Nonpolar GaN grown on Si by hydride vapor phase epitaxy using anodized Al nanomask

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GaN growth by the hydride vapor phase technique on (100) Si substrates masked by porous Al anodic oxide is described. The masks were prepared by vacuum deposition of Al with subsequent anodic oxidation in dilute sorrel acid. The grown GaN layer is nonpolar, with $(11\bar{2}0)$ *a*-orientation and a full width at half maximum of the $(11\bar{2}0)$ reflection below 500 arc sec and showing small anisotropy. This result is comparable with the results obtained for *a*-GaN growth using selective epitaxy or advanced buffer growth routines. Microcathodoluminescence spectra of the grown films confirm a low density of stacking faults. Possible growth mechanisms are discussed. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3072614]

GaN has applications in light emitting devices operating in the UV-visible range and in high-frequency/high-power microwave devices.[1,2] Most devices are prepared by heteroepitaxy using sapphire or SiC as substrates. GaN substrates grown by hydride vapor phase epitaxy (HVPE) have also become available.[3] In HVPE, thick GaN is deposited on sapphire substrates and separated by self-separation due to high stress. The key is in designing buffers that provide separation at the interface without breaking or cracking the wafer. This is challenging in terms of achieving high yield. The situation would be easier if the growth could be performed on a substrate that could be readily removed by etching or polishing, such as Si or GaAs. Some groups have reported impressive results with HVPE growth on GaAs substrates,[4] but protecting the substrate during the initial stages of growth in an aggressive HVPE ambient requires careful optimization. Growth of GaN on Si substrates has achieved an advanced stage using metal organic chemical vapor deposition[5,6] and high-performance GaN-based transistors or light emitting diodes (LEDs) can be realized. However, growth of thick films that could be used as GaN substrates is a problem because of the high stress.

In this letter, we demonstrate that thick GaN can be deposited on Si substrates by HVPE if the surface of the substrate is masked by porous anodic oxide of Al. By subjecting thin Al films to anodic oxidation in electrolytes based on dilute aqueous solutions of weak acids, such as sorrel acid, one can produce porous amorphous Al_2O_3 oxide layers with a regular network of open channels with submicron diameter.[7–10] Such layers can be prepared on various substrates and can be used as a mask for growing semiconductor nanorods.[7–10] We demonstrate that using such a mask is advantageous in preparing good quality thick GaN films on Si substrates.

N-type Si (100) substrates with sheet resistivity of 1 Ω cm were used. 1.5 μm thick Al films were deposited by vacuum evaporation. Anodic oxidation was performed in 0.1*M* solution of sorrel acid $H_2C_2O_4$ at a constant voltage of 66 V. The process was: (1) initial oxidation for 30 min, (2) etching off the top oxide layer in phosphoric and chromic acids at 60 °C, (3) repeated oxidation to form deep channels going down to almost the Si surface, and (4) etching the structure in 2*M* solution of H_2SO_4 at 50 °C. Stage 2 was introduced to make the structure more regular and stage 4 to open the channels all the way down to Si, although getting through the barrier layer and the layer of Si oxide exposing a clean Si surface is difficult. The diameter of oxidized Si was 1 cm^2. X-ray diffraction, infrared spectrometry, and Raman spectrometry show that the films are amorphous Al_2O_3 with no measurable traces of hydroxyl group and no captured acid radicals.

Growth of GaN by HVPE was performed in a vertical system.[11] First a thin (~30 nm) film of GaN was deposited at 550 °C to protect the unoxidized surface and to create a low temperature buffer for growth of GaN in the anodic oxide channels. The temperature was brought to 1000 °C in ammonia flow and high temperature growth was performed. The nitrogen carrier gas flow was 60 l/h, the HCl flow through the Ga source was 1 l/hr, and the Ga source temperature was 870 °C. The growth time was 2 h. The thickness was measured by observation of the cleaved surface in optical microscope and was 160–180 μm, or a growth rate of 80–90 μm/h. The orientation of the film was determined from $\theta/2\theta$ scans. The crystalline quality of the films was evaluated by the full width at half maximum (FWHM) of the double-crystal x-ray rocking curve. In both cases a diffractometer system using Cu $K\alpha$ radiation was used. The surface morphology of the anodic oxide and the GaN film was studied by scanning electron microscope (SEM). The luminescence spectra were measured by microcathodoluminescence

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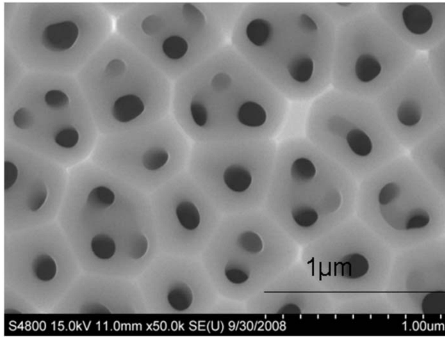

FIG. 1. SEM plan-view of the Al anodic oxide layer.

(MCL) at 90 K. Imaging of the GaN surface was performed in the MCL mode.[12]

Figure 1 shows the plan-view image of the anodic oxide layer. The open channels with dimensions of ~100 nm form a regular structure with a pitch of 300–500 nm. X-ray $\theta/2\theta$ scans performed on the GaN layer deposited on the anodic oxide showed only one reflection at $2\theta=57.77°$, close to the reflection from the $(11\bar{2}0)$ planes. Thus the film is single crystalline with nonpolar *a*-orientation. The FWHM of the double-crystal rocking curve for this reflection was 450 arc sec and showed a weak dependence on rotation around the axis normal to the surface. A low value and a slight anisotropy of the FWHM value indicate a relatively low density of stacking faults (SFs) and of associated partial dislocations.[13–18] The formation of a high density of SFs and partial dislocations plagues *a*-GaN layers grown by metal organic chemical vapor deposition on *r*-sapphire and is strongly favored by the growth mechanism. Typically the FWHM of such *a*-GaN films is ~1° and is several times higher when the diffraction plane is parallel to the $[1\bar{1}00]$ *m*-direction compared to the [0001] *c*-direction[13–15] A high dislocation density and SF density in *a*-GaN films is currently the main obstacle for growing nonpolar GaN LEDs in which the detrimental impact of the electrical polarization field for growth in the polar [0001] direction is minimized.[16,17] To suppress this high defect density in *a*-GaN, selective epitaxial growth on patterned *a*-GaN templates[19] or growth using an AlGaN/GaN superlattice buffer[14] schemes has been proposed. The FWHM values in such improved *a*-GaN layers are in the 300−700 arc sec range, i.e., comparable the FWHM value observed for our *a*-GaN films.

The mechanism of growth is clarified by Fig. 2, showing

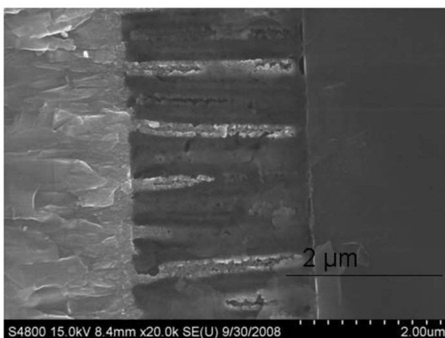

FIG. 2. Cross-section SEM of the GaN film grown on the Al anodic oxide on (100) Si substrate.

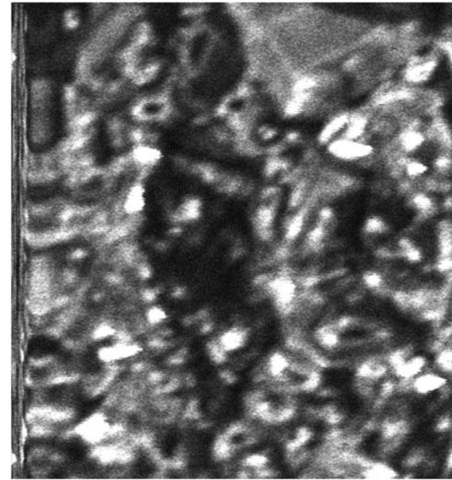

FIG. 3. 90 K MCL image of the grown GaN surface. The full dimensions of the image are 100×100 mm^2.

a cross section of the grown GaN layer together with the anodic oxide layer. This demonstrates that the open channels do not reach down to the Si surface (the right hand side of the layer) and thus subsequent growth is not epitaxial growth of GaN on Si. Rather, one observes that at the initial stage small GaN crystallites are deposited within the channels. The growth rate of these is higher, closer to the mouth of the channels, most likely due to higher supply of reagents in the gas phase. In time, the channels are blocked by these crystallites that then grow outside the channels preferentially in a lateral mode so that the grain size increases rapidly within the first micron of the film. After this, the layer displays a well defined columnar structure with the preferential growth direction of $[11\bar{2}0]$ as follows from the x-ray data. The surface morphology remains rough even after ~200 μm thickness.

Figure 3 shows a surface image taken at 90 K in MCL mode for the 3.46 eV bandedge line. The surface has relatively large bright grains with a high intensity of the bandedge luminescence interspersed by dark regions corresponding to deep depressions in the surface profile. Figure 4 compares the 90 K MCL spectra taken for the bright and dark parts of the image. The spectrum of the bright parts of the image consists of the 3.46 eV bandedge line, whereas the spectrum of the dark parts is dominated by defect bands at 3.43 and 3.25 eV, which are associated with SFs and partial

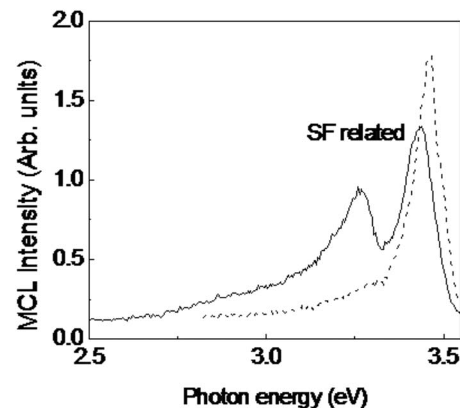

FIG. 4. (Color online) 90 K MCL spectra taken in the bright (dashed curve) and dark (solid curve) parts of the image in Fig. 3.

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dislocations.[19,20] Thus the elevated parts of the grown *a*-GaN layer show low SF and partial dislocation density, while thinner portions of the films still display a relatively strong signal from SFs.

In summary, growing thick GaN films by HVPE on Si (100) with Al anodic oxide nanomasks yields good quality nonpolar *a*-GaN with lowered density of SFs comparable to the results obtained by selective epitaxy or by using advanced buffer schemes.[14,18] Commonly when growing on Si(111) or Si(110) one gets polar *c*-GaN films,[5,6] while for growth on Si (100) one gets either cubic GaN (Ref. 21) or wurtzite *c*-GaN (Ref. 22) depending on the buffer scheme. The growth mechanism starts by growth of small crystallites in the open channels of the mask with subsequent preferential growth of the grains in the $[11\bar{2}0]$ direction. The GaN films self-detach from the Si substrates, with the breaking plane going through the substrate close to the interface with the anodic oxide.

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