Self-Formed Thin Buffer Layer Assisted Growth of MgZnO Nanowall Structures on GaAs Substrates

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ABSTRACT: This study reports the growth of MgZnO nanowall structures on GaAs substrates through the incorporation of Mg by metalorganic chemical vapor deposition at a growth temperature of 500 °C. Through Mg incorporation, a 5-nm-thick MgGa2O4 layer was initially self-formed on GaAs substrates, which acted as a buffer layer with reduced lattice mismatch for nanowall growth. However, due to the large difference in lattice parameters, the MgZnO seed crystals grew on the MgGa2O4 layer with a pyramidal shape showing a Volmer–Weber growth mode. Moreover, by the random motion of the adatoms on these MgZnO seed crystals, nanowalls with high crystalline quality were grown along the grain boundaries in the MgZnO seed crystals. On the basis of the microstructural characterization of the synthesized nanowall structures, the growth evolution of the MgZnO nanowall structures on GaAs substrates was first proposed.

1. Introduction

From the early 21st century, zinc oxide (ZnO) has been studied extensively owing to its wide direct bandgap of 3.37 eV, high transparency in the visible region, and large exciton binding energy of 60 meV at room temperature. In particular, low-dimensional ZnO nanostructures, such as nanowires, nanotubes, and nanowalls, are expected to show extraordinary properties due to quantum confinement effects. In addition, such low-dimensional ZnO nanostructures have high surface-to-volume ratios, which is good for applications to optoelectronic devices and chemical sensors. In the case of ZnO nanowall arrays, the surface-to-volume ratio is comparatively high and device fabrication using lithography and etching is relatively simple due to the two-dimensional vertical alignment, compared to nanowire arrays. Most studies on the growth of ZnO nanowall structures focused on the use of sapphire and Si substrates with ZnO or Si3N4 buffer, where epitaxial ZnO nanowall structures were grown with an orientational relationship. In most cases, Au metals were used as a catalyst to grow the ZnO nanowall structures, and the growth temperatures were also high (> 700 °C). However, the adoption of catalysts normally degrades device performance because the catalysts act as thermally activated non-radiative recombination centers. Moreover, the high growth temperature limits the possibility for versatile applications due to a restriction in the use of glass or polymer substrates. In addition, most nanowall structures were grown on nonconducting sapphire substrates, which have an epitaxial relationship and low defect density in the ZnO layers. However, the fabrication of electrical devices on nonconducting substrates requires a complex process, due to the difficulty in constructing a vertical device structure. Therefore, a method to grow nanowall structures with high crystallinity on conducting substrates should be developed without using catalysts at relatively low temperatures. Among the conducting substrates, representative Si substrates have an indirect bandgap and a large band offset in the ZnO/Si heterojunction. On the other hand, GaAs is a commercially available substrate with a direct bandgap and relatively small band offset that provides promising characteristics for optoelectronic device applications with a vertical device structure.

ZnO thin films and nanostructures on GaAs substrates have been studied for the formation of n-type ZnO employing the diffusion of As atoms from a GaAs substrate. In addition, p-type GaAs can be obtained easily as a hole injection layer instead of n-type ZnO. GaAs substrates have already been used in optoelectronic devices owing to their superior optical and electrical properties, and merit for high speed devices. However, there are only a few reports on the synthesis of ZnO nanostructures on GaAs substrates, and no reports on the synthesis of ZnO nanowall structures on GaAs substrates. This study reports for the first time the growth of high quality MgZnO nanowalls (2.4 at % in Mg contents) on GaAs substrates through the incorporation of Mg and the formation of a self-formed MgGa2O4 layer by metalorganic chemical vapor deposition (MOCVD). The growth evolution of the MgZnO nanowall structures on GaAs substrates was examined at different growth times by transmission electron microscopy (TEM). In addition, the detail growth procedure of nanowall structures grown on the GaAs substrates is summarized based on the microstructural characterization of the resulting MgZnO nanowall structures.

2. Experimental Section

Well-aligned high density MgZnO nanowall structures were grown on (100) GaAs substrates by low-pressure metal–organic chemical vapor deposition (MOCVD). Before the growth of the MgZnO nanowall structures, the GaAs substrates were cleaned ultrasonically in acetone, ethanol, and deionized water in sequence for 5 min each. The precursors used to grow the MgZnO nanowall structures were diethylzinc (DEZn, purity 99.9995%), bis-cyclopentadienyl-magnesium (Cp-Mg, purity 99.9995%), and oxygen gas (O2, purity 99.9999%). Argon (Ar, purity 99.9999%) was supplied as
a carrier gas. DEZn and O₂ were supplied separately into the reactor chamber to prevent a prereaction of the precursors. The MgZnO nanowall structures were grown at 500 °C and a reactor pressure of 1 Torr. During the growth process of the MgZnO nanowall structures, the Zn and Mg flow rates were kept constant at 6.1 and 0.71 μmol/min, respectively, and the resulting Mg contents in the nanowalls were 2.4 at%. To further understand the growth evolution of MgZnO nanowall structures, the growth time was varied from 1 to 30 min.

The morphology of the MgZnO nanowall structures was observed by field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F), and microstructural characterization was carried out by high-resolution transmission electron microscopy (TEM) (HRTEM, JEOL JEM-3010) and X-ray diffraction (XRD) (RIGAKU, D/MAX-2500). Cross-sectional TEM samples were thinned by mechanical polishing and ion-milled at a low current Ar⁺ ion dose to prevent deformation during ion-milling.

3. Results and Discussion

The formation mechanism of MgZnO nanostructures grown on (100) Si substrates was reported previously, where the MgZnO nanowire arrays were synthesized by self-phase separation through the incorporation of Mg. In the case of Si substrates, a native oxide exists on the surface of the Si substrate. Therefore, Mg atoms supplied to the reactor are incorporated preferentially with a native oxide, and as a result, MgSiO₃ or Mg₂SiO₄ phases are formed in the initial stage. MgSiO₃ or Mg₂SiO₄ phases play a key role in the formation of MgZnO nanostructures on a Si substrate with different crystal structures and large lattice mismatch. On the other hand, for GaAs substrates, the native oxide is virtually absent on the surface of substrates due to its high formation energy. Therefore, the formation mechanism of the MgZnO nanostructures on GaAs substrates is completely different from that of a Si substrate and the growth evolution of MgZnO nanowall structures on GaAs substrates will be determined.

To examine the growth evolution of the MgZnO nanostructures on GaAs substrates, SEM images of the samples were obtained at various growth times (1, 5, 10, and 30 min) (Figure 1a). As shown in Figure 1a, no nanostructures were observed up to a growth time of 5 min, whereas randomly oriented nanowall structures with a sheet-like morphology were observed at a growth time of 10 min. Subsequently, further growth induces the formation of high density nanowall structures with interlinked networks on the GaAs substrates. XRD pole figure analysis corresponding to the MgZnO [1011] reflection was carried out to determine the in-plane orientation of the nanostructures on the GaAs substrates. The results show the random distribution of planes diffracted from the MgZnO nanowalls like polycrystalline films, as shown in Figure 1b.

In general, the growth mechanism of the nanostructures can be revealed by microstructural characterization from the bottom to the top of the nanostructures synthesized using a bottom-up process. Therefore, the microstructural characteristics of the nanowall structures grown on the GaAs substrates were investigated. At the initial growth stage (5 min growth) with no nanostructures, nanosized dimples were formed on the surface of the GaAs substrates (Figure 2a), as indicated by the arrow in Figure 1a. The density of the dimples increased with growth time up to 5 min. The formation of nanosized dimples is due to the prior evaporation of volatile As atoms from the surface of the GaAs substrates, where As atoms have a low vapor pressure and low sublimation temperature (603 °C). As atoms evaporated preferentially from the atomically stepped or defective sites on the GaAs substrates, and the opposite Ga atoms, which lost an ion-pair (As), were finally depleted due to possible evaporation from the newly created steps and additional nucleated desorption sites.24
By continuing the growth process, the dimples in the surface were filled with the deposited adatoms, as shown in Figure 2b. On the basis of the HRTEM analysis, the filled regions have different crystal phases with GaAs and correspond to a tetragonal MgAs$_4$ (a = b ≠ c, α = β = γ = 90°) phase that has a similar crystal structure with cubic GaAs (a = b = c, α = β = γ = 90°), as shown in Figure 2c. The dimples are considerably unstable sites due to the high density of dangling bonds. As a result, the adatoms deposited on the substrate surface were initially trapped at the dimpled regions. Among the adatoms trapped in the dimples, the supplied Mg atoms may react preferentially and rapidly with the As atoms from the GaAs substrate, leading to the formation of a MgAs$_4$ phase. Interestingly, all the dimples on the substrate surface were filled with the MgAs$_4$ phase, not other phases such as MgGa$_2$O$_4$, Ga$_2$O$_3$, Zn$_2$As$_2$. In addition, the MgAs$_4$ phases in the dimple sites maintained their phase and were not converted into other phases. This is because the lattice parameters of GaAs are almost identical to those of MgAs$_4$, as shown in Figure 2b,c. Therefore, it is possible that the MgAs$_4$ phases with low lattice mismatch exist stably in the dimple sites.

Subsequently, interlayers, approximately 5 nm thick, were formed between the MgZnO seed layers and GaAs substrates on the entire substrate surface at the middle growth stage, as shown in Figure 3a,b. Surprisingly, the thickness of the interlayers are quite uniform. HRTEM revealed a lattice spacing along the in-plane and out-of-plane of 0.292 and 0.471 nm, respectively. Their crystal structure was cubic MgGa$_2$O$_4$ with a spinel structure. During growth, there were many candidate products that can be formed by a surface reaction. From the formed interlayer (i.e., MgGa$_2$O$_4$), some possible reactions 1–5 are proposed. A comparison of the change in Gibb’s free energy at 500 °C (773 K) and 1 Torr revealed the MgGa$_2$O$_4$ layer to be most thermodynamically stable phase compared to MgO, Ga$_2$O$_3$, and ZnO, assuming that the sticking coefficients of all reactants could be ignored. The details are as follows:

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\begin{align*}
\text{Mg} + \frac{1}{2} \text{O}_2 & \rightarrow \text{MgO} \quad \Delta G = -633.5 \text{kJ/mol} \quad (1) \\
2\text{Ga} + \frac{3}{2} \text{O}_2 & \rightarrow \text{Ga}_2\text{O}_3 \quad \Delta G = -1182 \text{kJ/mol} \quad (2) \\
\text{Zn} + \frac{1}{2} \text{O}_2 & \rightarrow \text{ZnO} \quad \Delta G = -395.9 \text{kJ/mol} \quad (3) \\
\text{Mg} + 2\text{Ga} + 2\text{O}_2 & \rightarrow \text{MgGa}_2\text{O}_4 \quad \Delta G = -1816 \text{kJ/mol} \quad (4) \\
\text{Zn} + 2\text{Ga} + 2\text{O}_2 & \rightarrow \text{ZnGa}_2\text{O}_4 \quad \Delta G = -1578 \text{kJ/mol} \quad (5)
\end{align*}
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The misfit strain was considered to determine the origin of the formation of interlayers. On the basis of the HRTEM results, the crystallographic orientation relationships (ORs) between the MgGa$_2$O$_4$ interlayer and GaAs substrate were MgGa$_2$O$_4$ [220] // GaAs [023] and MgGa$_2$O$_4$ [112] // GaAs [011] on the in-plane, leading to lattice mismatches of 46.4 and 15.5%, respectively. In addition, the MgGa$_2$O$_4$ (111) plane is parallel to the GaAs (200). Therefore, the misfit strain and residual stress are anisotropic along two in-plane directions. If the MgZnO nanostructures with a c-axis preferred orientation were grown directly on the GaAs substrate without an interlayer, the large lattice mismatches are expected to be 40.7 and 18.8% along the [10T0] MgZnO and [1120] MgZnO directions, respectively, assuming that the lattice parameters of the MgZnO are similar to those of the ZnO due to the low Mg composition and similar ionic radius of Zn$^{2+}$ and Mg$^{2+}$. On the other hand, if an interlayer was introduced between the MgZnO nanostructures and GaAs substrate, the lattice mismatch can be reduced significantly to 3.9 and 11.0% along the [10T0] MgZnO and [1120] MgZnO, respectively, in the MgZnO nanostructure and MgGa$_2$O$_4$ interface. The lattice mismatch of 11.0% is the effective lattice mismatch reflecting the domain matching condition. It indicates that the MgGa$_2$O$_4$ interlayer can effectively act as a buffer layer for the growth of MgZnO nanostructures on GaAs substrates.

It should be noted that the average size of a dimple increased and the MgGa$_2$O$_4$ interlayer was slightly thickened as the growth time increased (not shown here). This means that the diffusion reaction occurred during the growth process. Mg atoms that came from the MgGa$_2$O$_4$ interlayer diffused toward the dimples and reacted with As atoms that came from decomposed materials from the dimple sites, resulting in the formation of MgAs$_4$. The Ga atoms which lost a pair of As also diffused into the MgGa$_2$O$_4$ interlayer and contributed to the thickening of the MgGa$_2$O$_4$ interlayer. This indicates that an equilibrium state of ionic diffusion between the substrate and the interlayer is expected by the interdiffusion of Mg and Ga atoms under a growth temperature of 500 °C.

As mentioned previously, although the MgGa$_2$O$_4$ interlayer has excellent thermodynamic stability and a reduced misfit strain as a buffer layer, there is still a large misfit strain between the MgGa$_2$O$_4$ interlayer and the GaAs substrate, which will affect the growth of MgZnO nanostructures on the MgGa$_2$O$_4$ interlayer. As a result of the large misfit strain
acting on the MgZnO nanostructure/MgGa$_2$O$_4$ interlayer interface, the MgZnO seed crystals were initially formed with a facet shape on the interlayer, as shown in Figure 4a, which indicates that the wurtzite MgZnO crystals had nucleated and grown with the island growth behavior of a pyramidal shape on the MgGa$_2$O$_4$ interlayer through Volmer–Weber growth mode. Figure 4b shows a cross-sectional HRTEM image along the [11\overline{2}0] ZnO zone axis of the MgZnO seed crystals on the interlayer. As shown in Figure 4b, the seed crystals with a pyramidal shape have many stacking faults (SFs), as indicated by the arrows. They are formed by the release process of the strain stored in the MgZnO seed crystals. The type of generated SFs is classified as intrinsic type I SFs, which have the lowest formation energy.\textsuperscript{27} In addition, although the facets of MgZnO seed crystals were inclined with an angle of $32^\circ$ in the low magnification TEM image of Figure 4a, they actually consisted of various planes, as shown in Figure 4b. These high indexed facets with relatively high surface energy, such as \{01\overline{1}4\}, \{01\overline{1}2\}, and \{01\overline{1}1\}, transit to low indexed planes. This is believed to provide circumstantial evidence for the structural transition from two-dimensional seed crystals to nanostructures, which was further confirmed by the formation of nanowires with \{10\overline{1}0\} side surfaces on the top of the MgZnO seed crystals, as shown in Figure 4c. The surface energy of the ZnO \{10\overline{1}0\} plane is considerably lower than high indexed planes, such as \{01\overline{1}4\}, \{01\overline{1}2\}, and \{01\overline{1}1\}.\textsuperscript{28}

Polycrystalline films were formed near the interface by the coalescence of seed crystals. Therefore, many grain boundaries were observed, as indicated by the arrows in Figure 4c. The nanowall structures were formed at temperatures $\geq 500^\circ$C higher than the melting temperature of Zn (419.53 °C) (Figure 4d). It was reported that the Zn adatoms drift freely by random motion and can finally be adsorbed in the high density grain boundaries because these grain boundaries are the most thermodynamically activated sites for the saturation and precipitation of adatoms.\textsuperscript{8,11} As a result, nanowall growth is initiated along the grain boundaries.\textsuperscript{8,11,31} A model explaining the growth evolution of nanowall structures grown on GaAs substrates was proposed considering the results concerning the microstructural characterization of the nanostructures synthesized on the conducting GaAs substrates, as summarized in Figure 5. First, As and Ga atoms were evaporated from atomically stepped or defective sites on the GaAs substrates due to the low sublimation temperature of As at 500 °C. As a result, the dimples were formed on the GaAs substrate. The MgAs$_2$ phase was formed preferentially in the dimple regions by a chemical reaction between Mg and As atoms for planarization. The 5 nm-thick self-formed MgGa$_2$O$_4$ interlayer was formed spontaneously as a buffer layer with a uniform thickness on the GaAs substrate due to the lower Gibb’s free energy and lower lattice mismatch with the nanostructures. This was followed by the formation of pyramidal-shaped MgZnO seed crystals and nanowires on the MgGa$_2$O$_4$ buffer layer, where the MgZnO seed crystals had many grain boundaries. Finally, the formation of nanowalls was initiated along the grain boundaries by Brownian random motion of adatoms at above a critical high temperature.

It was difficult to obtain microstructural information of single nanowall from the cross-sectional TEM samples prepared by mechanical polishing and ion-milling due to the high density of synthesized nanowall structures and the limited aperture size of TEM. Therefore, the nanowalls were dispersed on the Cu mesh grid by ultrasonic agitation, and for the

![Figure 4](image1.png)

**Figure 4.** (a) Cross-sectional bright-field TEM image of the sample grown for 10 min. (b) HRTEM image from the top region of the MgZnO seed crystal. The white arrows indicate the stacking faults. (c, d) Cross-sectional bright-field TEM image of the sample grown for 30 min. The black arrows in (c) indicate the grain boundaries between the adjacent MgZnO seeds.

![Figure 5](image2.png)

**Figure 5.** Schematic model showing growth evolution of the nanowall structures grown on the GaAs substrates.
sake of accuracy, individually existing 30 nanowalls on a mesh grid were examined by TEM. Figure 6a shows a representative bright-field TEM image and corresponding selected area diffraction pattern (SADP) of individually existing nanowalls. The nanowall on the mesh grid was attached slightly to the mesh grid due to van der Waals force. As shown in SADP of Figure 6a, the zone axis of the nanowall is the MgZnO [11 \bar{2} 0] direction, which means that the synthesized nanowalls have [11 \bar{2} 0] planes as the major plane. Fujimura et al. reported that ZnO [11 \bar{2} 0] and {10 \bar{1} 0} had surface energies of 0.123 and 0.209 eV/A\(^2\), respectively. Therefore, the nanowalls were grown by maximizing the area of the [11 \bar{2} 0] planes, which have a relatively low surface energy for the reduction of total energy.

As shown in the cross-sectional HRTEM image of Figure 6b, no crystallographic defects, such as stacking faults and dislocations, were observed in the nanowalls. The synthesis of high crystalline nanowalls with a considerably large surface area using commercially available GaAs substrates and MOCVD facilities for optoelectronic devices has potential for a range of optoelectronic applications.

4. Conclusions

ZnO-based nanowall structures with high crystalline quality were grown on conducting GaAs substrates at 500 °C through Mg incorporation. After the formation of self-formed ~5 nm-thick MgGa\(_2\)O\(_4\) interlayers with reduced lattice mismatch with MgZnO seed crystals, the MgZnO seed crystals were formed into polycrystalline films with a pyramidal shape. With increasing growth time, these seed crystals showed a structural transition to one-dimensional nanowires. At the same time, the nanowalls were grown along the grain boundaries by the random motion of adatoms at high temperatures because grain boundaries are thermodynamically activated sites for the saturation and precipitation of adatoms. The synthesized nanowalls exhibited high crystallinity without structural defects as well as a uniform distribution on a large area using commercially available facilities.

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Figure 6. (a) Cross-sectional bright-field TEM image and corresponding SADP from a single nanowall on a mesh grid. The SADP was obtained using a field limiting aperture with a diameter of 1.35 μm. (b) Enlarged HRTEM image from the rectangular region marked with the dashed line in (a). The nanowall has no structural defects, such as stacking faults and dislocations.