Growth and Patterning of ZnO Nanowires on Silicon and LiNbO3 Substrates

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Abstract

ZnO nanowires provide enormous advantages such as high aspect ratio, good field electron emission property and excellent molecular absorption and desorption characteristics in catalyst applications. Fabrication technologies with nanometer resolution will enable us to realize complex solid state devices with novel mechanical, electronic or optical functions. In this paper, two most popular substrates, silicon and LiNbO3, are chosen for the study on such integration issues. The influences from substrate, process procedures and etching solutions on the growth and patterning of ZnO nanowires are discussed. The results are quite promising.

Key Words: ZnO, Nanowire, Integration, Patterning.

1. Introduction

Semiconductor nanoparticles and nanowires have attracted much attention in recent years due to their excellent photonic and electronic properties. A crystalline wirelike structure was first formed by the vapor-liquid-solid (VLS) reaction in the 1960s. In that reaction, a liquid metal cluster or catalyst acts as an energetically favored site for absorption of gas-phase reactants. Then the cluster supersaturates and grows the material in a 1D structure. However, today Zinc Oxide (ZnO) nanowires with diameters of 40–200 nm can be grown with or without a gold catalyst in bulk quantities on a lot of substrates. This synthesis procedure could be achieved by heating a 1:1 mixture of ZnO and Zn powder to 500°C with trace water vapor as an oxidizer [1–2]. X-ray diffraction and transmission electron microscopy show that the nanowires are in the pure wurtzite phase. ZnO nanowires provide enormous advantages such as high aspect ratio, good field electron emission property [3–4] and excellent molecular absorption and desorption characteristics in catalyst applications.

The study here is concentrated on the paving the road from nano-world to micro-world, so-called bottom-up approach. By leveraging from the well developed infrastructure of IC and micro-electro-mechanical system (MEMS) technology, the ZnO nanowires could be easily integrated with current technologies and their advantages can be taken. In the other way, fabrication technologies with nanometer resolution enable us to realize complex solid state devices with novel mechanical, electronic or optical functions. In the following, the influences from substrate, process procedures and etching solutions on the growth and patterning ZnO nanowires are discussed. In the meantime, a Surface Acoustic Wave (SAW) device is being prepared for further experiments and research on the integration issues.

2. Growth of ZnO Nanowire

Two kinds of substrate are chosen here for study: sili-
con and lithium niobate (LiNbO₃). Silicon is the most popular substrate for microelectronics and is also widely adopted in MEMS applications. It serves as a good integration platform. LiNbO₃ substrate is widely used for making SAW devices due to its large piezoelectric characteristics. SAW devices need piezoelectric material to transform between acoustic wave and electromagnetic wave. SAW devices are also the candidates for making various sensors by using the mass loading mechanisms along the wave propagation path.

Conventionally, gold (Au) catalyst is usually used for growth site of ZnO nanowires. However, this process may cause contamination problems and put restrictions, e.g. temperature limitation, for the subsequent processes. Therefore, a new two-step growth method is developed to solve this problem. By adopting sputtering as the growth mechanism first, the ZnO stoichiometric value could be adjusted by controlling the level of vacuum and O₂ working pressure. Thus, the PVD ZnO layer could be used to replace gold as growth site for future ZnO nanowires growth.

Before growing ZnO nanowires, different treatments of silicon and LiNbO₃ substrates are made to make sure that conductive ZnO films can be deposited as growth sites.

(1) Silicon substrate base: due to the lattice mismatch between silicon and ZnO, ZnO nanowires are difficult to have nice microstructures and exhibit random orientations. Usually, a thermal oxide is deposited on the silicon as a buffer layer first, and then titanium, platinum and ZnO thin film are sputtered on top of the buffer layer respectively by radio frequency (RF) sputtering. The metal layers are used here as a bottom electrode and could be omitted in some cases. If additional gold layer is used as a catalyst for the growth of ZnO nanowires, the nanowires could be even denser and deposited more easily.

(2) LiNbO₃ substrate base: LiNbO₃ is a stable material; therefore no buffer layer is needed. The ZnO thin film could be deposited directly on the substrate. Generally speaking, ZnO nanowires on LiNbO₃ substrate are denser in distribution and more easily grown than on silicon substrate.

After preparing and cleaning on the above two kinds of substrates, the synthesis is performed by vapor-phase deposition method, as shown in Figure 1. The zinc vapor source is a purity of 99.9% Zn metal powder. The substrates and zinc vapor source in an alumina boat are inserted into the quartz tube and put close to the middle of

![Figure 1. ZnO Nanowire synthesis equipment.](image1)

![Figure 2. Si/SiO₂/Nanowire.](image2)

![Figure 3. Si/SiO₂/Ti/Pt/ZnO/Nanowire.](image3)
the furnace. A mechanical pump is used to evacuate the system to maintain the pressure inside the quartz tube at about 10 torr. A programmable temperature controller is used to keep the heating ramp and furnace temperature in the range of ± 1°C [1–2].

In our study, needle-like ZnO nanowires have been grown relatively vertical over an entire conductive ZnO film at 500°C by vapor-phase deposition, with or without employing any metal catalysts. In Figure 2, sparse and random orientation nanowires are grown on the top of Si/SiO₂ substrate because no catalysts are used. In Figure 3, dense and quite vertical ZnO nanowires are grown on the top of Si/SiO₂/Ti/Pt/ZnO substrate. In Figure 4, inclined ZnO nanowires are grown on the top of LiNbO₃/ZnO substrate. However, this may be due to the property problems from the purchased LiNbO₃ substrates. The nanowires were grown preferentially in the c-axis direction on the ZnO film. High-resolution transmission electron microscopy (HRTEM) was used to confirm that the nanowires are single crystals.

3. Nanowires Patterning

Using the above growth techniques, a surface full with ZnO nanowires could easily be obtained. But nanowires alone could not be used as devices, some sensing and actuation mechanisms must be integrated. Similar patterning techniques for nanowires like those used in MEMS are developed here, thus ZnO nanowires could be easily integrated into micro-scale devices, such as SAW device.

The substrate used for study here is LiNbO₃. Photoresists are spun on the top of Nanowires first. After lithographic process, several chemical acid solutions are used
to etch nanowires growth areas that are not protected with photoresists.

Figures 5 and 6 show some results of nanowires etched by different acid solutions. All the tested acid solutions could etch nanowires very efficiently in about 2 minutes, except H₃PO₄ takes more time. After the patterning process, the microstructures of protected nanowires surface are checked by several methods and no property changes appear. Obviously, the patterning process would not make any influences on the nanowires.

In our experiments, two phenomena are observed. First, lithographic process will not damage nanowires structure. This may be due to the fact that nanowires are so dense and have high aspect ratio; the photoresist could not fill in between due to the high surface force. But if the adherence of nanowires to the substrate is too weak, nanowires could be peeled off in the subsequent development and stripping process. Acid solutions could easily remove nanowires probably because acid liquid could easily break molecular bonding among meta-oxide. Since nanowires structure exhibits high aspect ratio, which makes them also easily attacked.

4. Conclusions

Silicon and LiNbO₃ substrates are chosen for the study on the integration issues of the growth and patterning of ZnO nanowires. The results are quite encouraging and a SAW device with ZnO nanowires on the propagation path, as shown in Figure 7, is being prepared for further research. The preliminary results do show good performance.

References


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