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Laser-induced electrical property patterning of Ag nanowire transparent electrode

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ABSTRACT

We here introduce a laser-driven method to pattern Ag nanowire (AgNW) transparent electrode without material removal. Our approach is to block the current flow in selected areas by cutting nanowires, which is fundamentally based on the Rayleigh instability. AgNW film spin-coated onto a glass substrate was selectively irradiated using a nanosecond-pulsed ultraviolet laser beam. This made it possible to fabricate a patterned structure consisting of spatially separated conducting and insulating regions. The feasibility of this electrical property patterning was demonstrated with white light emitting diodes attached to the fabricated pattern.

1. Introduction

Transparent conducting electrode (TCE) is an essential component for many optoelectronic devices such as solar cells, displays, light emitting diodes (LEDs), and touch screen panels. While indium tin oxide (ITO) is the most widely used TCE material to date, it is not suitable for next-generation flexible devices due to its inherent brittleness. This has led to a fervent search for materials to replace ITO. Potential TCE materials have thus been extensively investigated, which include carbon nanotubes, graphene, conducting polymers, metal meshes, and silver nanowires (AgNWs). Carbon-based materials and polymers may be highly flexible but their electrical conductivities are still very low, limiting the practical applications. Among these alternatives to ITO, AgNWs are particularly promising because a random network of AgNWs possesses excellent conductivity, good flexibility, and compatibility with low-temperature solution process. However, there are two problems associated with AgNWs that should be solved for their widespread use in real devices. The first issue is related to the thermal stability of AgNWs [1–3]. When integrated with other layers during device fabrication, AgNW networks are likely to be heated to high temperatures, which may increase the sheet resistance due to oxidation. This ultimately degrades the electrical performance of TCE. Meanwhile, patterning is inevitable in device integration. A number of methods to pattern AgNWs have been suggested, including etching [4,5], lift-off [6], dry transfer [7], and laser ablation [8]. Another important issue to be addressed is that patterned AgNW electrode can be visible to naked eyes. The visible electrode is especially problematic in transparent displays. While the display images need to have high visibility, the electrode pattern should be invisible. This visibility issue is common to any metal-based TCEs including metal mesh electrode. The origin of the electrode visibility is quite simple. As illustrated in Fig. 1(a), AgNW electrode patterned on a transparent substrate exhibits a small difference in reflectance/transmittance between the patterned and unpatterned regions. This can make it visible to our eyes. AgNWs slightly scatter light, which also contributes to the pattern visibility. Regardless of whether the AgNW electrode is patterned either by etching, ablation, or selective deposition, the conventional methods always entail the visibility problem due to the regions absent from AgNWs. Our approach is to control the conductivity of the AgNW network by a laser, which plays a role to block the current flow in selected areas by cutting nanowires. This method can be referred to as a kind of “property patterning”, since the cut nanowires still remain on the substrate (Fig. 1(b)). This work shows that the electrical property of AgNW film coated on a glass substrate can be patterned by selective laser irradiation.

2. Experimental procedure

The AgNWs used for this study were supplied from NANOPYXIS

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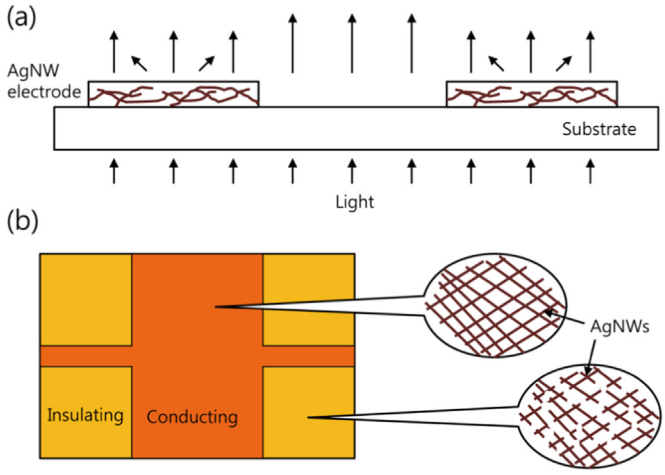

Fig. 1. (a) Origin of the pattern visibility, (b) schematic of the concept of property patterning.

Inc. The as-received product was a 1 wt% solution of AgNWs dispersed in ethanol, where the wire length and diameter are 25 ± 5 μm and 32 ± 5 nm, respectively. After being diluted to 0.3 wt%, a 200 μL drop of the solution was spin-coated onto a slide glass substrate at 1000 rpm for 1 min.

The coated solution was then dried at 100 °C for 5 min. A nanosecond-pulsed ultraviolet (UV) laser (Coherent AVIA 355-5; wavelength = 355 nm, pulse width < 20 ns, repetition rate = 30 kHz, maximum output power = 5.0 W, output beam diameter = 2.85 mm) was employed as the laser source. The output laser beam was made 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 sample was stationed on a z-translation stage so that its vertical position with respect to the focal plane can be varied. The laser spot size on the focal plane was calculated to be ~30 μm. The estimated beam size increased to 0.5 mm when a 50 mm-defocused beam was used, i.e., when the sample was vertically displaced by 50 mm from the focal plane. The power and scan rate of the beam were independently controlled. The sheet resistances of the AgNW films were measured using a 4-point probe. Transmission spectra were measured by a UV–visible spectrophotometer and structural analysis was carried out using field-emission scanning electron microscopy (SEM, Model: JSM-7001F, JEOL Inc. 15 kV).

3. Results and discussion

As-coated AgNW films exhibited a sheet resistance of 15–25 Ω/sq and a transmittance of ~85% at 550 nm. This transmittance value is 7% lower than that of a bare substrate. At first, the films were scanned in a line-by-line fashion using a laser spot with a size of 0.5 mm. The power was varied from 3.0 to 4.5 W with an increment of 0.5 W and the scan rate, from 2 mm/s to 10,000 mm/s. For a fixed beam size, the laser energy absorbed by the film increases with an increasing power and a decreasing scan rate. However, the morphological change and sheet resistance of the irradiated film were more sensitive to the power than to the scan rate. For a power of 3.0 W, the sheet resistance and morphology of the AgNW network remained little changed regardless of the scan rate. The minimum scan rate achievable with the used galvanometric scanner is 1.3 mm/s. Only when the scan rate was reduced to an almost minimum value of 2 mm/s, the sheet resistance increased by one order of magnitude. At an increased power of 3.5 W, the sheet resistance was immeasurable (i.e., infinite) under various scan rates of 3 mm/s, 10 mm/s, 50 mm/s, 100 mm/s, and 150 mm/s, indicating that the Ag nanowires are disconnected at these conditions. When the power was further increased to 4.0 W, the infinite sheet resistance was observed at scan rates of 100 mm/s, 300 mm/s, 500 mm/s, and 700 mm/S. For higher scan rates of 1000 mm/s, 3000 mm/s, and 5000 mm/s, the measured sheet resistance values were mixed. For instance, when multiple samples were tested, some exhibited finite sheet resistances and others, infinite values. With an increased power of 4.5 W, however, the sheet resistances of all investigated samples were infinite even at these high scan rates.

To verify the feasibility of the conductivity patterning, an AgNW film was selectively coated onto a bare glass substrate in the form of an “H” letter and the center of this “H” letter-shaped film was vertically scanned using a laser beam with a 0.5 mm size, as illustrated in Fig. 2(a). Fig. 2(b) shows the I–V relations measured before and after the laser scan. The morphologies of the scanned area are compared in Fig. 2(c). It can be seen that some wires are already cut by laser irradiation and others, in a stage just before cutting. This blocks current flow across the scanned region. Our approach is fundamentally based on the Rayleigh instability [9,10], which states that a stream of fluid breaks up into smaller droplets with the same volume when its length relative to the diameter is above a certain threshold value. Since a nanomaterial exhibits a much lower melting temperature than its bulk state, individual Ag nanowires can be easily melted by laser irradiation. Therefore, any fluidized wires will not maintain their original shapes, ultimately being cut in the middle. Meanwhile, AgNWs may contain grain boundaries that can serve as preferred locations for the formation of thermal grooves [11]. In addition, the grain boundaries of melted materials can be completely or incompletely wetted depending on the misorientation angle [12]. Since all these may contribute to the breaking of AgNWs, further detailed analysis will be necessary to find out the exact mechanism. As mentioned above, the sheet resistance of the AgNW film was influenced by the laser power and scan rate. Thus we checked the consistency between the sheet resistance obtained in a specific irradiation condition and the performance of an electrode pattern fabricated using the same condition. For this purpose, an AgNW film was prepared on a bare glass substrate (2×2 cm^2). Then it was selectively irradiated using a laser beam (0.5 mm size), leaving one “L”-shaped and one “inverted L”-shaped regions unirradiated (Fig. 3). Now the film has a patterned structure consisting of two separate conducting regions and the remaining insulating area. A series of white LEDs were attached to the fabricated pattern and their light emission was investigated. Bright light was emitted from the LEDs when the film was patterned with the condition that led to an infinite sheet resistance. This means that the AgNW network of the irradiated area was completely disconnected and the current flows through the LEDs. If the two electrodes were not electrically isolated, the LEDs would not be turned on due to a leakage current. Of course, when the film was patterned using the condition that resulted in a finite sheet resistance, no light (or very weak light) was emitted.

The ultimate goal of this work is to develop a patterning method that does not entail the visibility problem. To do so, laser irradiation should not alter the transmittance of AgNW film. A current limitation is that the film became slightly yellowish after irradiation. The yellowish color is attributed to a localized surface plasmon resonance peak caused by Ag nanoparticles that are generated as a result of the laser-induced melting and cutting of nanowires. Fig. 4 compares the transmittance spectra of as-coated and laser-irradiated films. The plasma resonance absorption peak, centered about 470 nm, became stronger as the used laser power increased, since more particles were generated at a higher power.