

Regular ZnO nanopillar arrays by nanosphere photolithography

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Abstract

Highly regular vertical ZnO nanopillar arrays were hydrothermally grown through a nucleation window pattern generated by nanosphere photolithography. The in-plane intensity modulation of the exposing ultraviolet light in the photoresist was performed by Stöber silica or polystyrene nanospheres in the masking Langmuir–Blodgett monolayer. By comparing six different nanosphere diameters in the 180–700 nm range only those with diameter above the exposure wavelength of 405 nm generate a pattern in the thin photoresist layer. The pattern quality is improving with increasing diameter, therefore, the masking for nanopillar growth was demonstrated with 700 nm polystyrene nanospheres. The results of the nanosphere photolithography were supported by finite-difference time-domain calculations. This growth approach was shown to have the potential for low-cost, low-temperature, large area fabrication of ZnO pillars or nanowires enabling a precise engineering of geometry.

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1. Introduction

Nanopillar arrays are currently attracting a great interest due to their potential applications in photonics. Although the official classification of the different quasi-one-dimensional materials is still missing, the term nanopillar (NPL) or sometimes simply pillar usually refers to an elongated object of diameter in the 150–500 nm range standing perpendicularly to the substrate [1]. For certain applications, where the manipulation of the visible light is required, the NPLs are more adequate than thinner

nanowires or nanorods. For example Si and II–VI compound semiconductor pillar arrays are intensively investigated as promising architecture for solar-energy-harvesting. These NPL-based photovoltaic cells possess several advantages over their thin-film counterparts such as enhanced light absorption [2], compatibility with low-cost or even flexible substrates [3], reduced amount of active material with less stringent quality requirements [4].

On the other hand, NPLs of similar geometry made of ZnO are promising for ultraviolet (UV) optoelectronic exploitation because of the wide direct band-gap (3.37 eV) and the high exciton binding energy of 60 meV. As it was recently pointed out by Zimmler et al., the amplified spontaneous emission from ZnO thin nanowires are usually misinterpreted as lasing, while the real lasing effect with the characteristic threshold and a superlinear region can only be

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obtained from thicker ($D > 150$ nm) NPL resonators [5]. The confined light experiences a refractive index contrasts at both hexagonal facets, thereby limiting the amount of reflection and feedback. The mirror losses explain the size dependence: the smaller the diameter of the NW/NPL the smaller is the fraction of the field confined inside the laser cavity. On the other hand, ZnO p–n homojunction type UV photodiode [6], UV light emitting device (LED) [7], and electrically pumped lasing [8] were also realized recently due to the development of reliable p-type doping. This progress will further increase the need for large scale, low cost, and low temperature fabrication techniques of highly regular ZnO NPL arrays.

In previous works, it was demonstrated that regular ZnO NRs can be formed on ZnO single crystal [9,10] or epitaxial ZnO layer [11] using a seed window pattern generated by e-beam lithography. However, to reduce the cost and to up-scale the fabrication in most applications, an alternative patterning method is needed. Among the available techniques both conventional photolithography and nanoimprint lithography require expensive, high resolution masks. Moreover, with the former technique the sub-micron resolution is always challenging. Nanosphere lithography, on the other hand is a powerful alternative where the high resolution of the pattern is ensured by the small diameter of the self-assembled particles [12,13]. In these methods the nanosphere monolayers are used as shadow mask during a subsequent metal deposition [14], ion implantation [15] or deep reactive-ion etching (DRIE) [16] step. The nanosphere photolithography (NSPL), as a novel nanopatterning technique combines the merits of both nanosphere lithography and conventional photolithography. In this process the self assembled monolayer of nanolens-like polystyrene or silica nanospheres on top of a photoresist layer is able to focus the UV light to exceed exposure dose limit just in the focus region [17] in the photoresist. In this work a novel fabrication route, the NSPL assisted wet chemical growth of vertical ZnO nanopillars is demonstrated.

2. Experimental

2.1. Growth of the ordered ZnO nanostructures

The fabrication process is illustrated in Fig. 1. Two different substrates were selected a Zn-terminated c-polar (0 0 0 1) single crystal ZnO (CrysTec GmbH) and a DC reactive magnetron sputtered ZnO thin film (150 nm) on Si wafer [18]. The cleaned and dehydrated wafers were spin-coated with a 200 nm thick

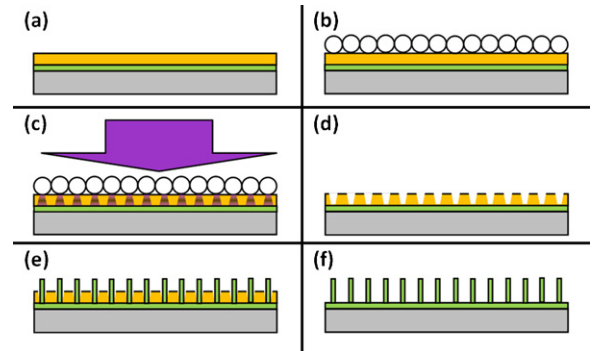


Fig. 1. Schematic process flow of nanosphere photolithography assisted wet chemical growth. The processing steps are: photoresist spin coating onto the ZnO surface (a), nanosphere deposition by Langmuir–Blodgett technique (b), exposure (c), removal of the nanospheres and the development of the photoresist (d), hydrothermal growth of ZnO nanopillars/nanowires (e), removal of the photoresist in acetone (f).

photoresist (Shipley S1805) and pre-baked on hot-plate (110 °C) for 60 s. The hexagonal close-packed (HCP) monolayer of Stöber silica [19,20] and polystyrene (MicroParticle) spheres with various diameters (180, 350, 430, 500, 700 nm) were deposited on the resist using Langmuir–Blodgett technique in an orange box to avoid the UV illumination. After the 0.4–0.6 s long exposure with 405 nm UV light (Hg-lamp h-line, 20 mW/cm²) in a mask aligner, in few seconds the nanospheres were removed by a 1:20 HF solution. The development was carried out in a 1:2 developer-water solution followed by a 10–15 min long post-bake procedure at 110 °C in an oven.

The ZnO nanorods were grown hydrothermally from the window pattern on the ZnO single crystal or on ZnO thin film covered Si substrates. The solution contained 10–10 mM of zinc nitrate hexahydrate (ZNH) and hexamethylenetetramine (HMT) in deionized Millipore water (18.2 Ω cm) [21]. The growth process lasted 2 h at 95 °C in a multipurpose laboratory oven. The resulting ZnO nanostructures were imaged using a Zeiss 1540XB field emission scanning electron microscope (SEM) and further studied by atomic force microscopy (AFM) in semicontact mode (AIST-NT, SmartSPM 1010).

2.2. Finite-difference time-domain simulations

The finite-difference time-domain (FDTD) simulations were carried out using commercial FDTD software. The 3D computational domain (4 μm × 4 μm × 1.2 μm) involved a silicon substrate (250 nm), a photoresist layer, a silica sphere monolayer

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