Determination of the epitaxial growth of zinc oxide nanowires on sapphire by grazing incidence synchrotron x-ray diffraction

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This letter shows that aligned zinc oxide (ZnO) nanowires growth on sapphire substrates is epitaxial and demonstrates the crystallographic relation between the two using grazing incidence synchrotron x-ray diffraction (XRD). The in-plane lattice match between the sapphire and the nanowires was directly probed by using XRD at grazing angles of incidence, where the lattice match between the (0001) plane of the sapphire and the (11−20) plane of the ZnO were observed simultaneously. It will also be shown that gold acts as a catalyst to initiate ZnO nanowire growth, but it does not interfere with the epitaxial mechanism between the nanowires and the sapphire substrate.
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The ability to grow one-dimensional (1D) nanomaterials with controlled crystallographic orientation is essential for their application in future devices. The growth of vertically aligned quasi-1D nanowires (NWs) has attracted much attention since nanowires have great potential for optical applications such as nanowire lasers[1] and three-dimensional-nanoelectronic devices.[2] Preferential alignment of nanowires in the vertical direction has been demonstrated using catalyst-assisted physical vapor deposition (PVD) methods.[3,4] The physical origin for the alignment has been attributed extensively to an epitaxial relationship between the material and an appropriate substrate. However, an absolute epitaxial relationship between the material and the substrate is seldom demonstrated.[3,5] This is important since at certain growth conditions, complete alignment of the nanowires can be obtained without any lattice correlation between the nanowires and the substrate. It is also worth noting that although epitaxial growth is often observed in molecular beam deposition or metal organic chemical vapor deposition systems,[6] the occurrence of such epitaxy is surprising in PVD systems using evaporation/condensation processes without any further control at pressures achievable using a rotary pump.

A system that has been widely explored recently is the growth of zinc oxide (ZnO) nanowires on sapphire (Al_2O_3) substrates. Epitaxial growth of ZnO can occur on two different surfaces of sapphire, the *c* surface (0001) and the *a* surface (11−20). ZnO nanowires grown on *a*-plane sapphire are mostly oriented in the [0001] direction, which is parallel to the sapphire (11−20) plane. For ZnO films grown on *a*-plane sapphire, the in-plane orientation relationship has been found to be [11−20]ZnO//[0001]Al_2O_3,[7–9] and although it is believed that the same relationship holds for the growth of ZnO nanowires, the in-plane measurement of the epitaxial relationship between the ZnO wires and the sapphire substrate has not been realized thus far. Baxter and Aydil indicated which crystallographic ZnO planes cause the epitaxial relationship with the sapphire substrate (11−20), but this measurement was not direct.[10] In this letter we will show the epitaxial relationship between the ZnO nanowires and sapphire substrates by using grazing incident synchrotron x-ray diffraction.

The samples were grown in a horizontal tube furnace by evaporating a 1:1 weight ZnO:carbon mixture at 1000 °C and using sapphire substrates with a 1−10 nm gold (Au) film as the catalyst under a nitrogen/oxygen (79%/21%) gas flow. The deposition temperature and pressure were varied from 680 to 890 °C and from 1 to 9 mbar, respectively. Figures 1(a) and 1(b) show side and top view micrographs of typical aligned nanowire growth on [11−20] sapphire. The degree of vertical alignment is visible from these micrographs. From the top view of the nanowires, one can observe a hexagonal symmetry showing the sixfold symmetry of ZnO in the [0001] growth direction. Transmission electron microscopy (TEM) analysis (not shown) confirms this result showing that the growth direction of the ZnO NW is [0001]. The growth was catalyzed using a thin film of gold; however,

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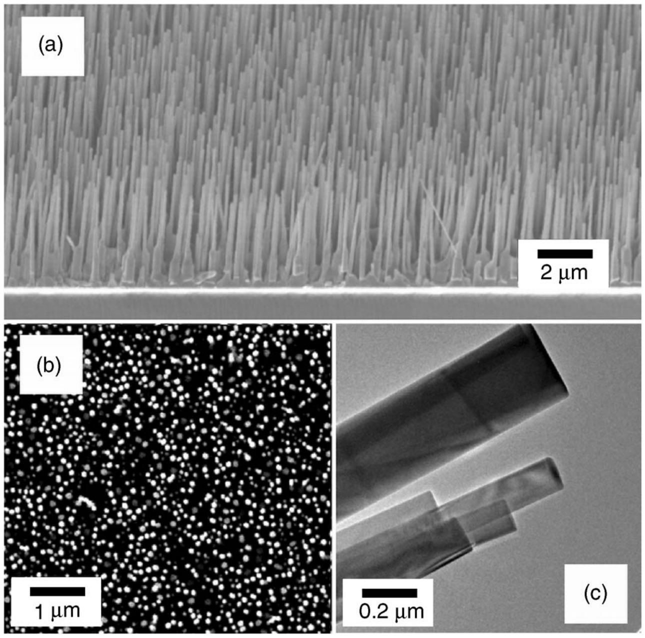

FIG. 1. Scanning and transmission electron microscopy images of aligned ZnO nanowires on sapphire substrates [11−20]. (a) and (b) show side and top view micrographs of typical aligned nanowire growth. (c) TEM micrograph of ZnO nanowire tips showing a flat end with no catalyst ball.

no metal particle was found on the tip of the nanowires [see Fig. 1(c)]. This information is very important as it raises fundamental questions about the nature of the epitaxy. As the gold is not found on the tip, or in the body of the nanowires, the gold must be located and must play a role at the nanowire-substrate interface. This also poses a complicated question about whether the nanowires can grow epitaxially from the substrate while still having a metal or alloy present at the interface.

X-ray diffraction on the vertically aligned ZnO NWs on sapphire was performed using a conventional diffractometer (Cu $K\alpha$). Grazing incident synchrotron radiation x-ray diffraction ($\lambda = 0.15426$ nm) was done on the beam line XRD1 of the Brazilian Synchrotron Light Laboratory (LNLS). Conventional (theta-2theta) measurements were performed first to confirm that the aligned ZnO wires were oriented in the

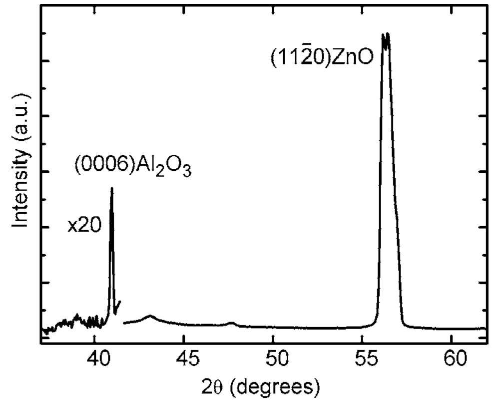

FIG. 3. Grazing incident diffraction (theta-2theta measurement) along the direction of the plane $(0006)Al_2O_3$. This result shows that the plane (11−20)ZnO is parallel to the (0006) of the Al_2O_3 substrate.

[0001] ZnO direction parallel to the [11−20] sapphire (Fig. 2). The purpose of this measurement was to look for crystalline planes parallel to the plane of the sapphire substrate. The ZnO diffractogram shows two peaks with higher intensity, (0002) and (0004), which are both multiples of the [0001] ZnO growth direction.

In order to prove directly the in-plane lattice match between the sapphire and the NWs, we performed an XRD experiment at a grazing incidence angle of 0.5° where one can study the crystallographic planes perpendicular to the substrate surface that are responsible for epitaxy. To prove the epitaxy, theta-2theta measurements using grazing incidence diffraction were performed where the (0006) plane of the sapphire and the (11−20) plane of the ZnO were observed simultaneously and showed a lattice match (Fig. 3). Additionally, the x-ray detector was positioned at the (11−20) ZnO peak of the wires and the sample was rotated by 360° (Fig. 4). This measurement showed six peaks of the (11−20) ZnO plane with each peak separated by 60° showing the sixfold symmetry indicating a global orientation of this plane among all nanowires. A similar experiment was performed by positioning the x-ray detector at the (0006) sapphire plane which shows a twofold symmetry with two peaks separated by 180°, as expected. The results presented

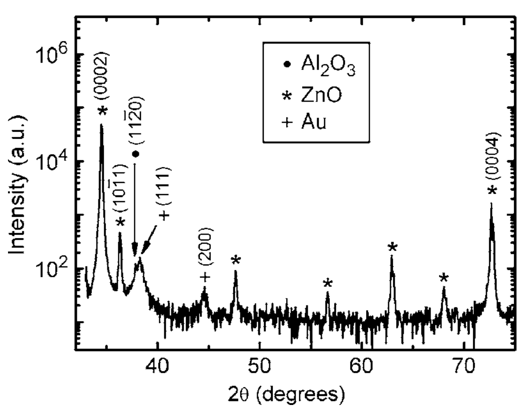

FIG. 2. Conventional x-ray diffraction of the sample in the direction parallel to the $[11-20]Al_2O_3$. The diffractrogram shows higher intensity peaks of ZnO planes from multiples of the [0001]ZnO growth direction proving that the wires are vertically aligned. The gold (111) and (200) diffraction peaks are also highlighted. The sapphire Al_2O_3 (11−20) peak was slightly detuned to avoid detector overflow.

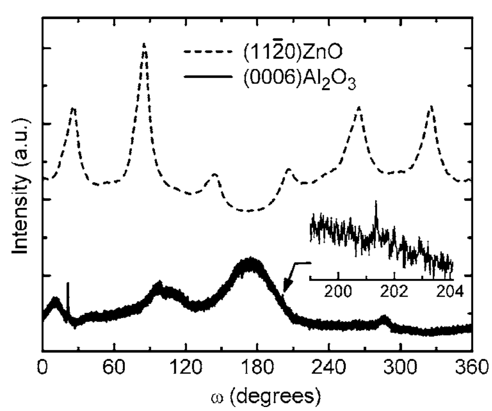

FIG. 4. X-ray diffractions using grazing incident diffraction. The detector was positioned in the (11−20) plane of the ZnO and the sample was rotated over 360°. Six peaks separated by 60° (dotted lines) were obtained showing that these planes are parallel between different nanowires and have a sixfold symmetry. A similar measurement was performed by positioning the detector in the (0006) plane of the sapphire which shows a twofold symmetry (solid line) with two peaks separated by 180 °C.

above directly prove that the substrate surface is strongly correlated with the orientation of the interfacial planes of the nanowires and, consequently, their growth direction. This work definitively establishes that there is epitaxial growth between zinc oxide nanowires and the *a* plane Al_2O_3 substrate. The epitaxy is a consequence of the match of four times the (11−20) ZnO planes with three times the (0006) sapphire planes (0.99 lattice parameter ratio).

This provides valuable clues about the epitaxial growth mechanism. Transmission electron micrograph images demonstrate that there is no catalyst particle at the tip of the nanowires, which is consistent with the TEM micrographs presented in Fig. 1(c). This result raises unanswered questions about the role of the gold catalyst on the epitaxial growth and whether the vapor-liquid-solid process (usually applied to explain the growth mechanism of catalyst-assisted nanowires) is the mechanism of growth in this case.

The analysis of the conventional XRD spectrum depicted in Fig. 2 shows the presence of peaks from gold catalyst metal. The peak at the position of 38.2° is characteristic of (111)Au and the peak at 44.3° is characteristic of (200)Au reflection. This suggests that the gold is either in the form of nanoparticles with random orientation or of a polycrystalline film. However, as mentioned earlier, this gold is not located at the tip [Fig. 1(c)] nor in the body of the nanowires which indicates that the gold must remain near the base. The question then is whether or not epitaxy occurs with a layer of gold between the sapphire and the zinc oxide nanowire. We believe that the answer is no, since the XRD measurements indicate that the gold crystals have random orientations. This means that a triple epitaxial relationship between ZnO, gold, and sapphire is not feasible. We propose that gold acts essentially as a catalyst to initiate ZnO nucleation at the substrate, but that it does not interfere at the interface between the ZnO nanowires and the sapphire substrate. The role of the gold catalyst has also been explored by Fan *et al.*[11] They show using cross sectional TEM that Au nanoparticles much smaller than the diameter of the nanowire help nucleate nanodisks. These then form the base of the nanowire that sits directly atop the sapphire substrate. This two-step mechanism still needs to be explored in greater detail.

In conclusion, using grazing incident x-ray diffraction, we have proven that the aligned growth of the ZnO nanowires on sapphire is epitaxial and the gold catalyst although fundamental to the growth process does not participate in the epitaxial mechanism because it is not preferentially aligned.

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