FACILE AND CONTROLLED INTEGRATION OF FUNCTIONAL
NANOSTRUCTURES IN MICROFLUIDIC DEVICE

J. Kim * and I. Park

School of Mechanical, Aerospace, and Systems Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Republic of KOREA

ABSTRACT
Nanostructure integration within microfluidic device has a great potential for substantial improvement of performance and widening of applications by taking advantages of unique nanoscale material properties. We introduce a novel and simple method for the integration of functional nanowires by controlled hydrothermal reaction within microfluidic device. By modulating synthesis parameters such as reaction seeds, temperatures, periods, and heating locations, the morphology and location of synthesized nanowires can be well-controlled. We also demonstrate a preliminary result of pH sensing experiment by using the ZnO nanowire bridges fabricated by this method.

KEYWORDS: In-situ nanostructure synthesis, nanowires, nanostructured microfluidics, pH sensor

INTRODUCTION
Recently, nanostructures are becoming extremely useful components for many functional electronic devices such as sensors, catalysts, electrodes, etc. Similarly, the usefulness of nanostructures becomes more obvious for microfluidic devices as sensing and pre-concentration components. Accordingly, there have been many attempts to integrate nanostructures in microfluidic devices for better device performance. Examples include CNT-modified working electrode in the capillary electrophoresis (CE) microchip for detecting hydrazine, phenol, purine, and amino acid compounds[1], nickel nanowires working as magneto-switch for sensing and separation[2], vertical germanium nanowire arrays for biological sensing [3], single ZnO nanorod for pH sensing microfluidic chip [4]. However, most of these nanostructures were integrated in microfluidic device using sequential fabrication process: ex-situ synthesis of nanostructures (by CVD, reactive ion etching, etc.) followed by additional steps for alignment and integration with microfluidic packaging. Here, we propose a novel method for in-situ, low-temperature, and hydrothermal nanostructure synthesis, by which direct integration and controlled fabrication of nanowire arrays within microfluidic device is possible. We have applied this method to the fabrication of ZnO nanowire bridge between neighboring microelectrodes and used it for the real-time pH level sensing of sample solution.

EXPERIMENTAL
ZnO nanowires were grown either globally (i.e. along the entire microchannel) or locally (i.e. on the microheater) within the PDMS microchannel by hydrothermal method. To control the morphologies of synthesized nanowires, three different kinds of seeds (texture, e-beam, particle seed) were prepared and coated on top of the silicon chips. The precursor solution was prepared with zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%, Sigma Aldrich®), hexamethylenetetramine (HMTA, C₆H₁₂N₄, 99+%®, Sigma Aldrich®) and polyethylenimine (PEI, (C₂H₅N)n, Sigma Aldrich®) by following the protocols given in Ref. [5].

PDMS microchannel was prepared by photolithography of SU-8 and PDMS molding techniques with 10-20μm height and 150μm width. Microheaters were fabricated by photolithography and lift-off of e-beam evaporated metal film (Cr 20nm/ Au 200nm). Texture and particle seeds were coated on the chip by dispensing the seed solutions, drying for 10 seconds, and rinsing with ethanol. This coating step was repeated three times for sufficient coverage of the seeds on the chip, and further annealing process was conducted at 350°C for 20 min for stabilization. Alternatively, e-beam evaporated ZnO thin film (10 nm) was also used as a seed layer for nanowire synthesis. Fabricated PDMS microchannel was aligned and bonded on the chip after treatment with ozone plasma.

Figure 1: Schematic diagram of (a)global and (b)local synthesis of ZnO nanowires in microfluidic chip
Figure 1 shows the schematics of global and local synthesis processes of ZnO nanowires within microfluidic channel. For both processes, fresh ZnO nanowire precursor solution was continuously supplied through the microchannel by syringe pumps. For the global synthesis, the injected precursor was pre-heated at 60°C before flowing into the microchannel that is heated at 95°C for the ZnO nanowire synthesis by heating plate. For local synthesis, localized thermal energy was supplied through the microheater while the precursor was flown in the microchannel. The nanowire synthesis rates were dependent on the supplied electrical power density (power consumption divided by the microheater volume). We synthesized nanowire arrays at the power densities of $2.0 \times 10^{15}$ W/m$^3$, $2.6 \times 10^{15}$ W/m$^3$, and $3.0 \times 10^{15}$ W/m$^3$.

For the pH sensor application, ZnO nanowire bridge was fabricated by using two adjacent microheaters. Nanowire arrays were grown on two microheaters simultaneously until they were interconnected. The change of electrical current through the ZnO nanowire bridge was monitored for the real-time electrical sensing of pH level of sample solution.

RESULTS AND DISCUSSION

ZnO nanowires were grown globally on the seeded silicon wafer only within the microchannel where the precursor was flown and heated for several hours (Figure 2). S. Cai et al., [7] have shown that the substrate preparation affects the ZnO nanowire morphology. In this study, we used two kinds of ZnO nanowire seeds (texture and e-beam seed) for global synthesis. Texture seed resulted in vertically well-aligned nanowires compared to those with e-beam seed. On the other hand, the aspect ratio of the nanowires grown from e-beam seed is larger than those from texture seed and this difference became larger for longer synthesis period. As shown figure 2 (d), nanowire diameter distribution of nanowires from e-beam seed is narrower than texture seed and the growth rate on the longitudinal axis is much faster than that of the texture seed.

Local synthesis of the ZnO nanowires was examined at 3 different levels of electrical power densities. Figure 3 (e) shows the effect of the power density supplied to the microheater. As predicted, higher power density resulted in faster growth rate. Growth rates for power densities of $2.0 \times 10^{15}$ W/m$^3$, $2.6 \times 10^{15}$ W/m$^3$, and $3.0 \times 10^{15}$ W/m$^3$ were 0.01 $\mu$m/min, 0.19 $\mu$m/min, and 0.245 $\mu$m/min, respectively. Figure 3 (a)-(d) shows the SEM images of synthesized ZnO nanowires at $2.6 \times 10^{15}$ W/m$^3$ for different reaction periods. Nanowires were grown vertically only on the microheater due to the localized endothermal reaction at elevated temperature.
Figure 4 shows the microscopic images of ZnO nanowire bridge sensor and the real-time pH sensing result. The current through ZnO nanowire bridge decreased as the pH level was increased. The current was significantly dropped from 26.6 μA to 20.7 μA when the pH level was switched from pH=5 to pH=6. However, the current change became smaller at higher pH levels (e.g., I = 19.2 μA $\rightarrow$ 18.8 μA for pH=8 $\rightarrow$ 9). Although the response to the pH level was not linear, the sensor exhibited reasonable sensitivity to the pH levels from pH=5 to pH=9. The sensitivity of ZnO nanowire bridge to the pH level can be explained by the bonding of H$^+$ ions on the ZnO surface and the change of surface charge as a consequence [4]. The H$^+$ specific bonding sites residing at the ZnO surface can hydrogenate after contact with the electrolyte solution at lower pH level. These sites can protonate or deprotonate, leading to a surface charge and change of surface potential [8]. Commonly, ZnO nanowire is intrinsically n-type material. Therefore, more binding of H$^+$ ions (at low pH level) results in the accumulation of electrons, resulting in higher electrical conductivity. Oppositely, at high pH level, more binding of OH$^-$ ions occurs and this results in the depletion of electrons, causing lower electrical conductivity.

CONCLUSION

In this paper, we demonstrated a new method for the in-situ nanowire array integration inside the microfluidic chip. The ZnO nanowires were controllably grown within microchannel either globally or locally. We also have demonstrated pH sensor based on ZnO nanowire bridges fabricated by this method. We anticipate that our method can provide facile, economic, and eco-friendly route to the fabrication of nanostructure-enabled microfluidic assay devices for biomedical, environmental, and microchemical applications.

ACKNOWLEDGEMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0015290) and Open Innovation Research Program of Hewlett Packard (HP) Company.

REFERENCES


CONTACT

*J. Kim, tel: +82-42-3505233; jkim0811@kaist.ac.kr