Growth and replication of ordered ZnO nanowire arrays on general flexible substrates

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Vertically aligned and site controllable ZnO nanowire arrays have been synthesized and replicated *via* hydrothermal method on general flexible substrates. The replication was demonstrated for three generations. The morphology and density of the nanowire arrays could be optimized in the original generation by adjusting the chemical reaction parameters. The pattern of the original generation was inherited by the succeeding generations by a new transferring method. The growth mechanism of the replicated nanowire arrays was investigated with the help of inductively coupled plasma (ICP) etching and AFM tip scanning. The robustness of the ZnO nanowire arrays was obviously improved compared with the seedless ZnO nanowires grown on Au (111) surface, according to the excellent morphology preservation after ultrasonic wave treatment.

Introduction

During the past several years, there has been a growing interest in one-dimensional ZnO nanostructures for their potential applications in fabricating electronic, optoelectronic, electromechanical and electrochemical devices, such as solar cell,[1,2] light-emitting diode,[3] chemical sensor,[4] strain sensor,[5] ultraviolet (UV) laser,[6] nano-generators,[7,8] and piezotronic devices.[9] Among the various methods that have been reported for the synthesis of ZnO one-dimensional nanostructures, catalytically vapor–liquid–solid (VLS) process[10] and catalyst-free metal–organic chemical vapor deposition (MOCVD)[11,12] are typically used. These methods produce high quality single crystal ZnO nanostructures. However, the strict requirement of the single crystallinity of the substrate and the high growth temperature seriously limit the compatibility of these methods with organic substrate for applications in flexible electronics. Comparatively speaking, hydrothermal synthesis is an attractive alternative because it could be carried out at a relatively low temperature around 70–90 °C, and could allow for multiple crystalline and even amorphous substrates.[13,14]

Using hydrothermal methods, one-dimensional ZnO nano-structures have been synthesized on Si substrate with ZnO seeds in the form of thin film or nanoparticles,[15,16] and on Au surface.[17] However, it is of great importance to synthesize ZnO nanowires on flexible organic substrate to integrate with foldable and portable electronic, photoelectronic and piezotronic devices. In the existing literature, ZnO nanowire arrays have been grown on organic substrates such as polydimethylsiloxane (PDMS), Kapton film, and polystyrene beads.[18–20] However, those methods either synthesize randomly distributed ZnO nanowire arrays or require an external electrical field to promote the growth of ZnO nanowire arrays, which is expensive and time-consuming. Besides, so far, there have been few investigations on the synthesis of density-controllable, finely patterned, vertically aligned ZnO nanowire arrays on multiple organic substrates *via* simple hydrothermal method.

Here in this work, we develop a new approach of synthesizing, transferring and replicating vertically aligned, density and site controllable ZnO nanowire arrays on a general flexible substrates (conductive and nonconductive) *via* simple hydrothermal method. The original pattern is generated by electron beam lithography (EBL), and then later the pattern could be replicated and multiplied on a large scale. Thus, the throughput of patterned ZnO nanowire arrays is greatly enhanced. This approach is adaptable to various kinds of organic materials, and the synthesis process could be carried out at a lower temperature (70 °C), rendering it a useful technique for flexible electronic application.

Experimental

The fabrication process flow is shown in Fig. 1. Firstly, the original ZnO nanowire arrays were synthesized on an inorganic substrate *via* hydrothermal method. Vertically aligned straight ZnO nanowire arrays are originally synthesized on two kinds of substrates: (1) a flat Au (111) surface on a Si(100) wafer by sputtering 20 nm Ti (200 Å min^{-1}) and 50 nm Au (400 Å min^{-1}), consecutively and (2) Si doped n-type GaN thin film on a sapphire substrate. EBL was used to generate the original pattern and thus the density and position of the ZnO nanowires can be well controlled. The lattice mismatch between the wurtzite GaN (0001) plane and ZnO (0001) plane is 1.8%, thus GaN (0001) plane serves as an excellent template for vertically aligned straight ZnO nanowire arrays growth.[20] The substrate was put facing down floating on the nutrient growth solution (1 : 1 ratio of zinc nitrate and hexamethylenetetramine (HMTA) 2 mM) and was kept in an oven at 70 °C for 16 hours.

The original ZnO nanowire arrays were then transferred to a thin layer of polymer. The liquid state prepolymer was solidified on the nanowire arrays and was later separated from the substrate together with the nanowire arrays. The prepolymer was dropped onto the substrate where the original ZnO nanowire arrays stand. After curing, the prepolymer polymerized and solidified, embedded the nanowire arrays firmly. Then the polymer layer was peeled off from the substrate, together with the nanowires. In this way, the bottom terminals of the nanowire arrays are exposed. In our study, three kinds of polymers were used to transfer the nanowire arrays: PDMS (Sylgard® 184 from Dow Corning), polymethyl methacrylate (PMMA) and resin (SPI-PON™ 812 resin). Different prepolymers have different polymerization process.

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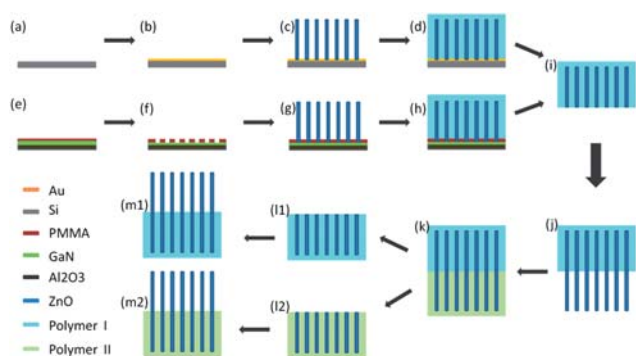
Fig. 1 The process flow of density controllable ZnO nanowire arrays growth and transferring for regrowth onto the flexible organic substrates. (a) Si wafer. (b) A thin layer of Au was thermally evaporated (0.3 Å s⁻¹ deposition rate, 50 nm) to the nucleation sites on the substrate. (c) ZnO nanowire arrays vertically grown on Au surface. (e) On Si doped n-type GaN on a sapphire substrate, a layer of PMMA was spin-coated. (f) EBL was employed to generate a patterned mask. (g) Patterned vertically aligned ZnO nanowire arrays grow on n-type GaN surface. (d and h) Polymer I (usually PDMS) was dropped on the nanowire arrays and polymerized. (i) Polymer I was peeled off together with the ZnO nanowire arrays. (j) Second generation ZnO nanowire arrays regrowth *via* hydrothermal method. (k) Polymer II was dropped and polymerized on the second generation nanowire arrays. (l1 and l2) Two kinds of polymers were separated. (m1 and m2) Succeeding generation nanowire arrays regrow from the polymer substrates.

The secondary ZnO nanowire arrays were then synthesized *via* hydrothermal method under the same reaction parameters as the original ones. Following the same procedures, the secondary ZnO nanowire arrays can be replicated and transferred to the later generations of polymers.

To illustrate the robustness improvement of the ZnO nanowire arrays on organic substrate, we prepared two samples. One is the secondary growth nanowire arrays on PDMS and the other is the original nanowire arrays on Au surface. The two samples were treated with ultrasonic wave in water for 15 minutes separately and then dried in oven for SEM observation.

Results and discussion

1. Chemical mechanism and morphology optimization

In this work, we used hydrothermal method to grow ZnO nanowire arrays. The growth mechanism has been well documented.[21–24] The ZnO nanowires were formed by the hydrolysis of zinc nitrate in water. Zinc nitrate provides Zn^{2+}, which is necessary to build up ZnO nanowires. Although the detailed function of HMTA during the ZnO nanowires growth is still under investigation, it is believed to act like a Lewis base to hydrolyze in the water solution and gradually produces OH^-.

By adjusting the reaction parameters, such as precursor concentration and growth temperature, the morphology of the nanowires can be readily controlled. The influences of the parameters have been analyzed in details.[17] Generally speaking, the nanowires density is determined by the precursor concentration, while the morphology and shape of the nanowires are controlled by the growth time and temperature. In our case, it is important to control the density of the

original nanowires and the aspect ratio of the secondary nanowires, because the density of the original nanowire arrays will be inherited by the succeeding generations of nanowire arrays. To find out the best experimental parameters, a series of experiments were performed with varying precursor concentration and temperature with the fixed 1 : 1 ratio of zinc nitrate/HMTA and a growth time of 16 hours.

To explore the influence of the precursor concentration to the density, we carried out a series of experiments with varying precursor concentrations. The experimental results show that the density of the nanowire arrays on Au surface has a close relationship with the precursor concentration. There is distinct increase of the nanowires density when the precursor concentration increases from 0.1 to 5 mM. The dense nanowire arrays result from the increase of the nucleation sites, which might balance the high zinc chemical potential caused by the increased precursor concentration. The density of the succeeding generations of nanowire arrays on the organic substrate is determined by the original nanowire arrays on Au surface. Temperature is also an important factor in maintaining a good hexagonal prism shape of ZnO nanowires. When the temperature decreased to 60 °C, the aspect ratio becomes smaller. When the temperature increased to 90 °C, pyramid-shaped ZnO nanowires were grown. The mechanism of the shape variation to the temperature has been documented.[17] From our experimental result, concentration of 2 mM, temperature of 70 °C, and growth time of 16 hours are the optimum combination to obtain well-defined hexagonal prism shape ZnO nanowires with appropriate density and aspect ratio (Fig. 5a).

2. Growth mechanism of the second generation ZnO nanowire arrays and the robustness improvement

To investigate the growth mechanism of the secondary ZnO nano-wire arrays, we treated secondary nanowires sample grown on PDMS with a plasma reactive ion etching process—ICP (15.0 mTorr, 55.0 °C, 15 min, Ar, O_2, and CF_4 as the etching gases). After the etching process, the PDMS base was lowered for about 6 μm, thus exposing a section of the original nanowires. The junctions connecting two sections of nanowires are clearly shown in Fig. 2a and b. From the uniform heights of the junctions, we can naturally estimate that the junctions are the ends of the original ZnO nanowires (bottom part), which also serve as the seeds for the secondary nanowire growth, *e.g.*, the upper part growth. The SEM image with higher magnification (Fig. 2b) shows that the upper part is wider than the bottom part. Actually this is a general case that the succeeding generation nanowires become fatter than the previous generation. This is because that the diameter of the nanowires is always larger than the size of the original seeds due to the lateral growth although it
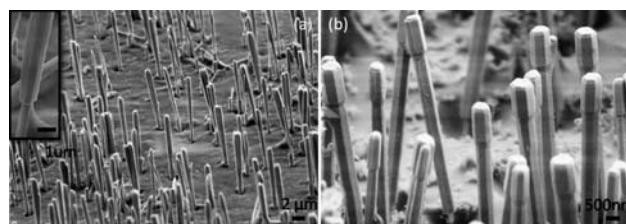
**Fig. 2** SEM images of ZnO nanowire arrays on PDMS after plasma etching.
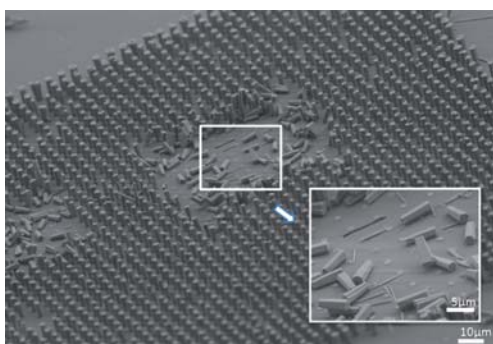
Fig. 3 SEM images of patterned ZnO nanowires grown on PDMS. The area with crushed nanowires is the area that was scanned by an AFM tip.

is much slower than the axial growth.[17] As for the second generation nanowires, the diameter of the first generation nanowires is the size of the "seeds" for the second generation.

To further illustrate the growth mechanism, the secondary nanowires on PDMS are scanned by an AFM tip. Fig. 3 shows the patterned ZnO nanowires on PDMS after scanned by an AFM tip. Unprotected nanowires were not rigid enough to resist the lateral force exerted by the AFM tip. The nanowires fell down after the scanning, leaving only the bare end of the original nanowires. Each bare end of the original nanowires corresponds to a single nanowire, which indicates that the ends of the original ZnO nanowires serve as seeds for the secondary nanowires growth.

The robustness of the secondary generation of nanowires was obviously improved compared with the first generation of ZnO nanowires grown by seedless hydrothermal method on smooth surface. To demonstrate the robustness improvement, the secondary nanowire sample prepared with our method and a seedless ZnO nanowires sample were treated respectively with the ultrasonic wave for 15 minutes. After the treatment, most of the seedless first generation of ZnO nanowires fell off from the substrate, while the secondary ZnO nanowires prepared with our method survived and preserved the original morphology, as shown in Fig. 4.
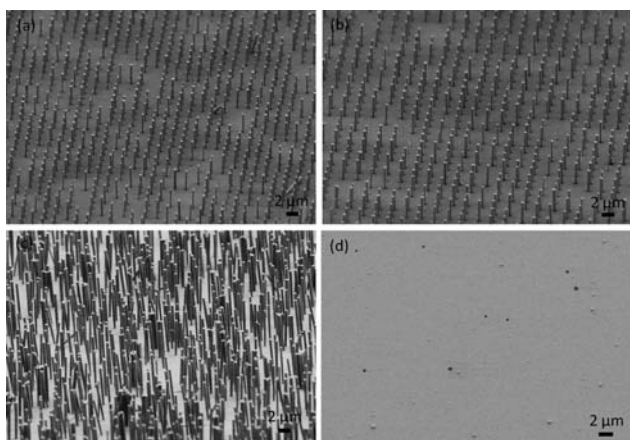
3. Nanowires transferring and replication

This nanowires transferring and replication method for growing ZnO nanowire arrays on organic substrates were demonstrated to be a general adaptable method to those polymers which have a solidification process during the polymerization. Several kinds of polymers have been demonstrated to transfer the original nanowires (Fig. 5a), and provide the basement for the secondary nanowires growth, such as PDMS, PMMA, resin (Fig. 5b–d) and carbon black mixed PDMS (C-PDMS) (Fig. 6b). The replication process was finely performed regardless of the different physical properties and the polymerization processes between different polymers.

To transfer the nanowire arrays, the viscosity of the prepolymer should be controlled precisely so that the prepolymer would be sticky enough to stay on the nanowire arrays and form a strong interface bonding, yet has a sufficient fluidity to infiltrate all nanowires without creating any possible bubbles that will reduce the fidelity of the pattern. After being heated, the prepolymer would have been fully solidified, ready to peel off from the substrate together with the nanowires. After the transferring, the pattern and the vertical alignment of the original nanowire arrays were perfectly preserved in the polymer. Furthermore, the bottom face of the polymer was exposed,

Fig. 5 (a) The first generation ZnO nanowire arrays on Au (111) surface. (b–d) The second generation nanowire arrays. The substrates are (b) PMMA, (c) resin, and (d) PDMS.
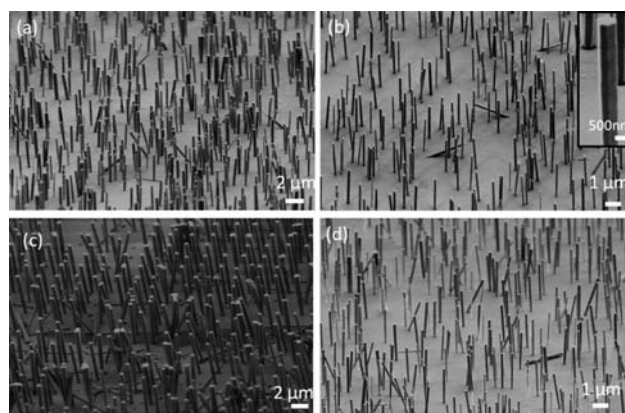

Fig. 4 Patterned ZnO nanowire arrays on PDMS (a) before and (b) after the ultrasonic wave treatment. Seedless ZnO nanowire arrays on Au (111) surface (c) before and (d) after the ultrasonic wave treatment.
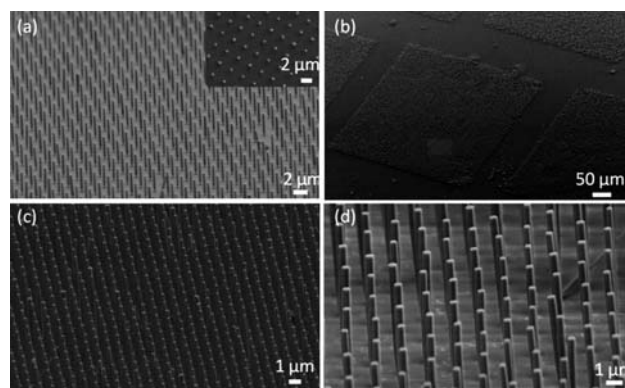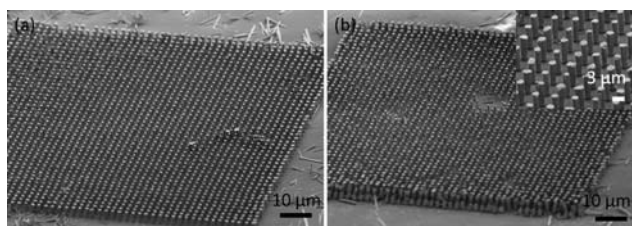

Fig. 6 (a) The patterned and vertically aligned first generation ZnO nanowire arrays on n-type GaN (0001) surface. Inset is enlarged top view. (b–d) The patterned second generation nanowire arrays on (b) carbon black mixed PDMS, (c) PMMA, and (d) resin.

Fig. 7 SEM images of the third (a) and fourth (b) generation nanowire arrays. The third generation nanowire arrays grow on resin substrate, while the fourth generation nanowire arrays on PDMS substrate.

with bared dotted ends of the original nanowires in it, which enabled secondary nanowire arrays growth. After being kept under the same reaction parameters used to grow the original nanowires, the secondary nanowire arrays grew out of the ends of the original nanowire arrays, which is called the replication.

C-PDMS was also used to demonstrate the adaptability of this pattern transfer and replication approach to conductive polymer. As shown in Fig. 6b, by mixing the carbon black (6 wt%) into PDMS during the polymerization process, the resistance of the C-PDMS block was reduced to around 15 kΩ cm^{-2}, which was significantly lowered compared with pure PDMS. The change of the viscosity and other physical properties of C-PDMS did not affect the transfer and replication processes at all. In this way, this approach enables the fabrication of patterned ZnO nanowire arrays for foldable and portable electronic devices.

Finely patterned vertically aligned ZnO nanowire arrays could be synthesized on organic substrates (Fig. 6b–d). By introducing EBL to generate a mask, the patterned first generation nanowire arrays could grow on n-type GaN (0001) (Fig. 6a). The pattern and the vertical alignment of the first generation nanowire arrays will be inherited by the succeeding generations of nanowires through the transfer and replication. The lattice mismatch between the wurtzite GaN (0001) plane and ZnO (0001) plane is 1.8%, so the GaN (0001) plane serves as an excellent epitaxial growth template for vertically aligned straight ZnO nanowire arrays.

ZnO nanowire arrays redefined growth could be performed for multiple times between different polymers. PDMS hardly glues to other polymers, which enables the repeated replications of the nanowire arrays between different organic substrates. We chose PDMS and resin for the transfer and replication of the nanowires by turns. PDMS was first used to transfer the first generation of nanowire arrays. After the growth of the second generation, the resin prepolymer was applied on the nanowire arrays on PDMS and then baked for polymerization. When the resin is fully solidified, it was peeled off from PDMS together with the ZnO nanowire arrays, ready for the third generation nanowire array growth. Following the same procedure, the nanowire arrays could be replicated for multiple times. Fig. 7 shows the third and fourth generation of nanowire arrays on resin and PDMS, respectively. After the multiple-generation growth, the nanowire arrays still preserved the original pattern. Besides resin, other polymers such as PMMA could also pair up with PDMS to accomplish the repeated replication of the nanowire arrays. The defect, defined as a ZnO nanowire missing from the pattern, became more prominent compared with the second-generation nanowire arrays, because every defect in the precious generation pattern was transferred to the succeeding generation pattern, thus the defects

accumulated and preserved as the pattern being transferred and replicated.

Conclusion

In summary, we developed a new technique of synthesizing patterned ZnO nanowire arrays on multiple flexible organic substrates using a novel chemical approach and a new transferring method. The nanowires arrays could be transferred and replicated between different organic materials. The pattern and density of the nanowire arrays were finely controlled in the original generation and were inherited by the succeeding generations through the transferring. The replication was demonstrated for three generations. The patterns were well preserved, although the defects accumulated. Compared with the seedless ZnO nanowire arrays grown on Au (111) surface, the robustness of the nanowires was strongly improved according to the excellent morphology preservation of the nanowires arrays after being treated by ultrasonic wave. This technique illustrates a low-cost and scalable approach of growing and replicating ZnO nanowire arrays on a general organic substrate, which could be integrated into flexible and wearable electronic and piezoelectronic devices.

Acknowledgements

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