Metal Organic Chemical Vapor Deposition of ZnO Nanowires

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ZnO is a wide band gap semiconductor (E_g = 3.37 eV) with applications in UV optoelectronics, varistors, piezoelectronics, and photovoltaics. Nanostructured ZnO can enable applications that require high semiconductor surface area such as sensors and dye sensitized solar cells [1]. We have grown nearly monodisperse ZnO nanowires by metal organic chemical vapor deposition (MOCVD) using zinc acetylacetonate ($Zn(AcAc)_2$) and oxygen gas. While monodisperse metal nanoparticles [2] or anodic alumina templates [3] have been used previously to pattern the size and location of nanowires, no effort was made to direct the nanowire growth in this work. Monodisperse diameter nanowires nucleate and grow spontaneously in this morphology on variety of substrates without a catalyst or template.

In our MOCVD process, the $Zn(AcAc)_2$ hydrate precursor is heated and sublimed at 80-135 ^oC and its vapor is transported into an MOCVD chamber using Ar carrier gas. $Zn(AcAc)_2$ and O_2 gas is injected over the substrate seated on a heated plate. $Zn(AcAc)_2$ dissociates and reacts with O_2 to deposit the nanostructures shown in Figure 1. Typical deposition pressures range from 0.2-10 Torr. Substrate temperatures between 500-550 ^oC yielded the nanowires shown in Figure 1

Nanowire diameters depend on the growth conditions and range from 16 nm to 100 nm. The nanowires grow from several to tens of microns long (Figure 1). The growth morphology depends sensitively on the partial pressure of $Zn(AcAc)_2$ and the substrate temperature. On amorphous oxides such as SiO_2 and F doped SnO_2 films ZnO nanowires grow in entangled webs. Long deposition times lead to secondary nucleation off the nanowires and result in dendrite-like growth morphology. Transmission electron microscopy indicate that the nanowires are single crystal and have wurtzite structure. In contrast to growth on amorphous oxide substrates, on a-plane sapphire, ZnO nanowires grow vertically from the substrate surface as densely packed arrays. In fact, ZnO nanowires grow epitaxially on a- and c-plane sapphire substrates. Nanowires with monodisperse diameters grow perpendicular to a-plane sapphire and with nearly perfect in-plane rotational alignment as confirmed by X-ray diffraction. The alignment is due to $[0001]_{ZnO} \| [11\bar{2}0]_{sapphire}$, $[11\bar{2}0]_{ZnO} \| [0001]_{sapphire}$ epitaxy. On c-plane sapphire multiple possible epitaxial relations give a mixture of nanowire orientations. The majority of the nanowires grow in one of three directions all at an angle of 51.8° off the substrate plane with $[0001]_{ZnO} \| [10\bar{1}4]_{sapphire}$, $[10\bar{1}0]_{ZnO} \| [1\bar{2}10]_{sapphire}$ epitaxy. A small fraction of the nanowires grow perpendicular to the substrate with $[0001]_{ZnO} \| [0001]_{sapphire}$.

We have used nanowires grown on F doped SnO_2 films to produce dye sensitized solar cells solar cells with short circuit current densities of 75 $\mu A/cm^2$, open circuit voltages of 0.63 V. A limitation of these preliminary solar cells is poor light harvesting, with less than 10% of incident light absorbed by the dye. We are currently investigating methods for seeding nanowire growth to improve the nucleation density, which will increase nanowire surface area and dye adsorption.

References

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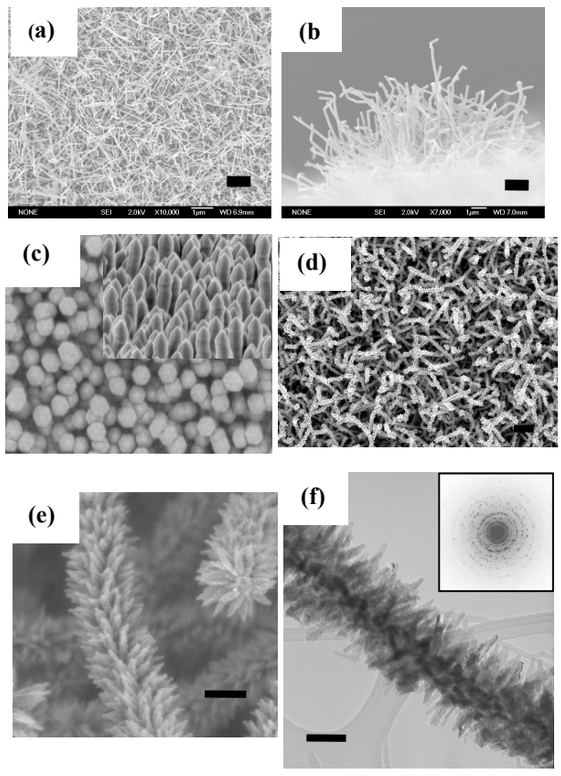

Figure 1. ZnO nanowires and nanostructures grown by MOCVD under various deposition conditions and times. Scale bars in (a), (b) and (d) are 1 μm whereas in (c), (e) and (f) it is 100 nm. (a) Plan view SEM of random network of 10s of μm long 30 nm diameter nanowires on F-doped SnO_2. (b) Glancing angle view of the nanowires in (a). (c) Plan view and grazing angle view (inset) of aligned 100 nm diameter several μm long nanowires grown on sapphire. (d, e, f) Nanowires with secondary nucleation on the nanowires to produce dendrite-like growth morphology. The nanowire backbone is single crystal with different orientation secondary nucleation off the backbone producing polycrystalline diffraction pattern [inset in (f)].