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SELECTIVE GROWTH OF 1D NANOSTRUCTURED OXIDE MATERIALS USING PDMS STAMP

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ABSTRACT

The approach for selective growth of 1D nanostructured oxide materials using poly (dimethylsiloxane) (PDMS) stamp consists of using microcontact printing, as such the soft lithography technique, for transferring the pattern of ZnO film on a substrate, followed by the hydrothermal growth of 1D nanowires on patterned areas. The nanowires have been grown in aqueous solutions of zinc nitrate at temperature at 95°C. The wettability of the glass and of the Si/SiO$_2$ substrates was investigated by contact angle measurements. The morphology of the nanostructures obtained was characterized by optical microscopy and scanning electron micoscopy.

KEYWORDS: ZnO nanowires, hydrothermal growth, microcontact printing, contact angle, morphology

1. Introduction

One-dimensional ZnO nanostructures (nanowires) have been studied intensively for the realization of various devices, such as light-emitting diodes [1], gas sensors [2], ultraviolet photosensor [3] and field effect transistors [4], due to their simple synthesis route.

Achieving selective, uniform and ordered arrays of ZnO 1D nanostructures on wanted areas of substrates via a one-step approach by the wet solution method remains a prominent challenge. For the selective pattern growth of ZnO nanowires various technologies have been developed: nanosphere litography [5], silane-based self-assembled monolayers [6], electron beam lithography [7] and conventional photolitography [8]. These procedures are time-consuming and require some expensive facilities. The new soft lithography techniques, such as microcontact printing, represent a very attractive alternative a nonphotolitographic strategy, using an element with surface relief (i.e. the stamp) to transfer material to a preselected area of the substrate [9-11]. Usually, stamps are produced by replication against a master that has the desired relief features.

A conventional PDMS stamp has a hydrophobic surface which enables nonpolar chemicals to be transferred onto substrates [12]. In this article, we report a selective growth of 1D nanostructures that combines the direct patterning of ZnO films via microcontact printing (1) and subsequent low-temperature hydrothermal growth of ZnO nanowires (2).

2. Experimental details

2.1. Preparation of Elastomeric Polymer Stamp

For the preparation of the elastomeric polymer stamp, a SU-8 photoresist was spin-coated onto the Si wafer and then exposed at 14.1mW UV radiation, through a photomask with 300x300 and 700x700 μm square model.

The exposed SU-8 thin film was developed to yield the pattern (master mold) and then cleaned with isopropyl alcohol and deionized (DI) water.

An polymer, PDMS (Sylgard 184 Silicone Elastomer KIT, Dow Corning)[13], fabricated by pouring a mixture of silicone elastomer and a curing agent, was poured onto the SU-8 mold and cured at 70°C.

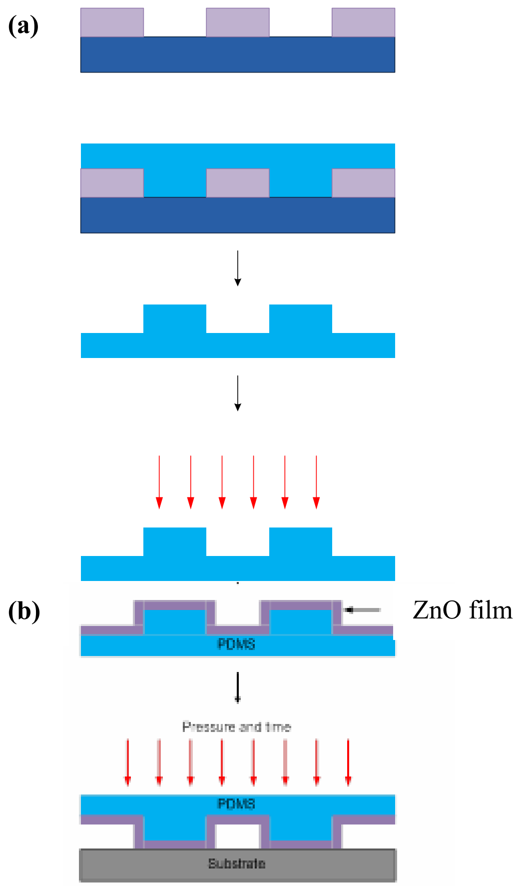
After the curing process, the PDMS was detached and cleaned in ethanol and ultrapure water, and treated with O$_2$ plasma (***Figure 1a***).

2.2 Patterning of ZnO film and growth of ZnO nanowires

For the deposition of the ZnO film, an alcoholic solution of zinc acetate dihydrate, $Zn(CH_3COO)_2{\cdot}H_2O$, (Sigma Aldrich, 99.5% purity) was used. The solution for the hydrothermal growth of nanowires, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 98% Sigma–Aldrich) was used as row material. Zinc nitrate salts provide Zn^{2-} ions required for building up ZnO nanowires, while water molecules in the solution provide O^{2-} ions. HMTA hydrolyze in the water solution and gradually release OH^- (***Figure 1b***).

2.3 Characterization of thin film and nanowire layers

The contact angle measurements were processed at 24°C with goniometer – *OCA 15 plus DataPhysics*, *Germany*. The surface morphology of patterned substrates was investigated by optical microscopy using a Olympus BX51 microscope. The effect of the morphology of the nanowires grown on patterned layers was investigated by scanning electron microscopy using an Zeiss Auriga microscope.



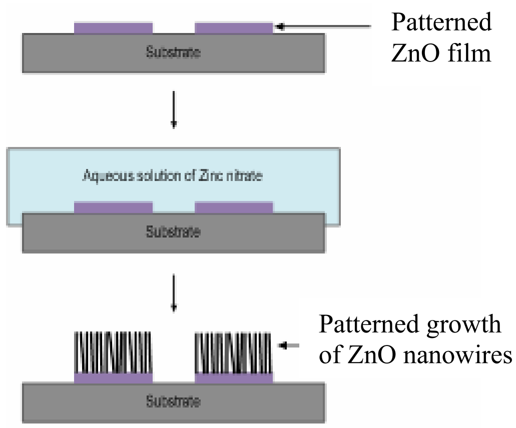


Fig. 1. *Cross illustration of the selective growth process: Elastomeric stamp preparation (a); Pattering of ZnO film and selective growth of ZnO nanowires (b)*

3. Results

Figure 2 shows the contact angle variation when measured on glass and silicon substrates. Using this technique, the wettability, in relation to zinc acetate solution used for the patterning of the ZnO film, was investigated.

The contact angle values show significant variation, it increasing from 37 to 92° for glass substrate, and from 52 to 100° for Si/SiO_2 substrate, when the substrates are pattern with ZnO seeds layer. Taking into consideration these results, one can conclude that the wettability of the glass substrate is higher than that of the silicon substrate, which implies a higher adhesion of zinc acetate dihydrate solution to the glass substrate.

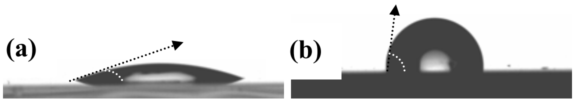


Fig. 2. *Illustration of contact angle variation on glass substrate (a) and silicon substrate (b)seeded with ZnO layer*

The model size and roughness have a significant effect on the quality of the resulted film pattern and on the aspect of the grown nanowires.

To control the geometry of patterned areas, the size of the square models of PDMS stamp was modified from 300x300 to 700x700 μm and the pressure carrying stamping was kept constant.

The optical images of the patterned substrates with different size of model are shown in ***Figure 3.*** The smoothest pattern surface was obtained for the 500x500 μm size.

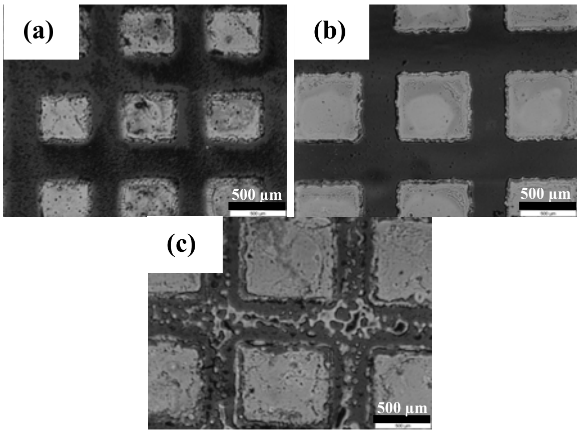


Fig. 3. *Optical images of Si/SiO$_2$ substrates stamped with PDMS stamp with dimension models 300x300 (a), 500x500 (b) and 700x700 µm (c)*

From the optical images, one can observe that the size model can affect the quality of the patterned areas. The square shape present a number of irregularities, but the advantage is that a very smooth surface will always be obtained so it will not affect the morphology of the 1D ZnO nanostructures.

In ***Figure 4*** are shown the SEM images of a Si/SiO$_2$ substrate stamped with a square model (right part) and non-stamped (left part). The patterned area obtained by microcontact printing shows some irregularities but very dense vertical nanowires grown inside of the square pattern can be observed (Figure 4c).

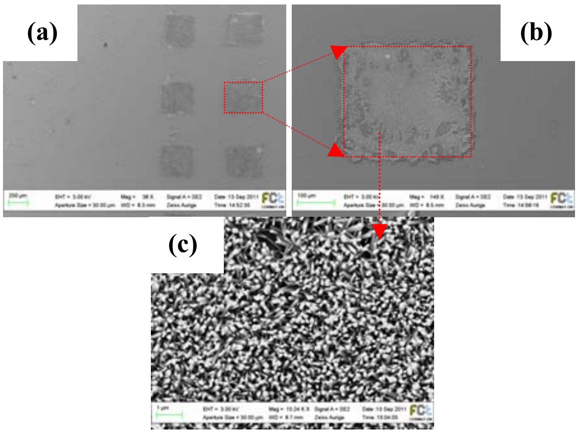


Fig. 4. *SEM images of ZnO nanowires localized grown on Si/SiO$_2$ patterned substrate (square model) by microcontact printing: images with non patterned and patterned zones (a), detail with patterned square model (b), detail with nanowires grown on patterned zones (c)*

The influence of the nature of the substrate on the stamping process is presented in ***Figure 5.***

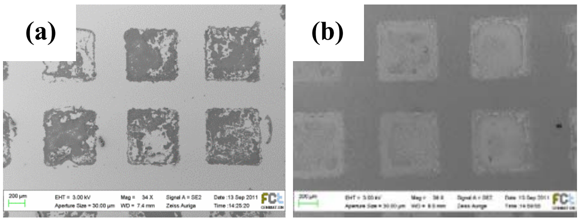


Fig. 5. *ZnO nanowires grown on glass substrate (a) and silicon substrate (b) patterned by microcontact printing*

It was mentioned before that the adhesion of the Zn (O$_2$CCH$_3$)$_2$ based stamping solution onto the silicon substrate is higher compared to that on the glass substrate.

On Si/SiO$_2$ substrates, the patterned areas are well shaped and defined, and the grown nanowires are dense and vertical; the edge of the model on the Si/SiO$_2$ substrate is more uniform than on the glass substrate. So, the quality of the created model is influences by the nature of the substrate, and in turn influence the direction and dispersion of the grown nanowires. In order to explore the relationship between the precursor concentration and the density of the ZnO nanowires arrays, the precursor concentration was varied between 0.01 - 0.025 M. As shown in ***Figure 6,*** the dimensions and the density of ZnO nanowires increase with solution concentration.

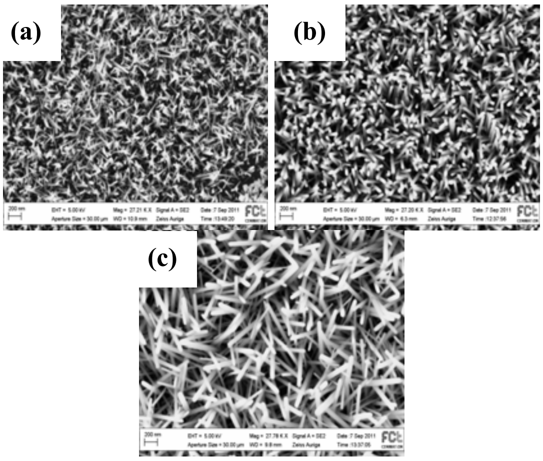


Fig. 6. *SEM images with ZnO nanowires growth with different concentrations of solution: 0.01 M (a); 0.02 M (b); 0.025 M (c)*

From ***Figure 7*** one can clearly see that, with increasing solution concentration, the nanowire length range from 323 to 667 nm, and diameters ranges from 12 to 29 nm.

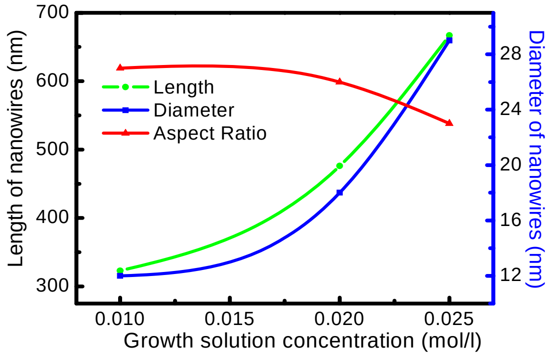


Fig. 7. *Length and diameter of ZnO nanowires vs. the concentration of grown solution*

4. Conclusions

A selective growth of 1D nanostructured oxide materials on glass and silicon substrates was obtained by combining the direct patterning of the ZnO film via microcontact printing and subsequent low-temperature hydrothermal growth.

The nature of the substrate influences the homogeneity of the patterned ZnO film and subsequently the direction of the growth and the aspect ratio of ZnO nanowires. Ordered and very good quality single-crystal ZnO 1D nanostructures can be grown from solution on a localized area of the substrate patterned by microcontact printing.

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