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Joule Heating of Metallic Nanowire Random Network for Transparent Heater Applications

Aekachan Pichitpajongkit, Hyeonjin Eom, and Inkyu Park[+]

Abstract

Silver nanowire random networks are promising candidates for replacing indium tin oxide (ITO) as transparent and conductive electrodes. They can also be used as transparent heating films with self-cleaning and defogging properties. By virtue of the Joule heating effect, silver nanowire random networks can be heated when voltage bias is applied; however, they are unsuitable for long-term use. In this work, we study the Joule heating of silver nanowire random networks embedded in polymers. Silver nanowire random networks embedded in polymers exhibit breakdown under the application of electric current. Their surface morphological changes indicate that nanoparticle formation may be the main cause of this electrical breakdown. Numerical analyses are used to investigate the temperatures of the silver nanowire and substrate.

Keywords: Silver nanowire, transparent electrode, Joule heating, hybrimer substrate, electrical breakdown

1. INTRODUCTION

Transparent conductive electrodes are very important in many modern applications such as photovoltaic devices [1-3], light-emitting diodes (LEDs) [4, 5], and flexible displays [6]. Indium tin oxide (ITO) is the most common material used as transparent conductive electrodes nowadays; however, the price of ITO has been increasing owing to the limited supply of indium. In terms of fabrication, ITO involves time-consuming processes under high temperature and vacuum conditions. However, the brittleness of ITO makes it unsuitable for use in flexible and bendable applications. Many candidates have been reported as prospective replacements for ITO, such as conductive polymers, carbon nanotubes, graphene, metal grids, and silver nanowire random networks. Amongst these candidates, silver nanowires have drawn much attention because of their excellent electrical conductivity and high optical transparency [7]. Furthermore, silver nanowire random networks can be fabricated through the solution process, which facilitates low cost and scalable roll-to-roll manufacturing. Prototypes of devices using silver nanowire random networks as transparent conductive electrodes have been reported, such as LEDs, touch screens, and solar cells [7-9].

Silver nanowire random networks have also been used as transparent film heaters, following the Joule heating characteristics of electrically conductive materials. Many researchers have attempted to utilize silver nanowire film heaters in real-life applications, such as for window defogging [10], in thermoacoustic speakers [11], and in thermochromic devices [12]. However, silver nanowire random networks breakdown under the flow of electric current and are unsuitable for long-term use [13]. Khaligh et al. concluded that silver nanowire transparent electrodes failed at elevated temperatures, owing to the instability of the silver nanowire and breakdown of the silver nanowire network [13]. However, the main reason for this instability was unknown, although some reasons were hypothesized. The temperature of the silver nanowires could have been higher than the average surface temperature, particularly, at the junction of the silver nanowires. The corrosion caused by the reaction with the sulfur in silver nanowires could be another possible reason, as silver sulfide (Ag_2S) was observed in the nanoparticles formed on the surfaces of the failed silver nanowires at elevated temperatures. Moreover, as all the sidewalls of the silver nanowires were {110} planes, which were not the lowest energy planes in the FCC structure, high temperatures could induce atomic diffusion at the sidewalls of the silver nanowires. Li et al. tried to conduct a numerical analysis of the Joule heating of the

Department of Mechanical Engineering, KAIST
Daejeon 34141, South Korea
[+]Corresponding author: inkyu@kaist.ac.kr
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silver nanowire networks and hypothesized that the failure could have been caused by the melting of the nanowires [14].

In this work, we studied the Joule heating and failure of silver nanowire random networks embedded in polymers. Numerical analyses were performed to compare the temperature of the silver nanowire with the average surface temperature.

2. EXPERIMENTAL AND NUMERICAL ANALYSIS

2.1 Synthesis of silver nanowires and fabrication of transparent film heater

Silver nanowires were synthesized using a modified polyol process. 5.86 g of polyvinylpyrolidone (PVP; molecular weight = 55,000) was dissolved in 190 ml of glycerol in a clean beaker and heated at 150 °C for 2 h to remove the moisture in the PVP. The PVP solution was then injected into a clean two-neck flask on a heating mantle and cooled down to 55 °C. 0.059 g of sodium chloride in 0.5 ml of deionized water and 10 ml of glycerol was added to the formerly prepared solution, along with 1.58 g of silver nitrate. The mixture was heated slowly to a temperature of 155 °C within 10 min, and maintained at that temperature for 20 min to facilitate reaction. The dimensions of the silver nanowire could be changed by controlling the reaction time. The product from the reaction was washed five times using the following process. The solution was filtered through a glass filter with pore sizes ranging from 10–16 and 16–40 μm. Then, the silver nanowires on the glass filter were sonicated in methanol to facilitate redispersion.

As it is well known that silver nanowires do not adhere well to polymer substrates, we embedded the silver nanowires into transparent polymer substrates, to improve the adhesion and mechanical robustness of the sample. The embedded samples were fabricated according to reference [9]. First, the silver nanowire solution obtained using the polyol process mentioned before was sprayed on to a glass slide. The back pressure of nitrogen used for spraying was 0.1 MPa and the flow rate of the silver nanowire solution was 3 ml/min. The distance between the substrate and nozzle was fixed at 13 cm. The substrate was heated to 100 °C to evaporate the solvent rapidly during spraying. The moving speed of the nozzle was set to 4,000 in/min and the relative humidity in the spray booth was maintained at 30%. The concentration of the silver nanowire solution was 0.6 mg/ml. The polymer resin (hybrimer) was prepared using the following process: 2-(3,4-epoxycyclohexyl) ethyl-trimethoxysilane (ECTS) and diphenylsilanediol (DPSD) were mixed in a two-neck flask at a molar ratio of 1:1.5. Barium hydroxide monohydrate was added along with 0.2 mol% silane precursors. The solution was left for 4 h under N_2 purging for sol-gel reaction. Then, 3-ethyl-3[(3ethyloxetane-3-yl) methoxy] methyl oxetane triarylsulfonium hexafluoroantimonate salt, in an amount equivalent to 2 wt% of the total resin solution, was added as a photoinitiator. Glass fibers were placed on another cleaned glass slide and the hybrimer was cast onto the prepared glass fiber. Presprayed silver nanowires deposited on glass were used to cover the uncured resin (hybrimer). Then, a sandwich sample was compressed and irradiated with UV light (λ = 365 nm) in order to cure the hybrimer. Finally, silver nanowires embedded in polymer were obtained after peeling off the resin from the glass.

2.2 Experimental and numerical characterization

Samples were cut into individual pieces with dimensions of 2 cm × 1 cm. Then, silver paste was applied onto the substrate, leaving an area of 1 cm × 1 cm exposed. Copper tape was then placed onto the silver paste to form the electrode. The sample was connected to DC power and an ammeter to collect the current data. A K-type thermocouple was attached to the surface of the sample and connected to a datalogger (OMEGA HH147U). COMSOL Multiphysics® was utilized, for the Joule heating feature. An isolated single unit of silver nanowire random network was fabricated using 50 nm diameter silver nanowires aligned orderly with a distance 500 nm between individual nanowires. The density was calculated to be ~20%, which was similar to that of the real sample characterized using the ImageJ software. The substrate surface dimensions were set to 6 μm × 4 μm and thickness was set to 100 μm. The parameters of the materials, required for the calculations, were taken from reference [15].

3. RESULTS AND DISCUSSIONS

Figure 1 (a-b) shows the scanning-electron microscope (SEM) image of the silver nanowires synthesized by the polyol method. The average length and width were 11±3.7 μm and 67±17.7 nm, respectively. The silver nanowire random network embedded in hybrimer is shown in Figure 1 (c-d). Typically, silver nanowires have poor adhesion to polymer substrates and thus, can be easily detached from the substrate surface. The embedding of silver nanowires in the hybrimer improved the adhesion between the

silver nanowires and substrate and simplified the handling of the heater sample.

Figure 2(a) shows a sample of the silver nanowire random network embedded in hybrimer. The optical transparency of the silver nanowire random network embedded in hybrimer is good, as the word "KAIST" underneath the sample can be seen clearly using naked eyes. The actual optical transmission spectrum of the silver nanowire random network embedded in hybrimer, measured by ultraviolet–visible (UV-Vis) spectroscopy, is shown in Figure 2(b). The optical transparency at wavelengths greater than 500 nm was ~80 % while the sheet resistance measured by a four-point probe was ~50 Ω/sq. When a voltage bias was applied to the silver nanowire random network, the surface temperature increased, according to the Joule heating effect. The time-dependent surface temperature profiles of silver nanowire random network (R_{sh} = ~50 Ω/sq.) with different voltages applied are shown in Figure 2(c). The result shows that the higher the voltage is applied, the higher the final surface temperature is obtained. The response time (T_{90}) and recovery time (T_{90}) are estimated as 170 s and 240 s, respectively.

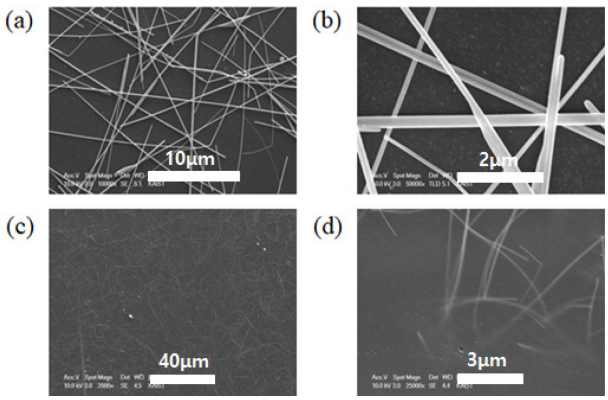

Fig. 1. SEM images of silver nanowire synthesized by polyol method (a-b) and silver nanowire random network embedded in hybrimer substrate (c-d)

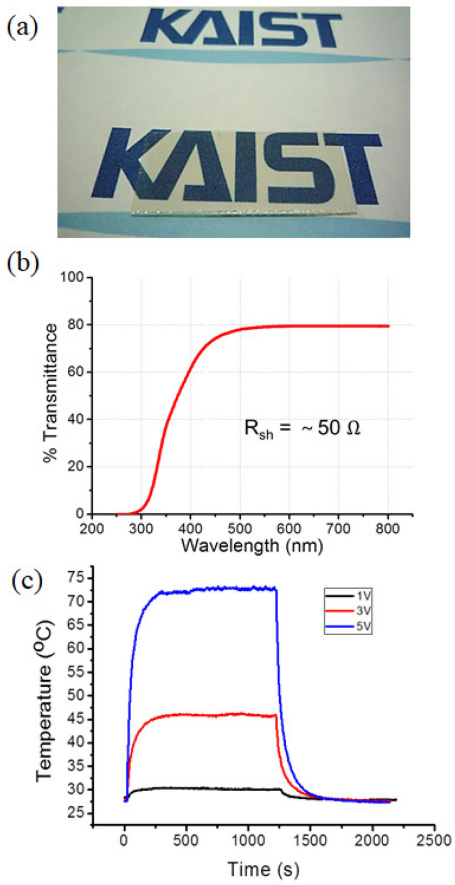

Fig. 2. (a) Sample of silver nanowire random network embedded in hybrimer. (b) Optical transmittance spectrum of silver nanowire random network embedded in hybrimer measured by UV-Vis spectroscopy. (c) Time-dependent surface temperature profile of silver nanowire random network (*R*sh = ~50 Ω/sq) for different applied voltages.

Figure 3(a) shows the scattering plot for the relationship between the electric power and increase in the surface temperature of the silver nanowire random network embedded in hybrimer. The result shows that the relationship between the electric power and increase in surface temperature is linear, by fitting with a linear equation (R^2 = 0.978). In order to observe the consistency of Joule heating of the silver nanowire random network, voltage cycles were applied to the

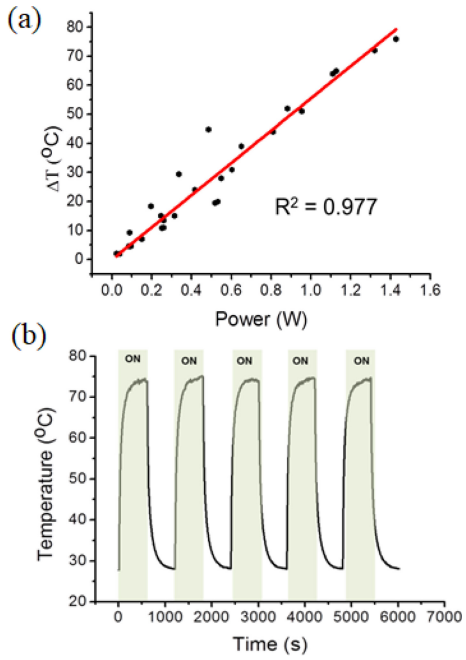

Fig. 3. (a) Relationship between electric power and the increase in surface temperature of silver nanowire random network embedded in hybrimer substrate. (b) Time-dependent surface temperature profile of silver nanowire random network when 5 V on/off cycles are applied.

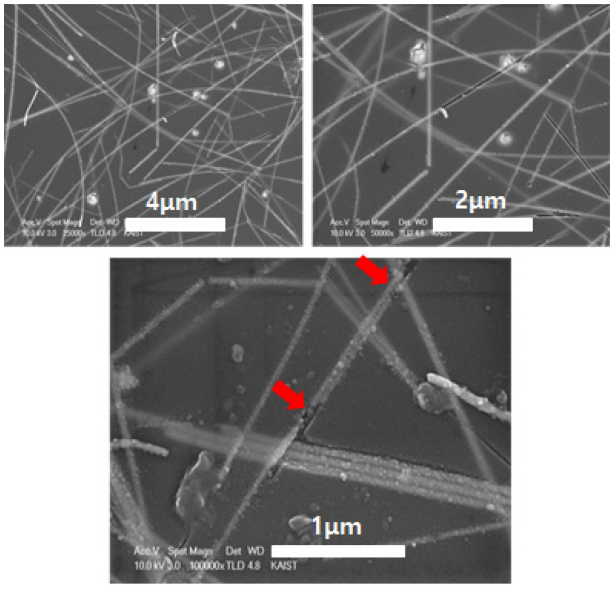

Fig. 4. SEM images of silver nanowire random network embedded in hybrimer after breakdown. Red arrows indicate the regions of physical breakdown within nanowires

silver nanowire random network (R_{sh} = ~50 Ω/sq) repeatedly. Figure 3(b) shows the time-dependent surface temperature profile of the silver nanowire random network when 5 V on/off cycles were applied. The result obviously shows that the silver nanowire random network was consistent in terms of Joule heating. In each voltage cycle, the surface temperature of the silver nanowire random network increased to ~75 °C and returned to the initial temperature after the voltage was turned off. Moreover, the surface temperature profiles for each on–off cycle were almost identical, with a rise time of~134 s and decay time of ~171 s.

However, the silver nanowire random network failed to operate for a long period. As the period increased, the sheet resistance of the silver nanowire random network increased and the surface temperature decreased until electrical breakdown of the network occurred. The broken down sample was investigated using a scanning electron microscope, as shown in Figure 4. There was no sign of silver nanowire melting at the surface. However, it should be noted that the melting point of silver is ~ 961.8 °C, although it had been reported to be lower for silver nanowires [16]. If the melting of the silver nanowire had interfered with the breakdown of the silver nanowire random network, traces of polymer melting should have been observed. However, we could not observe any sign of polymer melting on the surface of the silver nanowire random network embedded in the hybrimer (the melting point of the hybrimer was 400 °C) [15]. Instead of the silver nanowire melting, we observed morphological changes at the locations

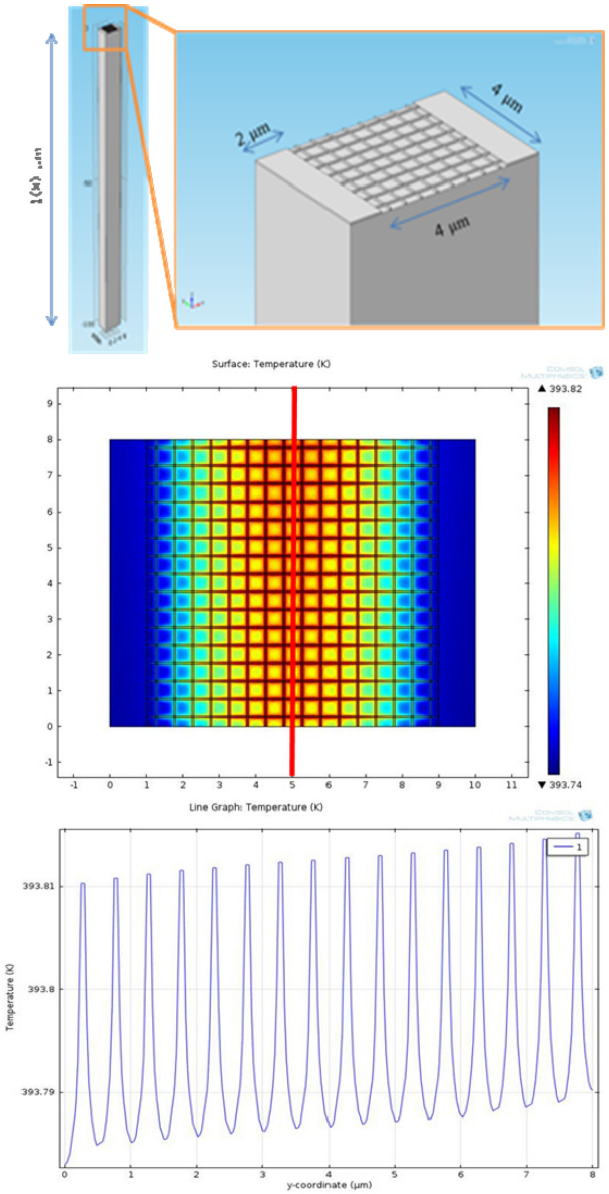

Fig. 5. (a) Numerical analysis model of silver nanowire network for Joule heating experiment. (b) Numerical analysis temperature distribution result for Joule heating of silver nanowire network. (c) Temperature profile along the red line in figure (b).

where the silver nanowires were exposed to the environment. The sidewall surfaces of the silver nanowires became rough and nanoparticles were observed to form on the sidewall surfaces. This result agreed well with the result of Khaligh et al. [13], which stated that silver nanowires could be unstable with the formation of nanoparticles at the sidewall surfaces at elevated temperatures, leading to disconnection of the electrical network.

In order to confirm the hypothesis, a numerical analysis was performed. As explained in the experimental section, the numerical simulation model shown in Figure 5(a) was utilized.

The surface temperature of the numerical analysis model was raised up to 373 K from 273 K. The surface temperature profile of the numerical analysis model was investigated and is shown in Figure 5(b-c). The result shows that the difference between the silver nanowire temperature and substrate temperature was very small (~0.1 °C). Therefore, the surface temperature during Joule heating could be considered highly uniform, which implied that melting may not have been the reason for the electrical breakdown of the silver nanowire network. As explained above, the formation of nanoparticles at the exposed areas of the silver nanowires could be the main cause of the electrical breakdown of the silver nanowire network.

4. CONCLUSIONS

We studied the Joule heating of silver nanowire random networks embedded in hybrimer substrates. The silver nanowire random networks embedded in hybrimer showed good response to Joule heating and consistent changes in temperature. However, an electrical breakdown could be observed during the long-term operation of Joule heating. The SEM images agreed well with the literature that stated that the silver nanowires became unstable at elevated temperatures and no signs of melting were observed. Numerical analyses were performed to estimate the local temperature of the silver nanowire and the substrate temperature; however, the results showed uniform temperature distribution. Therefore, it was unlikely that the melting of the silver nanowire caused the breakdown of the electrical network. Instead, nanoparticle formation could be the main cause of the breakdown.

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REFERENCES

[1] W. Gaynor, G. F. Burkhard, M. D. McGehee, and P. Peumans, “Smooth nanowire/polymer composite transparent electrodes”, *Adv. Mater.*, Vol. 23, No.26, pp. 2905-2910, 2011.

[2] F. S. F. Morgenstern, D. Kabra, S. Massip, T. J. K. Brenner, P. E. Lyons, J. N. Coleman, and Richard H. Friend, “Ag-nanowire films coated with ZnO nanoparticles as a transparent electrode for solar cells”, *Appl. Phys. Lett.*, Vol. 99, No. 18, pp. 183307-183309, 2011.

[3] M. Reinhard, R. Eckstein, A. Slobodskyy, U. Lemmer, and A. Colsmann, “Solution-processed polymer–silver nanowire top electrodes for inverted semi-transparent solar cells”, *Organic Electronics*, Vol. 14, No.1, pp. 273-277, 2013.

[4] S. Coskun, E. Selen Ates, and H. E. Unalan, “Optimization of silver nanowire networks for polymer light emitting diode electrodes”, *Nanotechnology*, Vol. 24, No. 12, pp. 125202-125209, 2013.

[5] Z. Yu, Q. Zhang, L. Li, Q. Chen, X. Niu, J. Liu, et al., “Highly flexible silver nanowire electrodes for shape-memory polymer light-emitting diodes”, *Adv. Mater.*, Vol. 23, No.5, pp. 664-668, Feb 1 2011.

[6] K. Lee, “Fabrication of transparent piezoresistors using carbon nanotube films and its application for piezoresistive touch display”, Ph.D. thesis, Korea Advanced Institute of Science and Technology, Republic of Korea, 2011.

[7] J. Lee, I. Lee, T. S. Kim, and J. Y. Lee, “Efficient Welding of Silver Nanowire Networks without Post-Processing”, *Small*, Vol. 9, No. 7, pp. 1-8, 2013.

[8] J. Y. Lee, S. T. Connor, Y. Cui, and P. Peumans, “Semi-transparent organic photovoltaic cells with laminated top electrode”, *Nano Lett.*, Vol. 10, No. 4, pp. 1276-1279, Apr 14 2010.

[9] L. Li, Z. Yu, W. Hu, C. H. Chang, Q. Chen, and Q. Pei, “Efficient flexible phosphorescent polymer light-emitting diodes based on silver nanowire-polymer composite electrode”, *Adv. Mater.*, Vol. 23, No. 46, pp. 5563-5567, 2011.

[10] T. Kim, Y. W. Kim, H. S. Lee, H. Kim, W. S. Yang, and K. S. Suh, “Uniformly Interconnected Silver-Nanowire Networks for Transparent Film Heaters”, *Adv. Func. Mater.*, Vol. 23, No. 10, pp. 1250-1255, 2013.

[11] H. Tian, D. Xie, Y. Yang, T.-L. Ren, Y.-X. Lin, Y. Chen, Feng-Yu Wang, Changjian Zhou, Ping-Gang Peng, Li-Gang Wang and Lai Lai, “Flexible, ultrathin, and transparent sound-emitting devices using silver nanowires film”, *Applied Physics Letters*, Vol. 99, No.25 p. 253507, 2011.

[12] C. Celle, C. Mayousse, E. Moreau, H. Basti, A. Carella, and J.-P. Simonato, “Highly flexible transparent film heaters based on random networks of silver nanowires”, *Nano Research*, Vol. 5, No. 6, pp. 427-433, 2012.

[13] H. H. Khaligh and I. A. Goldthorpe, “Failure of silver nanowire transparent electrodes under current flow”, *Nanoscale Res Lett*, Vol. 8, No. 1, pp. 235-240, 2013.

[14] Y. Li, K. Tsuchiya, H. Tohmyoh, and M. Saka, “Numerical analysis of the electrical failure of a metallic nanowire mesh due to Joule heating”, *Nanoscale Research Letters*, Vol. 8, No. 1, pp. 1-9, 2013.

[15] J. M. Yoon, D. O. Shin, Y. Yin, H. K. Seo, D. Kim, Y. I. Kim, J. H. Jin, Y. T. Kim, B. S. Bae, S. O. Kim, and J. Y. Lee, “Fabrication of high-density In(3)Sb(1)Te(2) phase change nanoarray on glass-fabric reinforced flexible substrate”, *Nanotechnology*, Vol. 23, No.25, p. 255301, Jun 29 2012.

[16] P. Ramasamy, D.-M. Seo, S.-H. Kim, and J. Kim, “Effects of TiO2 shells on optical and thermal properties of silver nanowires”, *Journal of Materials Chemistry*, Vol. 22, No. 22, pp. 11651-11657, 2012.