Materials Science in Semiconductor Processing 77 (2018) 24–30

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Maskless patterned growth of ZnO nanorod arrays using tip based electrolithography

A. Kathalingam[a], Dhanasekaran Vikraman[b], K. Karuppasamy[b], Hyun-Seok Kim[b,*], Hyun-Chang Park[b], Kumaran Shanmugam[c]

[a] Millimeter-wave Innovation Technology (MINT) Research Center, Dongguk University-Seoul, Seoul 04620, South Korea
[b] Division of Electronics and Electrical Engineering, Dongguk University-Seoul, Seoul 04620, South Korea
[c] Department of Biotechnology, Periyar Maniammai University, Vallam, 613403 Thanjavur, India

ARTICLE INFO

Keywords:
ZnO nanorod pattern
Maskless lithography
Electrolithography
Tip based writing method
PMMA resist
Hydrothermal method

ABSTRACT

We report patterned growth of ZnO nanorods based on electrochemical driven writing on a PMMA layer using a metal tip. Electric field induced breaking of the PMMA layer was used for pattern formation. ZnO nanorods were grown on the patterned PMMA layer using two step hydrothermal synthesis. After etching the unaffected PMMA using the conventional lift-off process, patterned growth of vertically aligned ZnO nanorods was produced. This strategy provides an easy and innovative solution for submicron lithographic patterning without requiring complex mask alignment, and allows micro-level semiconductor patterns to be easily formed. The process of pattern formation and ZnO nanorods growth are reported.

1. Introduction

Zinc oxide (ZnO) has a direct wide band gap (3.4 eV) with large exciton binding energy (60 meV), and has been recently applied to various electronic and photonic applications [1]. One-dimensional (1D) ZnO materials have been studied extensively, as they provide important building blocks for realizing various nanoscale devices due to their high surface-to-volume ratio [2]. Among the various ZnO nanostructures, vertically grown ZnO nanorod (NRs) arrays have attracted tremendous interest due to their remarkably versatile properties, suitable for many applications such as flexible photonics, nanogenerators, photovoltaics, and sensors [3,4]. Patterned growth of vertically aligned ZnO NRs provides significant advantage over randomly grown NRs for potential use in various applications.

However, conventional lithography techniques are expensive, as they require extreme environments, such as ultra-high vacuum, high temperature and specials molds [5,6]. For patterned growth of vertically aligned ZnO NRs, exclusively dedicated instrumental facilities and special masks pre-designed for a particular pattern are also required. For some other alternative lithographic patterning methods [7–9], such as scanning probe microscopy (SPM) techniques, dedicated instruments and vacuum systems or complex chemical procedures are required. Apart from the simple patterning process, the following basic requirements are required to economically grow device quality vertically aligned ZnO NRs arrays: low-temperature growth suitable for all substrate types; less experimental facilities; catalyst free; and good control over NR size, density and orientation [10–12]. Only a few reports have demonstrated patterned growth of vertical ZnO NRs, and all used expensive experimental facilities. Sheng et al. employed E-beam lithography (EBL) to generate patterned masks for the growth of patterned ZnO NRs using a hydrothermal method [10]. Hong et al. fabricated vertically patterned ZnO NRs using a catalyst-guided vapor- phase method with a template [11]. Su et al. also used an E-beam lithography designed mask in a hydrothermal method [12]. We propose an alternate lithography technique, where a simple metal tip with sufficient electric bias directly writes micro size patterns on any conducting substrate, i.e., a direct writing method onto a Polymethylmethacrylate (PMMA) layer without requiring a special mask or equipment, which significantly reduces the fabrication cost. In this electrochemical writing, a vertical electric field modifies PMMA layer surface forming a pattern [13,14]. PMMA is commonly used as a photoresist in electron beam and scanning probe lithography [15,16]. Spin coating methods are usually employed to coat PMMA film onto the substrate [17], which is an easy and fast method to producing uniform different thickness films. Although a resist is not required for a tip based local oxidation created in scanning tunneling microscopy (STM) and atomic force microscopy (AFM) techniques, the use of PMMA eliminates proximity effects due to high voltage application [18]. Moreover, the PMMA layer provides a masking layer for seed mediated hydrothermal growth of vertically aligned ZnO NRs.

* Corresponding author.
E-mail address: hyunseokk@dongguk.edu (H.-S. Kim).

https://doi.org/10.1016/j.mssp.2018.01.008
Received 14 September 2017; Received in revised form 26 December 2017; Accepted 9 January 2018
1369-8001/

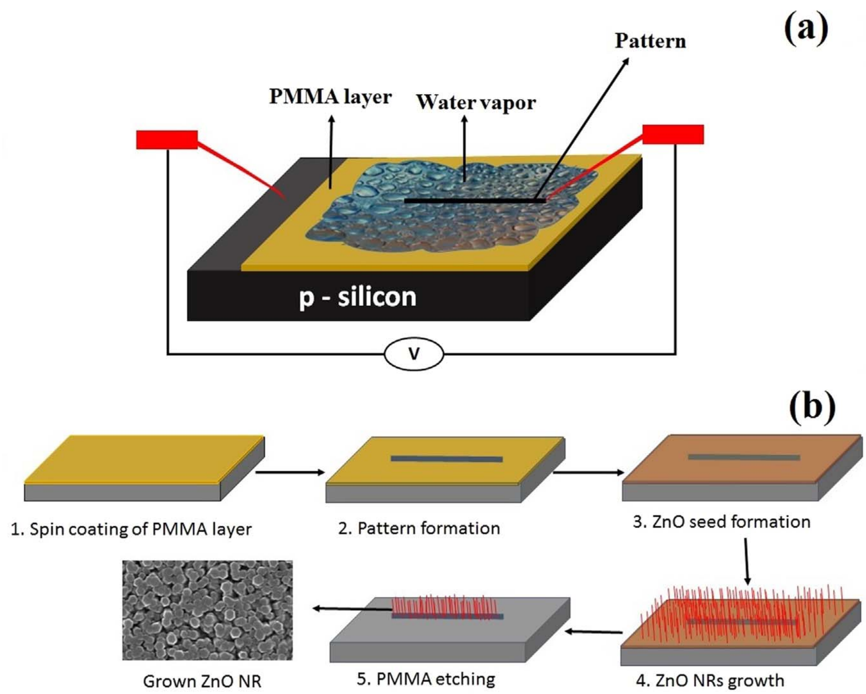

Fig. 1. Schematic representation of (a) different stages of the pattern formation process and (b) the electric field induced pattern formation.

This technique allows pattern formation by electric field induced local modification of the PMMA layer by an electric potential applied to the floating metal tip [19,20]. We discuss the mechanism of pattern formation and the properties of the resultant ZnO NRs. The purpose of this report is to provide an easy and innovative micro patterning technique for researchers working in high tech applications with minimum instrumentation facilities. This electric field induced patterning of polymer layers is a relatively new and promising technique for mask less patterning.

2. Experimental methods

All chemicals used were purchased from Sigma Aldrich. PMMA with molecular weight 850,000 g/mol was diluted in toluene at 2 wt%, then spin cast at 3000 rpm onto pre-cleaned p-type silicon for 30 s. The coated substrates were baked at 100 °C for 10 min to remove excess solvent. To provide an open area for electrode contact, a small portion in the substrate was shaded using adhesive tapes while spin coating. Dot and line patterns were created on the PMMA layer using a tungsten needle attached with a Keithly electrical parameter analyzer (4200 SCS) probe station. Manipulating the tungsten needle, the dots and straight line patterns were fabricated by applying negative potential (−25 to −50 V) bias to the tungsten needle under sufficiently high room humidity (> 75%). The substrate was given positive potential as shown in Fig. 1(a). After forming the pattern on the PMMA layer, vertically aligned ZnO NRs were grown using a two-step hydrothermal procedure as reported previously [21,22]. Finally, the PMMA was removed by wet chemical etching and lift-off using acetone, resulting in a patterned growth of vertically aligned ZnO NRs.

The various steps involved in the process of patterned growth of ZnO NRs are schematically represented in Fig. 1(b). The fabricated ZnO NR patterns were analyzed using X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive x-ray (EDAX), and Raman spectroscopy.

3. Results and analysis

Generally, conventional lithography uses a polymer layer as photo resist, and we have used the PMMA layer similarly as a resist for the proposed electrical field induced writing. The cross-linked PMMA can also provide a mask for electrochemical etching. Borini et al. demonstrated mechanical breaking of PMMA by prolonged application of an electric field [23]. The current proposed technique produced dots and line patterns on the PMMA layer by moving a tungsten needle with −50 V bias. Needle traces were produced on the PMMA layers as straight lines and arrayed dots by touching the substrate using a tungsten needle with electrical bias. After writing the pattern, ZnO seed layer was spin coated onto the patterned PMMA layer, and it was dipped into precursor solution for the growth of vertical ZnO nanorods. Finally, the unaffected PMMA layer was removed using a standard lift-off process with acetone, leaving the desired patterned array of ZnO nanorods. The wet chemical etching and lift-off did not completely remove the PMMA layer. Therefore, the etched samples were annealed at 350 °C for 1 h to completely remove the PMMA resist.

Fig. 2 shows microscopic view of the product at different stages of the proposed technique. The dark dots shown in Fig. 2(a) with blue backgrounds are the formed tungsten oxide. The blue region around the dots indicate the modification of PMMA as carbon and the white spots are scratches produced by mishandling and over pressure on the metal tip. The other black dots and lines are the PMMA surfaces modified due to the electric field applied via tip electrode. Thus, opening of the PMMA layer and oxide formation depends on tip pressure, moisture, and duration of tip contact with the PMMA layer. Fig. 2(b) shows the surface of the substrate after coating ZnO NRs onto the patterned PMMA layer, Fig. 2(c) shows the substrate after etching the PMMA layer, left with vertically grown ZnO in predetermined locations. The Fig. 2(d) shows an SEM image of the circled region in Fig. 2(c) highlighting the vertical ZnO NRs grown as patterned dots and lines.

Figs. 3 and 4 show two different samples highlighting ZnO NRs patterned growth as dots and lines, respectively. Fig. 3(a) shows SEM image of vertically grown ZnO NRs as dot and line patterns on Si substrate. The morphology of an individual dot is shown in Fig. 3(b), it displays rough surface of the dot with cauliflower-like shape. This rough surface of the dot denotes the growth ZnO NRs on tungsten oxide formed by local oxidation. Fig. 3(c) shows the edge of a circular dot, it illustrates the complete removal of unaffected PMMA showing clear demarcation between ZnO NRs dot and substrate surface. Fig. 3(d) displays the ZnO NRs grown on the patterned lines, showing typical