Applied Surface Science 399 (2017) 617–623

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Comparative analysis of serial and parallel laser patterning of Ag nanowire thin films

Harim Oh, Myeongkyu Lee*

Department of Materials Science and Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, South Korea

ARTICLE INFO

Article history:
Received 15 August 2016
Received in revised form 5 November 2016
Accepted 7 December 2016
Available online 8 December 2016

Keywords:
Ag nanowire
Patterning
Ultraviolet laser
Nd:YAG laser

ABSTRACT

Ag nanowire (AgNW) films solution-coated on a glass substrate were laser-patterned in two different ways. For the conventional serial process, a pulsed ultraviolet laser of 30 kHz repetition rate and ~20 ns pulse width was employed as the laser source. For parallel patterning, the film was directly irradiated by a spatially-modulated Nd:YAG laser beam that has a low repetition rate of 10 kHz and a shorter pulse width of 5 ns. While multiple pulses with energy density ranging from 3 to 9 J/cm^2 were required to pattern the film in the serial process, a single pulse with energy density of 0.16 J/cm^2 completely removed AgNWs in the parallel patterning. This may be explained by the difference in patterning mechanism. In the parallel process using short pulses of 5 ns width, AgNWs can be removed in their solid state by the laser-induced thermo-elastic force, while they should be evaporated in the serial process utilizing a high-repetition rate laser. Important process parameters such as threshold energy density, speed, and available feature sizes are comparatively discussed for the two patterning

1. Introduction

Transparent conductive electrode (TCE) materials with a combination of high electrical conductivity and optical transparency are essential components for various optoelectronic devices, including light-emitting diodes, liquid crystal displays, e-papers, touch-screen panels, and solar cells. Although indium tin oxide (ITO) film is the most commonly used TCE material to date, it suffers from several drawbacks such as high materials cost, scarcity of indium, and intrinsic brittleness. These problems have led to a fervent search for materials to replace ITO. Potential replacements include carbon nanotubes (CNTs) [1,2], graphene [3,4], conducting polymers [5,6], metal meshes [7–9], and silver nanowires (AgNWs) [10–13]. Carbon-based materials and polymers possess superior flexibilities but their conductivities still remain very low. Among these alternatives to ITO, AgNWs are particularly attractive because a random network of AgNWs that provides high conductivity and flexibility can be prepared by a simple solution process. In fact, plenty of articles have already reported the fabrication of highly flexible and cost-effective organic photovoltaic devices with AgNW electrodes [14–16].

Patterning is inevitable in device integration. A variety of methods have been suggested to pattern AgNWs, including photolithography and etching [17,18], soft lithography [19], printing [20–22], lift-off [23], dry transfer [24], and control of wettability [25,26]. All these methods have both merits and drawbacks. High-resolution patterns may be obtained by lithography but it is highly expensive, comprising a number of individual steps. Many of the suggested methods also require a sacrificial layer or release template to pattern AgNWs, which increases the overall process time and cost. For many electronic and optoelectronic applications, the challenge is not the feature size reduction any longer. The most important keywords are now “low-cost”; “flexible”; and “large area”. A simple alternative method to pattern AgNWs is ablation using a pulsed laser [27–29]. This laser ablation has also been extensively investigated to pattern ITO films [30–32]. Compared to wet chemical etching; the use of lasers can reduce the overall cost significantly and also eliminate the environmental concern associated with chemicals used in the etching process. However; the conventional laser ablation is a serial process based on the scanning of a focused beam and lacks the throughput speed necessary for cost-effective volume manufacturing. The speed is typically limited by the power and repetition rate of the laser. Here we present a new laser patterning scheme where a large area is simultaneously patterned by a spatially-modulated laser beam. The results of this parallel process are compared with those of a conventional serial process.

* Corresponding author.
E-mail address: myeong@yonsei.ac.kr (M. Lee).

http://dx.doi.org/10.1016/j.apsusc.2016.12.045
0169-4332/

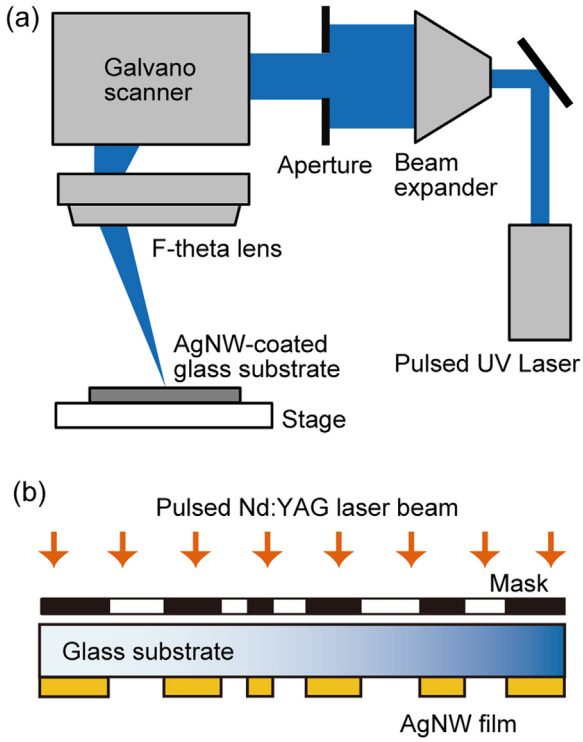

Fig. 1. Schematic illustration of the used set-up. (a) Serial laser patterning. (b) Parallel laser patterning.

2. Experimental procedures

A 1 wt% solution of AgNWs dispersed in ethanol (diameter = 32 ± 5 nm, length = 25 ± 5 μm) was supplied from NANOPYXIS Inc. The as-received solution was diluted to 0.3 wt% and then sonicated for 5 min. The sonication process reduced the average length of Ag nanowires to roughly half the original length and helped obtain more uniformly coated films. After sonication, the wires showed lengths of 10–15 μm, indicating that they are more probably cut in the middle. A 200 μL drop of the solution was spin-coated onto a slide glass substrate (2 cm × 2 cm) at 1000 rpm for 1 min. The coated AgNW film was then dried at 100 °C for 5 min. Two different pulsed laser sources were employed in this study. A nanosecond-pulsed ultraviolet (UV) laser (Coherent AVIA 355-5 model; wavelength = 355 nm, pulse width = ~20 ns, repetition rate = 30 kHz, maximum output power = 5 W, beam diameter = 2.85 mm) was employed as the laser source for serial laser patterning. Fig. 1(a) shows a schematic of the setup used for the conventional serial process. The output laser beam of Gaussian profile was incident into a galvanometric scanner and an F-theta lens (focal length = 205 mm) combined with the galvanometric scanner was used to steer the laser beam and maintain a uniform spot size on the sample surface. The laser beam was automatically scanned by computer software that controlled the gavanometric system. The power and scan rate of the beam were independently varied. When the output beam was directly focused, the laser spot size at the focal plane, i.e., on the sample suface was calculated to be ~37 μm. In order to reduce the laser spot size further, the output beam was expanded by a beam expander before entering the galvanometer. Spatial filtering of the beam by an aperture helped achieve AgNW patterns with clear-cut edges. Since the UV laser used for serial patterning has a repetition rate of 30 kHz, it is hereafter referred to as "high-repetition rate laser".

Another laser source empolyed in the study is a pulsed Nd:YAG laser (Quantel Brilliant B: wavelength = 1064 nm & 355 nm, pulse width = 5 ns, repetition rate = 10 Hz, maximum pulse energy = 850 mJ at 1064 nm & 350 mJ at 355 nm). The output beam of 0.9 cm diameter was spatially-modulated through a shadow mask in contact with the backside of the substrate and then made incident into the AgNW film, as shown in Fig. 1(b). The shadow mask consists of regular line openings whose width is 200 μm. The laser beam directly illuminates the film through the shadow mask without scanning. Both the fundamental 1064 nm and its third harmonic 355 nm were used for this parallel patterning. Since the output beam has a near hat-top profile, no beam homogenizer was used. The Nd:YAG laser has a repetition rate of 10 Hz and it is here denoted as "low-repetition rate laser". When the output powers of the lasers are on the same order, the energy of an individual pulse is much higher in this low-repetition rate laser. For 5 W, a single pulse of the low-repetition rate laser has energy of 0.5 J, while a pulse from the high-repetition rate laser has energy of 0.167 mJ. The sheet resistances of the films were measured using a 4-point probe. Transmission spectra were measured by a UV–vis spectrophotometer and structural analysis was carried out using field-emission scanning electron microscopy (SEM, Model: JSM-7001F, JEOL Inc. 15 kV). As-coated films exhibited a sheet resistance of 25–35 Ω/sq and a transmittance of 82% at 500 nm.

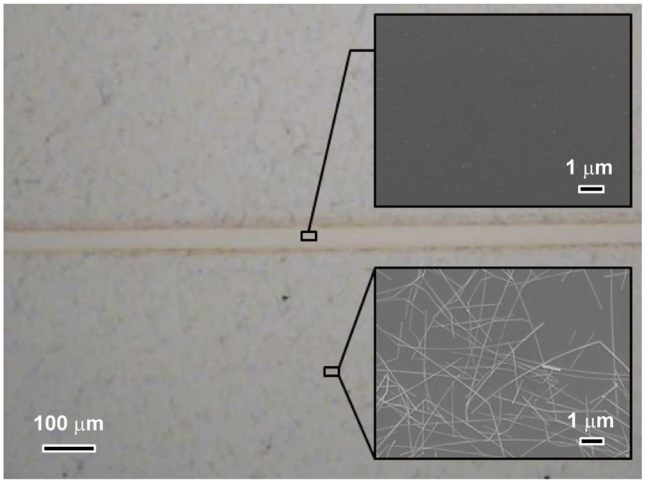

Fig. 2. Optical microscopic image of a line pattern. Insets are SEM images.

3. Results and discussion

Fig. 2 shows a line pattern formed by scanning a focused high-repetition rate UV laser beam over the film. SEM images shows that AgNWs in the irradiated region are completely ablated. Although the line width also depended on the power and scan rate of the beam, it was most dominantly affected by the laser spot size. A minimum line width of 16 μm was obtained under the conditions of power = 1 W, scan rate = 2 mm/s, beam expansion = 8 X, and no spatial filtering. Two critical parameters determining whether AgNWs are completely removed or not were the pulse energy density and scan rate of the beam. Here, the pulse energy density represents the energy of an individual pulse divided by the laser spot size. Fig. 3(a) plots the threshold pulse energy density as a function of the scan rate, which was obtained at a fixed laser spot size of ~37 μm. The threshold pulse energy density was defined as the pulse energy density at which AgNWs were completely ablated. It was measured by finding the pulse energy leading to complete ablation and dividing it by the laser spot size. As the scan rate increased, the pulse energy density required to completely ablate AgNWs also increased. With an increase in the scan rate, the film is exposed to the laser spot for a shorter time, thereby absorbing