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Vertically aligned ZnO nanowire arrays on GaN and SiC substrates

Wenjie Mai [a], Puxian Gao [a], Changshi Lao [a], Zhong Lin Wang [a,*], Ashok K. Sood [b], Dennis L. Polla [c], Martin B. Soprano [d]

[a] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States
[b] Magnolia Optical Technologies, Inc., 52-B Cummings Park, Suite 314, Woburn, MA 01801, United States
[c] Defense Advanced Research Projects Agency, DARPA/MTO, 3701 North Fairfax Drive, Arlington, VA 22203, United States
[d] DARPA Programs Office, US Army, AMSRD-AMR-WS-DP-SB, Redstone Arsenal, AL 35898, United States

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ABSTRACT

Growth of vertically aligned ZnO nanowire arrays has been extensively studied on a variety of important semiconductor substrates, such as SiC and GaN. Systematic experiments were carried out to investigate the effect of growth parameters to the quality of the nanowires. In addition, the growth of nanowalls connecting individual aligned nanowires was studied and a growth mechanism was proposed. These conductive and interconnected nanowalls are indispensable for nanodevices to be fabricated on nonconductive substrates for serving as a common electrode. Finally, these nanowire arrays have been integrated as ultra violet detectors, which show good optical performance.

As a direct wide band-gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV), ZnO is one of the most important semiconductor materials for applications in optoelectronics, sensors, and actuators [1,2]. For the known one-dimensional (1D) nanomaterials, ZnO nanowires nanobelts are among the most promising and most extensively studied 1D nanostructures due to their interesting properties [3,4]. Recently, growth of vertically aligned nanowire arrays have received considerable attention not only for fabricating arrays of vertical field effect transistors [5], but also more importantly due to their applications in nanogenerators and nanopiezotronics for converting mechanical energy into electrical energy and fabricating piezoelectric-semiconducting coupled devices [4,6].

Systematic study on the growth of vertically aligned ZnO nanowire arrays on different substrates are of practical importance for various applications. Our previous studies have been focused on the growth of ZnO nanowires on substrates such as Al_2O_3 and GaN [3,4,7,8], by systematically changing the growth conditions such as vapor pressure, oxygen partial pressure, and the thickness of catalyst layer. In this paper, we report our study on the growth of ZnO nanowires on some of the technologically important substrates such as SiC and GaN for light emitting diodes, laser devices, and light detectors [9,10]. We have studied the dependence of length, aspect ratio and percentage of the vertically aligned nanowires on synthesis conditions. This study is important because it gives the conditions under which the well-aligned nanowires can be grown for application in optical sensors, nanogenerators, and field emissions.

All syntheses were performed in our high temperature tube furnace by vapor–liquid–solid process. Equal amount (by weight) of ZnO and graphite powder (0.6 g each) were loaded in an alumina boat located at the center of an alumina tube, which was later placed in a single-zone tube furnace. Argon was used as carrier gas at a flow rate of 49 sccm with additional 1 sccm oxygen to facilitate the reaction. Substrates were coated with a thin layer (7–8 nm) of Au as catalyst and placed 7–12 cm downstream from the center of the tube. The source materials were heated to 970 °C at a rate of 50 °C/min, and the temperature was held at the peak temperature for 30–90 min under a pressure of 160 Torr, while the local temperature of the substrates was between 930 and 970 °C. All previous parameters were chosen after careful optimization.

The morphology of the as-grown products was examined using scanning electron microscopy (SEM, LEO 1530 and LEO 1550). Vertically aligned nanowire arrays were found covering the entire SiC(0001) (Fig. 1a) and GaN(0001) (Fig. 1b) substrates (size is ~0.3 × 0.3 cm^2). The energy dispersive spectroscopy (EDS) experiment confirmed the nanowires to be ZnO (Fig. 1d inset). However, for CdTe and Si substrates, even after a series of designed experiments, only a few of random ZnO nanowires were detected on these substrates, and the rest area either was bare or covered with ZnO particles. Thus, we just concentrate on discussing the experiments about ZnO nanowire arrays growth on SiC and GaN substrates. The best nanowire growth in term of high percentage of vertically aligned nanowires and uniform length was located around 960 °C for both SiC and GaN substrates, and detailed statistical analysis will be discussed later. The product was also characterized using transmission electron microscopy. The growth orientation of ZnO nanowires was along (0001), and a tiny Au

* Corresponding author. Fax: +1 404 894 9140.
E-mail address: zhong.wang@mse.gatech.edu (Z.L. Wang).

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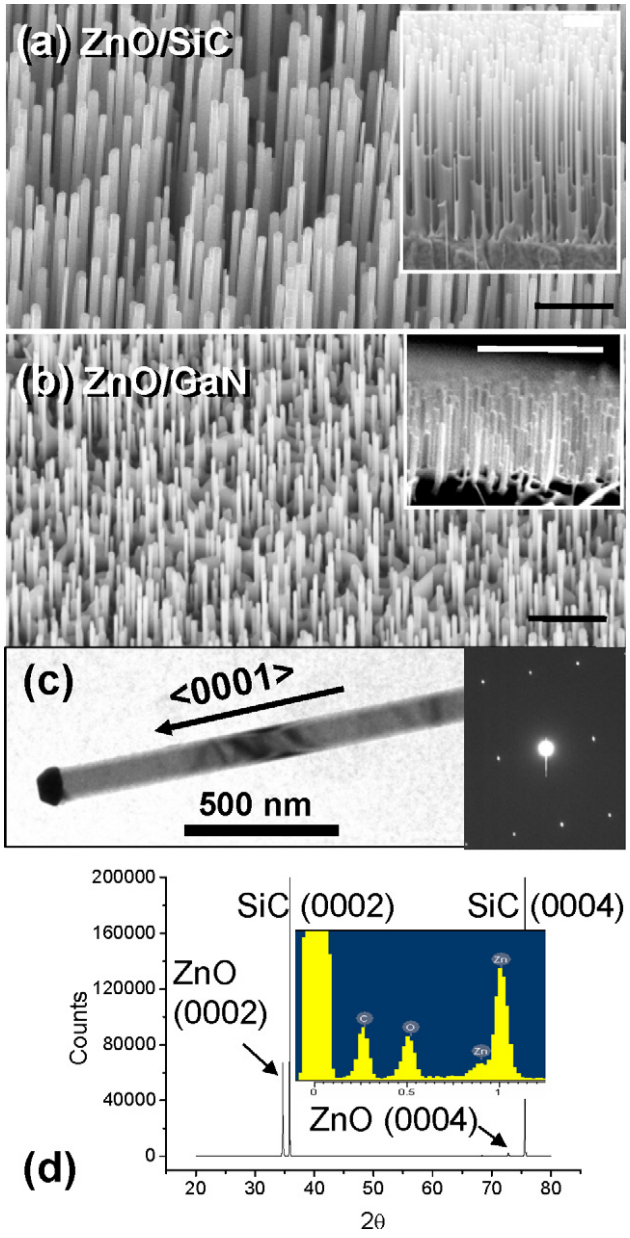

Fig. 1. (a) About 30° tilted and cross-sectional SEM images of vertically aligned ZnO nanowires arrays grown on SiC(0001) substrate with 1 μm scale bar; (b) 30° tilted and cross-sectional SEM images of vertical aligned ZnO nanowire arrays grown on GaN(0001) substrate with 1 μm scale bar; (c) TEM image of a ZnO nanowire grown along (0001) direction with Au catalyst sphere, and the inset shows the corresponding TEM diffraction pattern; and (d) X-ray diffraction pattern of the same sample in (a), and the inset is EDS analysis.

catalyst sphere was found at the growth front (Fig. 1c). Although, EDS can barely show the elemental composition of SiC and GaN substrates due to the short sampling depth, strong peaks of substrates can be detected in X-ray diffraction (XRD) curves (Fig. 1d), indicating the high orientation of ZnO nanowires and substrates. The experiments showed that perfect vertically aligned ZnO nanowire arrays (wurtzite, $a = 0.3249$ nm, $c = 0.5207$ nm) only occur on SiC(0001) (wurtzite, $a = 0.3076$ nm, $c = 0.5048$ nm) and GaN(0001) (wurtzite, $a = 0.3189$ nm, $c = 0.5185$ nm) substrates. ZnO(0001) plane has small lattice mismatch (<6%) with SiC(0001) and GaN(0001) planes, and has significant mismatch with other substrates that we have tried. The small lattice mismatch between the nanowires and substrates is believed to play a key role in heteroepitaxial growth of vertically aligned arrays. For nanowires, which have a significant surface to volume ratio, the surface energy dominates nanowires' growth process, especially, at their nucleation and initial growth stage. The bigger lattice mismatch results in higher strain energy. Higher strain energy state becomes unstable and other lower strain energy states associated with other ZnO planes can occur, effectively reducing the total energy of the system. However, at our synthesis condition, ZnO nanowires prefer (0001) direction as the fastest growth direction. Thus, if the (0001) plane of ZnO is not the boundary with the lowest energy, ZnO nanowires would have higher possibility to lose the coherence with the substrates, and the fastest (0001) growth direction could point to any random direction. Therefore, vertical aligned ZnO nanowire array is much easier to achieve when there is a small lattice mismatch between ZnO nanowires and substrates.

Typical samples A–F were obtained on SiC substrates at 970, 965, 960, 953, 946, and 937 °C temperature region, respectively, after 30 min synthesis, and their spatial distance between closest two samples was 1 cm. The following discusses the synthesis results by using statistical method. Five random locations (10×2 μm^2) were chosen for each sample; percentage of vertical aligned nanowires, length, diameters, and aspect ratio of nanowires were measured and calculated for all nanowires on the chosen locations. Nanowires were regarded as vertical if their axial direction is within 5° deviation of vertical line of the substrate. The length of nanowire was measured from the growth end to the nanowall that underlies of the nanowires, since it is practically impossible to precisely determine the original substrate surface, if the surface is away from the edges and has interconnecting nanowalls on it. The aspect ratio of length to diameter was also calculated. In order to accurately obtain these parameters, sometimes the samples were tilted to 30° or close to 90°. The statistical results showed that sample B has almost 100% vertically aligned nanowires, while this percentage drops sharply below 50% at 5 °C or even lower temperature zone (Fig. 2a). The length of nanowires of sample B is 447 ± 10 nm, and corresponding aspect ratio of length to diameter is 8.0 ± 2.8 (Fig. 2b), in which errors indicate statistical standard deviation. This means that nanowires in sample B location are probably the best for device application since they have relatively highest uniformity, which is required for reliable nanodevices. The linear fitting (Fig. 2a inset) indicates that the nanowires grew at a rate of 54 nm/min. Theoretically, nanowire arrays with any length can be achievable as long as the catalyst particle is still active and the synthesis time increases according to previous discovery. However, in practice, a poisoning of the catalyst particles limits the length of vertical nanowires.

Generally, the vertically aligned nanowires are not separated from one another and they are connected by nanowalls (Fig. 3a). Through SEM and TEM, we found that the residue Au catalyst at the bottom of aligned nanowires induced the sides (01–10) of ZnO nanowires to grow into triangular nanosheets (Fig. 3b and c). These triangular nanosheets could meet another nanosheets or nanowires and became interconnected nanowalls. This proposed growth mechanism has been visually explained in a schematic diagram shown in Fig. 3d. These conductive nanowalls are indispensable for some device applications, especially, when nanowire arrays are grown on the nonconductive substrates. The electric signals can only be transported to each aligned nanowire through the interconnected nanowalls instead of the underlying substrates.

The nanowalls interconnecting ZnO nanowire arrays can serve as an electrode, and the other top electrode will be required for device fabrications. The top electrode can be a tiny conductive atomic force microscopy (AFM) tip [4], or a large piece of metal coated substrate [6]. In our experiment, a new setup of device was

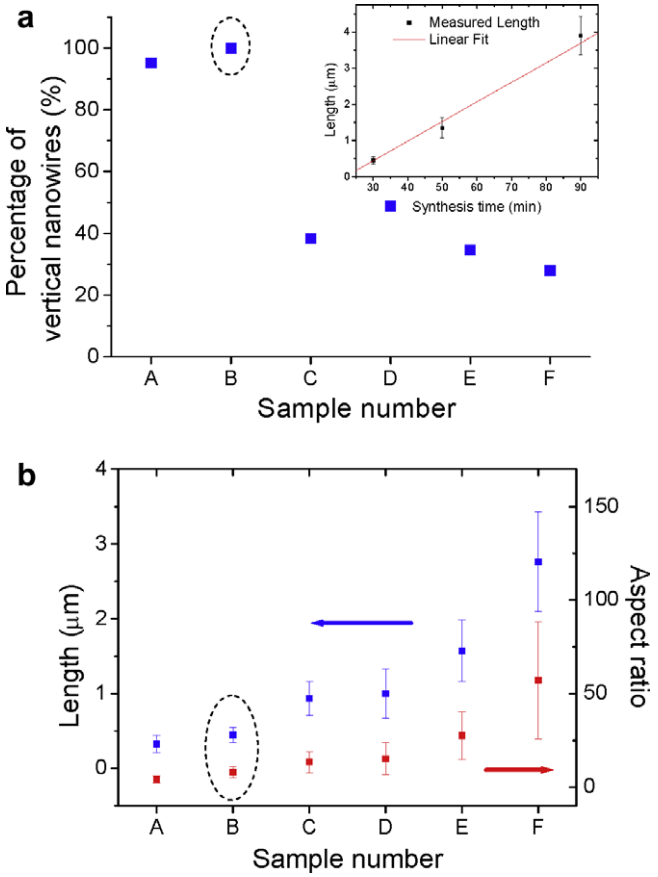

Fig. 2. Growth of ZnO nanowires on SiC substrates. (a) Diagram indicates the percentage of vertically aligned nanowires, and the inset shows the length dependence on synthesis time at sample B location and (b) diagram represents length distribution and aspect ratio of length to diameter distribution for samples A–F, with circles highlighting the best results.

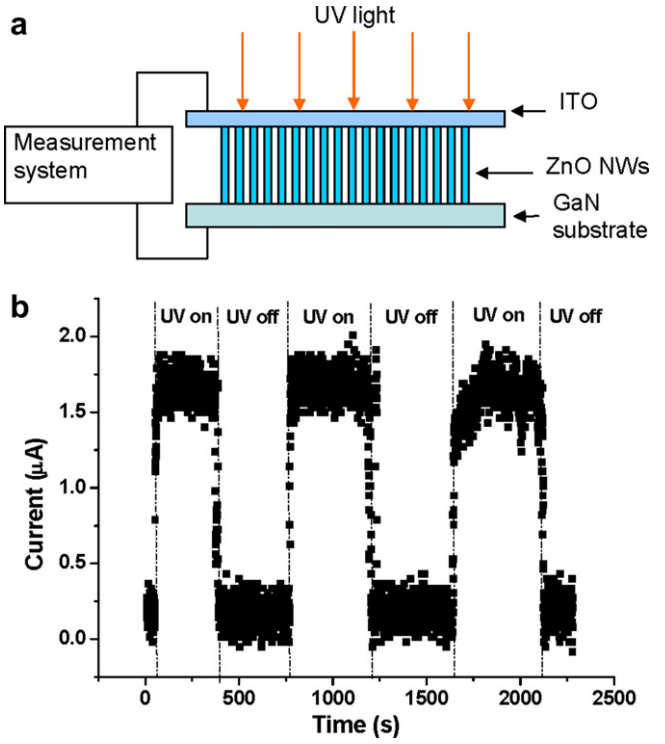

Fig. 4. (a) The schematic diagram of a UV detector based on vertically aligned ZnO nanowire arrays and (b) the diagram displays the current response of functionalized ZnO nanowire arrays to UV light.

designed to accommodate the ultra violet (UV) detector requirement. A transparent and conductive indium tin oxide (ITO) coated glass was deliberately chosen as our top electrode and placed on the top of vertically aligned ZnO nanowire arrays (Fig. 4a). This device was connected in a constant voltage circuit and was demonstrated as an UV detector. The UV source used in this experiment has a wavelength distribution around 365 nm and incident intensity ~20 mW/cm^2. As UV turned on, UV can penetrate through the top electrode and illuminate on the tremendous parallel ZnO nanowires. Because the photon energy of the incident UV light is higher than the band-gap of ZnO, electron–hole pairs are generated inside ZnO nanowire arrays by light absorption. At the same time, the electron–hole pairs are separated by electric field and induce the photocurrent. The current through a typical device sharply

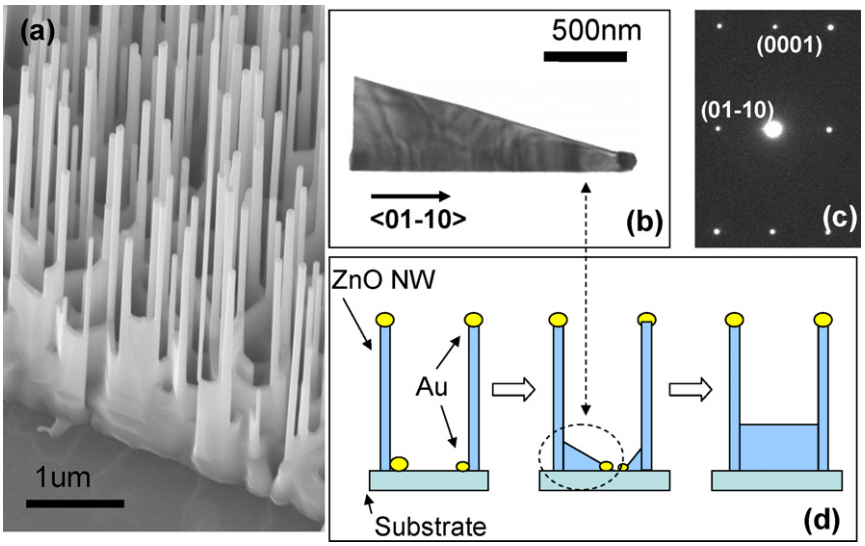

Fig. 3. (a) The SEM image shows nanawalls connecting individual vertically aligned nanowire; (b) the TEM image of a triangular nanosheet, which is the early stage of nanowalls; and (c) the corresponding TEM diffraction pattern of (b); schematic diagram demonstrating the growth mechanism of nanowalls.

increased approximately three times when UV was on. The performance of device could be further improved by using uniform length of nanowire array or by chemically functionalizating nanowires arrays [11]. After layered coating a positively charged polymer poly(diallyldimethylammonium chloride) (PDADMAC) and a negatively charged polymer polystyrene sulfate (PSS), the conductance of the device increases about eight times when UV illumination is on (Fig. 4b). It should be noted that neither PDADMAC nor PSS is conductive itself and shows almost no response to UV illumination. The increase in conductance for the polymer coated ZnO array must attribute to a coupling effect between the polymer and ZnO.

In summary, a systematic study on growth of vertically aligned ZnO nanowire arrays has been performed on a variety of important semiconductor substrates by physical vapor deposition method. Excellent results have been achieved on SiC and GaN substrates. Statistical techniques have been employed to investigate some growth related issues, such as percentage of vertically aligned nanowire, length distribution, and aspect ratio distribution and growth rate. In addition, the growth of nanowalls connecting individual aligned nanowires has been discussed and a growth mechanism has been proposed. These conductive nanowalls are useful for a variety of device application, especially for nanowire arrays on nonconductive substrates. Finally, the UV response of the nanowire arrays was measured for potential applications as photon detector.

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