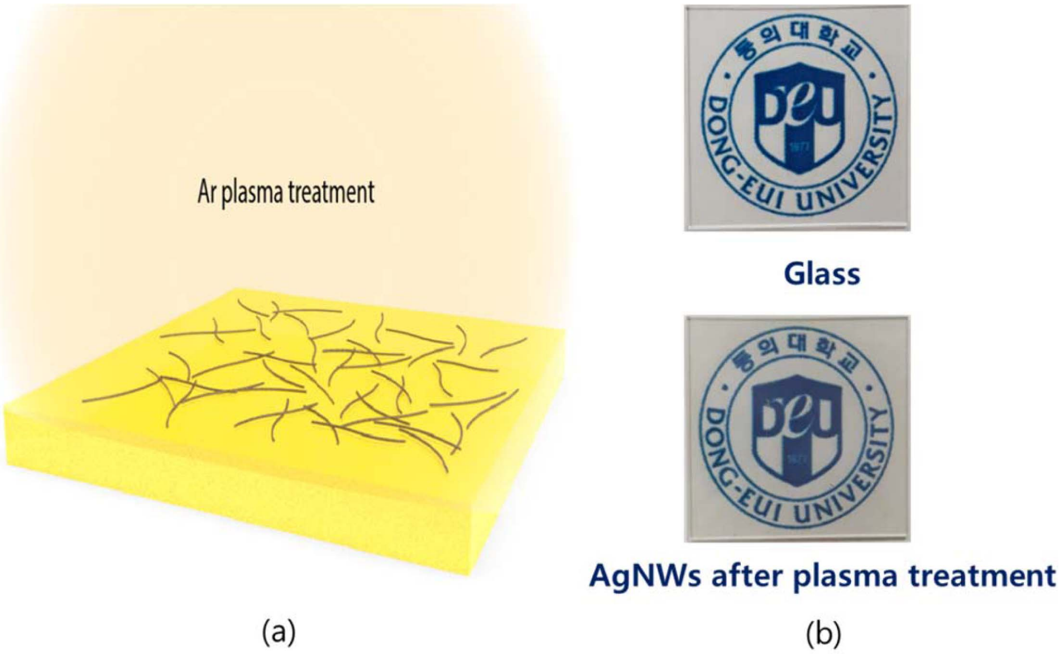


Fig. 1. (a) Schematic structure of AgNWs prepared on top of a glass substrate with Argon plasma treatment, (b) Optical photographs of the glass substrate and AgNWs after Argon plasma treatment.

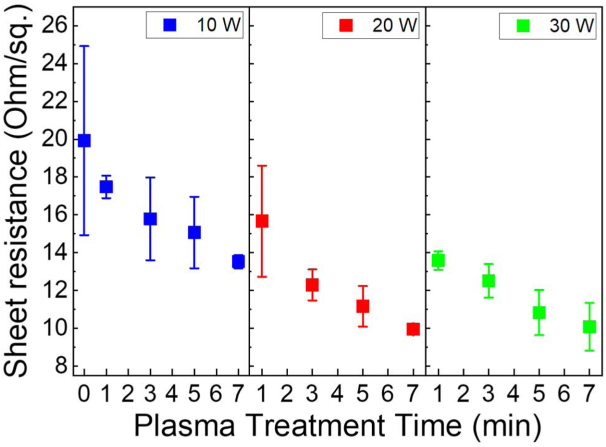


Fig. 3. The sheet resistance of AgNWs as a function of plasma treatment condition at 10 W, 20 W, and 30 W with a concentration of 0.4 ml AgNW and 1.6 ml IPA, 20 drop mixture solution AgNWs on glass substrate by 8000 rotations per minute.

AgNWs modified by different surface treatments. Overall, the plasma-treated samples showed lower sheet resistance values than that of the pristine sample due to the effect of ArP treatment. This enhances the contact between AgNWs junctions which leads to the increased conductivity of AgNWs.[13] It was shown that the selection of 20 W generally exhibited lower sheet resistance relative to the values for 10 and 30 W. For all conditions, the sheet resistance values platued above modification duration of 7 min.

Fig. 4 shows the maximum and average visible light (λ: 400-800 nm) transmittance measured with respect to the air baseline. Despite the significant difference in sheet resistance, the ArP did not result in appreciable differences in optical transmittance values (i.e., maximum and average values of 76.6 % and 70.6% for the pristine AgNWs and 76.8% and 71% for the ArP-processed AgNWs). The transmittance values were not affected by the ArP power and duration.

The Joule heating properties for the AgNW electrodes such as electrode temperature and electrical current are given in Fig. 5. As clearly shown, temperature and current levels are inversely proportional to the AgNWs sheet resistance in Fig. 5, as is expected by the Joule heating mechanism, i.e., higher currents and higher heater temperatures for samples with lower resistance at given applied voltages (P=IV, where P, I, and V represent power, current and voltage, respectively).[2]

Fig. 6(a) shows the typical voltage-dependent Joule heating characteristics for the AgNW-heaters before ArP and after ArP. As discussed earlier, the ArP-treated samples show significantly improved heating capability at given voltages due to the lower sheet resistance. The AgNW-

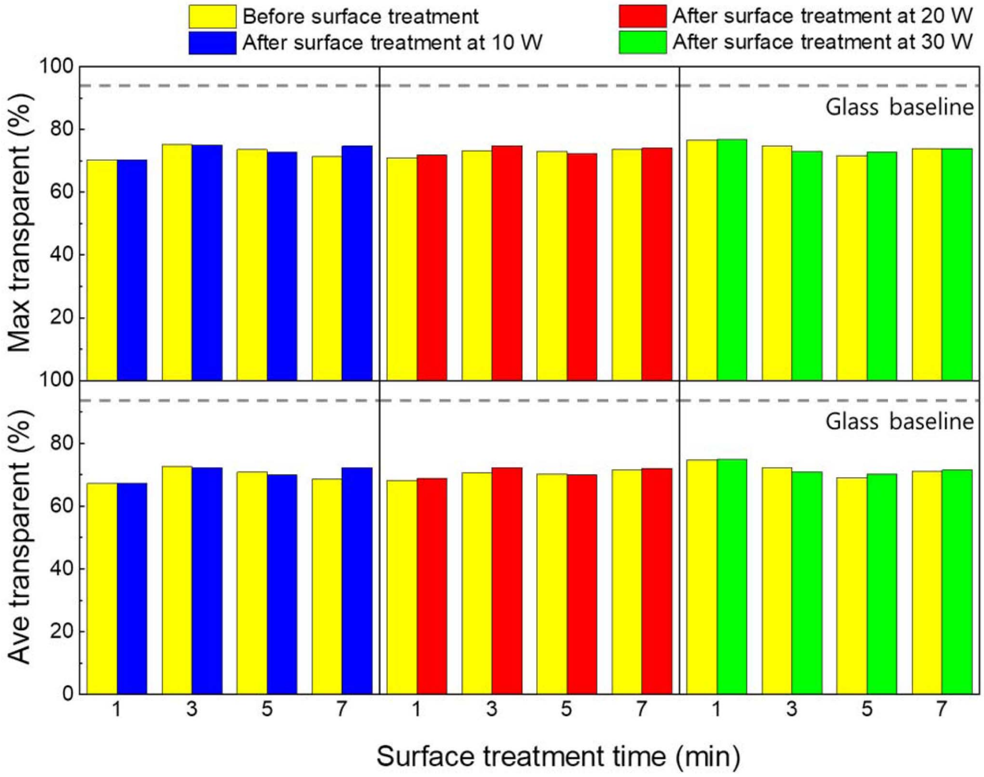


Fig. 4. Maximum and average transmittance of AgNWs as a function of plasma treatment. Red, orange, and green bar represent the glass, before surface treatment and after surface treatment sample, respectively. (x-axis change) The transmittance for the glass usbstrate was provided for reference.

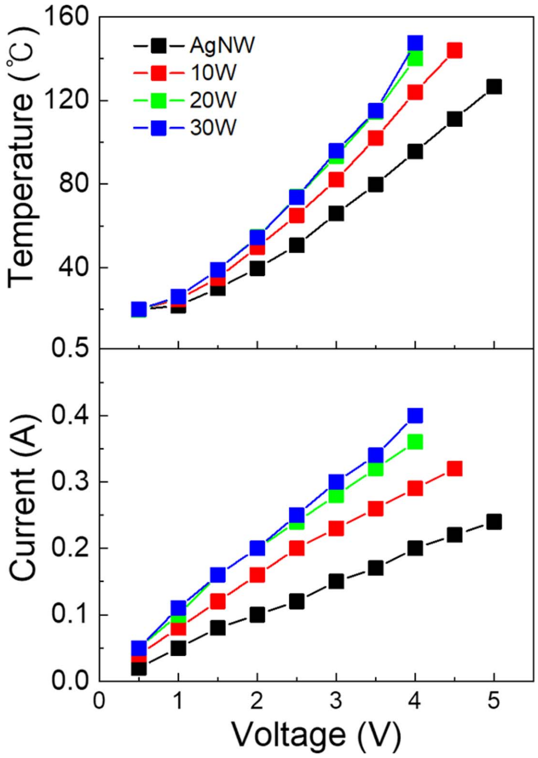


Fig. 5. Current vs. voltage and temperature vs. voltage characteristics are given, where applied DC voltage is increased by 0.5 V every 3 min until the limit temperature of the IR camera. The presented temperatures correspond to the maximum temperature of the heater.

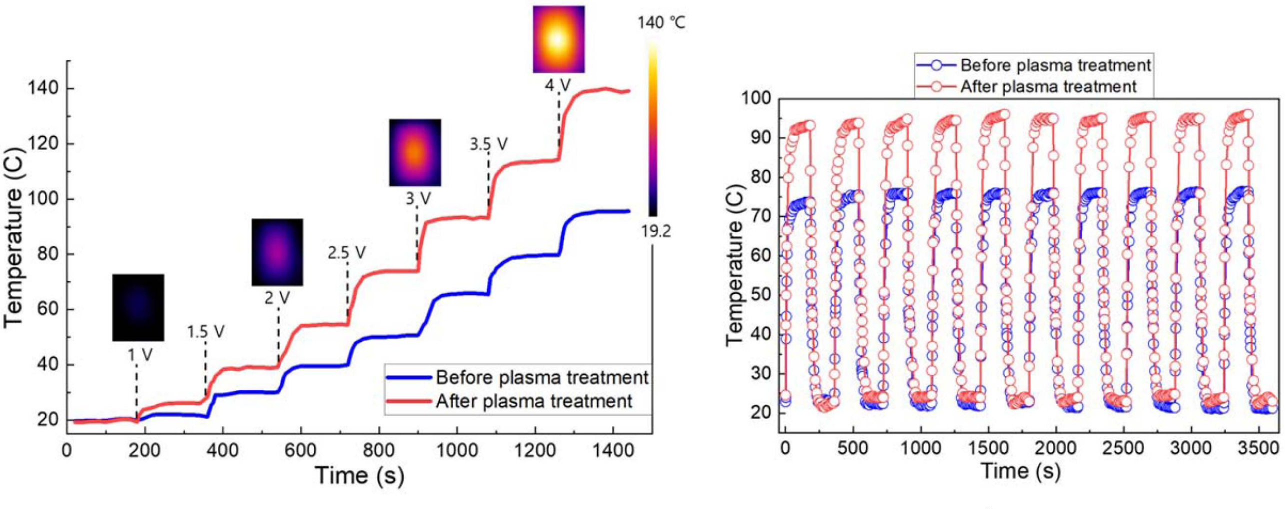
heaters exhibited fast thermal response, i.e., 97% of the final temperatures were reached within 30 s. Fig. 6(b) shows a cyclic heating test where the heaters were repetitively switched on by applying 3 V for 6 min and switched off for 6 min. The enhanced heating capability of the ArP-AgNWs with fast thermal response and high reproducibility, clearly proves that the methodology explored in this study has a great potential in the applications in flexible devices.

4. Conclusion

In this study, we examined the effects of argon plasma modification of Ag nanowires by varying the plasma power and duration. With the optimized conditions, sheet resistance values were reduced by more than a factor (10 ohm/sq. relative to the value of 21 ohm/sq. for the pristine sample). Such a reduction can be attributed to the welded junctions between Ag nanowires formed following the ArP process. The maximum and average transmittance were 76.8% and 71%, respectively. Finally, we fabricated transparent heating devices based on the methodology, which exhibited superior heating capability.

Acknowledgments

D.C. acknowledges financial supports by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (grant number NRF-2019R1A2C1003089). This research was also supported by Basic Science Research Capacity Enhancement Project through Korea Basic Science Institute (Core-facility for Converging Materials) grant funded by the Ministry of Education (2019R1A6C1010045) and Korea Institute for Advancement of Technology(KIAT) grant funded by the



(a) (b)

Fig. 6. (a) Temperature evolution of the AgNWs heater at stepwise bias increase up to 4 V until the IR camera temperature limit. IR camera images corresponding to the applied bias of 1, 2, 3, and 4 V are also given, (b) Temperature profiles for the two samples in (a) by repetitively switching on for 6 minutes and switching off for 6 minutes. The switch-on voltage was 3 V.

Korea Government(MOTIE) (P0012451, The Competency Development Program for Industy Specialist).

Reference

1. F. Wan, H. He, S. Zeng, J. Du, Z. Wang, H. Gu and J. Xiong, “Silver nanowire network for flexible transparent electrodes based on spray coating at a low DC electric field and plasma treatment”, Nanotechnology, 31(32), 302-325 (2020).
2. D. Lee, G. Bang, M. Byun and D. Choi ,“Highly flexible, transparent and conductive ultrathin silver film heaters for wearable electronics applications”, Thin Solid Films, 697, 137835 (2020).
3. P. Zhang, I. Wyman, J. Hu, S. Lin, Z. Zhong, Y. Tu, Z. Huang and Y. Wei, “Silver nanowires: Synthesis technologies, growth mechanism and multifunctional applications”, Materials Science and Engineering: B, 223, 1-23 (2017).
4. J. Li, Y. Tao, S. Chen, H. Li, P. Chen, M.-z. Wei, H. Wang, K. Li, M. Mazzeo and Yu Duan, “A flexible plasma-treated silvernanowire electrode for organic light-emitting devices”, Scientific Reports, 7, 16468 (2017).
5. V. H. Dao and B. J. Mapleback, “Generation of highly porous silver nanowire networks by plasma treatment and their direct application as supercapacitor electrodes”, Nanoscale, 12, 11868-11877 (2020).
6. M. Lagrange, D. P. Langley, G. Giusti, C. Jiménez, Y. Bréchet and D. Bellet, “Optimization of silver nanowire-based transparent electrodes: effects of density, size and thermal annealing”, Nanoscale, 7, 17410-17423 (2015).
7. D. Zhou, H. Wang, J. Bai and J. Cao, “Effects of oxygen plasma treatment and ebeam evaporation on AgNWs/PDMS based stretchable electrode”, Smart Mater. Struct., 23, 104001 (2014).
8. K. Terpilowski and D. Rymuszka, “Surface Properties of Glass Plates Activated by Air, Oxygen, Nitrogen and Argon Plasma”, Glass Phys. Chem., 42, 535-541 (2016).
9. Y.-J. Song, J. Chen, J.-Y. Wu and T. Zhang, “Applications of Silver Nanowires on Transparent Conducting Film and Electrode of Electrochemical Capacitor”, Journal of Nanomaterials, 2014, 193201 (2014).
10. A. M. Bernal, A. M. Ardila, M. Vega-Verdugo, “Fabrication and study of thin transparent conductive films prepared by Spin Coating from metal nano-wires”, Ing. Compet., 18(2), 125-132 (2016).
11. M. Sadegh-cheri, “Design, Fabrication, and Optical Characterization of a Low-Cost and Open-Source Spin Coater”, J. Chem. Educ., 96(6), 1268-1272 (2019).
12. M. Song, D. S. You, K. Lim, S. Park, S. Jung, C. S. Kim, D.-H. Kim, D.-G. Kim, J.-K. Kim, J. Park, Y.-C. Kang, J. Heo, S.-H. Jin, J. H. Park and J.-W. Kang, “Highly Efficient and Bendable, Organic Solar Cells with Solution-Processed Silver Nanowire Electrodes”, Adv. Funct. Mater., 23(34), 4177-4184 (2013).
13. T. Tokuno, M. Nogi, M. Karakawa, J. Jiu, T. T. Nge, Y. Aso and K. Suganuma, “Fabrication of Silver Nanowire Transparent Electrodes at Room Temperature”, Nano Res., 4, 1215-1222 (2011).
14. K. Gayantha, N. Thilawala, J.-K. Kim and J.-M. Lee, “Improvement of conductivity of graphene - silver nanowire hybrid through nitrogen doping using low power plasma treatment”, Journal of Alloys and Compounds, 773, 1009-1017 (2019).
15. W. Kim, and J. W. Roh, “Suppressed Sheet Resistance of Ag Nanostructure Films by O2 Plasma Treatment”, J. Microelectron. Packag. Soc. 26(3), 37-41 (2019).
16. Y. B. Shin, Y. H. Ju, and J.-W. Kim, “Technical Trends of Metal Nanowire-Based Electrode”, J. Microelectron. Packag. Soc. 26(4), 15-22 (2019).