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Synthesis of dimension-controlled silver nanowires for highly conductive and transparent nanowire films

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Abstract—High-quality silver (Ag) nanowires with specific dimensions were synthesized by a polyol method with detailed control of the synthesis conditions. For the same amount of $AgNO_3$, the Ag nanowire density became higher as the nanowire diameter decreases and the length increases. This trend was replicated in Ag nanowire films coated on poly(ethylene terephthalate) films and higher densities of Ag nanowires and their junctions were observed in thinner and shorter nanowire networks. Nanowire films with a low sheet resistance ($<100\ \Omega\ sq^{-1}$) and a high transmittance (>90%) resulted from thin, long Ag nanowires. A modified percolation model, which emphasized the importance of the nanowire junction density, was in good agreement with the experimental observations. Meanwhile, long Ag nanowires were found to be undesirable in respect of their uniform coating over a large area. These results offer important design rules of Ag nanowires for highly conductive and transparent nanowire films.

Keywords: Silver (Ag) nanowires; Nanowire dimensions; Nanowire films; Sheet resistance; Transmittance

1. Introduction

The need for a unique material that is electrically conductive and optically transparent has been ever growing due to the consistently expanding use of optoelectronic devices such as light-emitting diodes, solar cells, liquid crystal displays and photodiodes [1]. To date, indium–tin oxide (ITO) has been the single most widely used material for that purpose owing to its low sheet resistance ($<100\ \Omega\ sq^{-1}$) and high transmittance (~90%). However, ITO is mechanically brittle and ITO film, which is usually grown by a sputtering process, is not suitable for flexible applications [2–4]. Several alternatives have been developed to replace ITO, including single-walled carbon nanotube networks [5,6], graphene films [7–14], silver (Ag) nanowire films [15–18], and poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) [19–22]. Of those, however, only Ag nanowire films were reported to equal or even surpass the performance of ITO [23,24]. Furthermore, Ag nanowire films showed good endurance to repeated bending, which is a major weakness of ITO [25,26].

The attractive features of Ag nanowire films are strongly dependent on the dimensions and the distribution of individual Ag nanowires since Ag nanowire films are a network of Ag nanowires rather than a continuous array. It has been argued that thin and long Ag nanowires lead to low sheet resistance and high optical transparency. In order to systematically study the effect of nanowire dimensions, nanowire diameter and length need tobe independently controllable. However, independent control of Ag nanowire dimensions is in general difficult to achieve since increasing the nanowire length is generally accompanied by a thickening of nanowire diameter. Recently, Bergin et al. reported the effect of nanowire length and diameter on the properties of Ag nanowire film by synthesizing Ag nanowires at different temperatures (130–160 °C) for varying growth times (0.3–7.5 h) based on a polyol method [27]. Although they presented experimental data on the length-dependent sheet resistance and transmittance for a given diameter, the diameter dependence was not clearly addressed. In addition, they used area coverage as a main

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variable from the basic assumption of random nanowire distribution, which may not be exactly true.

In this work, we synthesized Ag nanowires with clear distinctions in diameter and length, employing an ionic-liquid-assisted polyol method [28]. The independent control of Ag nanowire dimensions made it possible to reveal their electrical and optical effects experimentally, and thereby provide guidelines for optimal Ag nanowire film design for conductive and transparent electrodes. Moreover, the effect of nanowire dimensions on the uniformity of Ag nanowire film was further discussed.

2. Experimental

2.1. Silver nanowire synthesis

Silver nanowires with different dimensions were synthesized using a polyol method. Under standard conditions, 0.129 g of poly(vinylpyrrolidone) (PVP)($M_w \approx 55{,}000$ gmol^{-1}) and 0.004 g of 1-butyl-3-methylimidazolium chloride (BMIM-Cl) were predissolved in propylene glycol (PG) at room temperature. To change the dimensions of the resulting nanowires, the amount of PVP was modulated in the range of 0.065–1.032 g while the amount of BMIM-Cl was changed from 0.004 to 0.016 g. Then the mixture was heated up to 90 °C in a heating mantle while stirring. Silver nitrate ($AgNO_3$) solution (in PG, 0.95 M, 0.8 ml) was added to the mixture slowly after the temperature of the mixture was stabilized. The mixture underwent a reaction for Ag nanowire growth for 24 h and was then cooled down to room temperature. The as-synthesized Ag nanowires were washed with ethyl alcohol (99.5%) and isolated by centrifugation at 1500 rpm for 20 min. This washing process was repeated twice to remove the solvent and chemical agents completely.

2.2. Silver nanowire film preparation

The as-prepared Ag nanowires were dispersed again in a deionized water solution, in which cellulose binder was predissolved. This formulation was coated onto an optical-grade poly(ethylene terephthalate) (PET) film 100 μm thick, using a bar-coater, which comprises a bar wound with a continuous wire. A uniform Ag nanowire film was coated immediately behind the moving bar-coater. The thickness of the coated Ag nanowire film was controlled by adjusting the wire size and the inter-wire volume of the bar-coater and the relative concentrations of the formulation components. Finally, the coated Ag nanowire film was dried in a convection oven at 100 °C for 2 min.

2.3. Characterization

The shape and the distribution of the Ag nanowires were investigated using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and laser scanning microscopy (LSM, Olympus OLS 4000). More specifically, SEM was used to study nanometer-scale features such as the morphology, diameter and junction density of Ag nanowires, while LSM was used to examine micrometer-scale features such as the length and the distribution of the nanowires. The diameters and the lengths of Ag nanowires were measured under a magnification of more than 200,000× and 2,160×, respectively. To ensure the reliability of dimension measurements, these were obtained from more than 50 nanowires selected from three different locations. Both SEM and LSM images were obtained at two major stages in the process, i.e. Ag nanowire synthesis and Ag nanowire film coating. To obtain the SEM images of just-synthesized Ag nanowires, the as-synthesized Ag nanowires were washed with ethyl alcohol and filtered through a glass microfiber filter with a pore size of 1.2 μm, and were then dried in a convection oven at 80 °C for 24 h. Immediately prior to SEM measurement, a platinum (Pt) thin film was sputter-deposited over the Ag nanowires. For the LSM images of the as-synthesized Ag nanowires, the nanowires were diluted with ethanol and dropped on a PET film, followed by drying in an oven at 100 °C for 2 min. The sheet resistance of a Ag nanowire film was measured using a standard four-point probe method (AIT CMT-100MT). Optical transmittances for both a complete Ag nanowire film/PET system and an Ag-only nanowire film were analyzed at a wavelength of 550 nm (Otsuka MCPD 3700; Cary Varian 5000 UV-VIS-NIR spectrophotometer). Here, the transmittance of a Ag nanowire film was estimated from the total transmittance compensated by the absorbance of the PET substrate. X-ray diffraction (XRD) measurements were also performed to analyze the structure and the crystallinity of the Ag nanowires at a scan rate of 2° min^{-1}with a Cu K_α ($\lambda = 1.54056$ Å) radiation (Rigaku Model D/MAX-2500V/PC).

3. Results and discussion

Fig. 1 shows SEM images (Fig. 1a–c) and LSM images (Fig. 1d–f) of Ag nanowires synthesized at varying concentrations of PVP. Here, the molar ratio of PVP to $AgNO_3$ was controlled to be 3, 1.5 and 0.75 for a/d, b/e and c/f, respectively, with a fixed ratio of BMIM-Cl to $AgNO_3$ of 0.03. It can be seen from the SEM images that the average nanowire diameter increases in reverse proportion to PVP concentration (45 nm for Fig. 1a and 95 nm for Fig. 1c), while long, smooth Ag nanowires are three-dimensionally entangled for all cases. Precise diameter measurements on multiple nanowires revealed that the nanowire diameter is distributed in the range of 30–60, 40–70 and 50–140 nm, respectively for Fig. 1a, b and c. These results verify that PVP effectively suppresses nanowire growth in the radial direction. Provided that the same amount of $AgNO_3$ was used for the synthesis, this increasing diameter should lead to a decrease in the nanowire density and the number of crossing points. This is observed more clearly from LSM images. Thick nanowires are sparsely distributed with a lower frequency of nanowire crossing in Fig. 1f as compared to Fig. 1d. Despite the difference in diameters, nanowire length was measured to be in the same range of 20–45 μm for all synthesis conditions. It is also noteworthy that a considerable number of Ag nanoparticles appear along with nanowires in Fig. 1e and f.

The length of the Ag nanowires was also modulated by controlling both concentrations of PVP and BMIM-Cl relative to $AgNO_3$, as shown in Fig. 2. The combination of molar ratios of PVP and BMIM-Cl to $AgNO_3$ was adjusted at 6:0.03, 6:0.12 and 12:0.12 for a/d, b/e and c/f, respectively. SEM images (Fig. 2a–c) show that thin, uniform Ag nanowires (diameter distribution of 35–50 nm) are