

GaN growth on Si(111) substrate using oxidized AIAs as an intermediate layer

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We have demonstrated that GaN can be grown epitaxially by atmospheric pressure metalorganic chemical vapor deposition on an aluminum oxide compound layer utilized as an intermediate layer between GaN and a Si(111). X-ray diffraction measurement indicates that single-crystal hexagonal GaN with its basal plane parallel to the Si(111) plane is grown. Using a scanning electron microscope, the macroscopic evolution of GaN grown on the $\text{AlO}_x/\text{Si}(111)$ substrate is found to be similar to that of GaN grown on a sapphire(0001) substrate. Cathodoluminescence (CL) spectrum shows a unique emission that consists of several peaks with the intensity comparable to that of the near-band-edge emission. Unique characteristics in CL spectrum are discussed in terms of a possible oxygen contamination of GaN grown on the $\text{AlO}_x/\text{Si}(111)$ substrate. © 1997 American Institute of Physics. [S0003-6951(97)03048-9]

Group III nitride semiconductor materials have been grown on several different types of substrates because there are no commercially available bulk GaN substrate. In view of potential applications in field-emission display devices and high-power microwave devices, Si is an interesting substrate to consider for group III nitride growth. In all attempts to grow group III nitrides on Si substrates, an intermediate layer such as aluminum nitride,^{1,2} silicon carbide,³ and nitrized GaAs⁴ were used to initiate growth of high quality nitride layers. Another approach using a compliant substrate consisting of SiC formed by carbonization of a silicon-on-insulator (SOI) substrate has also been demonstrated.⁵ In this letter, we have demonstrated that GaN can be grown epitaxially on a Si(111) substrate using an aluminum oxide compound (AlO_x) as an intermediate layer between the GaN epitaxial layer and a Si(111) substrate.

The samples studied were prepared by the following sequence. (The sequence is also shown in Fig. 1 schematically.) First, an undoped AIAs layer (2500 Å) followed by an undoped GaAs cap layer (300 Å) were grown on a *p*-type ($N_A \sim 1 \times 10^{18} \text{ cm}^{-3}$) Si(111) substrate by atmospheric pressure metalorganic chemical vapor deposition (MOCVD) using trimethylaluminum, trimethylgallium, arsine (a V/III ratio of 27 and a growth rate of 12 Å/s were used for the AIAs growth) and hydrogen as a carrier gas. A two-step growth technique was employed for the AIAs growth, involving a low-temperature (460 °C) grown AIAs buffer layer (350 Å thick) followed by a high-temperature (760 °C) grown AIAs overlayer. The surface of the GaAs/AIAs/Si(111) is specular when viewed with an optical microscope. Subsequently, the AIAs layer was selectively oxidized and converted to AlO_x by etching features through the AIAs layer and heating the AIAs layer in a water vapor/ N_2 ambient.⁶ After the AlO_x

layer was selectively formed, the GaAs cap layer was removed and an anneal was performed at 1000 °C in an oxygen ambient for 1 h. Finally, using a multistep growth approach⁷ that consists of multiple undoped GaN layers grown at successively higher temperatures, GaN was grown on $\text{AlO}_x/\text{Si}(111)$ by MOCVD. The reactor chamber, manufactured by Thomas Swan & Co. Ltd., is a vertical reactor equipped with a closed spaced showerhead and operated at atmospheric pressure. Trimethylgallium and ammonia were used as sources with a hydrogen carrier gas. Sapphire(0001) substrates and Si(111) substrates, as references, were also loaded with the $\text{AlO}_x/\text{Si}(111)$ substrate in the same GaN growth run.

Θ - 2Θ scan x-ray diffraction (XRD) profiles taken to trace each step of the sample preparation sequence are shown in Figs. 2(a)–2(c), corresponding to Figs. 1(a)–1(c). As seen in Fig. 2(a) two major peaks originating from the Si(111) substrate and the AIAs(111) layer (the peak associated with the thin GaAs cap layer is expected to have very small intensity) are seen, indicating that the AIAs layer is grown epitaxially on the Si(111) substrate.

After the AIAs layer is oxidized and the GaAs cap layer is removed, the peak associated with AIAs(111) disappears

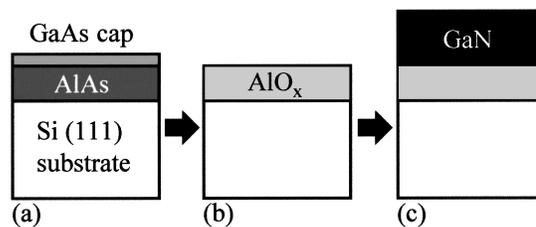


FIG. 1. A schematic of the procedure to prepare the GaN/ $\text{AlO}_x/\text{Si}(111)$ sample. (a) An AIAs layer followed by a GaAs cap layer is grown on a Si(111) substrate. (b) Subsequently, the AIAs layer is selectively oxidized and converted to AlO_x . The sample is further annealed at a high temperature. (c) GaN is finally grown on $\text{AlO}_x/\text{Si}(111)$.

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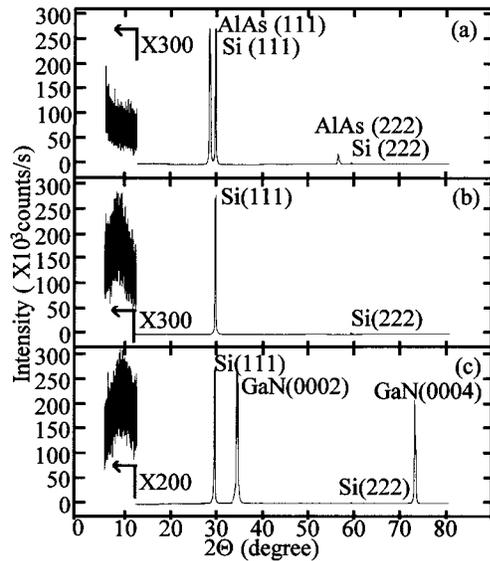


FIG. 2. XRD profiles taken from the different stages, corresponding to Figs. 1(a), 1(b), and 1(c), of the procedure to prepare GaNAlO_x/Si(111) sample. (a) Two peaks associated with the (111) plane of the AlAs layer and the Si substrate respectively are observed. (b) The peaks associated with the AlAs layer disappears and a broad peak in the lower diffraction angle appears. (c) Besides the peaks originating to the Si substrate, peaks associated with the basal plane of the hexagonal GaN can be seen.

as shown in Fig. 2(b). More importantly, a noticeably broad peak extending over the low diffraction angle range ($2\theta \sim 10^\circ$) appears. In general, a broad peak seen in the low diffraction angle range is a typical indication that the structure contains an amorphous and/or a fine-grain phase. Indeed Al_xGa_{1-x}As ($x=0.8-0.98$) oxidized with a similar oxidation process was found to contain both amorphous and fine-grain phases.^{8,9} Aside from this, there is no indication, within the detection limit of our XRD measurement, for the formation of single-crystalline or polycrystalline Al₂O₃ phases such as γ , η , χ , δ -Al₂O₃ or AlO(OH). Therefore we attribute this broad peak to an amorphous/fine-grain phase contained in the AlO_x layer. From GaN/AlO_x/Si(111) [Fig. 2(c)], only the peaks associated with GaN(0001) plane are seen in addition to the peaks seen in Figs. 2(b), indicating that GaN with hexagonal space lattice was grown on the AlO_x layer.

A remarkable consequence implied by the data presented here is that highly oriented GaN can be grown epitaxially on an AlO_x layer that contains predominantly an amorphous/fine-grain phase. It is unlikely that the order necessary for GaN to grow epitaxially on the AlO_x layer is transmitted from the Si(111) surface through the AlO_x layer because the thickness of the AlO_x layer is ~ 2500 . It is also unlikely that hexagonal GaN just grows with the most preferential plane, namely the basal plane, without having the order necessary for epitaxy, because, in the experiment done simultaneously, GaN grown on an AlO_x layer formed on a Si(100) substrate using similar procedures resulted in polycrystalline GaN even though the AlAs layer, being oxidized to form AlO_x, was grown under optimized conditions [different from that for Si(111)] for Si(100). At this point, we do not observe substantial macroscopic difference in the surface morphology on AlO_x/Si(100) and on AlO_x/Si(111), thus we are cur-

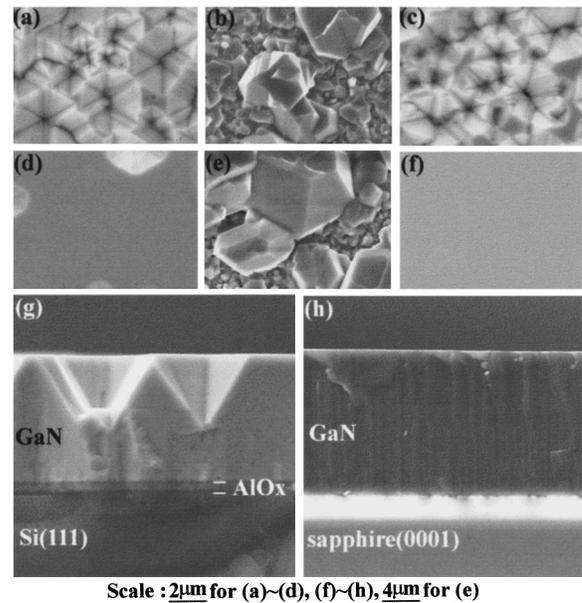


FIG. 3. PV- and CS-SEM images of the macroscopic evolution of GaN grown on three different substrates: AlO_x/Si(111) is shown in panels (a), (d), and (g); Si(111) is shown in panels (b) and (e); and sapphire is shown in panels (c), (f), and (h). In panels (a), (b), and (c) PV-SEM images of GaN grown for 1 h are shown. In panels (d), (e), and (f) PV-SEM images of GaN grown for 3 h are shown. In panels (g) and (h) CS-SEM images of GaN corresponding to the panels (d) and (f) are shown, respectively.

rently investigating these samples to see if there is any microscopic morphological difference.

Although it is not clear at this point what positively leads to the epitaxy of GaN on the AlO_x layer, we briefly enumerate several possibilities that can initiate the GaN epitaxy on the AlO_x layer. (1) We have not observed, within the detection limit of XRD measurement, any indication that the amorphous/fine-grain phase AlO_x layer was transformed to the crystalline phase even after GaN growth. It is possible that the order necessary for GaN to be grown epitaxially can be transferred from a selected ensemble of fine grains, that have well-defined crystallographic planes and suitable orientation. (2) Even though majority volume of the AlO_x layer contains an amorphous/fine-grain phase, the surface, including a region beneath the surface, of the AlO_x can possibly have regular atomic arrangement on which GaN epitaxy can be initiated. Cross-sectional transmission microscope study of an AlO_x layer formed by a similar oxidation procedure has shown that the interface between an AlO_x layer and a GaAs layer has an atomically sharp transition region different from the region inside the AlO_x layer.¹⁰

In Fig. 3, plan-view and cross-sectional scanning electron microscope images of the macroscopic evolution of GaN grown on three different substrates are shown. In the early stage of nucleation and growth (after 1 h GaN growth), as shown in Figs. 3(a)–3(c), GaN grown on AlO_x/Si(111) appears to grow in a similar fashion to GaN grown on sapphire(0001), while GaN directly on Si(111) grows in the form of spatially separated crystallites. As growth is continued (after 3 h GaN growth), the hexagonal pits existing on the surface of the GaN at the earlier evolution stage are filled up, leading to the formation of smooth surface area as shown in Figs. 3(d) and 3(f). On the contrary, Fig. 3(e) indicates

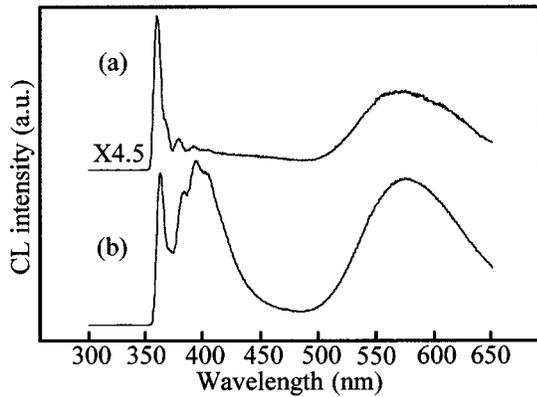


FIG. 4. CL spectrums taken from GaN grown (a) on sapphire(0001) and (b) on $\text{AlO}_x/\text{Si}(111)$ are shown. In the panel (b), in addition to I_2 line a broad emission band that appears to be composed of at least three different emissions with the intensity comparable to I_2 line is apparent.

that GaN grown on Si(111) evolves without revealing a major transition of surface features seen at the earlier evolution stage. The cross-sectional SEM images corresponding to the plan-view images shown in Figs. 3(e) and 3(f) are also shown in Figs. 3(g) and 3(h), respectively. It should be noted that in the cross sectional images in Fig. 3(g) the AlO_x intermediate layer is clearly seen between GaN and a Si(111) substrate.

Cathodoluminescence (CL) spectra taken from GaN grown on sapphire(0001) and on $\text{AlO}_x/\text{Si}(111)$ are shown in Figs. 4(a) and 4(b), respectively. In Fig. 4(a) the most intense line at 3.461 eV is interpreted as the emission from the excitons bound to neutral donors (I_2 line).¹¹ The shoulder on the I_2 line at 3.375 eV and the lines at 3.283 and at 3.177 eV are attributed to phonon replicas of the I_2 line.¹² A broad emission peaked at 2.169 eV, generally observed in CL spectra of undoped GaN, is also seen.

The CL spectrum shown in Fig. 4(b) indicates several significant features. A sharp peak at 3.425 eV is thought to originate from a redshifted (40 meV) I_2 line. An emission band that appears to be composed of at least three different emissions with the intensity comparable to I_2 line is apparent and peaked at 3.155 eV. Although the emission peaks that compose this emission band are fairly close to the positions expected from the phonon replicas associated with I_2 line, the intensity comparable to the I_2 line implies that these lines are not simple phonon replicas as seen in Fig. 4(a). The intensity of the broad emission peaked at 2.129 eV is also comparable to that of I_2 line.

The origin of the CL emission near 3.155 eV is unknown at present. However, in most III–V semiconductors, oxygen is known to create a deep donor level.^{13,14} Oxygen has been reported to create a deep donor level in GaN at around 78–110 meV below the conduction band.^{15,16} Furthermore, a deep acceptor level, at around 200 meV above the valence band, associated with the existence of oxygen impurities during GaN growth has been also reported.^{15,16} Considering the

structure of our samples, we speculate that oxygen atoms, which are expected to have weak bonds in the AlO_x layer, may diffuse into the growing GaN layer, resulting in the oxygen-related impurity emission. Moreover, nitrogen vacancies substituted by doubly ionized oxygen ions have been reported to be the origin of high electron background of undoped GaN,¹⁷ which also could contribute to increased intensity of the wideband emissions as seen in Fig. 4(b). Recently, secondary ion mass spectroscopy studies have shown that oxygen atoms tightly bonded in a sapphire substrate can diffuse into growing GaN for distance greater than 1 μm from the GaN/sapphire interface.¹⁸ However, Auger electron spectroscopy (AES) performed on the GaN grown on the $\text{AlO}_x/\text{Si}(111)$ substrate did not show any indication of oxygen contamination, implying that any oxygen contamination that may occur is present at levels below the detection limit of AES (~ 0.1 at %).

In summary, we have demonstrated that GaN can be grown epitaxially on AlO_x layer selectively formed on a Si(111) substrate. The overall macroscopic evolution of the GaN on the $\text{AlO}_x/\text{Si}(111)$ substrate was found to be identical to the GaN grown on a sapphire(0001) substrate. In CL measurement, the unique emission peaks, not seen on the GaN grown on a sapphire(0001) substrate, were observed. Oxygen contamination from the AlO_x layer was suggested as a possible source to explain the unique CL emission peaks.

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