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High-density hydrothermal growth of zinc-oxide nanowires using printed resistive heater

Dongil Nam [a,1], Janghoon Park [a,1], Sungsik Park [a], Yoonki Min [a], Youngwook Noh [a], Dongjin Lee [b,c,*]

[a] Department of Mechanical Design and Production Engineering, Konkuk University, Seoul, South Korea
[b] School of Mechanical Engineering, Konkuk University, Seoul, South Korea
[c] Flexible Display Roll-to-Roll Research Center, Konkuk University, Seoul, South Korea

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ABSTRACT

A method for synthesizing high-density grown zinc-oxide (ZnO) nanowires (NWs) is proposed. A resistive heater printed on the backside of a substrate using a roll-to-roll gravure printing process was employed as a heat source for the NWs. Hydrothermal synthesis was used to grow the ZnO NWs on the backside of the printed resistive heater in a polydimethylsiloxane mold. After the reaction, the characteristics of the locally grown ZnO nanowires, including the density and verticality, were measured. The synthesis results indicated a high growth density, with an enhanced heat transfer efficiency and selectivity, compared with the comparison group.

1. Introduction

Zinc-oxide (ZnO) nanowires (NWs) are promising for use in a variety of electronic devices [1–3]. They exhibit excellent performance owing to their high surface-to-volume ratio and have several favorable properties as a semiconductor material, including a wide direct band gap (~3.3 eV) and large exciton binding energy (60 meV) [4].

Generally, NWs are synthesized by vapor–liquid–solid growth, chemical vapor deposition, or similar methods [5–7]. However, selecting a substrate for these methods is difficult because they involve high temperatures and require long cooling periods despite the quality of the substrate. In contrast, aqueous-solution epitaxy, also known as hydrothermal growth, provides advantages of low process temperature and low costs [8–10]. Nevertheless, the hydrothermal method is slower than the aforementioned methods.

Effective heat transfer is essential for reducing NW growth time. Ma et al. [11] reported that the heating conditions can affect the density of ZnO NWs. In recent studies, methods involving hot plates, conduction, convection ovens, etc., have been used for fabricating the heat source. In particular, ZnO NWs have been widely fabricated in convection ovens because they provide uniform heating. Goodsell et al. [12] synthesized nanostructures using a hot plate as a heat source. However, in these methods, the distance between the substrate and the heat source is high, resulting in insufficient heat transfer during NW growth. In this study, we synthesized ZnO NWs via the localized hydrothermal growth method, using the backside of a printed resistive heater as a direct and selective heat source.

2. Experimental details

The patterns were printed in a cleanroom using a roll-to-roll (R2R) gravure printer, as shown in Fig. 1(a) [13,14]. Polyimide (PI) with a thickness of 25 μm and width of 300 mm was used as a substrate. Ag-flake conductive paste (FP Co., Korea) whose viscosity was brought to 16570 cps by adding 2-ethoxyethylacetate solvent was employed. The inset of Fig. 1(a) shows the printed resistive heater after the printing process. The heater pattern had a line width of 350 μm, thickness of 2–3 μm, and resistance error of 10% (36 ± 0.7 Ω) in a 500-m sampling length. A heating pot, i.e., a ZnO NW platform (Fig. 1(b)), was fabricated using the printed resistive heater and a polydimethylsiloxane (PDMS) mold. The PDMS mold was cured in a vacuum oven at 90 °C for 10 min.

* Correspondence to: School of Mechanical Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 143-701, South Korea. Tel.: +82 2 450 0452; fax: +82 2 447 5886.
E-mail address: djlee@konkuk.ac.kr (D. Lee).
[1] Contributed to this work equally.

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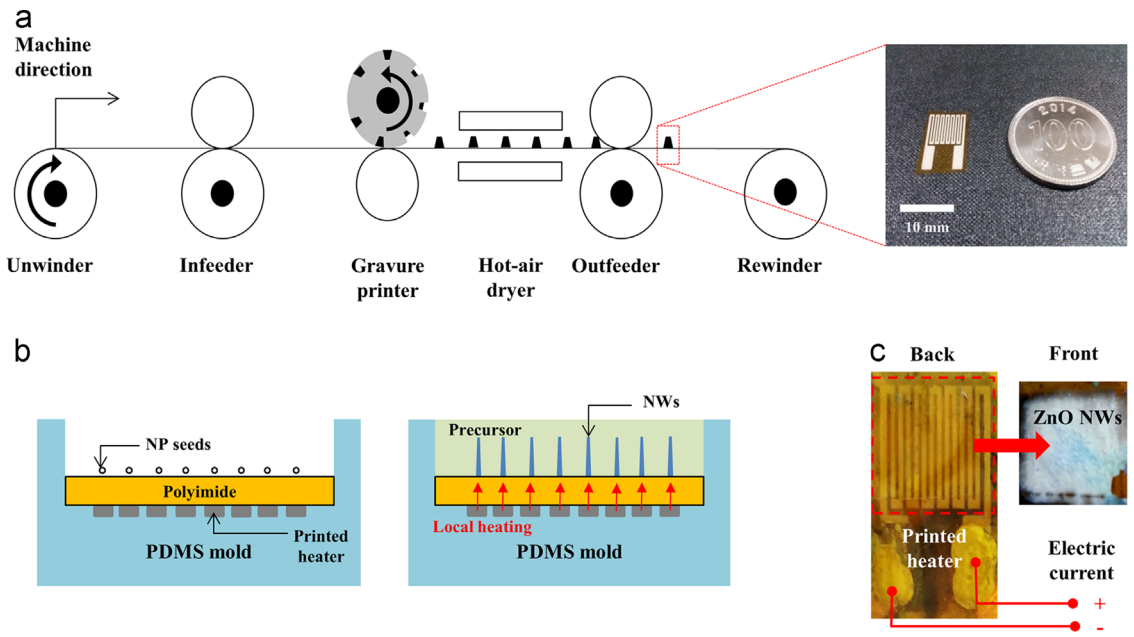

Fig. 1. (a) Schematic of R2R gravure printing process of resistive heater (inset: photograph of printed heater). (b) Fabrication process for ZnO NWs in PDMS heating pot. (c) Photograph of synthesized ZnO NWs on printed heater.

To synthesize ZnO NWs, a catalyst and a reaction solution are essential. These two materials were fabricated according to a previous study [15,16]. First, ZnO seed nanoparticles (NPs) were prepared by mixing 25 mM of zinc acetate with methanol. The precursor used as the reaction solution comprised 25 mM zinc nitrate hydrate [$Zn(NO_3)_2 \cdot 6H_2O$], 25 mM hexamethylenetetramine ($C_6H_{12}N_4$, HMTA), and 5–7 mM polyethylenimine (PEI) in deionized (DI) water [17]. The ZnO NW growth is influenced by the temperature and pH. In this case, we controlled the pH by adjusting the HMTA amount [18,19].

Fig. 1(b) shows the ZnO NW synthesis in the heating pot. A few droplets of ZnO seed particles in methanol were applied uniformly on the PI substrate by rotating and manually tilting the sample for about 5 s. This was followed by rinsing with ethanol and drying with N_2 gas. This process was repeated 5 times before annealing at 150 °C for 20 min. The entire process was then repeated thrice to ensure that the seed layer was uniformly applied. Subsequently, the precursor solution was injected into the heating pot (200 μl).

Various currents were applied to the printed heater and generated local heating using a sourcemeter (Keithley, 2611A), as shown in right side of Fig. 1(b). During NW growth, the change in temperature due to the evaporation of the precursor was minimized by steadily injecting an additional quantity of precursor into the heating pot using a syringe pump (LEGATO 100, KD scientific). After the reaction completed, the sample was rinsed with DI water and dried in the oven at 65 °C to remove any residual polymer and complete the ZnO NW growth process (Fig. 1(c)).

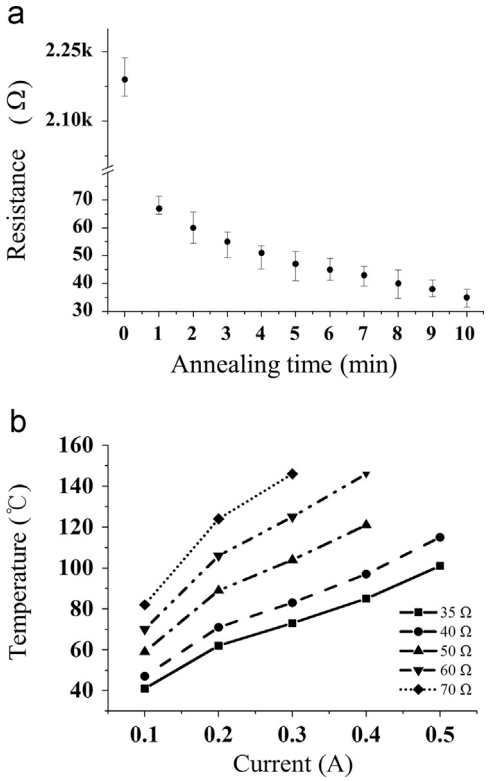

Fig. 2. (a) Resistance change during annealing at 350 °C. (b) Temperature increase by current application with various resistances, achieved using printed heaters.

3. Results and discussion

After the printing process, an additional annealing process was performed at 350 °C for various annealing times, as shown in Fig. 2(a). The printed heaters exhibit various resistance values according to the annealing times. The initial resistance of the printed pattern must be determined before it can be used as a heater.

To compare the characteristics of the fabricated NWs, the applied current was varied for an applied voltage of 20 V. Fig. 2(b) shows a comparison of the resistance and temperature of the precursor with respect to the applied current. Here, the ideal resistance was determined as below 40 Ω. At a resistance of 35 Ω, we could choose currents from 0.1 to 0.4 A. In other cases where the resistance was