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Direct Evidence of Self-catalysis effect in ZnO Nanobelt Growth

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Uniformly aligned ZnO nanobelt arrays have been grown on a (0001) GaN substrate without foreign catalyst such as Au. The nanobelts mainly grew along [01 $\bar{1}$ 3] at beginning when the temperature was relatively low, then switched to [01 $\bar{1}$ 0] at high temperature, and finally switched to [01 $\bar{1}$ 3] when the temperature was lowed. The alignment of the nanobelts was due to not only the epitaxial orientation relationship with the substrate but more importantly the presence of metallic Zn nanoparticles at the tip of the ZnO nanobelts, which were produced by reduction of ZnO source material. The Zn nanoparticle has a fixed orientation relationship with the ZnO nanobelt, indicating that the growth follows the self-catalyzed vapor-liquid-solid process.

Each belt we examined by TEM is only part of the whole nanostructure grown from the substrate. Different sections of nanobelts can be identified using their morphologies. During vapor deposition process, a seed layer was first epitaxially grown on the substrate, and then ZnO nanobelts grew up form such a thin film layer. Therefore, the nanobelt in Figure 1a, which looks like peeled off from a thin film layer, can be considered as the root of nanobelt binding with the GaN substrate. Figure 2b is a HRTEM image of the rectangle area in Figure 1a. The growth direction can be uniquely identified as [01 $\bar{1}$ 3], which corresponds to the starting growth direction. In figure 1c, an arrow points to a particle at the growth front of the nanobelt. The uniform contrast of the nanobelt and the inserted SAED pattern indicate that it is a single crystal with two growth directions along [01 $\bar{1}$ 0] and [01 $\bar{1}$ 3], respectively. The turning points of growth directions between [01 $\bar{1}$ 0] and [01 $\bar{1}$ 3] are circled in Figure 3c.

Figure 2a confirms that the ZnO nanobelts grew along [01 $\bar{1}$ 3] at the tip. From the analysis above, we can see that the NBs initially grew along [01 $\bar{1}$ 3], then switched to [01 $\bar{1}$ 0] during growth, and then the final part of the ZnO NBs took the [01 $\bar{1}$ 3] as its growth direction. Also in Fig. 2, it shows a single crystalline Zn particle that is covered by a thin ZnO layer, which was formed due to the oxidation of Zn when exposed to air. The particle's SAED pattern is displayed in Figure 4b, which is composed of two patterns; one is ZnO [2 $\bar{1}$ $\bar{1}$ 0], and another one is the Zn [0001] pattern as indicated by white arrowheads. The lattice match configuration can be described as $(2\bar{1}\bar{1}0)_{ZnO} \mid (0001)_{Zn}$, $[0001]_{ZnO} \mid [01\bar{1}0]_{Zn}$. The observation of Zn particle and its lattice match to ZnO NB indicates the existence of a self-catalyzed growth process. In our experiment the only source material was pure ZnO powder and there was no foreign catalyst deposited on the substrate. The Zn self-catalyzed growth of ZnO nanowires/nanobelts has been proposed previously.[2] Our experiment gives the direct evidence of such self-catalyzed growth using ZnO decomposed Zn particle.

Reference:

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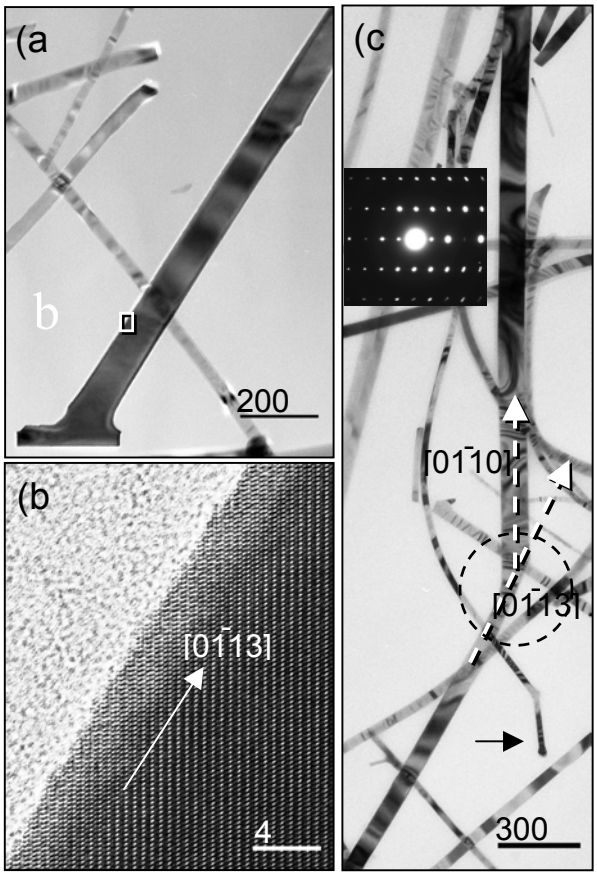

Fig. 1. (a) Low-magnification TEM image of the root of a ZnO nanobelt in contact with the GaN substrate. (b) High-resolution TEM image from the rectangular area in (a). The root of the nanobelt grows along [01 $\bar{1}$ 3] direction. (c) TEM image shows the turning point (circled area) of the growth direction from [01 $\bar{1}$ 3] to [01 $\bar{1}$ 0]. Inset: the SAED pattern of the largest nanobelt shown in (c).

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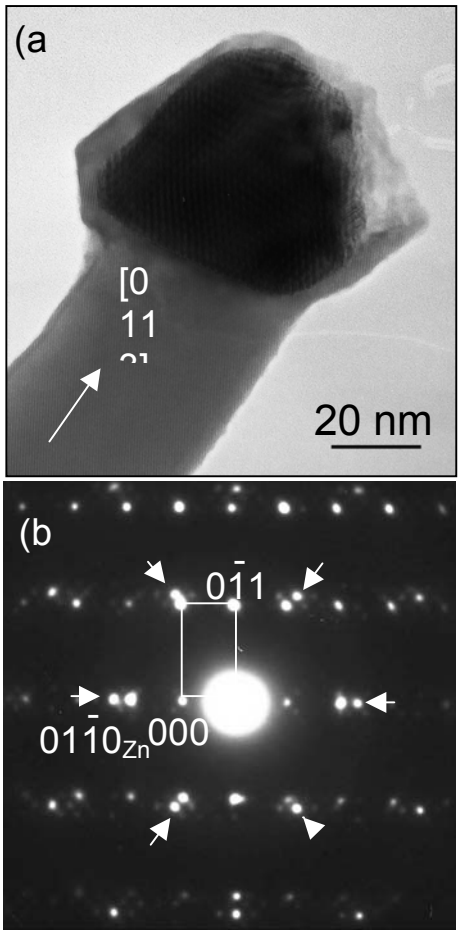

Fig. 2. High-resolution TEM image (a) and corresponding SAED pattern (b) of a ZnO nanobelt with a Zn particle located at its tip. Note the relative rotation of the diffraction patterns in reference to the image was not adjusted for nice display purpose.

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