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Labyrinth patterns of zinc oxide on porous silicon substrate

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ABSTRACT

The substrate treatment dependent formation of different micromorphologies of zinc oxide over PS substrate has been reported. Effect of substrate oxidation and annealing has been studied. Changes in the structural properties were seen in the form of labyrinth patterns developed on the surface and were studied with the help of scanning electron microscope (SEM), atomic force microscope (AFM). X-ray diffraction (XRD) along with UV–visible absorption and photoluminescence (PL) spectroscopy were performed for characterizing the zinc oxide film and the hybrid structure. A relatively flat film of nanostructured zinc oxide particles is found to form on the oxidized substrate as compared to the nanostructured labyrinth patterns formed on the un-oxidized substrate with enhanced aspect ratio. Such micromorphologies can be very promising for fabricating highly sensitive gas sensors.

1. Introduction

Some of the unique properties of zinc oxide, such as direct band gap semiconductor (3.37 eV), large excitation binding energy (60 meV), near UV emission and transparent conductivity and various applications for nanodevices like varistors [1], UV light emitting devices [2], photo detectors, gas sensors and nanolasers [3], have attracted remarkable attention of the scientific community. Different morphologies of nanostructures like nanowires, nanorods, belts, tubes, nanobridges, whiskers, nanonails [4–7] have generated interest due to their potential for fundamental studies related to the effect of

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dimensionality, morphology and size on their physical and chemical properties along with their application in optoelectronic devices [8–11]. Moreover, recent reports on lasers from nanowire arrays [12] have caused great interest in the studies related to various morphologies of nanostructures. These nanostructures have been successfully prepared by various physical and chemical methods [13]. Apart from that, various kinds of porous substrates, such as porous alumina [14] and porous silicon [15] have also been employed to design different morphologies and have possible sensing applications.

In particular, porous silicon (PS) is one of the important porous materials since Canham in 1990 [16] presented the first observation of efficient photoluminescence from PS at room temperature. Its open structure, tunable pore dimensions, large surface area, convenient surface chemistry, compatibility with the silicon IC technology [17], combined with the unique optical and electrical properties, make PS a good candidate for templates [18–21] and an alternative material for gas sensing, operating at relatively low temperatures [22–24]. Possibility to further increase the surface area and hence, the optical and electrical properties of such porous substrates, has invoked the interest of many researchers to investigate the growth of different microstructures of semiconducting oxides on porous silicon substrate. Recently, Hashim et al. [25] demonstrated fabrication of nanorods on porous silicon by thermal evaporation method. In the present work, ZnO films were spin coated over freshly etched and oxidized low porosity nanostructured mesoporous silicon followed with annealing and laser treatment to obtain to microstructures such as nanoribbons, and granular labyrinth patterns.

2. Experimental details

PS samples were fabricated by wet electrochemical etching of p^{++}-type Si, (100) orientation wafers with a resistivity of 0.002–0.005 Ω cm. The samples were prepared with 1:1 concentration of hydrofluoric acid (48 wt.% HF) and ethanol (99.9%). Multilayered porous structure was fabricated with anodization time and current density as A/B and 7.4/118 mA/cm^2 for high/low porosity layer respectively. After the fabrication, the samples were rinsed by ethanol and dried in pentane [26]. ZnO was synthesized via wet chemical route i.e. sol–gel method and thin films were deposited onto the PS substrates using spin coating. In order to see the effect of substrate oxidation, on the morphological properties of zinc oxide films, PS substrates were oxidized with 99.9% of oxygen at 600 °C for a duration of 30 min.

Preparation of ZnO via sol–gel technique consisted of dissolving zinc acetate dehydrate [$Zn(CH3COO)_2 2H_2O$] in ethanol along with monoethanolamine (MEA), which is highly water soluble, non-ionic and a sol stabilizer. A homogeneous transparent solution with a concentration of 0.2 M zinc acetate and a 1:1 M ratio of MEA/zinc acetate dehydrate was kept for an hour in ultrasonic bath at 50 °C and later left at room temperature for 48 h (hydrolysis). The above solution was spin coated at 3000 rpm for 25 s. After each deposition, the film was dried at 200 °C for 3 min and the process was repeated 10 times to get the desired film thickness. The morphology and the topographical characteristics were studied before (ZB2A) and after annealing (ZB2B) the hybrid structures at 500 °C for 30 min. in nitrogen environment. Similarly, hybrid structures formed on the oxidized substrate, without (OZB1A) and with annealing treatment (OZB1B) were studied. The structural properties were analyzed using high resolution field emission scanning electron microscope (Quanta 3D FEG) and atomic force microscopy (AFM) (Vecco Nanoscope V model). The orientation and crystallinity of the ZnO crystallites were analyzed by XRD spectrometer (Xpert'PRO) equipped with Cu anode X ray tube (with Kα radiation wavelength of 1.54 Å) from the angle 2 ranged from 20° to 60°. The steady state photoluminescence properties were studied using Varian Fluorescence spectrometer (Cary Eclipse) under the excitation wavelength of 325 nm using a Xenon lamp and the reflectance was measured using Perkin–Elmer UV–Vis–NIR spectrometer (Lambda 950). For localized heat treatment, 532 nm laser with single-frequency green output, generated from a compact solid-state diode-pumped frequency-doubled Nd:Vanadate (Nd:YVO_4), Verdi V-8 coherent high intensity laser system (1W) was used.

3. Results and discussion

Fig. 1 shows the cross-sectional view of a typical hybrid structure with thin ZnO layer deposited over nanostructured PS substrate (ZB2B). The cross sectional image shows the approximate thickness