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XPS investigation of vacuum annealed vertically aligned ultralong ZnO nanowires

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ABSTRACT

The surface properties of vertically aligned ZnO nanowires grown by chemical vapour deposition on GaN using a gold layer as a catalyst are investigated by X-ray Photoelectron Spectroscopy as a function of annealing temperature in ultra high vacuum (UHV). The nanowires are 8.5 μm long and 60 nm wide. 87% of the surface carbon content was removed after annealing at 500 °C in UHV. Analysis of the gold intensity suggests diffusion into the nanowires after annealing at 600 °C. Annealing at 300 °C removes surface water contamination and induces a 0.2 eV upward band bending, indicating that adsorbed water molecules act as surface electron donors. The contaminants re-adsorbed after 10 days in UHV and the surface band bending caused by the water removal was reversed. The UHV experiment also affected the nanowires arrangement causing them to bunch together. These results have clear implications for gas sensing applications with ZnO NWs.

1. Introduction

Zinc Oxide (ZnO) nanostructures are widely regarded as a very promising material system for a multitude of nanotechnology applications in the fields of optoelectronics (nano-lasers, waveguides) [1], microelectronics (transparent transistors [2], spintronics, piezotronics [3]), gas sensing [4], bio-sensing [5] and energy harvesting (nano-generators [6]). This interest is a consequence of the attractive intrinsic properties of ZnO (3.37 eV direct band gap, 60 meV exciton binding energy, piezoelectric, pyroelectric, high isoelectric point, high refractive index, biocompatible), combined with the availability of a large variety of nanostructure geometries of high crystalline quality, such as wires, rods, ribbons, helices, rings, cages, combs and many others [7].

ZnO quasi 1D nanostructures can be synthesised by several techniques including vapour processes using MOCVD, MBE, sputtering and pulsed laser deposition as well as wet chemical processes, such as hydrothermal decomposition and electrochemical reaction [7,8]. The most employed vapour process method is the vapour transport technique, where zinc oxide powder is evaporated in the middle of a horizontal tube furnace heated at 950 °C–1050 °C. The vapour is then carried downstream by an argon flow and condenses, forming the nanostructures. The growth parameters, such as the temperature of source and substrates, pressure, catalyst, Ar flow rate and oxygen content can be adjusted to grow the structures of interest. The growth process typically takes from 15 min to 1 h. Nanowires (NWs) can be grown via a vapour–liquid–solid (VLS) [9,10] process where the semiconductor material (in a vapour form) is absorbed by liquid nanodroplets of an appropriate catalytic material such as gold. Continued growth occurs at the boundary of the metal droplet and the NW, gradually extending its length. ZnO NWs also form vertically aligned arrays when grown on lattice matched hexagonal substrates such as GaN, SiC, Al_2O_3 and single crystal bulk ZnO [11,12]. These vertical arrays have an extremely high surface area and could be used for gas sensing and biosensing applications. Additionally, the presence of the Au catalyst nanoparticles at the tip could provide a convenient route for contacting the NWs. However, many device fabrication processes involve high temperature anneals (dopant activation, ohmic contact formation, implantation repairs) so the effect of temperature on the properties of the NWs is crucial to the realisation of nanodevices based on ZnO NWs. Additionally, vacuum annealing is commonly used to clean surfaces of contaminant adsorbed during exposure to air in order to study the intrinsic properties of the materials. This is especially relevant to surface active nanomaterials like ZnO, where intrinsic properties such as the resistivity of nanowires are very difficult to measure because of surface states created by adsorbed molecules [13]. In this article, we present an investigation of the effect of vacuum annealing on the chemical, electronic and structural properties of vertically aligned catalytic ZnO NWs using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). XPS has been used before on various ZnO nanostructures and thin films, mostly to investigate the surface chemical composition of growth products [14–17], rather than focussing on the electronic properties.

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2. Experimental details

The vertically aligned ZnO NWs were grown on a GaN substrate coated with a 3 nm thick Au layer. The GaN substrate was cleaned in acetone and dried with N_2 prior to Au deposition. The GaN substrate was placed in a tube furnace 8 cm downstream from a source consisting mixed ZnO and graphite powders (1:1 in weight). The furnace was heated to 1030 °C for 1 h in a 50 sccm Ar flow with a 2% O_2 content. The thermocouple measured temperature of the substrates was 950 °C during the growth. The vertical NWs sample was characterized using SEM (JEOL 3600) and then loaded in an ESCALAB XPS system (base pressure 5×10^{-10} mbar). The sample was scanned before and after each incremental anneal from 100 °C to 600 °C in steps of 100 °C. The sample was heated by electron beam bombardment on a customised sample holder equipped with a tungsten filament and a high voltage connection. The sample holder had been calibrated with a thermocouple prior to the experiment. The sample was left in ultra high vacuum (UHV) for 10 days and scanned before and after a second 600 °C anneal to investigate the build-up of contamination. Finally the sample was placed in the SEM again to assess the impact of the UHV anneal on the structure of the array. The XPS spectra were recorded using Al K_α X-ray radiation (1483.6 eV) and with a pass energy of 50 eV and 10 eV for the survey scans and detailed core level scans, respectively.

3. Results and discussion

Fig. 1 shows SEM images of the vertically aligned NWs before the annealing experiment, with the substrate tilted at 45°. Size analysis from the SEM images revealed that the length of the NWs is 8.5 μm (±0.5 μm) and very uniform over large areas (mm^2). The NWs diameter ranges from 30 to 70 nm, with an average of 60 nm and a standard deviation of 14 nm. The aspect ratio of the NWs is therefore in excess of 100:1 and is one of the largest ever reported for vertically aligned ZnO NWs. This extremely large surface to volume ratio is attractive for sensing applications. [18] The SEM image of Fig. 1(b) clearly shows the presence of Au catalyst particles at the tip of the NWs while the role of the 3 nm Au layer is evidenced on Fig. 1(a) where the regions without Au on the substrate are bare of NWs. Fig. 2 shows the same area of the sample after the UHV anneals. The tips of the NWs appear to have bunched together as a result of the UHV experiment. It could have been caused by a combination of thermal annealing and electrostatic interaction induced by the removal of photoelectrons during the XPS scans, causing localized charging at the tips of the NWs.

The XPS survey scans of Fig. 3 showed the expected Zn, O and C peaks plus small Ga peaks from the exposed parts of the substrates, caused by scratches during handling before and after growth. A small Au signal was also observed.

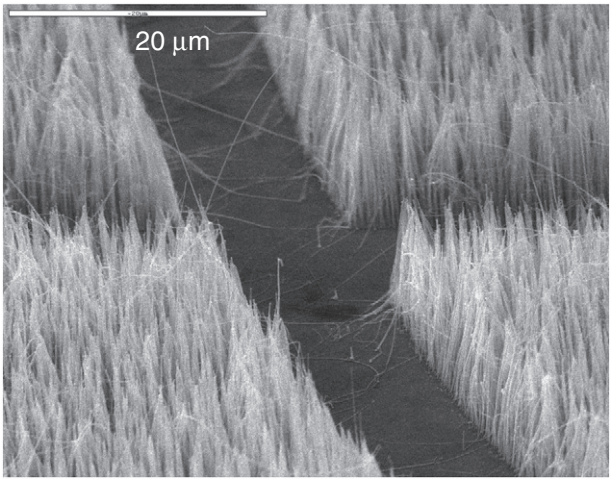

Fig. 2. 35° tilt SEM image of the same area shown in Fig. 1, after annealing in UHV at 600 °C.

The shape of the Zn2p peak (not shown) does not change with temperature apart from a slight decrease in FWHM from 1.95 eV up to 200 °C, to 1.85 eV at 300 °C and higher. The O1s peak shape however, changes significantly as the anneal temperature increases. Fig. 4 shows the curve fitted O1s peaks for the as loaded surface, after the 600 °C anneal and after the sample was left in UHV for 10 days. The O1s peak was fitted with 3 Gaussian–Lorentzian components corresponding to the Zn–O bond, a $Zn(OH)_2$ hydroxyl component 1.35 eV on the high BE side and a water vapour component 2.3 eV away from the Zn–O bond. These BE offsets are in good agreement with various previously published results [19,14]. It should be noted that some groups have fitted the O1s peak with C–O components, and attributed the hydroxide component to defective ZnO_x and the water component to adventitious CO_2 [15,16] or chemisorbed oxygen [17]. The energy offsets and FWHM of the components were kept constant for all surface treatments. Table 1 summarises the relative composition of each of the 3 components as a function of surface treatment. The hydroxyl and water vapour components make up 16% and 9% of the total O1s intensity for the as loaded surface, respectively. The water vapour content decreases after the 200 °C anneal, and disappears after 300 °C while the hydroxyl content is reduced to 11% at the same point. Subsequent anneals at 400 °C, 500 °C and 600 °C did not change the composition of the O1s peak significantly and the 600 °C

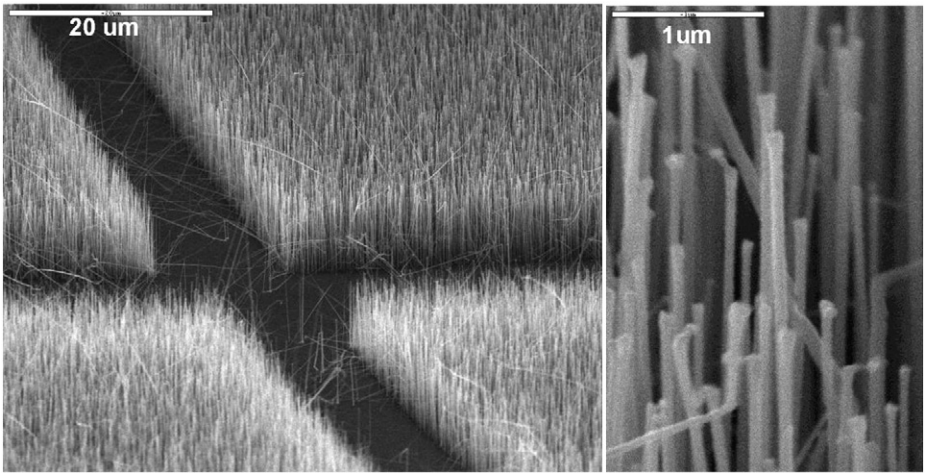

Fig. 1. 45° tilt SEM images of high aspect ratio vertically aligned ZnO NWs grown on GaN using a 3 nm layer of Au. (a) The area devoid of NWs corresponds to where the Au had been scratched away prior to growth. (b) Higher magnification image showing the Au catalyst particles at the tip of the NWs.