EXPERIMENTAL METHODS FOR THIN LAYER COATING OF METAL NANOWIRES WITH INERT METALS

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Abstract

Metal nanowire (NW) films are recently studied as transparent electrodes for flexible display applications. On account of both high conductivity and persistence against bending, metal nanowires of copper and silver proved suitable for these applications. Silver and copper can form nanowires of high aspect ratio; whereas making nanowires of inert metals (gold, platinum, palladium) is relatively difficult and material cost rises if whole nanowire is composed of these. In order to exploit their surface physics and chemistry, it is more cost-effective to make cheap metal/inert metal core/shell nanowires. However, uniform coating of large-scale nanowire system is not easy.

We propose to coat metal nanowires with a thin shell of heavier metals, which are inert against oxidation and sulfurization. Coatings can be implemented efficiently and uniformly in two methods: portionwise and biphasic titration. Metal (Au, Pt, Pd) salts can be used as galvanic exchange agents for oxidation and substitution of a thin layer of copper and silver. This will provide with passivation of copper and silver against most chemical changes. Another advantage of thin layer coating is the exploitation of differences in optical parameters of those metals.

Keywords:

Metal Nanowires, Metal Coating, Silver Nanowires

1. INTRODUCTION

Currently used Indium Tin Oxide (ITO) transparent electrode has limitations including scarcity of indium, high costs of materials and processing as well as mechanical brittleness that could be fatal to flexible displays and touch screens. Promising candidates being studied for replacing ITO are carbon nanotubes (CNT), graphene, and metal nanowire electrodes. Among them, metal nanowire electrode is especially promising since it is able to overcome the limitations of ITO listed above while providing similar or superior optical and electrical properties compared to those of ITO [1]. Metal nanowires (NW) can be fabricated using the solution synthesis methods with high yield, and the solution suspended nanowires can simply be spin-coated or sprayed onto a large scale substrate [2]. This revolutionary technology is expected have a significant impact for the display industry, especially for flexible displays that requires mechanical flexibility.

Among different methodologies of making nanowires, the currently reported method for AgNW synthesis is the polyol reduction method [3], which results in high quality single crystalline NWs with high yield. Ultra-long and thin CuNWs can also be synthesized by solvo-thermal methods. Our research groups are currently focusing on synthesizing metal NWs with enhanced aspect ratios to improve the sheet resistance and using electro-spray deposition method to apply this technology at large scale.

Although the nanowire electrode has shown comparable performance to that of ITO, the current level of haze is ~15% at 8 ohm/sq sheet resistance and 80% diffusive transmittance as reported by Hu et al [1]. Such a

high levels of haze is an advantage for solar cell applications that benefits from scattering of light, but it needs to be reduced significantly below 5% for highly transparent displays for various applications.

The metal nanowire electrode has been shown to possess desired electrical and optical performance, but a large portion of the total transmittance is haze (up to ~15%), which can result in blurriness that is unsuitable for display applications. In order to minimize haze, methodologies for maximizing the total transmittance, such that the haze will reduce as a consequence per targeted sheet resistance, have to be explored. It is known that the metal (Ag, Cu) nanowire itself has very low resistance, and most of the sheet resistance of the nanowire electrode is originating from the junction resistance. The junction resistance is known to be due to thin oxide layer as well as to surfactant that surrounds the metal NW during synthesis [4]. While the resistance of a single NW is around 300 ohm, junction resistance between two NWs might be as large as 1 gigaohm (AgNW). The aim of this work is to address the nanowire synthesis methodologies to enhance the total transmittance per given sheet resistance or reduce the sheet resistance per given target total transmittance.

2. EXPERIMENTAL SECTION

Metal nanowire (NW) films are recently studied as transparent electrodes for flexible display applications. On account of both high conductivity and persistence against bending, metal nanowires of copper and silver proved suitable for these applications. Silver and copper can form nanowires of high aspect ratio; whereas making nanowires of inert metals (gold, platinum, palladium) is relatively difficult and material cost rises if whole nanowire is composed of these. In order to exploit their surface physics and chemistry, it is more cost-effective to make cheap metal/inert metal core/shell nanowires. However, uniform coating of large-scale nanowire system is not easy.

We propose to coat metal nanowires with a thin shell of heavier metals, which are inert against oxidation and sulfurization. Coatings can be implemented efficiently and uniformly in two methods: portionwise and biphasic titration.

2.1 Synthesis of Silver Nanowire Solution:

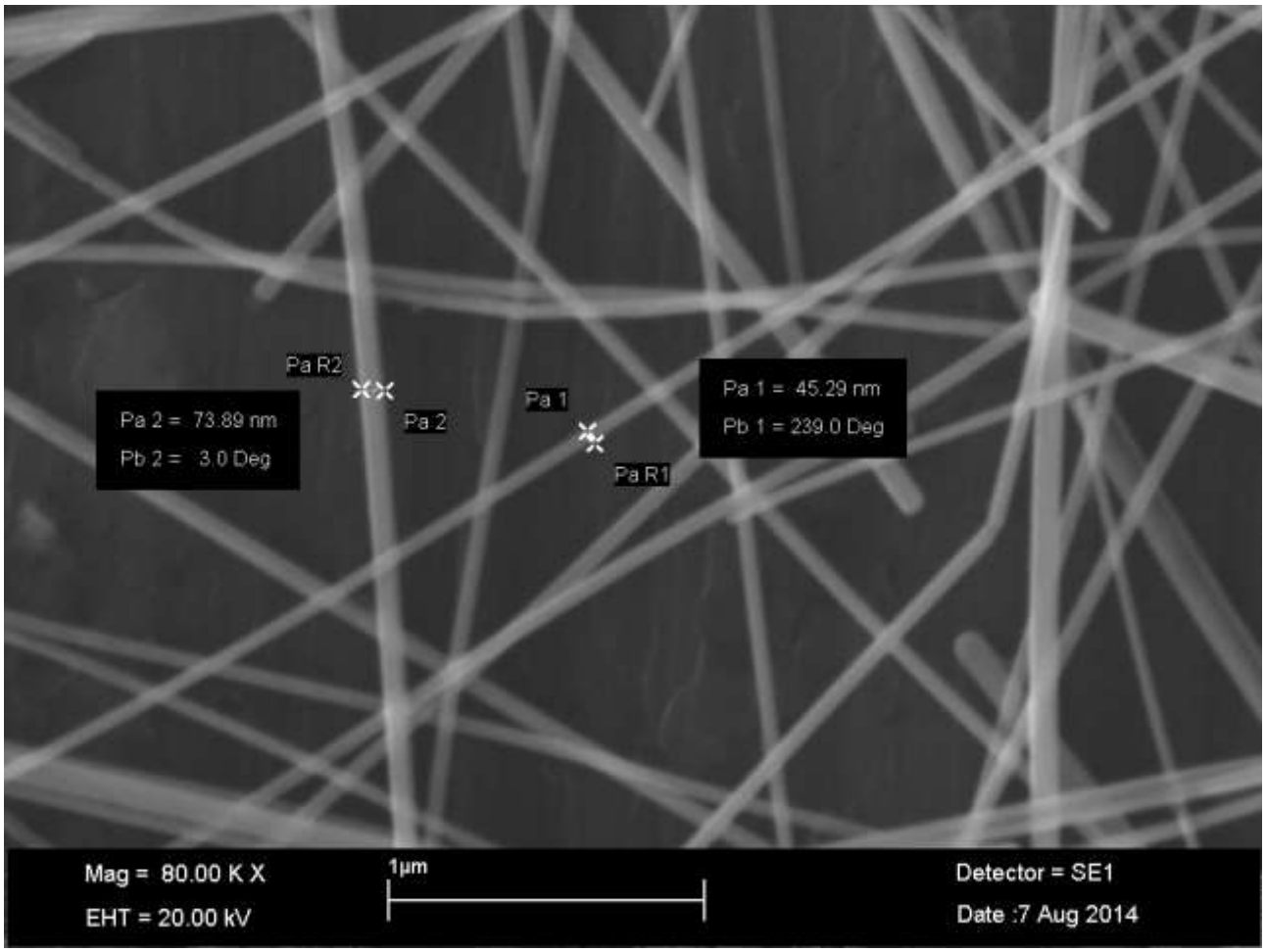
Silver nanowires were made by a solution processing method known as the polyol process [5] with some modifications. First, 6.68 g of PVP was added to 200 mL of ethylene glycol in a three necked round-bottom flask and stirred at 400 rpm using a magnetic stirrer. The mixture was then heated to 170 °C, and 0.1 g of KBr, 0.2 g of NaCl, and 2.793 g of AgNO3 were added to the solution and stirred at 200 rpm. The solution was then kept at 170 °C for 4 h to allow the Ag nanowire growth reaction to take place and then was cooled down to room temperature. The nanowire solution was filtered using a glass filter in order to get rid of particles that can reduce transmittance. Collected silver nanowires were finally dispersed in methanol according to the desired concentration.

2.2 Synthesis of Copper Nanowire Solution:

Synthesizing copper nanowires, 2 mmol octadecylamine (ODA) was added to 80 mL of copper (II) chloride (12.5 mmol L^{-1}) aqueous solution and vigorously stirred for 5 h forming a blue emulsion. Then the solution was transferred into a Teflon-lined autoclave of 100-mL capacity and heated at 160 ^{0}C for 48 h. After the autoclave was cooled down to room temperature naturally, the supernatant was decanted and the final product was obtained after washing the solid part with n-hexane, deionized water and ethanol, respectively.

2.3 Portionwise titration

NW solvent is separated into volumes. Each portion was titrated by Au complex salt solution until the desired Ag/Au exchange ratio (8%). Similar process also repeated for Pt and Pd complex salt solution. Figure 1 shows that AgNW coated with Pd by using $[Pd(en)_2]Cl_2$ complex.



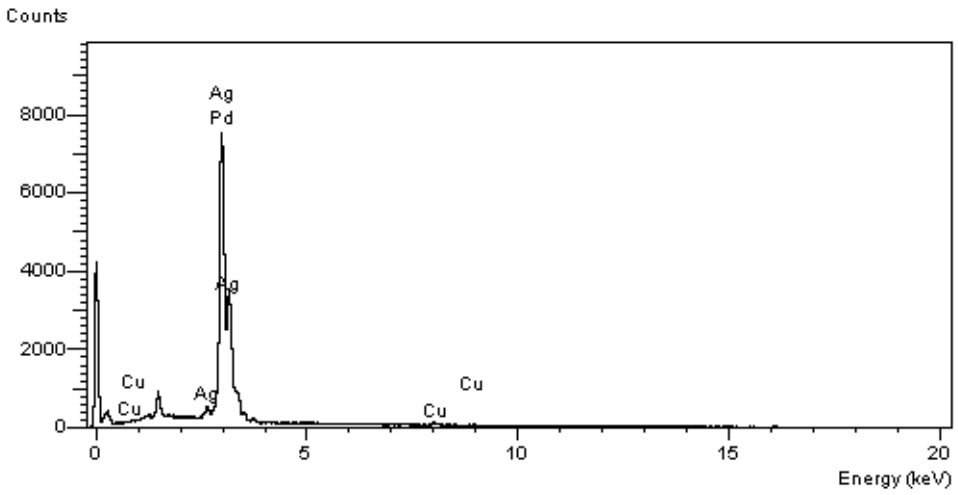


Figure 1: SEM image and EDX spectrum of Pd coated Ag nanowire by using $[Pd(en)_2]Cl_2$ complex

2.4 Biphasic titration

An immiscible solvent (ethyl acetate) is added atop the AgNW solution in water. Au complex salt solution is

added dropwise (titration). Au complex is diluted in ethyl acetate, and then spent by AgNW solution slowly. Similar process also repeated for Pt and Pd complex salt solution. Figure 2 shows that AgNW coated with Au by using $[Au(en)_2]Cl_3$ complex.

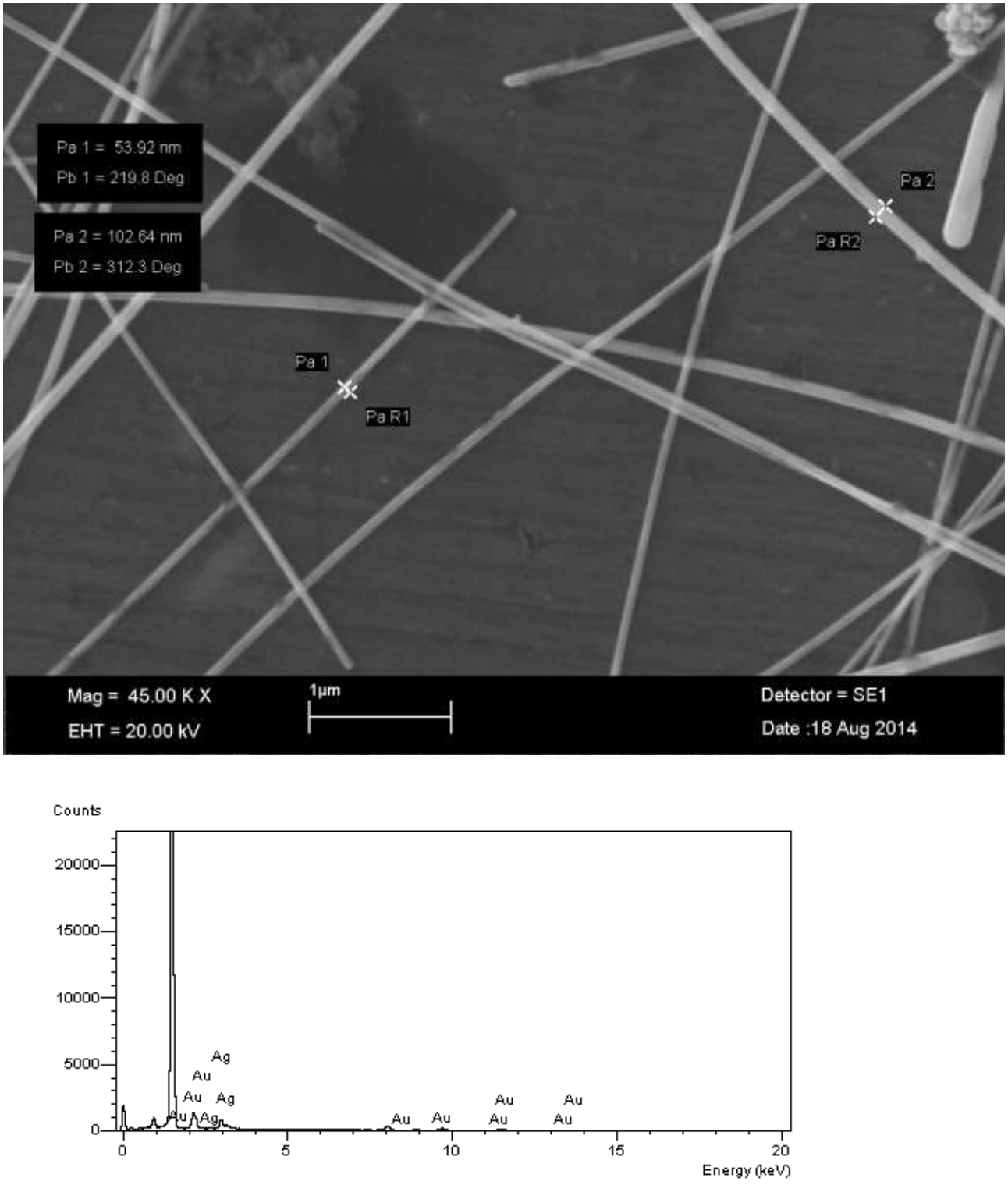


Figure 2: SEM image and EDX spectrum of Au coated Ag nanowire by using $[Au(en)_2]Cl_3$ complex

3. CONCLUSION

In this study, portionwise and biphasic titration methods successfully used to coat the surface of the nanowire with a thin layer of metal. Metal (Au, Pt, Pd) salts can be used as galvanic exchange agents for oxidation and substitution of a thin layer of copper and silver. The mild galvanic exchange reaction resulted in a slower reaction rate to only replace the outer surface with metal without truncating the nanowires. This will provide with passivation of copper and silver against most chemical changes.

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LITERATURE

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