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Alignment nature of ZnO nanowires grown on polished and nanoscale etched lithium niobate surface through self-seeding thermal evaporation method

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ABSTRACT

High aspect ratio catalyst-free ZnO nanowires were directly synthesized on lithium niobate substrate for the first time through thermal evaporation method without the use of a buffer layer or the conventional pre-deposited ZnO seed layer. As-grown ZnO nanowires exhibited a crisscross aligned growth pattern due to step bunching of the polished lithium niobate surface during the nanowire growth process. On the contrary, scratches on the surface and edges of the substrate produced well-aligned ZnO nanowires in these defect regions due to high surface roughness. Thus, the crisscross aligned nature of high aspect ratio nanowire growth on the lithium niobate surface can be changed to well-aligned growth through controlled etching of the surface, which is further verified through reactive-ion etching of lithium niobate. The investigations and discussion in the present work will provide novel pathway for self-seeded patterned growth of well-aligned ZnO nanowires on lithium niobate based micro devices.

1. Introduction

High aspect ratio ZnO nanowires are known for their higher selectivity and sensitivity in detecting certain gas molecules. Accordingly, they are widely adopted as nanostructured sensing medium in chemical sensors [1–5]. For instance, 1-D ZnO nanostructures such as nanowires and nanorods have been used as sensing medium in acoustic wave devices like surface acoustic wave (SAW) devices [6–11] and quartz crystal microbalance (QCM) [12,13] for gas sensing and UV detection purposes. These kinds of acoustic devices are generally made of piezoelectric substrates such as quartz, lithium niobate, lithium tantalate, gallium orthophosphate and langasite. Lithium niobate is a commonly chosen SAW device substrate for its reasonable cost and favorable material properties like high electromechanical coupling coefficient and low attenuation at high operating temperatures [6]. For example, Giffney et al. [6] demonstrated a highly sensitive lithium niobate based SAW ethanol sensor using vertically aligned ZnO nanorods as sensing medium. The ethanol vapors were selectively adsorbed by the ZnO nanorods and introduced mass loading to the acoustic path of the SAW sensor, which was then characterized by measuring the change in SAW device parameters.

It is also reported that vertically aligned ZnO nanowires are preferred as sensing medium as they show higher sensitivity as compared to randomly aligned ZnO nanowires. For instance, it is found that ammonia gas sensitivity of vertically aligned ZnO nanowires is directly proportional to the length of the nanowires [13]. Moreover, aligned ZnO nanowires can be employed as numerous nanoelectrodes for enhanced electrochemical sensing while the spaces available in between the aligned nanowires can increase the surface area for better electrolyte access [14]. Thus, it is important to find suitable methods to grow well-aligned ZnO nanowires on substrates specifically for sensing applications. In recent years, considerable research has been conducted to identify methods to grow nanowires, nanorods, and nanobelts [15]. Researchers have adopted aqueous solution growth method [6–8,10] and vapor phase transport method [16] to grow ZnO nanostructures such as ZnO nanorods and nanowires on lithium niobate substrates. However, all these methods require pre-deposition of a seed layer made of ZnO film to nucleate the growth of nanowires. The disadvantage of having a pre-deposited ZnO seed layer prior to the ZnO nanowire growth process is that it usually produces nanowires with fusion among their roots which in turn reduces the exposed surface area, thereby affecting the sensitivity of the nanowires [12]. Further, solution grown method is prone to contamination of the ZnO nanowires grown [17] which is unfavorable for sensor applications. Moreover, all the previous reports of ZnO nanowire growth on lithium niobate

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showed that the nanowires had minimal alignment. Also few reports mention that direct growth of one-dimensional ZnO-based arrays on a ceramic substrate is possible without the use of seeds or growth catalysts through a particular solution grown method [18,19]. The substrate used in their work was functionalized for nucleation of ZnO nanowires by the introduction of glucose into the Zn^{2+} solution [18,19]. However, there are no reports that suggest the possibility of such growth on lithium niobate or any other piezoelectric substrate. Accordingly, in the present work, we have investigated synthesis of catalyst-free ZnO nanowires on lithium niobate substrate through a self-seeding thermal evaporation technique without using a buffer layer or pre-deposited ZnO seed layer and further, identified a possible technique for growth of well-aligned ZnO nanowires on the substrate.

A conventional chemical vapor deposition (CVD) setup consisting of one end open quartz tube was employed for the experiment. We observed that the as-grown ZnO nanowires had a crisscross type of growth alignment pattern on the overall surface of the lithium niobate substrate. However, it was noted that the crisscross alignment pattern of the ZnO nanowires was affected and resulted in well-aligned ZnO nanowires at defects sites induced through scratches on the lithium niobate substrate. The following paragraphs present investigations on the ZnO nanowire growth method and discussions on the growth behavior of the nanowires on lithium niobate.

2. Experimental procedure

The experimental setup for synthesis of the ZnO nanowires is shown in Fig. 1. A horizontal quartz reaction tube of 1 m length and inner diameter of 19 mm was placed inside a horizontal split 3 zone tube furnace consisting of three heating zones of 20 cm each. One end of the quartz tube was kept open and hence, maintained at atmospheric pressure throughout the growth time, while other end had sealed inlet to inflow reaction gas: argon gas and purified air. The flow of these gases was controlled by conventional variable area flow meters (Dwyer Instruments, Inc.). Argon was used as the carrier gas for ZnO vapors in the reaction and oxygen content in the purified air was used to assist the oxidation of Zn source. Temperature of the heating zones was controlled by Carbolite 3216 programmable controller (Carbolite Limited). 128° Y-cut X-propagating lithium niobate substrate samples of size 5 mm × 5 mm were diced out from a 4 inch wafer (Precision Micro-Optics LLC). The samples were cleaned by rinsing them in acetone, followed by rinsing in methanol and de-ionized water. Further the samples were dried with purified air and heated at a temperature of 125 °C for 2 min over a hotplate to evaporate any residual solvents. The sample was then loaded on a quartz boat along with 0.25 g of metallic Zn powder (purum grade, Sigma–Aldrich). The lithium niobate sample and Zn powder were separated by a horizontal distance, l of 8 mm (see Fig. 1); and the vertical distance between the lowest point of the Zn powder and surface of the sample was maintained at distance, d of 2 mm (see Fig. 1). The quartz tube was initially heated at a temperature of 620 °C under an argon flow of 100 sccm. Once the temperature of the furnace was stabilized, a mixture of argon and purified air were allowed to inflow at a flow rate of 250 sccm and 5 sccm, respectively. The quartz boat containing the Zn powder and lithium niobate sample was then inserted into the quartz tube such that the boat was positioned at the center of the heated furnace. The reaction time was set to 60 min after which the lithium niobate sample was cooled to room temperature under a flow of 100 sccm of argon. It should be also noted that the nanowire growth temperature of 620 °C in the experiment is well within acceptable temperature range for lithium niobate which possess a curie temperature of 1140 °C [20]. Further, there are reports indicating that lithium niobate retains its piezoelectric properties up to 800 °C [21]. The morphologies, elemental composition, crystallographic properties and growth mechanism of the as-grown ZnO nanostructures were characterized using field emission scanning electron microscopy (FE-SEM, SU8010, Hitachi HHT), energy-dispersive X-ray spectroscopy (EDX, SU8010, Hitachi HHT), X-ray diffraction (XRD, D8 Discover, Bruker Corporation) and high resolution transmission electron microscopy (HRTEM, JEM2100, JEOL) respectively. The effect of ZnO nanowire growth temperature on the morphology and composition of lithium niobate surface was investigated using atomic force microscopy (AFM, XE-100, Park Systems) and XRD (D8 Discover, Bruker Corporation) respectively.

3. Results and discussion

FE-SEM image of ZnO nanowires grown on the surface of the lithium niobate substrate is shown in Fig. 2(a) with a magnified

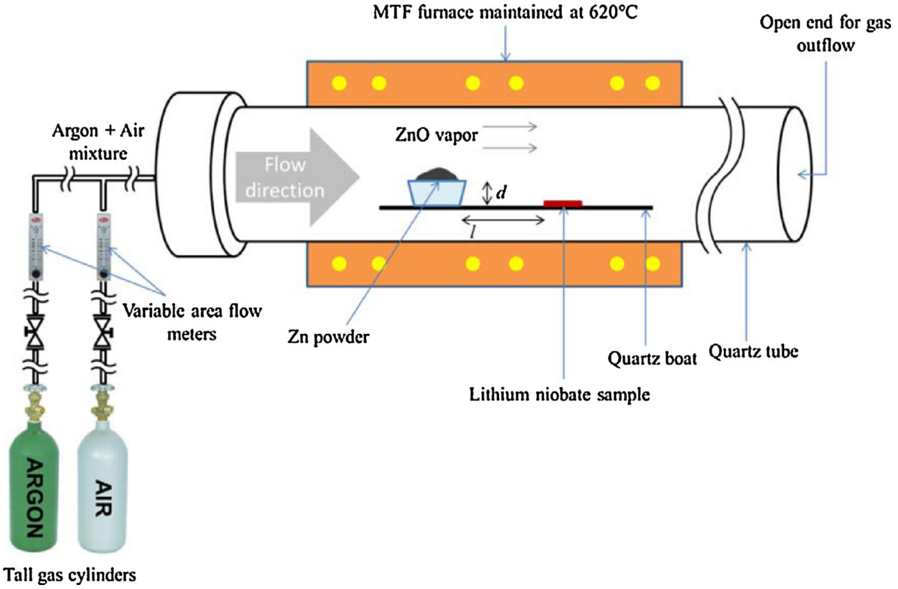

Fig. 1. Experimental setup for self-seeded thermal evaporation synthesis of ZnO nanowires.