



Study on optical films with AgNWs using UV laser patterning

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ABSTRACT

Silver nanowires (AgNWs) with excellent conductive properties can be used to make transparent electrodes with high transmittance, low haze, high electrical conductivity, and high mechanical strength. AgNWs could be a promising material to replace indium tin oxide (ITO). In this study, a polyol method was used to synthesize one-dimension AgNWs. Molecular dynamics simulation software of the Large-scale Atomic/Molecular Massively Parallel Simulator was applied to analyze the micro/nano-scale behavior and predict basic mechanical properties of the materials. For optical properties, a near-field electrospray was combined with ultraviolet 355-nm laser ablation process to direct-write patterning of the transparent conductive AgNWs films as electrodes. Three conductive films with various thicknesses of AgNWs prepared by the near-field electrospray process were coated on glass substrates to analyze the surface morphology and optical properties. A scanning electron microscope and energy dispersive spectrometer were utilized to observe the surface morphology and material composition. An optical integrating sphere and a four-point probe were used to examine the transmittance, haze, and electrical conductivity, respectively. In this study, the optical, electrical and mechanical characteristic as a function of thickness of the films, and laser power levels were characterized.

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1. Introduction

Much attention has been paid to nanocrystalline materials with a grain size ranging from 1 to 100 nm because they may provide unique mechanical, physical and chemical properties, compared to the conventional polycrystalline materials [1,2]. With micro/nano size, surface area increases accompanied by high chemical activity in the metallic materials. Development, synthesis and properties analysis of various nanomaterials have become popular research topics in the field of nanotechnology. However, the mechanical and behavior properties cannot be observed or measured precisely. Simulation software and measuring equipment were applied to analyze the properties of nanomaterials. Atomistic simulations are more useful to predict the changes of composition in alloy systems than the actual experiments [3]. In 2005, Hyde et al. proposed that the molecular dynamics (MD) simulation on silver nanowires (AgNWs) with various wire geometries and found that they are

inherently unstable, due to the high surface energy and various axial orientations [4]. In 2014, Huang et al. simulated the mechanical behavior of nanomaterials and structures at the molecule scale and accurately reported the interatomic potential for nanofilms [5].

Silver nanoparticles (AgNPs) and AgNWs exhibit the highest electrical and thermal conductivities among all metals. Besides, it has antibacterial activity [6–9]. Nano silver particles are widely used in medical and optical industries. A study showed that AgNPs mixing with the materials of dentures enhanced its antimicrobial activities in the dental industry [10]. A nanoindenter was mainly used to measure the indenter load in normal and tangential directions with continuous change of displacement of thin film materials. Nanoindenter was also used to examine the electrical contact behaviors, microstructural failure modes [11–14], and to assess the mechanical stability [15]. Through the load and indentation depth control, the mechanical properties and material deformation behaviors can be identified. AgNWs are currently applied in optoelectronic and electronic components, and the most popular flexible transparent conductive films. Nowadays, the most commonly used materials of transparent conductive films are

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indium tin oxide (ITO), carbon nanotube [16,17], graphene [18], metallic nanowire and metallic nanonet [19–21]. AgNWs with excellent electrical conductivity and high transmittance become the most potential material to replace the transparent conductive ITO. The previous studies proposed a sandwich-structured graphene/AgNWs/graphene transparent conductive film (TCF) by chemical vapor deposition (CVD)-grown graphene layers. The graphene/AgNWs/graphene TCF exhibited excellent optical and electrical properties [22]. Therefore, AgNWs flexible films used for transparent conductive electrodes have been studied. To fabricate films, the previous reports described that AgNWs were deposited in aqueous solution with dispersing agent, and AgNWs was collected through coating process [23,24]. The near-field electrospray process takes fewer steps to make fibers and films, compared with the deposition/coating method. The near-field electrospray with the high-voltage electric field can be used to fabricate continuous fibers, ranging from micrometer to nanometer. The electrospray process is a simple, convenient, versatile, and effective technique to prepare oxide nanofibers. Also, the electrospray process was able to control the composition, diameter and porosity of materials [25–27]. The nanofibers formed by electrospray were continuously one dimension with good physical and chemical stabilities, such as small fiber diameter, large surface area, high porosity and high surface-to-volume ratio. These advantageous properties of the nanofibers have been proved in many applications [28–30].

There are many investigations on the practical applications of AgNWs films as transparent electrodes. Photolithography is the most widely used patterning technique for fabricating transparent electrodes. However, multiple steps in the process include photoresist coating followed by soft-baking, exposure, developing, etching, and stripping. A laser ablation technology was used to direct-write patterning of the AgNWs films with high ablation speed, throughput and resolution, in just a single-step patterning, compared to the traditional photolithography process. Moreover, laser ablation is a non-toxic and convenient method [31–33]. For electrode manufacturing, Lin and Hsu [34] patterned ITO films which were deposited on a glass substrate by using a fiber laser-ablated process at a wavelength of 1064 nm, with repetition rates ranging from 100 to 400 kHz. There are many types of industrial lasers, which were classified by the wavelength and the oscillation of the medium. The wavelengths mainly include 266, 532, 808 and 1064–1070 nm. It is essential to select different types of laser for different materials. Although the diode pump solid state laser technology is mature, it does not become the major procedure due to the impact of thermal effects on the patterning quality. For Nd:YAG laser (1064 nm), studies showed that most of the input energies were absorbed by working medium, which rendered an increase of system temperature, and caused heat-affected zone (HAZ) on the specimen [35]. Accordingly, the UV laser has been widely studied. In 2008, Wang et al. used UV laser with 355-nm wavelength to cut printed circuit boards. During the cutting process, the O₂ auxiliary gas was added to explore the cutting quality [36]. But for the cutting process of an excimer laser, the temperature was not increased, also known as cold treatment. After the process, the samples were not damaged by thermal effects.

In this study, we combined the process of a near-field electrospray and a 355-nm UV laser ablation to prepare and direct-write patterning of the AgNWs films as electrodes. A four-point probe was used to examine the electrical properties of the AgNWs films. An integrating sphere with a spectrometer was used to measure optical properties including haze and transmittance. In addition, the relationships in terms of thickness of the films and the laser power levels as a function of the conductivity and transmittance were characterized.

2. Materials and methods

2.1. Molecular dynamic simulation

The molecular dynamics simulations for the tensile and bending tests were carried out to study the mechanical properties of AgNWs with different defect concentrations. For the tensile simulation, the displacements along the opposite directions were imposed at two endpoints of AgNWs, as shown in Fig. 1(a). For the bending simulation, the midpoint of AgNWs is used as the bending center. Two endpoints of AgNWs were imposed by the bending forces to evaluate the strain value of AgNWs, as shown in Fig. 1(b). With these two simulations, the mechanical properties of AgNWs in the structure were predicted.

All MD simulations were conducted using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [37]. The interaction between Ag atoms was described by the second nearest-neighbor modified embedded-atom method (2nn-MEAM) potential developed by Lee [38]. It has been previously reported that this 2nn-MEAM potential can accurately predict the lattice constant, cohesive energy and elastic constants of bulk Ag material [39]. For the temperature control, the AgNW was first equilibrated at 300 K for 100 ps using the canonical (NVT) ensemble. Then the velocity scaling method was used to maintain the system temperature of 300 K before applying the next tensile and bending increments.

2.2. Fabrication of AgNWs films

The polyol method was used to synthesize AgNWs. The process is described as follows; first, the chemicals were prepared including the PVP (#9003-39-8, Alfa Aesar), EG with 99% purity (99%, #107-21-1, JT Baker), AgCl (99.99%, #7783-90-6, Sigma-Aldrich) and AgNO₃ (99%, #7761-88-8, Sigma-Aldrich). The complete process of AgNWs is shown in Fig. 2. Then, 0.21 g poly-vinylpyrrolidone (PVP) with an average molecular weight 1,300,000 was put into the ethylene glycol (EG) solution with 20 mL. After the solution mixed uniformly, 0.065 g silver chloride (AgCl) and 0.22 g silver nitrate (AgNO₃) were afterward added into the mixture step by step under 170 °C at 350 rpm stirring.

The AgNWs films were fabricated by a near-field electrospray, providing a uniform surface area on a glass substrate. The electrospray system was integrated by X-Y control table with high voltage power supply (YOU-SHANG TECHNICAL CORP., Japan), motor (57BYGH56, SHENG-FU MACHINERY, Taiwan), controller (2M542-N, SHENG-FU MACHINERY, Taiwan), and infusion pump (KDS-100, Kd Scientific, USA). Fig. 3 is the schematic illustration of the near-field electrospray. This technique was developed based on the electro-hydrodynamic theory. When the solution goes through high voltage electric field, Taylor cone is formed due to the charge accumulation. The parameters include the electric field, needle diameter, solution feeding rate and solution viscosity. In this research the thin films of AgNWs are fabricated at the electric field of 5 kV with a feed rate 1.4×10^{-5} mL/s. Fig. 4 is the size dimension of the sample for electrospray process. The substrate is 900 mm². The film was electrosprayed within an area of 400 mm². The thicknesses of films were measured as ~0.61 μm, 0.89 μm, 1.07 μm and 1.39 μm, respectively. Different thicknesses of AgNWs films were prepared.

2.3. UV laser patterning

A 355-nm UV laser (K-JET Laser Tek Inc., MMS-1000F, 3-W max, Taiwan) was used in this study, with a stable light source and a smaller heat affected zone. The mechanism of laser system is

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