Epitaxial Growth of ZnO-GaN Hetero-Nanorods and GaN Nanotubes

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We report about the successful realization of a coaxial hetero structure grown by MOVPE around ZnO nanocolumns. At higher overgrowth temperatures, the ZnO cores completely dissolved leaving GaN nanotube structures with excellent properties. Such tubes could be sheathed by a GaInN-GaN single quantum well structure, as confirmed by photoluminescence and transmission electron microscopy.

1. Introduction

Various methods to grow high quality and perfectly arranged ZnO nanorods have been reported over the recent years (see, e.g., [1, 2] and references therein). However, due to the material properties of ZnO and its related compounds, there are many restrictions in designing more complex heterostructures or even devices based on such nanorods. In particular p-type doping of ZnO is still a big, yet unsolved challenge. On the other hand, GaN and its related compounds, having similar band gap and lattice constant as ZnO, have been successfully used for the realization of a huge number of various devices owing to the fact that many issues related to heterostructures and to n- and p-type doping could be successfully solved. However, for this material class, the deposition of ordered low-dimensional structures like nanorods is very difficult, typically leading only to a very disordered growth of nanowires in contrast to the above mentioned highly ordered ZnO nanorod structures. Therefore, we have investigated the combination of these two material approaches by growing GaN epitaxially around ZnO nanorods. Similar studies have been reported by An et al. [3].

One significant obstacle for this approach is the high sensitivity of ZnO in GaN growth environment: At elevated temperatures, ZnO decomposes by reacting with hydrogen or ammonia (NH_3). Therefore, we have established a multi-layer growth process (MGP) based on our experience about the growth of GaN layers on ZnO templates by metalorganic vapor phase epitaxy (MOVPE) [4–6]. However, even then the ZnO may easily dissolve leaving GaN nanotubes on the wafer [7]. In the current studies, we investigated whether such nanotubes can be used as templates for coaxial GaInN quantum well structures.

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2. Experimental

The ZnO nanopillars used as templates in these studies have been grown catalyst-free by a vapor-solid process on a-plane sapphire wafers. This process started with a ZnO nanocrystal nucleation layer using zink acetate as precursor. The nanorods were deposited at 845°C with Ar as carrier gas following a carbo-thermal method [8]. We could achieve perfectly vertically aligned ZnO nanorods with good homogeneity (Fig. 1) with typical diameters and heights of 100 – 300 nm and 1 – 2 µm, respectively. They showed mostly perfect hexagonal shape with flat side facets. These templates have then been transferred to our AIXTRON AIX 200 RF low pressure (LP) MOVPE system. Here, the precursors were trimethylgallium (TMGa), and NH_3. The In containing layers including the adjacent GaN barrier layers have been grown in our 2nd MOVPE system in order to make use of the respective experience for the deposition of GaInN. The shape of the grown nanopillars was mainly investigated by scanning electron microscopy (SEM), whereas transmission electron microscopy (TEM) was applied to measure the dimensions of single rods and to evaluate the heterostructure details. Photoluminescence carried out at room and low temperature was applied to investigate the band gaps of the grown multi-layer nanostructures.

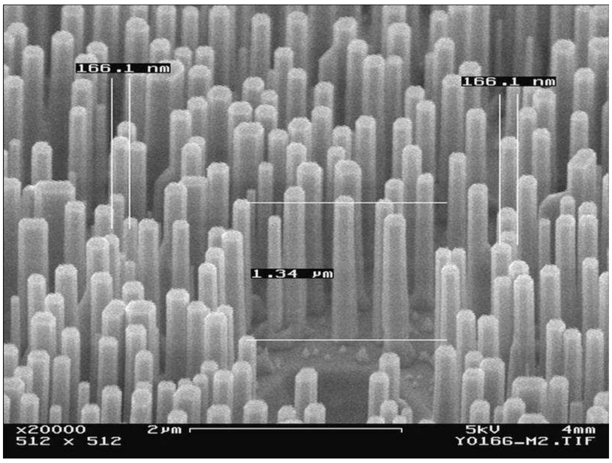

Fig. 1: ZnO nanorods grown on a-plane sapphire.

3. ZnO-GaN Coaxial Nanorods

Following our experience for the growth of GaN layers on ZnO templates [4,6], the growth was started with a low temperature covering layer of GaN grown at 550°C using N_2 as carrier gas to protect ZnO from being etched at the onset of the growth process. Then, the temperature was raised to 800°C, still using N_2 as a carrier gas. This resulted in a lightly yellow colored sample indicating that the grown GaN is not completely defect-free. SEM micrographs showed that the outer surface of the overgrown sheath layer of GaN is not as smooth as that of the original ZnO nanopillar. Low temperature photoluminescence spectra revealed a peak of ZnO with a GaN related shoulder (Fig. 2). From TEM images, the thickness of the GaN sheath was evaluated to be about 30 nm thick.

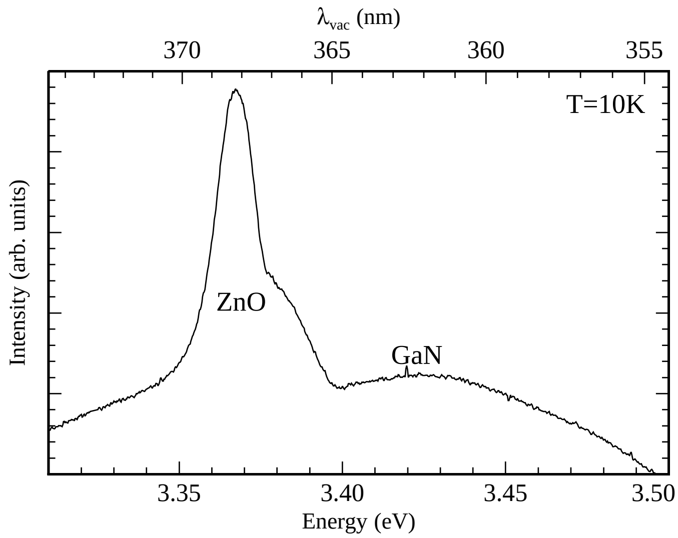

Fig. 2: Low temperature photoluminescence of GaN-ZnO coaxial nanorods.

4. GaN Nanotubes

In order to improve the GaN quality, we have investigated the sheathing growth at higher temperatures. After growing the thin GaN covering layer at 550°C, we deposited three thin intermediate layers of GaN at 800°C, 900°C, 1000°C, and finally a layer at 1050°C using H_2 as carrier gas. In contrast to the previous samples, the color of this sample was transparent white. The SEM micrograph (Fig. 3) shows very smooth well-defined facets of the structures. The top view (Fig. 3, right) reveals hollow tubes with large diameters. In low temperature PL, a sharp near-band-edge GaN related peak at around 3.47 eV without yellow band luminescence is observed (Fig. 4) demonstrating the high quality of the GaN crystal. Obviously, the ZnO nanopillar cores disappeared completely during the high temperature overgrowth leaving perfectly aligned GaN nanotubes. The latter still reflect the arrangement of the original ZnO nanopillars, which hence acted as templates for the GaN nanotubes. The wall thickness of the nanotubes was analyzed by transmission electron microscopy (TEM) to be about 40 nm. This thickness is fairly uniform along the full length of the tubes. It fits to the growth data taking into account the surface area of the tubes as compared to the areal size of a normal flat layer. High-resolution TEM images confirmed the high crystalline quality of the GaN tubes. Moreover, we could not find any evidence for remaining ZnO inside the tubes by EDX analysis in TEM.

5. Coaxial GaInN Quantum Well

As mentioned above, we then transferred the samples to our 2nd MOVPE machine for the deposition of a GaInN quantum well. Here, the growth was re-established by growing a thin GaN layer (about 7 nm) at 885°C with triethylgallium (TEGa) as Ga precursor and N_2 as carrier gas. Then, the trimethylindium (TMIn) flow was switched to the reactor to grow a GaInN quantum well with nominally about 10 % In at a temperature of 830°C.

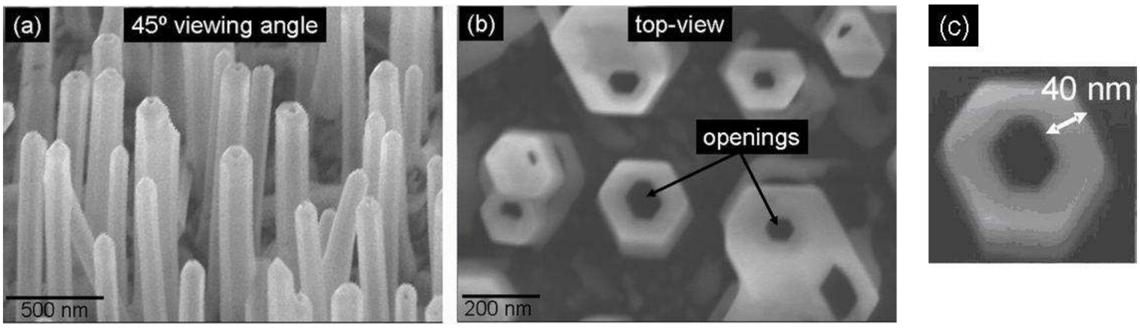

Fig. 3: GaN nanotubes grown around ZnO nanorods which dissolved during the MOVPE process: (a) bird eye's view, (b) top view, (c) determination of wall thickness.

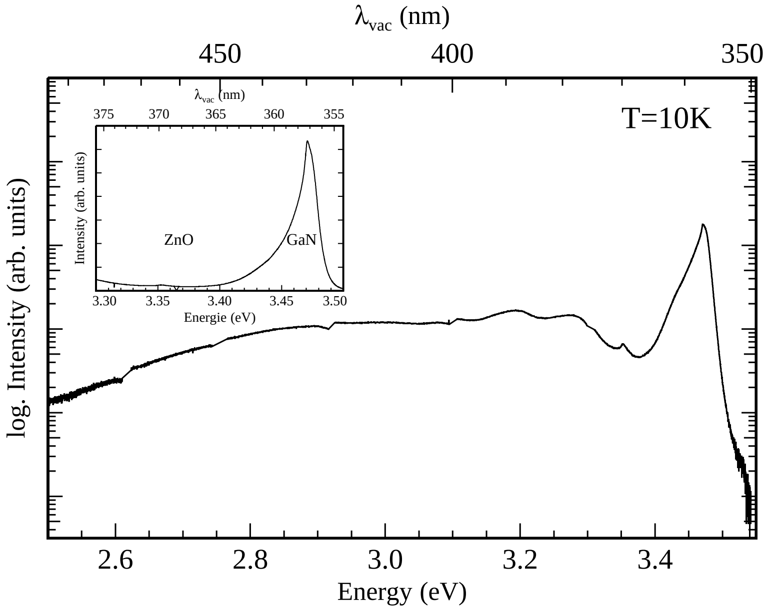

Fig. 4: Low temperature photoluminescence of GaN nanotubes.

Finally, the temperature was set back to 885°C for the growth of the outer GaN barrier layer under H_2 as carrier gas.

SEM inspection showed that the diameters of the nanotubes have significantly increased (Fig. 5). Obviously, most material was deposited at the top of the tubes, indicating a less pronounced precursor diffusion down to the template surface. This may be a consequence of the fairly densely packed nanotubes and of the lower diffusivity of TMIn and TEGa as compared to TMGa, being even further pronounced by the lower growth temperature.

In photoluminescence, we could determine a fairly sharp and intense peak at about 3 eV, the position expected for the GaInN quantum well (Fig. 6). This interpretation was confirmed by a local EDX analysis of the chemical composition in TEM (Fig. 7): No In can be found in spectrum (A), whereas (B) and (C) show a weak In signal. Moreover, the thicknesses of the inner GaN tube, the GaInN quantum well and the outer GaN barrier could be determined by high resolution TEM to be about 40 nm, 4 nm, and 20 nm, respectively.

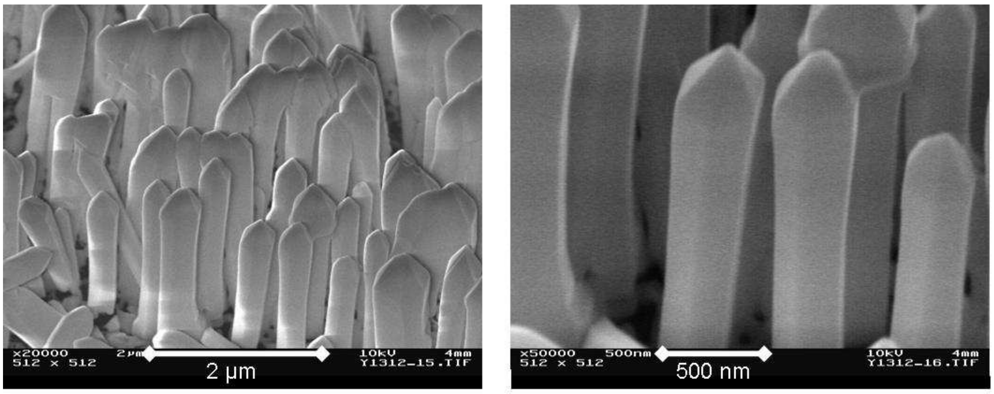

Fig. 5: GaInN GaN coaxial nanotube structures: Overview (left), close-up (right).

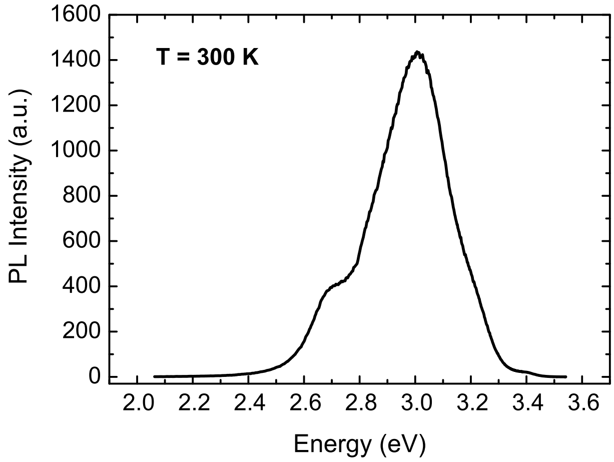

Fig. 6: Room temperature photoluminescence of GaInN GaN coaxial nanotube structures.

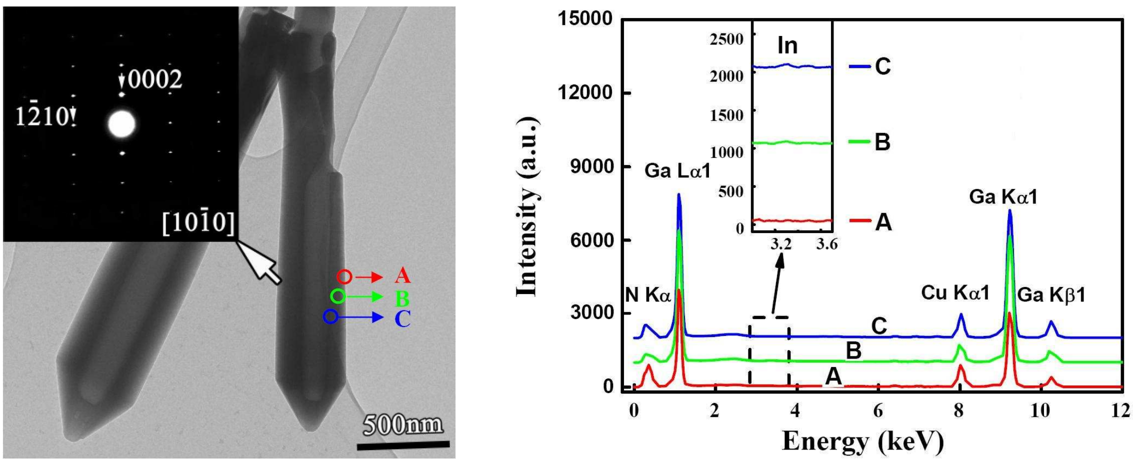

Fig. 7: TEM analysis (left) and related EDX analysis of a GaInN GaN coaxial nanotube structure. The inset (left) shows an electron diffraction signal taken along the [10$\bar{1}$0] zone axis of the nanocolumn confirming its crystalline character.

6. Summary

When growing GaN around ZnO nanocolumns by MOVPE at elevated temperatures, the ZnO core could completely be dissolved leaving well arranged GaN nanotubes. These tubes could be overgrown by a GaInN-GaN double hetero structure resulting in a coaxial GaInN quantum well of about 4 nm thickness. Photoluminescence and transmission electron microscopy studies confirmed the very good properties of these novel nanostructures.

References

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