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Growth of GaN free from cracks on a (111)Si substrate by selective metalorganic vapor-phase epitaxy

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The selective metalorganic vapor-phase epitaxy of wurtzite GaN was performed on a (111) silicon substrate using SiO_2 grid mask pattern. Within window regions of (0.2–0.5) mm×(0.2–0.5) mm, GaN films free from cracks were achieved. The full width at half maximum of the (0004) X-ray rocking curve was as narrow as 388 arcs and that of the band edge emission was 18.6 meV at 77 K. The band edge emission peak energy was redshifted. The redshift is reduced slightly in a sample grown on small windows. This suggests that the biaxial strain due to the thermal expansion coefficient mismatch is partly relaxed on small windows. *© 2002 American Institute of Physics.* [DOI: 10.1063/1.1432764]

The growth of III nitrides on a silicon substrate will open a new possibility in the field of opto-electronics devices. By molecular-beam epitaxy, thin GaN films have been successfully achieved on silicon (111) or (001) substrates. But the sample is often a mixture of cubic and wurtzite structures.[1,2] The GaN grown on a Si substrate by metalorganic vapor-phase epitaxy (MOVPE) exhibits, on the other hand, high crack density which is attributed to the large mismatch in the thermal expansion coefficients between GaN and Si (55%).[3–7] Several attempts were reported to improve the crystal quality by optimizing the formation process of an AlN intermediate layer,[8] or utilizing multiple step growth method.[9] But the effect of the thermal expansion coefficient mismatch is too large to suppress the formation of cracks in the grown films.

An elegant method was proposed by Matsuda and Akasaki to suppress cracks in the hetero-epitaxial growth of a material with large thermal expansion coefficient mismatch.[10] They made a grid mask pattern with a SiO_2 film on a GaP substrate to restrict the growth area and succeeded in obtaining crack free ZnS films within the window area. Following them, Shibata *et al.*[11] tried to get high quality GaN thick films on sapphire substrate by hydride vapor phase epitaxy and proved the feasibility of the selective area growth (SAG) method. In a recent paper, Zamir *et al.*[12] studied the MOVPE growth of GaN on Si(111). With a simple analysis, they found that the critical size free from crack is on the order of 15 μm if the thickness of the GaN film is 0.7 μm.

The crack density depends strongly on the growth conditions and quality of the crystals achieved, i.e., the average size of the crack free sample can be increased by manipulating the growth conditions as well as the postgrowth heat treatment. But the appearance of the cracks is quite random on the film, which gives a fatal difficulty in device applications. Thus, the control of the crack distribution in a large area film is the main issue of the present study.

We used a (111) silicon wafer as the substrate for the growth of wurtzite GaN.[3] A 70 nm thick SiO_2 layer was deposited by sputtering. Various grid mask patterns were formed with conventional photolithography on the substrate. The window region was a square of (200–500) μm×(200–500) μm and divided by (5–200) μm wide SiO_2 mask region. The SAG of GaN was performed in an atmospheric pressure horizontal MOVPE chamber, using trimethylaluminum (TMA), trimethylgallium (TMG), and ammonia (NH_3) as the source materials. After a heat treatment of the substrate, an AlN intermediate layer was deposited at 1150 °C by supplying ($TMA{:}NH_3$)=(1.83 μmol/min:2.5 slm). The AlN thickness was 30–50 nm. Immediately after the formation of the intermediate layer, the SAG of GaN was performed at 1090 °C for 40 min by supplying ($TMG{:}NH_3$)=(18.3 μmol/min:2.5 slm). A single crystal GaN was grown selectively within the window region, of which the *c* axis was normal to the (111)Si substrate surface and the ⟨1-101⟩ axis was parallel to the ⟨−1−12⟩ axis of the silicon substrate. The thickness of the GaN crystal was typically 1.5 μm at the center region of the window area. More details of the heat treatment of the substrate and the growth process were reported elsewhere.[8,13]

The device size of the modern light emitting diode (LED) and laser diode (LD) is on the order of or less than several hundreds of micron. This is the reason why we have tested the SAG on square windows of which width is 200–500 μm. In case of 500 μm windows, the GaN grown on the window often exhibited cracks. For windows less than 400 μm, we could have obtained GaN films free from cracks over a wide area on the substrate. In case of 200 μm windows, we have found no cracks on the whole area. Typical surface microscope images of the SAG-GaN are shown in Fig. 1. In case of SAG, we can see that the GaN is free from cracks. Figure 1(b) represents the result obtained using masks of 200 μm wide. The peripheral morphology is due to ridge growth, which is attributed to the lateral diffusion of chemical species on the mask region.[13] The ridge growth should be suppressed if we are to fabricate uniform thin films such as quantum-well structures. To make the layer as uniform as possible, the effect of the mask width on the ridge growth was studied. In case of samples obtained by using a

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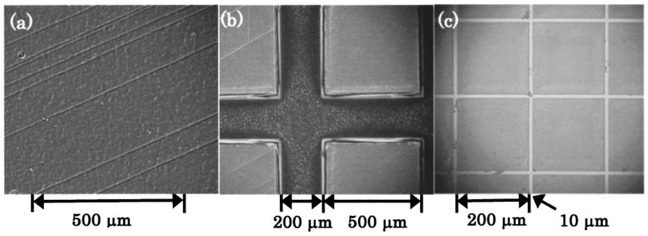

FIG. 1. Microscope picture of GaN/AlN/Si. (a) GaN film grown without grid mask. (b) GaN grown on 500 μm wide square windows with 200 μm wide masks. (c) GaN grown on 200 μm square windows with 10 μm wide masks. By the SAG method the crack density is much reduced and in (c) no cracks are observed. In (b) and (c), the ridge growth took place. The width of the ridge growth is around 20 μm.

50 μm wide mask, the ridge growth was also observed. But by reducing the mask less than 10 μm, the ridge growth was practically suppressed. At the edge of the square crystal, the grown layer is only 10% thicker than at the center. These results show that use of masks less than 10 μm will give uniform and crack free GaN films on a (111) silicon substrate, which might be applicable to modern LED or LD.

The results shown here are in contrast to those shown by Zamir *et al.*,[12] where the film size free from cracks was one order of magnitude smaller. In the case of ZnS/GaP, the difference in the thermal expansion coefficient is 35%, which is a little bit smaller than the present GaN/Si case. Matsuda *et al.* achieved crack free 500 μm$\times$500 μm ZnS film at the thickness of 30 μm.[10] According to their results, the surface morphology is rather rough and includes hillocks/pits. This suggests presence of grain boundaries due to the columnar structure of the ZnS, which may reduce the strength against the tensile strain. The fact that we could have achieved crack free films of the same size but as thin as 1.5 μm might be due to the high quality of the material.

Figure 2 shows typical x-ray rocking curves of the samples. The ω-scan axis was along the $\langle$11-20$\rangle$ axis of GaN. Apparently, the full width at half maximum (FWHM) of the (0004) diffraction peak of the SAG-GaN is much improved as compared to that for a sample grown by a conventional method. Moreover, the samples on narrower windows exhibit narrower FWHM. The value of 388 arcs obtained for a 200 μm window is extremely narrow for GaN grown on silicon substrate by MOVPE. The c-axis orientation might be fluctuated by the cracks and/or the appearance of ridge growth, but the narrower value obtained in the present experiments proves that the SAG method is effective to improve the crystal quality of GaN as well as to reduce crack density.

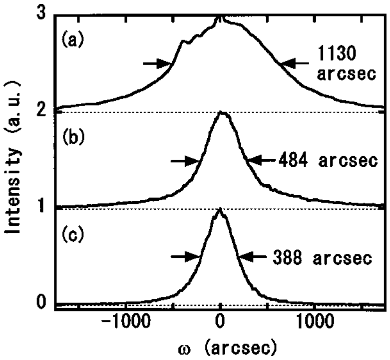

FIG. 2. (0004) X-ray-rocking curves of GaN/AlN/Si in ω-scan modes. (a) GaN by conventional method, (b) SAG-GaN grown on 500 μm square windows, (c) SAG-GaN grown on 200 μm square windows.

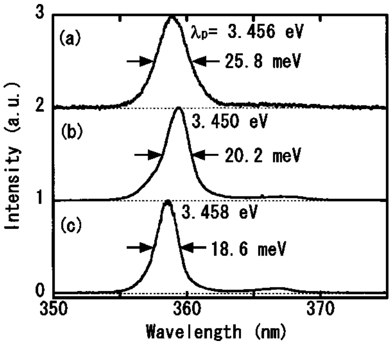

FIG. 3. PL spectra of GaN/AlN/Si at 77 K (a) GaN by conventional method, (b) SAG-GaN grown on 500 μm square windows, (c) SAG-GaN grown on 400 μm square windows. (d) SAG-GaN grown on 200 μm square windows. The peak energy is shown in eV and the FWHM in meV.

The photoluminescence (PL) spectra were investigated at 77 K. In all samples, we observed strong band edge emission and weak yellow band emission, which suggested the low point defect density in these samples. Figure 3 shows the edge emission spectra. The relative intensity of the edge emission was weak in samples on 500 μm wide windows but each spectrum was normalized by the peak height in Fig. 3. The FWHM is apparently reduced in narrow windows. The narrowest one has 18.6 meV. The weak subsidiary peak at 70 meV below the main peak is attributed to the incorporation of oxygen.[14] But we could not observe the donor–accepter pair emission, which suggests high optical quality of the samples.

As shown in Fig. 3, the edge emission peak for SAG-GaN is at around 358 nm which is redshifted as compared to the peak shown for samples grown on sapphire substrate. The difference is as large as 3 nm (or 30 meV). This is attributed to the tensile strain given by the thermal expansion coefficient mismatch between GaN and Si. It is notable that the magnitude of the redshift and FWHM depend on the window size as shown in Fig. 4. On windows less than 400 μm, on the other hand, the redshift is slightly reduced as compared to those on 400 or 500 μm wide windows. Since we could not find any cracks on 200 μm windows, the strain is supposed to be partially relaxed already by virtue of the small size of the films. Since some of the samples on 500 μm wide windows exhibit cracks, the wide FWHM is attributed to the fact that the strain has been partially relaxed by the cracks which are however not uniformly distributed over the sample surface.

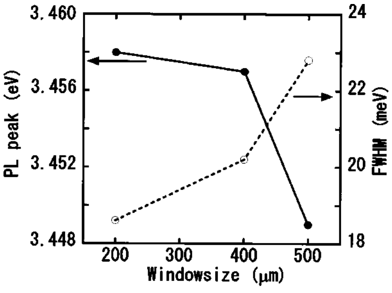

FIG. 4. Dependence of the PL peak energy (solid line) and FWHM (broken line) on the window size.

In summary, we have achieved GaN films free from cracks on Si by SAG-MOVPE. The area of the crack free GaN can be more than 200 μm$\times$200 μm for 1.5 μm thick sample. X-ray-rocking curves showed that the orientation fluctuation of the c axes was much reduced by the SAG method. The PL spectra showed strong band edge emission and weak yellow band emission. It was found that the red-shift of the edge emission is determined by the size of the windows.

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