High-Performance Silver Nanowire Film on Flexible Substrate Prepared by Meyer-rod Coating

Junaidi¹, K Triyana², Harsojo² and E Suharyadi²

¹Department of Physics, Universitas Lampung, Bandar Lampung, 35145 Indonesia
²Department of Physics, Universitas Gadjah Mada, Yogyakarta, 55281 Indonesia
Email: triyana@ugm.ac.id

Abstract. Flexible and transparent conducting (FTC) films based on silver nanowires (AgNWs) were fabricated onto a polycarbonate (PC) substrate by a simple Meyer-rod coating process. AgNWs were synthesized using polyvinyl alcohol by polyol process with a diameter and length of 500 nm and 10 µm, respectively. The FTC film was fabricated by varying the number of layers. The FTC film exhibited a sheet resistance of 12.1 Ω sq⁻¹ with a transparency of 89.5%. The optical conductivity of FTC films was obtained about 4.7 - 13.1 × 10⁵ S.m⁻¹ with a refractive index about 1.2 to 1.7. The number of layers is an important to influence on the sheet resistance and transmittance of the FTC films. The sheet resistance and transmittance decreases with the number of layers.

Keywords: conductive film, flexible substrate, silver nanowire, transparent electrode.

1. Introduction

Transparent conductive electrode (TCE) has emerged rapidly and attracted much attention due to its fascinating features and applications in recent years. For the reasons, many TCE materials, such as indium tin oxides (ITO), graphenes, carbon nanotubes (CNTs), and silver nanowires (AgNWs). ITO has excellent transparency throughout the visible spectrum and low sheet resistance. However, ITO has certain limitations in application for next-generation devices: (i) indium is a rare material, so it has a high price, (ii) the process of making ITO is also expensive because it requires high temperature and vacuum to control its thickness [1], (iii) ITO is brittle and can easily wear out or crack when used in the applications which involve bending, and (iv) ITO has a high refractive index. Such disadvantages make ITO unsuitable for display applications because it will reflect light and reduce the brightness of the screens [2].

The deposition techniques are performed on transparent substrates such as glass, quartz, and poly (ethylene terephthalate) or PET [3–5]. The main focus of the TCE manufacture is getting low sheet resistance ($R_s$) and high optical transmittance ($T$). TCE based on AgNWs can simultaneously realize outstanding flexibility, conductivity, and transparency compared with other electrode materials, and its low-cost deposition techniques [6]. The spin coating method for producing AgNWs films was demonstrated by Chen et al. and produced sheet resistance and transmittance of about 10 Ω/sq and $T \approx 80\%$, respectively [7]. Margulis et al. reported solution-process of AgNWs films by spray coating method with $R_s \approx 18$ Ω/sq and $T \approx 86\%$ [8]. Sachse et al. reported a dip coating method for AgNWs
film fabrication with $R_s \approx 15$ Ω/sq and $T \approx 85\%$ [9]. Fabrication of AgNWs film with a meyer-rod coating has been done by Kumar et al. with $R_s \approx 300$ Ω/sq and $T \approx 90\%$ [10].

In this paper, we performed the synthesis of AgNWs using polyvinyl alcohol (PVA) as a capping agent and stabilizer. Furthermore, the resulted AgNWs created a thin layer on polycarbonate (PC) substrates using Meyer-rod coating method. The number of AgNWs layers was varied to produce optimum optical and electrical properties. The produced AgNWs films can be used as TCE for various optoelectronic applications, such as touch screens, organic light-emitting diodes (OLEDs), solar cells, and transparent heaters.

2. Experimental Method

2.1 Materials
The materials used included: silver nitrate (AgNO$_3$, 99%, Merck), polyvinyl alcohol (PVA, Mw. 31000-50000 g/mol, Sigma-Aldrich), copper (II) chloride dihydrate (CuCl$_2$.2H$_2$O, Sigma-Aldrich), ethylene glycol (EG, 99%, Merck), and ethanol (EtOH, 98%, Merck).

2.2 Synthesis of AgNWs
The AgNWs were synthesized by polyol method with several modifications [11]. Firstly, 0.5 g of PVA was mixed with 10 mL of ethylene glycol (EG) and 20 µL of CuCl$_2$.2H$_2$O 0.1 M using an Erlenmeyer flask at 150 °C for 1 h. After that, 5 mL of AgNO$_3$ 0.5 M in EG was added dropwise using a syringe for about 10 min followed by stirring at 350 rpm for 1 h. Furthermore, the solution containing the produced AgNWs then cooled naturally to room temperature. It was followed by several times of centrifugation using ethanol at a speed of 6000 rpm.

2.3 Fabrication of AgNWs Films
Firstly, the PC substrates were ultrasonicated in ethanol at room temperature for 30 min and rinsed thoroughly with deionized water. The PC substrates had been dried at room temperature under ambient conditions. The AgNWs with a diameter ($\phi$) and length ($l$) of ($\phi$ = 500 nm, $l$ = 10 µm) as shown in SEM images in Figure 1 were used in this study. The samples of AgNWs were dried to determine their mass and concentration by evaporating ethanol in a heating chamber at a temperature of 60 °C. The as-prepared AgNWs was dispersed for one more time in an ethanol solution with a concentration of 10 wt. %. The dispersion solution of the AgNWs was coated onto 25 mm × 25 mm PC substrates by varying the number of layers manually using a bar-coater (RDS-20). After coating the AgNWs, the samples were dried on a hot plate at 90 °C for 15 min to remove the solvent.

2.4 Characterization
The crystal structure of AgNWs suspension was analyzed via X-ray diffraction (Shimadzu R6000) by CuKα ($\lambda = 1.54184$ Å) with a 2θ scanning in the temperature range of 20 to 90°. Furthermore, the electrical and optical properties of the flexible AgNWs films were recorded using a four-point-probe (Keithley) and UV-vis spectroscopy (Shimadzu, UV-1700) in the wavelength range of 300 to 800 nm. The morphology, size, and thickness of AgNWs films were observed using a transmission electron microscope (JEOL, JEM-1400) and scanning electron microscope (JEOL, JSM-6510).

3. Results and Discussion
Figure 1(a) shows the UV-vis spectra of AgNWs in an ethanol solution. From the UV-vis spectra, the absorption peaks of AgNWs solution formed at a wavelength of 360 nm and 378 nm when synthesized using PVA as a capping agent and stabilizer [12]. The characteristics and the optical phenomenon of metal nanomaterials, especially Ag nanostructures regarding the absorption spectrum depend on the geometry and size. The absorbance peak that occurs at a specific wavelength results from the interaction of light and matter (sample).

The XRD pattern of the AgNWs is depicted in Figure 1(b). The crystal structure of AgNWs produced four diffraction peaks. All peaks can be indexed to Ag cubic phase of which each angle of
diffraction 2θ was at 38.21° (111), 44.49° (200), 65.59° (220), 77.41° (311), and 81.59° (222). The number in the parentheses indicates the corresponding crystal plane. According to standard JCPDS card of 04-0783 from ASTM, the XRD pattern indicates the crystallization of the AgNWs. The crystalline of the AgNWs can be identified as a face-centered cubic (fcc).

Figure 1. (a) UV-vis Spectra of AgNWs solution and (b) XRD pattern of AgNWs.

The AgNWs synthesized in this study also showed a high aspect ratio. This case showed the diffraction signal peak of XRD at (111) was larger than that at (200). The calculated lattice constant according to the spacing distance ($d_{hkl}$) of the {111} planes was 4.080 Å. Such lattice constant was very close to the literature value of 4.085 Å [12]. The SEM images of AgNWs solution and AgNWs film are shown in Figure 2.

Figure 2(a) shows that the diameter and length of AgNWs were (500 ± 100) nm and (10 ± 5) μm. The diameter and length of different AgNWs will have an impact on changes in optical and electrical properties when used as TCEs. The SEM image of the AgNWs film with one layer was shown in Figure 2(b). The thickness of AgNWs film was analyzed using cross-sectional techniques. The thickness of AgNWs film obtained was about of 40 μm (Figure 2(c)).

PVA is an effective polymer capping agent and stabilizer in the synthesis of AgNWs. PVA can control the process of the Ag nanocrystal seeds with various sizes. The presence of PVA can change the free surface energy that influences anisotropic formation mechanism of AgNWs. Anisotropic growth is retained by the PVA on (100) facets. The mechanical strength of PVA caused a single crystal and MTP seeds grow into AgNWs. The bonding capabilities of PVA depend on the shape of the Ag nanocrystal. The Ag atoms will be attached to the (111) facets that cause MTPs seeds grew and formed pentagonal NWs [13,14]. The NWs structure can grow to form Ag-O bond on the (111) facets. PVA can effectively inhibit the growth on the (100) so as to control the growth on the
(111) with various Ag nanocrystals [15,16]. The transmittance and band gap energy of AgNWs film are illustrated in Figure 3.

![Figure 3](image)

**Figure 3.** The curve of (a) transmittance and (b) band gap energy of AgNWs film.

Figure 3(a) shows that the transmittance of AgNWs film was approximately 70.7 to 89.5%. The AgNWs film transmittance decreased along with the increasing number of layers. The measurement of absorbance as a function of wavelength and thickness of thin films conducted to determine the value of the band gap energy ($E_g$) of the thin films. The energy gap of AgNWs film was about 4.15 eV as shown in Figure 3(b).

The extension coefficient ($k$) is a measure of the fraction of lost light due to scattering and absorption of light per distance units of the medium or thickness. The extension coefficient decreased together with the increasing wavelength of light which subjected to the surface of the sample. The decline in the extension coefficient resulted in the increasing of the wavelength shows that the light fraction has been reduced or lost due to the decreasing light intensity scattered and absorbed by the sample [17].

The refractive index was calculated using the reflectance values, and the extension coefficient. The resulting refractive index is used to calculate the optical conductivity of the AgNWs film. The optical conductivity is the ability of material to conduct photon energy. The curves of the refractive index and optical conductivity of the AgNWs film as a function of wavelength are presented in Figure 3.

![Figure 4](image)

**Figure 4.** (a) Refractive index and optical conductivity and (b) transmittance and a sheet resistance of AgNWs film.
Figure 4(a) shows that the refraction index decreased in line with the increasing wavelength. The refractive index experienced saturation at a wavelength of about 550 nm, i.e. about 1.2 to 1.7 for the AgNWs film [18]. The obtained optical conductivity onto the PC substrate for AgNWs film was about $4.7 \times 10^5$ Sm$^{-1}$. The optical conductivity of AgNWs film is lower than the optical conductivity of metallic silver, i.e. $6.3 \times 10^7$ Sm$^{-1}$ [19,20].

I-V curves were used to determine the sheet resistance ($R_s$) of AgNWs film that measured using a four-point probe on a direct current from 0 to 0.5 mA as shown in Figure 4(b). Figure 4(b) shows that the sheet resistance of AgNWs film in one layer was 1470.5 $\Omega$sq$^{-1}$. A sheet resistance continues to decline consecutively about 454.2, 43.9, and 12.1 $\Omega$sq$^{-1}$ when the coating is done as much as 2x, 3x and 5x. Decrease of sheet resistance indicates the increasing in electrical conductivity ($\sigma_{dc}$) of AgNWs film. The number of layers can increase the electrical conductivity and decrease the optical transmittance of AgNWs film as seen in Figure 4(a) [21].

4. Conclusion

The synthesis AgNWs were conducted by polyol process using polyvinyl alcohol as a capping agent and stabilizer. The absorption peaks of AgNWs solution formed at the wavelengths of 360 nm and 378 nm with the face-centered-cubic (fcc) crystal structures. The Diameter and length of AgNWs solution are $(500 \pm 100)$ nm and $(10 \pm 5)$ µm. The AgNWs were coated onto the PC substrate by various numbers of coating. The thickness of AgNWs film obtained about of 40 µm prepared by Meyer-rod coating. The transmittance of AgNWs films was approximately 70.7 to 89.5% and the sheet resistance of AgNWs film was 12.1 $\Omega$sq$^{-1}$. The obtained optical conductivity for AgNWs film was about $4.7 \times 10^5$ Sm$^{-1}$.

5. References

[1] Hecht D S, Hu L and Irvin G 2011 Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures Adv. Mater. 23 1482–513

[2] Wang J, Jiu J, Araki T, Nogi M, Sugahara T, Nagao S and Koga H 2015 Silver nanowire electrodes: conductivity improvement without post-treatment and application in capacitive pressure sensors Nano-Micro Lett. 7 51–8

[3] Lim J W, Cho D Y, Jihoon-Kim, Na S I and Kim H K 2012 Simple brush-painting of flexible and transparent Ag nanowire network electrodes as an alternative ITO anode for cost-efficient flexible organic solar cells Sol. Energy Mater. Sol. Cells 107 348–54

[4] Naito K, Yoshinaga N, Tsutsumi E and Akasaka Y 2013 Transparent conducting film composed of graphene and silver nanowire stacked layers Synth. Met. 175 42–6

[5] Tokuno T, Nogi M, Jiu J and Suganuma K 2012 Hybrid transparent electrodes of silver nanowires and carbon nanotubes: a low-temperature solution process Nanoscale Res. Lett. 7 281

[6] Kim D, Zhu L, Jeong D J, Chun K, Bang Y Y, Kim S R, Kim J H and Oh S K 2013 Transparent flexible heater based on hybrid of carbon nanotubes and silver nanowires Carbon N. Y. 63 530–6

[7] Chen T-G, Huang B-Y, Liu H-W, Huang Y-Y, Pan H-T, Meng H-F and Yu P 2012 Flexible silver nanowire meshes for high-efficiency microtextured organic-silicon hybrid photovoltaics. ACS Appl. Mater. Interfaces 4 6857–64

[8] Margulis G Y, Christoforou M G, Lam D, Beiley Z M, Bowring A R, Bailie C D, Salleo A and McGehee M D 2013 Spray deposition of silver nanowire electrodes for semitransparent solid-state dye-sensitized solar cells Adv. Energy Mater. 3 1657–63

[9] Sachse C, Müller-Meskamp L, Bormann L, Kim Y H, Lehnter F, Philipp A, Beyer B and Leo K 2013 Transparent, dip-coated silver nanowire electrodes for small molecule organic solar cells Org. Electron. physics, Mater. Appl. 14 143–8

[10] Kiran Kumar A B V, Wan Bae C, Piao L and Kim S H 2013 Silver nanowire based flexible electrodes with improved properties: High conductivity, transparency, adhesion and low
haze Mater. Res. Bull. 48 2944–9

[11] Junaidi, Triyana K., Sosiati H., Suharyadi E. and Harsojo 2015 Effect of temperature on silver nanorods synthesized by polyol method Adv. Mater. Res. 1123 256–9

[12] Junaidi, Triyana K., Harsojo and Suharyadi E. 2016 Chloride ion addition for controlling shapes and properties of silver nanorods capped by polyvinyl alcohol synthesized by polyol method 020092 020092

[13] Sun Y., Mayers B., Herricks T. and Xia Y. 2003 Polyl synthesis of uniform silver nanowires: a plausible growth mechanism and the supporting evidence Nano Lett. 3 955–60

[14] Zhang Q. and Wang Q. 2013 Particle size distribution of silver nanoparticles in different water conditions J. Mater. Environ. Sci. 4 617–20

[15] Junaidi, Yunus M., Harsojo, Suharyadi E. and Triyana K. 2016 Effect of stirring rate on the synthesis silver nanowires using polyvinyl alcohol as a capping agent by polyol process Int. J. Adv. Sci. Eng. Inf. Technol. 6 365–9

[16] Junaidi, Triyana K., Hui H., Wu L. Y. L., Suharyadi E. and Harsojo 2016 The silver nanowires synthesized using different molecule weight of polyvinyl pyrrolidone for controlling diameter and length by one-pot polyol method 020014 020014

[17] Bakr N. A., Funde A. M., Waman V. S., Kamble M. M., Hawaldar R. R., Amalnerkar D. P., Gosavi S. W. and Jadkar S. R. 2011 Determination of the optical parameters of a-Si:H thin films deposited by hot wire-chemical vapour deposition technique using transmission spectrum only Pramana - J. Phys. 76 519–31

[18] Khanarian G., Joo J., Liu X., Eastman P., Werner D., Connell K. O., Trefonas P., Khanarian G., Joo J., Liu X., Eastman P., Werner D. and Connell K. O. 2016 The optical and electrical properties of silver nanowire mesh films The optical and electrical properties of silver nanowire mesh films 024302

[19] De S., Higgins T. M., Lyons P. E., Doherty E. M., Nirmalraj P. N., Blau W. J., Boland J. J. and Coleman J. N. 2009 Silver nanowire networks as flexible, transparent, conducting films: extremely high DC to optical conductivity ratios ACS Nano 3 1767–74

[20] Mi H. Y., Li Z., Turng L. S., Sun Y. and Gong S. 2014 Silver nanowire/thermoplastic polyurethane elastomer nanocomposites: Thermal, mechanical, and dielectric properties Mater. Des. 56 398–404

[21] Dinh D. A., Hui K. N., Hui K. S., Kumar P. and Singh J. 2013 Silver nanowires: a promising transparent conducting electrode material for optoelectronic and electronic applications Rev. Adv. Sci. Eng. 2 1–22

Acknowledgments
This work was supported by a research grant of “International Research Collaboration and Scientific Publication through Contract No. LPPM-UGM/998/LIT/2015 with the Directorate General of Higher Education (DIKTI), Ministry of Education and Culture, Republic of Indonesia.