Transparent Thin Film Heaters Based on Copper Nanowire Networks

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Abstract

One-dimensional nanostructures open up new avenues in materials science since materials' properties do change with the dimension and size. Silver is a highly appealing material both in nanosize and bulk form. This is because of its high electrical conductivity. Silver nanowires are widely used in electronic and optoelectronic applications. On the other hand, although copper is almost equally conductive and cheaper than silver, copper nanowires are relatively new to these application areas. In this study, transparent thin film heaters were produced using copper nanowire random networks. Initially, copper nanowires were synthesized with a simple solution-based method. After purification and dispersion of nanowires, thin films were deposited by spray coating. A major problem for copper nanowires in heater application is their oxidation since copper nanowires easily oxidize at elevated temperatures. The problem was solved by the deposition of an aluminum oxide shell layer onto copper nanowires via atomic layer deposition method. Bare copper nanowire thin films' heater performance was poor since the heater temperature can only be increased up to 100 °C under an applied bias, which then gradually dropped off due to oxidation. On the other hand, the heater temperature of aluminum oxide coated copper nanowire networks was increased up to 200 °C under an applied bias. Detailed analysis on the thermal, optical and electrical properties of copper nanowire network heaters will be presented.

1. Introduction

Thin film transparent heaters are visually transparent substrates with electrically conductive coatings on them. Typical applications include fog and ice prevention on optics and optical displays and extension of liquid crystal displays (LCDs) operating temperatures. There are basically two requirements for this application; high optical transmittance and high electrical conductivity. In electrically conductive materials, passage of current produces heat which can be explained by Joule's heating principle. According to this principle, when voltage is applied to a conductor, electrons are accelerated in the opposite direction of electric field, which gives them kinetic energy. Then, electrons collide with ions in the conductor and kinetic energy is transferred to scattering of particles which generates heat. This relationship can be explained by Joule's first law;

$$P = I^2 * R \qquad (1)$$

,where P is power, I is electrical current and R is resistance.

Commercially available thin film transparent heaters are generally made of transparent conductive oxide (TCO) materials, where the most common one is indium tin oxide (ITO). ITO has a lot of disadvantages such as high deposition temperature (above than 300°C), high brittleness and poor thermal stability [1]. To get rid of these disadvantages, some alternative materials are studied in literature such as fluorine doped tin oxide (FTO) and metallic nanowire random thin films. Metallic nanowire thin films are promising candidates as the next-generation transparent electrodes. When utilized in heaters they provide advantages such as low power consumption and fast thermal response [2]. They can also be deposited over large areas.

Silver nanowires based transparent heaters have already been explored in quite detail [3]. Copper nanowires, on the other hand, can also be used to replace silver nanowires in such applications since the electrical conductivity of both copper and silver are similar. In fact, copper is much cheaper than silver. However, copper nanowires can easily be oxidized when compared to silver nanowires, which is a major problem at elevated temperatures. Thus, a protective layer on copper nanowires is necessary so that they can be used as transparent thin film heaters.

There are some attempts to prevent oxidation of copper nanowires such as coating nickel, graphene and transparent oxide shells onto copper nanowires [4-5]. Transparent oxide shells coated by atomic layer deposition (ALD) shows improved oxidation stability without sacrificing transmittance and sheet resistance alteration [6]. ALD method has some advantages such as excellent conformality on high-aspect ratio structures and thickness control at the angstrom level which are important parameters for adjusting sheet resistance and transmittance of thin films.

Herein, we report on the heating performance of 15 nm thick aluminum oxide (Al_2O_3) deposited copper nanowire thin films. Spray deposition is used for the deposition of copper nanowire random networks on quartz substrates, which was followed by ALD deposition of Al_2O_3 onto copper nanowire networks.

2. Experimental Procedure

2.1. Materials

All chemicals were purchased from Sigma-Aldrich. Copper (II) chloride dihydrate ($CuCl_2$) (≥ 99.0 %), D-(+) - glucose monohydrate (anhydrous, 97.5-102.0%) and hexadecylamine (HDA) (≥ 94.0 % (a/a)) were used for copper nanowire synthesis. Ethanol (≥ 99.9 %) and polyvinylpyrrolidone (PVP) (MW= 55000) were used for the purification and dispersion of nanowires, respectively. Lastly, chloroform was used for the elimination of synthesis by-products.

2.2. Synthesis of Copper Nanowires

Copper nanowires were synthesized via a simple solution based method. 125 mg $CuCl_2$, 300 mg glucose and 1080 mg HDA were dissolved in 60 mL deionized water and the solution was left for stirring for 12 hours at room temperature. Then, the solution was placed in a teflon lined autoclave with 100 mL capacity. The autoclave was left at 100 °C for 12 hours under autogenous pressure and then allowed to cool to room temperature [7]. After the synthesis, nanowires were purified. Purification involved repeated centrifugation with distilled water and ethanol. Then, by-products were eliminated with the help of chloroform. In this step, the solution was mixed with water and chloroform. Due to surface tension, by-products sink at the water and nanowires were gathered in the chloroform [8]. At the end, dispersion of nanowires was done via centrifugation with 2% PVP-ethanol solution.

2.3. Thin Film Production

1 inch x 1 inch quartz substrates were placed on a hot plate at 100 °C. Then, dispersed and by-product free copper nanowires were deposited onto the substrates through spray deposition and then allowed to cool to room temperature. Spray deposition provided homogeneous copper nanowire network formation on quartz substrates. Finally, prepared copper nanowire thin films were annealed under inert atmosphere to get rid of the excess PVP.

2.4. Atomic Layer Deposition (ALD) onto Copper Nanowires

The ALD cycle was optimized before deposition onto copper nanowires. Trimethylaluminum (TMA) and water (H_2O) precursors were sequentially applied onto the substrates to obtain 1 cycle. The overall reaction for ALD of Al_2O_3 is;

$$2\ Al(CH_3)_3 + 3H_2O \longrightarrow Al_2O_3 + 6\ CH_4 \qquad (2)$$

120 cycles of ALD were applied onto copper nanowire thin films to obtain a 15 nm thick Al_2O_3.

3. Results and Discussion

SEM images of bare and 15 nm Al_2O_3 deposited copper nanowires are provided in Figure 1 (a) and (b), respectively. SEM image in Figure 1 (b) showed conformal coating of Al_2O_3 around the nanowires.

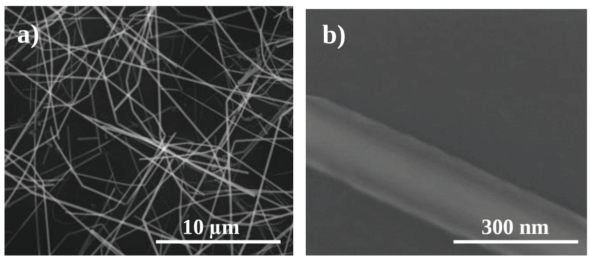

Figure 1. SEM images of (a) bare copper nanowire network and (b) Al_2O_3 deposited copper nanowire.

The two important parameters for transparent heaters are sheet resistance and optical transmittance, both of which were investigated both before and after Al_2O_3 deposition onto copper nanowires. While sheet resistance value (Rsh = 10 Ω/sq) was found to remain the same following Al_2O_3 deposition, optical transmittance (Figure 2) was found to decrease. Copper nanowire random network thin film had an optical transmittance of 78% at a wavelength of 550 nm, while the transmittance for 15 nm Al_2O_3 deposited copper nanowire thin film was found to be 73%.

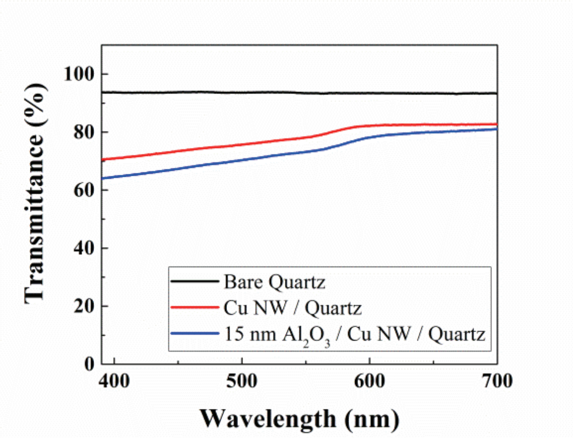

Figure 2. Transmittance of bare and Al_2O_3 deposited copper nanowire thin films. Transmittance of bare quartz is also provided for comparison.

Time dependent heating profiles of Al_2O_3 deposited copper nanowire thin films under different applied voltages (1, 3, 5 and 7V) are provided in Figure 3. The maximum temperature attained by the heaters was found to increase with the applied voltage. As it can be seen from the figure, the temperature increase was found to last for only 2 minutes. Then, the temperature remained stable until cutting the applied voltage. The maximum temperature attained was 225 °C under an applied voltage of 7V. However, following the application of 7 V for 12 minutes, the copper nanowire thin film's sheet resistance was started to increase. As a result of this, the temperature of the heater started to decrease. This result showed the stability limit of 15 nm thick Al_2O_3 deposited copper nanowire thin film, whose performance was distinctly better than bare copper nanowire thin film heaters that could not be stable even at 100 °C for 20 minutes.

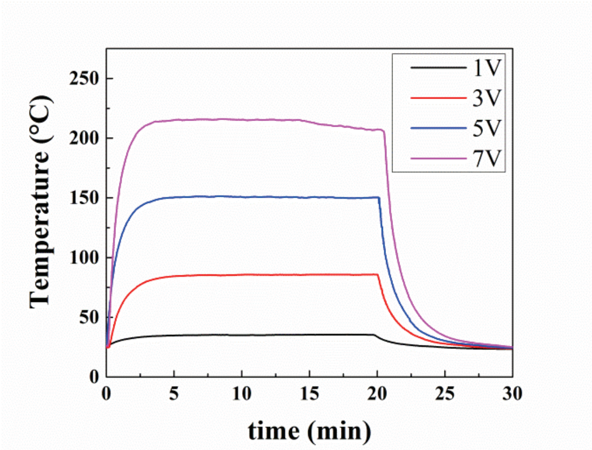

Figure 3. Time dependent heating behavior of 15 nm Al_2O_3 deposited copper nanowire thin film under different applied voltages.

4. Conclusions

In conclusion, copper nanowires were synthesized via simple solution based method and they were deposited on quartz substrates in the form of thin films by spray deposition. To prevent the oxidation, 15 nm thick Al_2O_3 was deposited onto copper nanowires by ALD. Then, optical transmittance, sheet resistance and time dependent heating behavior of Al_2O_3 deposited copper nanowire thin films were investigated. Deposition of Al_2O_3 was found to improve the stability of copper nanowire thin film heaters.

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