Controllable Dimension of ZnO Nanowalls on GaN/c-Al₂O₃ Substrate by Vapor Phase Epitaxy Method

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Vertically well-aligned ZnO nanowalls were successfully synthesized at 950–1050 °C. Ar gas was introduced into the furnace at a flow rate of 2000–2500 sccm. An Au thin film with a thickness of 3 nm was used as a catalyst. The ZnO nanowalls were successfully grown on the substrate and most of them had nearly the same thickness and were oriented perpendicular to the substrate. The morphology and chemical composition of the ZnO nanowalls were examined as a function of the growth conditions examined. It was found that the grown ZnO nanowalls have a single-crystalline hexagonal structure and preferred c-axis growth orientation based on the X-ray diffraction and high-resolution transmission electron microscope measurements. The room temperature photoluminescence showed a strong free-exciton emission band with negligible deep level emission, indicating the high optical property of our ZnO nanowall samples.

Keywords: ZnO Nanowalls, Vapor Phase Epitaxy, GaN Epilayer.

1. INTRODUCTION

ZnO has a wide direct band gap of 3.37 eV at room temperature (RT) and a large exciton binding energy of 60 meV. ZnO is a semiconducting and piezoelectric material and has high mechanical and thermal stabilities. As such, it is a promising semiconductor material for ultraviolet (UV) and blue light-emitting devices. In addition, it has practical and scientific importance in the areas of sensing, piezoelectric transduction, surface acoustic wave propagation and photonics. Currently, the realization of nanoscale functional devices depends on the ability to integrate semiconductor nanostructures into nano-scale building blocks. Various ZnO nanostructures, such as nanowires, nanorods, nanobelts, nanobridges and nanonails have recently been reported. Especially, research into two-dimensional nanostructures is rapidly increasing in importance, with a great deal of attention being directed toward the realization of nanowalls and nanosheets.

It has been suggested that ZnO nanowalls can be used as energy-storage devices, chemical and biological sensors and dye-sensitized solar cells, as well as memory devices, because they have a large surface-to-volume ratio. In this regard, the assembly and synthesis of these nanostructures manifesting multiple dimensionalities via a bottom-up method would be of strong potential importance. Up to now, a variety of methods have been developed for synthesizing one-dimensional ZnO nanostructures, such as vapor-liquid-solid (VLS) growth with metal-catalysts, metal-organic chemical vapor deposition (MOCVD), template-assisted growth, and other solution methods. The use of an insulating sapphire substrate might prevent the nanostructure array from being used in electrical devices. With this in mind, in this study, we synthesized vertically well-aligned ZnO nanowalls on GaN epilayer/c-Al₂O₃ substrates which have a single-crystalline hexagonal structure. Furthermore, the influence of the Ar gas flow rate and growth temperature was investigated.

2. EXPERIMENTAL DETAILS

The ZnO nanowalls were grown on GaN/c-Al₂O₃ using a vapor phase epitaxy (VPE) method at an atmospheric pressure of 760 Torr. The starting materials were ZnO (99.99...
purity) and graphite (99.99 purity) powder at a weight ratio of 1:1. A GaN thin film (thickness of 4 μm) deposited by MOCVD on a c-Al2O3 substrate was used for the growth of the ZnO nanowalls with an Au thin film with a thickness of 3 nm being used as a catalyst. High purity Ar (99.999%) gas was introduced into the quartz tube at a flow rate of 2000–2500 sccm as a carrier gas. The main growth of the ZnO nanowalls was performed at 950–1050 °C for 60 min. After the reaction, the system was allowed to cool down naturally to RT under Ar gas flow at the same rate. The substrate surface had a white-gray color. The morphology and chemical composition of the ZnO nanowalls were examined by a field-emission scanning electron microscope (FESEM, Jeol 7401) equipped with an energy-dispersive X-ray spectroscopy (EDX). The crystal structure was identified by X-ray diffraction (XRD, Rigaku D/MAX) with CuKA radiation. The crystallinity of a single ZnO nanowall was investigated with a high resolution transmission electron microscope (HRTEM, Jeol 3010). The optical properties of the ZnO nanowalls were observed by performing photoluminescence (PL) measurements with the 325 nm line of a He-Cd laser as an excitation source.

3. RESULTS AND DISCUSSION

Figure 1 shows the typical low and high magnification FESEM images of the well-aligned ZnO nanowalls synthesized at 950 and 1050 °C for 60 min. Ar gas was introduced into the furnace at a flow rate of 2000 or 2500 sccm. The nanowalls were successfully synthesized on the substrates and most of them had nearly the same thickness and were oriented perpendicular to the substrates. The distribution of the nanowall networks was uniform on the GaN substrates. Figures 1(a and b) show the ZnO nanowalls synthesized at 1050 °C with an Ar gas flow rate of 2000 sccm. The wall thicknesses are in the range of 50–150 nm. Figures 1(c and d) show the growth of the nanowalls at 950 °C with an Ar gas flow rate of 2500 sccm. The thicknesses of the nanowalls in this growth condition are in the range of 150–1000 nm. Figures 1(b and d) clearly show the differences in the thickness of the ZnO nanowalls.
nanowalls synthesized at different temperatures and carrier gas flow rates. It should be pointed that the growth of the ZnO nanowalls was found to be influenced by both the carrier gas flow rate and growth temperature. As the gas flow rate is increased at a lower growth temperature, the thickness and density of the nanowall networks are increased. The EDX result shown in Figure 2 also indicates that the ZnO nanowalls are composed of zinc and oxygen elements and there is no evidence of metal elements on their surface. Thus, we suggest that the ZnO nanowalls were directly grown on the Au networks rather than being grown by VLS mechanism. The Au networks on the GaN epilayer from a highly stable structure with lattice mismatch between ZnO and the GaN network channels. On the Au networks surface, ZnO nucleation results in the oxidation of the Zn-Au alloy and the ZnO nanowalls then start to grow on the Au network surface. Epitaxial ZnO growth is incited by the active sites of the ZnO network channels such as the grain boundary regions. Thus, the shape of the ZnO nanowalls that are formed resembles that of the Au networks. The orientation of the nanowall arrays with respect to the GaN epilayer was further investigated by XRD. Figure 3 shows that ZnO and GaN have almost XRD profiles, due to their similar lattice constants. This indicates the good alignment of the ZnO nanowalls along the c-axis direction on the GaN thin film.

This clearly shows that the synthesized ZnO nanowalls are vertically well-aligned along the [0001] direction and that they strongly preferred to be oriented along the c-axis. The diffraction peaks can be indexed to the wurzite hexagonal structure of the ZnO crystal with the lattice constants, \( a = 0.324 \) nm and \( c = 0.519 \) nm. In order to examine the crystallinity of a single nanowall, HRTEM measurements were conducted. Figure 4 reveals that the nanowall is a single-crystalline phase with a hexagonal structure. The inset of Figure 4(b) is the selected area electron diffraction (SAED) pattern, which provides more evidence of the oriented growth of the ZnO nanowalls on the GaN epilayers. Our ZnO nanowalls on GaN epilayers have a single-crystalline hexagonal structure and c-axis orientation. As shown in Figure 4(c), the HRTEM image clearly shows the well-resolved lattice of the nanowall grown along the [0001] direction. This result is consistent with the XRD results.

Figure 5 shows the RT PL spectrum of the ZnO nanowalls. A strong UV emission peak is clearly observed at 379 nm (3.27 eV). This strong free-exciton emission indicates the excellent crystallinity of our ZnO nanowalls. The deep-level emission is almost unobservable in the PL spectrum. Ordinarily, the optical properties and crystallinity of ZnO nanostructures synthesized by the VPE method tend to be degraded by the many unstable faceted planes that are formed, due to their high surface energy. The deep-level emission is mainly arises when there is a large amount of the impurities involved at the interface.
energy and oxygen vacancies in the ZnO nanostructure. Thus, we were able to conclude that our ZnO nanowall samples have a small number of point defects or impurities.

4. CONCLUSION

We successfully synthesized vertically well-aligned ZnO nanowall structures on GaN/\(c\)-Al\(_2\)O\(_3\) substrates using the VPE method. The thicknesses of the nanowalls can be controlled by adjusting the carrier gas flow rate and growth temperature. The XRD and HRTEM measurements showed that the ZnO nanowalls have a single-crystalline hexagonal crystal structure and \(c\)-axis orientation. The PL spectrum shows that the optical quality of the nanowalls is excellent. Two-dimensional ZnO nanostructures with a high surface-to-volume ratio such as nanowalls could be used as energy storage, data storage and memory devices.

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References and Notes


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