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ZnO nanowires strips growth: Template reliability and morphology study

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ABSTRACT

In this work we report on hydrothermal growth of ZnO nanostructures obtained by using strip-shaped resist templates made by electron beam lithography, with particular focus on: (i) the effects of materials used and processing on the template adhesion and its stability during wet growth; (ii) the influence of the template pattern dimensions on the nanowires morphology. Templates made of patterned films with methylmethacrylate–methacrylic acid copolymer showed greater adhesion and stability with respect to the commonly used poly (methylmethacrylate) electron resist or to the use of thin adhesion-promoter photoresist layers. The growth of nanowires in strip-shaped methyl methacrylate–methacrylic acid copolymer templates has been investigated using typical hydrothermal growth parameters and a marked dependence of nanowires length and diameter has been found on the template size for strips narrower than about 2 μm.

1. Introduction

Micro and nanoscale structured materials made of zinc oxide (ZnO) are particularly interesting for applications in electronics and photonics due to their outstanding properties including semiconductivity, piezoelectricity, pyroelectricity, direct bandgap and biocompatibility [1–3]. Many kinds of ZnO nanostructures have been obtained over large areas with good uniformity using the hydrothermal synthesis on different kind of substrates (including GaN [4], ZnO single crystal [5], ZnO seed on Si or on other substrates [6]). This low cost growth process is attractive, however it hardly provides structures with both precise spatial arrangement and custom size and geometry, which may be required by novel micro/nano-devices based on ZnO such as for instance micro-arrays of addressable sensors.

An approach to have a better control of the ZnO nanostructures is the localized growth by means of templates obtained using different techniques [4,7,8], such as electron beam lithography (EBL) patterned resist which is the most used material for templated hydrothermal growth on a ZnO seed layer on Si [9]. The most common template design used is made of circular holes in resist patterns. Many studies investigated the influence of growth parameters on the morphology of the nanostructures while only few works [9–11] deal with the influence of the template size on the morphological characteristics of ZnO NWs.

In this work we report on ZnO NWs obtained by hydrothermal growth on strip-shaped resist templates made by EBL. In particular we focus on: (i) the effects of materials used and processing on the template film adhesion and its stability during the wet growth; (ii) the influence of the template pattern dimensions (strips width) on the NWs morphology.

2. Materials and methods

The ZnO nanostructures were synthesized by hydrothermal growth on a Si substrate covered by a thin ZnO seed layer. The schematic in Fig. 1 shows the processing steps used for the templated growth. After cleaning a Si substrate, by using piranha solution for 3 min and a dip in HF (10%), a ~30 nm thick seed layer was deposited on the substrate by radio frequency sputtering technique at 150 W in argon atmosphere at a working pressure of $1.3 \cdot 10^{-2}$ mbar. The ZnO layer was deposited at room temperature

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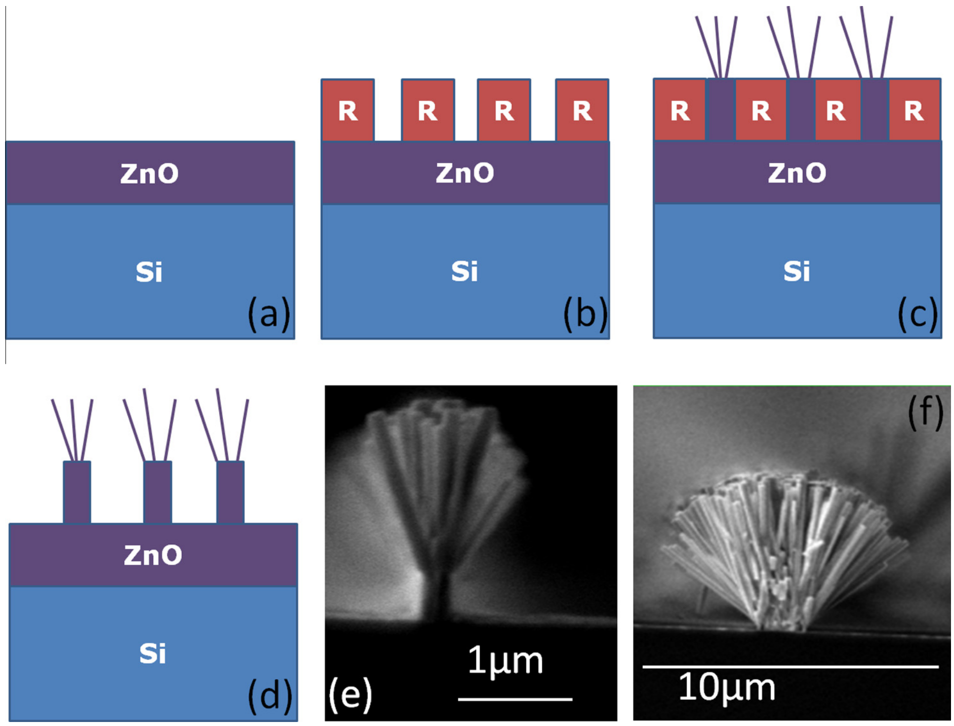

Fig. 1. Schematic of the templated growth process: (a) thin film seed layer deposition by sputtering; (b) resist patterning by EBL; (c) hydrothermal growth of ZnO nanowires; (d) resist removal; (e and f) 90° tilted SEM images of resulting ZnO structures showing the nanowires on top of a bulky ZnO buffer.

with a rate of 17 nm/min. The obtained seed layer shows an optical gap of 3.16 eV and a resistivity of 9.2 Ωcm [12] (Fig. 1a).

The templated growth was obtained by using a masking resist layer patterned by electron beam lithography (Leica EBPG 5 HR) (Fig. 1b). The following resist single-films and bilayers were considered in order to test their adhesion during the hydrothermal growth:

(i) Poly (methyl methacrylate) (PMMA) at 4% dilution in ethyl lactate, spin coated at 3000 rpm for 60 s and dried at 170 °C for 5 min. The resist thickness was ~350 nm.
(ii) Adhesion promoter photoresist layer (thickness ~30 nm) followed by PMMA as described in (i); the photoresists employed are Shipley 1813 and AZ 5214 diluted 1:25 in propylene glycol monomethyl ether acetate, spin coated at 2000 rpm for 60 s and dried at 90 °C for 5 min. The total resist thickness was ~380 nm.
(iii) Commercial methylmethacrylate–methacrylic acid (MMA–MAA) copolymer (MMA(8.5)MAA) at 11% dilution in ethyl lactate, spin coated at 5000 rpm for 60 s and dried at 170 °C for 5 min. The resist thickness was ~350 nm.

Different EBL doses are assigned depending on resist type and pattern size. The optimized dose using MMA-MAA copolymer for pattern width larger than 1 µm was 400 µC/cm^2, while a larger dose up to 800 µC/cm^2 was used for sizes smaller than 1 µm. For PMMA resist increased doses of 500 µC/cm^2 and up to 1000 µC/cm^2 respectively were used.

The resists were developed in 1:1 isopropyl alcohol (IPA):-methyl isobutyl ketone (MIBK) for 1 min. A gentle oxygen plasma treatment was made before the ZnO growth in order to remove any resist residue in the template apertures.

The hydrothermal growth of the NWs was performed by keeping the sample upside down, tilted by an angle of 60°, in an equimolar aqueous solution (10 mM) of zinc nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$ and hexamethylenetetramine (HMTA) in ultra pure water. The growth temperature (*T*) ranged from 60 °C to 90 °C and the growth time (*t*) was between 4.5 and 14 h. After growth the samples were rinsed in IPA and soft dried in N_2 (Fig. 1c). The resist was then stripped in acetone (Fig. 1d).

The sample surface morphology was characterized by atomic force microscopy (AFM) using a Digital Instruments D3100 microscope with Nanoscope IIIa controller operated in Tapping Mode. Commercial n$^+$-doped silicon probes with nominal tip radii in the 5 ÷ 10 nm range, and a typical force constant of about 40 N m^{-1} were used. For the morphological characterization of ZnO nanostructure a ZEISS EVO MA10 scanning electron microscope (SEM) was used at an accelerating voltage of 5 kV. The NWs diameter measurements were made by using top view images, while the NWs length was evaluated at 90° tilt angle after cleavage across the strip-template patterns (see Fig. 1e and f). The NWs length does not include the thickness of the bulky ZnO buffer grown within the template apertures, which height is equal to the resist thickness.

3. Results and discussion

3.1. Resist template stability and reliability

The hydrothermal growth of ZnO NWs using PMMA templates with circular holes on our sputtered seed layer showed similar results as reported in literature [9,10]. Frequently, we observed a poor PMMA adhesion which causes feed solution penetration, and thus ZnO growth, underneath the resist layer. This finding is more evident in the case of template patterns made of considerably long lines or trenches. Ultimately, in case of high growth temperature and growth time, the resist film might show dramatic swelling, as shown in Fig. 2a.

Even if there is no visible MMA damage after growth and before resist removal, a resist adhesion loss can occur producing a slight but not negligible ZnO growth underneath the resist film. Two examples of morphologies of such ZnO growth are reported in