Growth of ZnO nanowires on multi-layered polymer structures fabricated by UV liquid transfer imprint lithography

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Abstract

Among various growth processes, hydrothermal synthesis has been widely employed to produce ZnO nanowires because of its simplicity and cost effectiveness. However, the successful hydrothermal synthesis of ZnO nanowires on multi-layered polymer structures has been limited due to growth inhibitors in the polymer. For example, alpha-hydroxy ketone resolved in a UV-curable polyurethane acrylate (PUA) resin forms carboxyl groups (COOH) consisting of hydroxyl groups (O-H) on the α -position of a carbonyl group (C=O) during the UV-curing process. The carboxyl groups suppress the nucleation and growth of ZnO nanowires. In this paper, multi-layered polymer structures were fabricated by Liquid Transfer Imprint Lithography (LTIL), and the enriched carboxyl groups on the UV-cured PUA structures were pre-treated with hexamethylenetetramine (HMTA) solution to reduce the inhibitive influence of the carboxyl groups. The HMTA pre-treatment enabled ZnO nanowires to grow hydrothermally on multi-layered PUA structures despite the initial presence of carboxyl groups.

Keywords:

Liquid Transfer Imprint Lithography (LTIL), polyurethane acrylate, ZnO nanowires, carboxyl groups, multi-layered polymer structures, hydrothermal synthesis

1. Introduction

Zinc oxide (ZnO) is an attractive material because it has both semiconducting and piezoelectric properties [1]. In addition, nanostructured ZnO exhibits enhanced semiconducting, piezoelectric, and thermodynamic properties in comparison with macro-sized ZnO. For example, *wurtzite* structured ZnO nanowires exhibit strong piezoelectric characteristics, which can be successfully applied in technologies that require large electromechanical transduction, such as energy harvesting devices. Since the zinc and oxide planes are electrically charged by the polar Zn-O bonds [2], ZnO has been synthesized in a variety of nano-morphologies, including wires, rings, belts, flowers, and particles, each applicable to different device designs. ZnO nanowires in particular have been rigorously studied as one-dimensional (1-D) nanostructures for optical [3-8], biological [9-12], electrical [3, 7, 13-17], and sensing devices [7, 18].

Prior to the introduction of the hydrothermal synthesis process by Vayssieres [19, 20], methods of growing ZnO nanowires were restricted to processes that employed rigid substrates like Si and glass under high vacuum and high temperature environments. [21-25]. In contrast, hydrothermal synthesis is conducted at atmospheric pressure and temperatures below 100 °C in an aqueous growth solution, and this has allowed ZnO nanowires to be grown on a variety of different substrates [20], such as Si wafers [26, 27], PDMS [28], thermoplastic films [10, 29], paper [30], and carbon fiber [31]. Hydrothermal synthesis can also potentially be used to integrate ZnO nanowires on polymer structures using advanced lithographic fabrication methods, such as microcontact printing (μ CP) [14], nanoimprint lithography (NIL) [13, 32, 33], or liquid transfer imprint lithography (LTIL) [34-37].

The LTIL process is a popular technique for fabricating multi-layered structures with no-residuum, making it suitable for applications like cell lysis, optical waveguides, or printed circuit

boards. However, the process has limitations when used to hydrothermally integrate ZnO nanowires on UV-cured polymer structures. Specifically, the nucleation and growth of the ZnO nanowires can be suppressed by the inherent organic compounds of the polymers used for the LTIL process. Monomers, initiators, and functional groups generate inhibitors that make ZnO synthesis difficult [38]. Hydrophobicity disturbs the uniform coating of the ZnO seed layer. Carboxyl groups (COOH) decompose into carboxylate ions (COO⁻) and hydrogen ions (H⁺) which tend to combine with hexamethylenetetramine (HMTA, C₆H₁₂N₄), which is one of the main compounds used for continuous ZnO nanowire synthesis. This reaction consequently lowers the concentration of HMTA in the aqueous growth solution, limiting ZnO nanowire growth.

UV-curable polyurethane acrylate (PUA, MINS-511 RM, Minuta Tech.) polymer was used in this work to build multi-layered structures by the LTIL process. PUA is a siloxane-urethane-acrylate compound containing alpha-hydroxy ketone. Known as acyloin, the alpha-hydroxy ketone includes a hydroxyl group in the α -position of the carbonyl groups. It serves as an organic material polymerizing the initiators to acrylate with monomers. After UV-curing, the PUA substrate has a hydrophobic surface which includes siloxane and epoxy groups. To allow ZnO nanowires to grow properly with minimal inhibitive influence, the carboxyl groups and hydrophobicity of the UV-cured PUA need to be controlled. Oxygen plasma can be used to modify a hydrophobic polymer surface so that it becomes hydrophilic, but the oxygen plasma treatment forms more carboxyl groups. Thus, developing a method to control the carboxyl groups may be the principle solution for integrating ZnO nanowires on UV-cured PUA structures.

As previously stated, PUA contains alpha-hydroxyl ketone as a functional group, which consists of the ketone flanked by hydroxyl groups placed in the α -position of the carbonyl groups ($C=O$), which are derived from reductive coupling of the carboxyl groups. Hence, the UV-cured PUA is rich with carboxyl groups. The following equilibria explain the hydrothermal synthesis of ZnO in ZNH/HMTA aqueous solution [8, 38]. HMTA provides hydroxide ions (OH^-) for the growth of ZnO nanowires in the aqueous growth solution as shown in equilibria (1) and (2), and ZNH supplies the zinc ions (Zn^{2+}) as shown in equilibrium (3). These OH^- ions combine with Zn^{2+} ions to form $Zn(OH)_2$, facilitating the growth of ZnO nanowires upon dehydration, in equilibria (4) and (5).

However, the carboxyl groups ($COOH$) in the UV-cured PUA act as inhibitors, suppressing the nucleation and growth of ZnO nanowires. The carboxyl groups ($COOH$) lose their hydrogen ions (H^+) and form carboxylate ions (COO^-) due to their low binding energy. The hydrogen ions (H^+) combine with HMTA in the growth solution, and the HMTA- H^+ complexes composite to COO -HMTA- H on the PUA layer [38]. Accordingly, the concentration of HMTA in the ZnO growth solution is decreased by the reaction with the carboxyl groups, and this results in lower availability of OH^- ions that are used for ZnO synthesis.

Previously, ZnO or Ag thin films have been used as the seed or catalyst layer to block the inhibitive influence of carboxyl groups when growing ZnO nanowires [20, 39]. However, it is

difficult to cover the entire surface of 3D multi-layered polymer structures using conventional thin film deposition techniques. An alternative way to reduce the effect of the carboxyl groups is to increase the HMTA concentration in the growth solution. HMTA tends to combine with carboxyl groups, and this in turn decreases the carboxyl group's inhibitive influence. However, increasing HMTA concentration can lead to an unstable chemical condition because of competing reactions among the HMTA molecules.

In this paper, ZnO nanowires were grown on relatively thin PUA substrates by increasing the HMTA concentration in the growth solution. Additionally, thick PUA substrates were pre-treated with HMTA to interact with the carboxyl groups, and thus lower the inhibitive influence of the carboxyl groups during the subsequent ZnO nanowire growing process. All the PUA substrates were rendered hydrophilic with 10 min of oxygen plasma to achieve the uniform coating of the ZnO seed layer. ZnO nanowires grown on various thicknesses of UV-cured PUA substrates were examined to investigate the effect of HMTA concentration in the pretreatment, and in the hydrothermal growth solutions. Multi-layered PUA structures with enriched carboxyl groups were fabricated by the LTIL process, and ZnO nanowires were successfully integrated on the polymer structure using the HMTA pre-treatment.

2. Experimental Process

All of the chemicals for growing the ZnO nanowires were used without any further purification, and the aqueous solution was optimized according to the following references [40-42]. A p-type silicon wafer (100) was used as a substrate following an acetone, isopropyl alcohol (IPA), and DI water treatment in an ultrasonic bath for 10 min.

Figures 1 and 2 show the fabrication process for the PDMS master stamp and the multi-layer polymer structures using UV-curable PUA. The process began by fabricating line patterns

by photolithography using SU-8 2010 (MicroChem Corp.) as shown in Figure 1. SU-8 2010 was spin coated on a hexamethyldisilazane (HMDS) treated Si wafer at 3,000 rpm for 30 seconds, and soft-baked on a hot plate at 65 °C for 1 min, and 95 °C for 2 min. A UV dose of 100 mJ/cm² was applied to the SU-8 layer using a mask aligner (MJB4, SUSS MicroTec) as shown in Figure 1 (a). The exposed SU-8 was post-baked at 65 °C for 1 min and 95 °C for 2 min, then developed in SU-8 developer (MicroChem Corp.) for 2 min. The SU-8 line patterns were rinsed with IPA and hard-baked at 95 °C for 30 min. A silicone elastomer mixture of polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) with base and curing agent (10:1 wt% ratio) was poured over the SU-8 line pattern after vacuum desiccation, and then thermally cured at 65 °C for 4 hours (see Figures 1 (c) and (d)). The replicated PDMS line pattern had a 10 µm linewidth, 30 µm pitch, and a 1:1 aspect ratio.

The LTIL process is based on the transfer of an uncured polymer to an acceptor substrate without residuum. That is, the LTIL process needs a pair of substrates, one as a donor and the other as an acceptor. First, the UV-curable PUA was prepared as a mixture of polyurethane acrylate (PUA, MINS-511RM, Minuta Tech) and propylene glycol monomethyl ether acetate (PGMEA, CH₃CO₂CH(CH₃)CH₂OCH₃, Sigma-Aldrich, ≥ 99.5%) with a 2:1 vol% ratio to optimize thickness. Secondly, the donor and the acceptor substrates were treated by oxygen plasma at 11 W at 300 mTorr for 10 min, spin coated with PUA primer at 3,000 rpm for 30 sec, and baked at 200 °C for 20 min to improve the adhesion force between the Si wafer and PUA. Thirdly, the prepared UV-curable PUA mixture was spin coated on the donor substrate at 1,000 rpm for 30 sec. Immediately afterward, the line-patterned PDMS master stamp was applied to the PUA donor layer (Figure 2 (a)), and the liquid PUA filled the line patterns for 20 min. The uncured PUA held in the line patterns of the PDMS was transferred to the acceptor substrate

(Figure 2 (b)), and fully cured in a UV chamber (EC-500, Electro-Lite Corporation) at 36 W for 10 min (Figure 2 (c)). In this manner, the LTIL process produced the multi-layered structures by PUA transfer (Figure 2 (d)).

Figure 3 shows a process flow diagram for the hydrothermal growth of ZnO nanowires on the multi-layered polymer structures pre-treated in HMTA solution. The multi-layered polymer structures were annealed overnight at 200 °C and then exposed to oxygen plasma at 11 W at 300 mTorr for 10 min (Figure 3 (a)). In succession, the samples were treated in 75 mM aqueous hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, Sigma-Aldrich, $\geq 99.0\%$) solution at 90 °C for 3 hours as shown in Figure 3 (b). The HMTA treated samples were rinsed in DI water and gently dried by a rubber air blaster. Figure 3 (c) shows the seed layer coating process, which was performed with 17 mM zinc acetate dihydrate (ZAD, $Zn(CH_3COO)_2 \cdot 2H_2O$, Sigma-Aldrich, 99.999%) solution. ZAD was dissolved in pure ethanol (Ethanol 200 proof, Decon Laboratories, Inc.) and ultrasonicated for 10 min. Samples were submerged upside down in the ZAD solution for 2 min to allow zinc precursors to cover the surface of the polymer structures, followed by an ethanol rinse and nitrogen drying. This seed coating process was repeated 5 times, followed by an annealing process at 200 °C for 20 min to achieve ZnO nucleation (Figure 3 (d)). The zinc nitrate hydrate (ZNH, $Zn(NO_3)_2 \cdot H_2O$, Sigma-Aldrich, 99.999%) and HMTA were prepared in DI water with a 25 mM concentration. The ZNH and HMTA solutions were then mixed by vortex for 1 min. The ZnO nucleated seed samples, which covered the HMTA treated multi-layered polymer structures, were leaned against the wall of the container face down in the aqueous growth solution to avoid the development of a white precipitate, as shown in Figure 3 (e). The ZnO nanowires were grown in a convection oven at 90 °C for 3 hours by the hydrothermal

synthesis process. After the ZnO nanowire growth, the samples were tempered in an oven chamber, washed with DI water, and dried by a rubber air blaster.

PUA layers of 800 nm, 250 nm, 160 nm, and 95 nm thicknesses were prepared using mixtures of PUA and PGMEA with different viscosities by spin-coating at 3,000 rpm for 30 seconds. Carboxyl groups were produced by UV exposure and oxygen plasma. The vol% ratio of PGMEA used in the PUA to control the thickness was 1:1, 3:1, 5:1, and 10:1 for the thicknesses of 800 nm, 250 nm, 160 nm, and 95 nm, respectively. For 10 μ m thick PUA layers, the same dilution and spin coating parameters as those used in the LTIL process were used. The PUA was dissolved in PGMEA by vortex mixing for 3 min, ultra-sonication for 10 min, and then stored in a dark place at room temperature overnight. The 17 mM ZAD precursor was coated 5 times by dropping on various thicknesses of PUA layer, and was then annealed at 200°C for 20 min. The resulting ZnO nanowires were grown in an aqueous solution containing 25 mM ZNH and varying HMTA concentrations of 25 mM, 50 mM, and 75 mM at 90°C for 3 hours. Field emission scanning electron microscope (FE-SEM, Helios NanoLab 400 DualBeam system, FEI Co.) was used to analyze the geometries of the multi-layered polymer structures and measure the length of ZnO nanowires.

3. Results and discussion

In this research, ZnO nanowires were grown by hydrothermal synthesis on multi-layered polymer structures fabricated by LTIL using a UV-curable PUA. As shown in Figure 4, the ZnO nanowires that were hydrothermally grown on a 10 μ m thick UV-cured PUA substrate did not grow as long as those grown on a Si substrate (see the inset) even under the same growth conditions. The limited nanowire growth on the PUA layer was attributed to the inhibitive influences of the UV-cured PUA, specifically, its hydrophobicity and carboxyl groups. The PUA

used for this study contains the initiators, monomers, and functional groups needed to polymerize the siloxane-urethane-acrylate compound for UV nanoimprint lithography (UV-NIL). The siloxane and epoxy in the PUA generate a hydrophobic surface with a measured 93° contact angle after UV curing. This hydrophobic condition disturbs the uniform seed coating, and consequently the nucleation of ZnO only occurs in local aggregations. To achieve a uniform seed layer, the hydrophobic surface was modified to a hydrophilic surface with 34° contact angle via oxygen plasma with 11 W at 300 mTorr for 10 min.

3.1 Effect of HMTA concentrations

To reduce the carboxyl groups' influence, a thermal decarboxylation was attempted by annealing overnight at 200°C . The thermal decarboxylation breaks the dimer bonds of the carboxyl groups and produces CO, CO_2 , and H_2O , which is similar to a thermal degradation process. Although the PUA layer was already annealed, the ZnO nanowires grew poorly as shown in Figure 4. To investigate the relationship between the carboxyl groups and HMTA, the HMTA concentration was increased in the growth solution, and the ZnO nanowire growth process was repeated. The images in Figure 5 are organized according to HMTA concentration and PUA thickness. The HMTA concentrations are arranged horizontally, of 25 mM, 50 mM, and 75 mM, and the PUA thicknesses are arranged in the vertical direction, of 800 nm, 250 nm, 160nm, and 95 nm. The number of carboxyl groups was assumed to be proportional to the PUA thickness for the same sized substrates, and thin PUA layers were expected to demonstrate well-grown nanowires with less number of carboxyl group. According to the results shown in Figures 5 (a) and (b), the increased HMTA concentration produced smaller hexagonal shaped nanowires on the 800 nm and 250 nm thick PUA substrates. Figures 5 (b), (c), and (d) show that higher HMTA concentrations resulted in longer ZnO nanowires grown on 250 nm, 160 nm, and 95 nm

thick PUA substrates, respectively. Moreover, the uniformity of the nanowires' length and diameter was affected by HMTA concentration. It should be noted that the only variable parameter in the experiment was different thicknesses with the same exposed surface area (i.e. different volumes). With the same surface area under the same HMTA concentration, ZnO nanowires have grown longer with thinner PUA substrates. The carboxyl groups are present not only on the surface, but also inside of the UV-cured PUA substrate. During the hydrothermal synthesis, polymer inter-diffusion occurs to bring the carboxyl groups into the reaction boundary, especially at elevated temperature [43]. The thicker PUA layer is likely to include higher carboxyl group content and provide rich inhibitive reactant condition during the hydrothermal synthesis. Figure 5 shows that the thickness (i.e. volume) of the PUA correlates to the number of carboxyl groups, and that the carboxyl groups' role as an inhibitor was controllable, enabling the growth of nanowires by 50 mM and 75 mM HMTA concentrations on PUA layers thinner than 250 nm. The HMTA that did not react with the carboxyl groups remained in the growth solution, and continued to provide an environment for ZnO nanowire growth. On the PUA layers thinner than 250 nm, increasing the HMTA concentration in the aqueous growth solution provided an effective and facile way of overcoming the carboxyl groups' inhibitive influence against ZnO nanowire growth.

3.2 The length of ZnO nanowires

Figure 6 shows the aspect ratio and average length of ZnO nanowires grown on thin PUA layers at the different levels of HMTA concentrations in a fixed 25 mM ZNH solution. The length and diameter of ZnO nanowires were measured using tilted SEM images. Increasing the HMTA concentration facilitated longer ZnO nanowire growth, as well as better coverage of nanowires on the PUA layer. On 800 nm thick PUA, anisotropic ZnO nanowire growth did not

appear until the HMTA concentration was increased to 75 mM in the growth solution. The aspect ratios of ZnO nanowires were observed to increase with thinner PUA layers and higher HMTA concentrations in the growth solution as shown in Figure 6 (a). ZnO nanowires grown on the 800 nm thick PUA layer showed a lower aspect ratio of 2 even under the higher HMTA concentration of 75 mM, but the aspect ratios of ZnO nanowires grown on the relatively thinner PUA layer of 95 nm thick reached up to 13.5 to 20 with the HMTA concentrations in the range of 25 mM to 75 mM. Although the higher concentration of HMTA helped the growth of ZnO nanowires up to a certain level, concentrations of HMTA above 75 mM caused OH⁻ rich growth solution and the pH increase. The solubility of Zn²⁺ decreases with the OH⁻ rich solution and the low Zn²⁺ content is the limiting reactant for the growth of ZnO nanowires [44]. As a result, the length of the nanowires exhibited poor uniformity. Furthermore, it was observed that higher concentrations of HMTA deteriorated the adhesion of PUA on the Si substrates, and resulted in separation of the PUA layers from the substrate. These results limited any further increase in HMTA concentration, and thus placed an upper limit on its concentration for the hydrothermal growing process.

3.3 HMTA pretreatment

Since a thick UV-cured PUA layer includes a higher number of carboxyl groups, it's expected that the HMTA concentration would need to be increased to more than 75 mM for thick PUA to effectively reduce the number of carboxyl groups. However, it was found that higher HMTA concentration resulted in poor ZnO nanowire growth, and damaged the PUA layer. In order to avoid the adverse effects of higher HMTA concentration during the growing process, the UV-cured PUA substrate was instead pre-treated in a HMTA solution before seed coating of the ZnO layer to induce an initial reaction between the HMTA and carboxyl groups, and thus

reducing the number of active carboxyl groups on the PUA substrate prior to the growth synthesis. Figure 7 shows the ZnO nanowires grown on 800 nm and 10 μm thick PUA substrates that were pre-treated in HMTA aqueous solutions at different concentrations at 60 $^{\circ}\text{C}$ for 3 hours. Figures 7 (a-c) show the ZnO nanowires grown on 800 nm thick PUA substrates that were pre-treated in HMTA concentrations of 25 mM, 50 mM, and 75 mM, respectively. HMTA establishes a stable pH buffering activity, and introduces a strong steric hindrance effect, thus ensuring a vertical arrangement of ZnO nanowires [45]. The nanowires shown in Figure 7 were grown in a growth solution of 25 mM ZNH and 25 mM or 75 mM HMTA. Figures 5 (a-1) and (a-3) show poor ZnO nanowire growth on the same PUA thickness with the same HMTA concentration in the growth solution, while Figures 7 (a-c) show that the additional HMTA pre-treatment achieved a smaller diameter, and uniform growth of the ZnO nanowires perpendicular to the substrate. The HMTA pre-treatment enabled better nucleation of ZAD and lowered the number of active carboxyl groups, and in turn decreased the carboxyl groups' inhibitive influence during the following hydrothermal growing process. It also needs to be noted that an excessive supply of HMTA during the hydrothermal growth process causes horizontal growth, resulting in thicker and shorter ZnO nanowires, as shown in Figure 7 (c-2). The HMTA pretreatment allowed the growth of ZnO nanowires on thick PUA layers which were enriched with carboxyl groups. Figures 7 (d-1) and (d-2) show that ZnO nanowires were grown on even thicker PUA layers of 10 μm in 25 mM and 75 mM HMTA growth solutions, respectively, after pretreatment in the 75 mM HMTA solution.

Single and double layered polymer microstructures were prepared by LTIL as shown in Figures 8 (a) and (b). The fabricated multi-layered PUA structures were pre-treated in 75 mM HMTA solution at 90 $^{\circ}\text{C}$ for 3 hours, following oxygen plasma with 11 W at 300 mTorr for 10

min. The ZnO nanowires were grown with the same hydrothermal growth process as that used for the Si substrates. The single-layered structures shown in Figures 8 (c) and (e) demonstrate that defined ZnO nanowires were grown on the entire surface. Measured length and diameter of the ZnO nanowires were 200 ~ 300 nm and 20 nm, respectively, so the aspect ratio ranged between 10 to 15. ZnO nanowires grown on the double-layered structures show overall coverage, but local aggregation and shorter nanowires were observed, as shown in Figures 8 (d) and (f). In the case of flat PUA layers, the volume of the PUA was approximately 4.5 mm³ on a 15 mm by 30 mm substrate with a 10 µm thickness. The corresponding volume of PUA was reduced by 66 % for the single-layered sample, and increased by up to 58% for the double-layered structures. Since the estimated number of carboxyl groups is proportional to the number of PUA layers, the HMTA concentration should be increased to control the carboxyl groups.

4. Conclusion

ZnO nanowires were grown hydrothermally on multi-layered polymer structures fabricated by the LTIL process using a UV-curable PUA. Enriched carboxyl groups, produced from the alpha-hydroxy ketone of the PUA, were found to inhibit the nucleation and growth of ZnO nanowires on the UV-cured PUA substrates. HMTA in the aqueous growth solution contributes to the continuous synthesis of ZnO nanowires. However, HMTA in the growth solution is preferably consumed by the carboxyl groups in the PUA to create COO-HMTA-H. This reduces the HMTA concentration in the growth solution and the resulting shortage of HMTA limits the continuous synthesis of ZnO. To provide sufficient HMTA, higher concentrations of HMTA could be added to the growth solution to ensure the growth of ZnO nanowires on thin UV-cured PUA layers. However, excessive HMTA concentration was also found to limit ZnO nanowire growth by inducing competing reactions between HMTA

components, and also resulted in the peel-off of PUA from the substrate. As an alternative, the UV-cured PUA was pre-treated with HMTA at relatively low concentrations, and this pre-treatment enabled the growth of ZnO nanowires on multi-layered structures by reducing the active carboxyl groups. The proposed HMTA pre-treatment for the fabrication of multi-layered polymer structures integrated with ZnO nanowires can be used to improve diverse functionalities of microfluidic bioassay applications, such as cell separation, trapping, and lysis for intercellular analysis and single cell study.

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Figure 1. The process flow diagram for fabrication of PDMS master stamp. (a) UV exposure of 10 μm line pattern on SU-8 2010, (b) SU-8 development and rinse, (c) PDMS casting on the SU-8 line pattern, and (d) PDMS replication from the SU-8 line pattern.

Figure 2. The process flow diagram for LTIL to fabricate multi-layered structures using a UV-curable polymer, PUA. (a) PDMS line pattern filled with PUA on a donor substrate, (b) PUA transfer to an acceptor substrate, (c) UV curing of PUA on the acceptor substrate, and (d) compiling the line patterns to achieve the multi-layered polymer structures by repetition of the LTIL process.

Figure 3. The process flow diagram for the hydrothermal synthesis of ZnO nanowires (a) on the multi-layered polymer structures fabricated by LTIL, (b) pre-treatment in HMTA aqueous solution, (c) seed coating on the HMTA pre-treated PUA structures, and (d) annealing of the seed layer on a hot plate, (e) growth of ZnO nanowires in aqueous solution by hydrothermal synthesis, and (f) rinsing and drying of the ZnO nanowires on the multi-layered structure.

Figure 4. ZnO nanostructures grown on a UV-cured PUA substrate using the hydrothermal synthesis process. Inset shows ZnO nanowires grown on a p-type Si substrate (100) using the same synthesis process. Scale bars are 1 μm .

Figure 5. Effect of HMTA concentration in the growth solution on the growth of ZnO nanostructures on UV-cured PUA layers with thickness of 800 nm, 250nm, 160 nm, and 95 nm in rows. The HMTA concentrations of 25 mM, 50 mM, and 75 mM are shown in the columns. Scale bars are 500 nm.

Figure 6. (a) The aspect ratio and (b) average length of the ZnO nanostructures grown on UV-cured PUA layers with different thicknesses, as a function of HMTA concentration. The aspect ratio and length of the ZnO nanostructures increase with the concentration of HMTA in the growth solution.

Figure 7. ZnO nanowires grown on UV-cured PUA substrates with thicknesses of (a-c) 800 nm and (d) 10 μm . After the layers were pre-treated in (a) 25 mM, (b) 50 mM, and (c) & (d) 75 mM HMTA solutions, ZnO nanowires were grown in aqueous growth solution mixtures of 25 mM ZNH and (-1) 25 mM or (-2) 75 mM HMTA. Scale bars are 500 nm.

Figure 8. (a) Single-layered and (b) double-layered UV-cured PUA structures fabricated by LTIL. ZnO nanowires grown on (c) single-layered and (d) multi-layered PUA structures with HMTA pre-treatment. Magnified images of (c) and (d) are shown in (e) and (f), respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

HMTA pretreatment
Hydrothermal growth