Effect of intense pulsed light on hydrothermally grown ZnO nanowires

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Abstract

Hydrothermal growth of ZnO nanowires has been of great interest as it allows the use of organic substrates for flexible electronics applications. However, there are drawbacks on the growth technique as it is known to introduce defects in the nanowires. In this work, the use of intense pulsed light on hydrothermally grown ZnO nanowires on polyimide substrate was performed to enhance the physical and electronic properties of the nanomaterials. Such photonic annealing technique offers a rapid and effective improvement in material properties and importantly it is suitable for use on a wide variety of organic substrates, which are vital for flexible electronics.

Keywords: *photonic annealing; ZnO nanowires; flexographic printing; defects*

1. Introduction

Hydrothermal growth technique, which can be performed at a temperature of less than 100 ^{o}C, is suitable for low-cost mass production on organic substrates. However, it is known to produce nanowires with high density of defects that can influence the electrical and optical properties of the materials [1]. Therefore, post-synthesis treatment such as thermal annealing of ZnO nanowires is important to improve its properties. However, thermal annealing is time consuming and is unsuitable for organic substrates with low glass transition temperature.

Laser annealing was previously reported on ZnO nanowires, which enhanced the crystallinity of the material at much shorter time [2]. However, laser annealing is complex and unviable for high throughput production of nanowires device due to its small spot size.

Photonic annealing has previously been used to sinter printed metallic nanoparticles and to enhance the electrical properties of printed graphene [3, 4]. In this work, the use of intense pulsed light to anneal hydrothermally grown ZnO nanowires on printed silver on polyimide substrate is reported for the first time. Such photonic annealing technique would anneal the nanomaterials at high temperature without causing damage to the underlying substrates [5]. It offers significant advantages over other techniques as it allows the use of low-cost organic substrates and provides rapid annealing.

2. Experimental Details

2.1 Materials

Polyimide substrates were obtained from Lohmann Adhesive Tape Systems. Silver ink (PFI 722) was purchased from NovaCentrix. Zinc acetate (ZnA) precursor solution consisted of isopropanol (IPA) (Fisher scientific) and zinc acetate dihydrate (Sigma Aldrich). Zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) (Sigma Aldrich) were used in the hydrothermal growth of ZnO nanowires. Extra pure DI water and phosphate buffered silane (PBS) solution were purchased from Fisher.

2.2 Synthesis of ZnO nanowires

Flexographic printing technique (IGT Reprotest Printability Tester F1) was used to print silver electrodes and ZnA on polyimide substrate as reported in previous work [6]. After printing ZnA, the substrate was placed on a hotplate at 350 ^{o}C to allow the conversion of ZnA to ZnO seed layers suitable for hydrothermal growth of ZnO nanowires [6]. The nanowires

were also grown on silicon substrate in order to measure its length using cross-sectional scanning electron microscope (SEM).

2.3 Photonic annealing of ZnO nanowires

Photonic annealing of ZnO nanowires was performed using PulseForge 1200 (Novacentrix, USA). The sample was placed at a distance of 20 mm away from the xenon lamp (wavelength ranging from 200 to 1500 nm) and exposed to nitrogen during photonic annealing, which was performed at 350 V with a pulse envelope of 6.9 ms (comprising of three identical micro-pulses at a duty cycle of 95.65%) to deliver an energy density of 7.93 J cm^{-2}. Figure 1 illustrates the fabrication and photonic annealing process of ZnO nanowires.

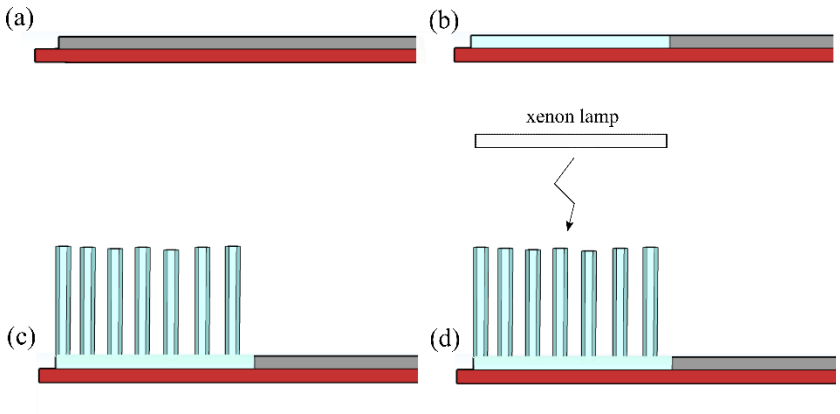

Figure 1. (a) Printing of silver electrodes and (b) ZnA layers on polyimide substrate. (c) Hydrothermal growth of ZnO nanowires and (d) photonic annealing of the nanowires.

2.4 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance measurements were carried out using Gamry (reference 600) potentiostat. As-grown and photonic annealed ZnO nanowires were introduced with 100 µL PBS. Measurements were carried out at 10 mV perturbation amplitude with reference to the measured open circuit potential in the frequency range of 1 Hz to 1 kHz. The impedance

parameters were calculated by fitting using an equivalent circuit illustrated in Figure 3(b). The fitting errors were below 5%.

3. Results and Discussion

SEM images of as-grown ZnO nanowires are shown in Figure S1. Figure 2a(i) and (ii) show SEM images of photonic annealed ZnO nanowires. The morphology of the nanowires was unchanged after photonic annealing. Figure S2 shows histograms on the diameter of as-grown and photonic annealed nanowires. The average length and diameter of as-grown nanowires were 545 ± 94 and 49 ± 20 nm, respectively. These were comparable to photonic annealed ZnO nanowires having average length and diameter of 534 ± 101 and 46 ± 15 nm, respectively.

EDX analysis was carried out on the ZnO nanowires to investigate its stoichiometry before and after photonic annealing. Figure 2(b) shows EDX spectrum of ZnO nanowires after photonic annealing. Zn and O peaks were from the ZnO nanowires, while the Ag peak originated from the silver electrodes. The stoichiometry of ZnO was almost 1:1 of zinc to oxygen, hence suggesting that photonic annealing did not affect the stoichiometry of the material.

X-ray diffraction (XRD) analysis of as-grown and photonic annealed nanowires is shown in Figure 2(c). Peaks from the substrate were observed between 20^{O} and 30^{O}. ZnO peaks were observed at 31.7^{O}, 34.4^{O}, 36.2^{O} and 47.5^{O}, which were associated with the hexagonal wurtzite phase of ZnO assigned as (100), (002), (101) and (102), respectively [7]. Diffraction peaks located at 38.1^{O} and 44.3^{O} can be indexed to (111) and (200) planes of printed silver electrodes, respectively [8]. The marginal increase in the intensity of ZnO (002) and Ag (111) peaks, after photonic annealing, is probably owing to a better orientation as suggested in previous reports [9].

Figure 2(d) shows photoluminescence (PL) spectra of as-grown and photonic annealed ZnO nanowires. Near band edge (NBE) and deep level emission (DLE) were observed from the spectra located at 376 and 600 nm, respectively. After photonic annealing, the DLE peak was highly quenched indicating a reduction of defects in the material [1]. The NBE peak intensity was remarkably increased as a result of photonic annealing. After photonic annealing, the ratio of NBE to DLE of the photonic annealed nanowires was 0.82, which was much larger than that of as-grown nanowires (e.g. 0.0064), suggesting a significant reduction in the defects.

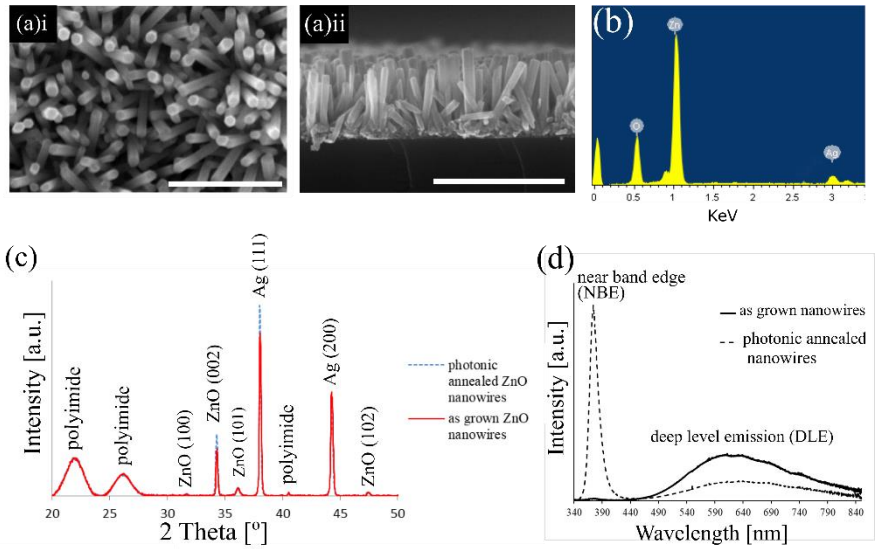

Figure 2. (a) SEM images showing (i) top and (ii) cross-sectional views of photonic annealed ZnO nanowires (scale bar is 500 nm); (b) EDX analysis of ZnO nanowires grown on silver electrodes on polyimide substrate after photonic annealing; (c) XRD analysis of as-grown and photonic annealed ZnO nanowires; (d) PL spectra of as-grown and photonic annealed ZnO nanowires.

EIS measurement was performed to investigate the effect of photonic annealing on the impedance of ZnO nanowires. The EIS technique was previously used to determine the resistance of various materials [10, 11]. Figure 3(a) shows the Nyquist plot of as-grown and photonic annealed ZnO nanowires. It can be observed that the impedance of ZnO nanowires has drastically decreased after photonic annealing indicating better conductivity than as-grown nanowires. Hydrothermally grown ZnO nanowires could exhibit high density of surface defects due to absorption of oxygen molecules at the surface of nanowires. These

defects would trap conduction electrons resulting in the formation of depletion layer near the surface of nanowires [1]. Photonic annealing would remove the absorbed oxygen molecules and reduce the depletion layer at the nanowires, thus leading to an enhancement in its electrical conductivity.

The impedance parameters of the nanowires (shown in Table 1) were obtained by fitting the EIS measurements using an equivalent circuit model as shown in Figure 3(b). The model reported here is similar to previously reported work by Jacobs *et al* [12]. Herein, the ZnO nanowires (in contact with PBS solution) were modelled as two parallel circuits connected to each other in series. The first circuit consisted of the ZnO resistance (R_{ZnO}) and capacitance (C_{ZnO}). The second circuit consisted of the charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}) at the ZnO/PBS interface. Since the PBS is not a redox probe, Rct was not considered in the simulation. Finally, Rs represents the resistance of PBS. The results showed that the resistance of ZnO nanowires has decreased by approximately six times after photonic annealing indicating an enhancement in the conductance of the nanowires. Furthermore, an increase in C_{dl} by two orders of magnitude was observed after photonic annealing. The reduction of defects in ZnO nanowires that led to enhancement in the conductance of the nanomaterials would attract more ions to the ZnO surface and increase polarization of electrolyte counter ions at the ZnO/PBS interface, thus increasing C_{dl} at the interface. Such improvement in the electronic properties of ZnO nanowires is pivotal to its applications in biomedical, optical and energy storage etc.

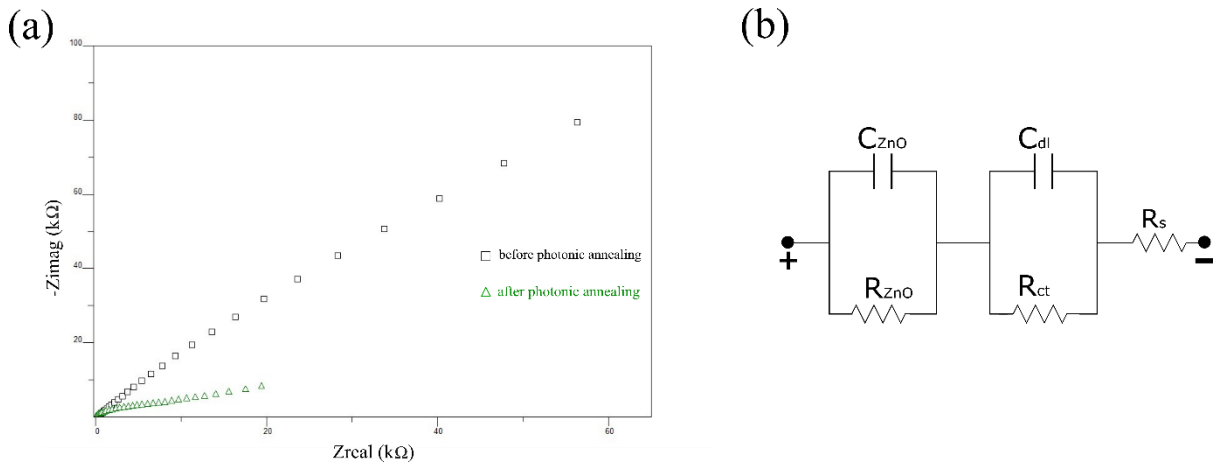

Figure 3. (a) Impedance spectra of ZnO nanowires before and after photonic annealing; (b) Simplified equivalent circuit.

Table 1. Impedance parameters of ZnO nanowires from EIS measurements.

	before photonic annealing	after photonic annealing
$R_{ZnO}(\Omega)$	8.9×10^{3}	1.53×10^{3}
C_{ZnO} (F)	3.26×10^{-7}	4.4×10^{-6}
C_{dl} (F)	8.48×10^{-7}	1.14×10^{-5}
R_s (Ω)	49	48

4. Conclusion

The results demonstrated an increase in the conductivity of hydrothermally grown ZnO nanowires due to the reduction of charge carrier traps after photonic annealing. Importantly, the annealing technique allows the use of organic substrates with low glass transition temperature and it has the potential to implement in series with roll-to-roll flexographic printing to facilitate low-cost mass production of high-performance flexible electronics.

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