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Single Crystalline GaN Epitaxial Layer Prepared on Nano-Patterned Si(001) Substrate

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The authors report the growth of GaN epitaxial layers on nano-patterned Si(001) substrates prepared by the standard facilities used in integrated circuit (IC) industry. It was found that we could achieve high-quality single crystalline GaN by using the 50 nm SiO_2 recess patterned Si(001) substrate. It was also found that we can reduce the tensile stress in GaN epitaxial layer by about 95% using the nano-patterned Si(001) substrate, as compared to the conventional un-patterned Si(111) substrate.
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GaN-based high-brightness light-emitting diodes (LEDs) were first demonstrated in 1993.[1] Since then, the development of these LEDs is very successful over the past few decades. With a wide direct bandgap, GaN-based materials can also be used as laser diodes,[2] high electron mobility transistors[3] and ultraviolet (UV) photodetectors.[4] Conventional GaN-based epitaxial layers were grown either on sapphire or on SiC substrates. However, SiC substrates are expensive while sapphire substrates are electrical insulators with poor thermal conductivity. Instead of using these substrates, epitaxy of GaN on Si is cost effective. To grow GaN on Si, Si(111) substrate is normally used due to its 6-fold atomic arrangement (i.e., 3-fold symmetry) at the surface which is more suitable for the epitaxial growth of hexagonal GaN.[5] However, Si(001) substrates are used in the mainstream silicon technology. Thus, growing GaN on Si(001) is preferred for the integration of GaN-based optical devices with Si-based microelectronics. However, previous studies showed that GaN growth on Si(001) leads to polycrystalline structures or very rough surface.[5] This is mainly due to the fact that the 4-fold symmetry of Si(001) allows GaN to grow with two preferred rotational alignments. The large mismatches in thermal expansion coefficient and lattice constant between Si and GaN also lead to high threading dislocation (TD) density in the epitaxial layer and possible formation of crack networks. It has been shown that these problems can be partially solved by using tilted Si(001) substrate[6] and/or by inserting a proper intermediate layer.[7]

Patterned substrate and epitaxial lateral overgrowth (ELO) are two commonly used methods to reduce TD density in GaN prepared on sapphire substrate. Similar reduction in TD density has also been reported for GaN on Si(111).[8,9] It should be noted the features used in conventional patterned substrate and ELO are both in the order of micrometers. Recently, it has been shown both theoretically and experimentally that TD density in GaN epitaxial layers can be further reduced by nanometer-sized patterns.[10] This was attributed to the fact that nano-scaled features can effectively minimize the strain energy induced by lattice mismatch. To prepare nano-patterns, one can use nano-sphere lithography,[11,12] laser holography[13] or anodic aluminum oxide (AAO) process.[14] Using these methods, it has been shown that nano-patterns can indeed further reduce TD density in GaN prepared on sapphire substrate.[15,16] However, it is difficult to apply these methods to large-sized substrates with good uniformity and good reproducibility. On the other hand, nanometer-sized patterns can be formed on large-sized Si(001) substrates easily in current integrated circuit (IC) industry. In this study, we report the growth of GaN on Si(001) substrates nano-patterned by e-beam lithography and dry etching. Physical and optical properties of the GaN epitaxial films will also be discussed.

Experimental

Prior to the growth of GaN epitaxial layers, we used standard IC processing facilities in Taiwan Semiconductor Manufacturing Company (TSMC) to form two different kinds of nano-patterns (i.e., SiO_2 recess and Si recess) on Si(001) substrates. We first cleaned the Si(001) substrates by standard RCA method. An e-beam lithography system was then used to define parallel stripes along the <100> direction on the chemically cleaned substrates. A dry etcher was subsequently used to define the nano-patterns with an etching depth of 200 nm. The etched regions were then filled with SiO_2 by plasma enhanced chemical vapor deposition (PECVD). For SiO_2 recess substrates, we immersed the substrates in dilute HF for 60 s to remove 50 nm of the deposited SiO_2. As shown in Fig. 1a, the width of the remaining Si nano-stripes was kept at 50 nm while the spacing between two neighboring Si nano-stripes was kept either at 50 nm (i.e., 50 nm SiO_2 recess) or at 200 nm (i.e., 200 nm SiO_2 recess). For Si recess substrates, we used dry etching to remove the exposed Si nano-stripes. As shown in Fig. 1b, the width of the remaining SiO_2 nano-stripes was kept at 50 nm while the spacing between two neighboring SiO_2 nano-stripes was kept either at 50 nm (i.e., 50 nm Si recess) or at 200 nm (i.e., 200 nm Si recess). The nano-patterned substrates were subsequently loaded onto a metalorganic chemical vapor deposition (MOCVD) system to grow the GaN epitaxial layers. Figures 2a and 2b show schematic diagrams of the growth steps for the samples prepared on SiO_2 recess substrates and Si recess substrates, respectively. After loading the nano-patterned substrates onto the MOCVD system, we treated the substrates in hydrogen ambient at 1080°C, followed by the growth of a 50-nm-thick low-temperature (LT) AlN nucleation layer at 720°C and a 1.5-μm-thick GaN layer at 1080°C.

For comparison, we also prepared GaN epitaxial layers on conventional un-patterned Si(111) substrate. As shown in Fig. 2c, the structure consists of a 50-nm-thick high-temperature (HT) AlN nucleation layer grown at 1240°C and a 2-μm-thick GaN layer grown at 1120°C. A transmission electron microscopy (TEM) was then used to analyze structural properties of the as-grown samples. Micro-photoluminescence (PL) characteristics of the samples were also measured by using a 3 mW continuous wave (CW) He-Cd laser operated at 325 nm as the excitation source. The luminescence signal generated from the samples was recorded by a lock-in amplifier at room temperature. Micro-Raman measurements were also performed at room temperature using a 532 nm yttrium aluminum garnet (YAG) laser as the excitation source.

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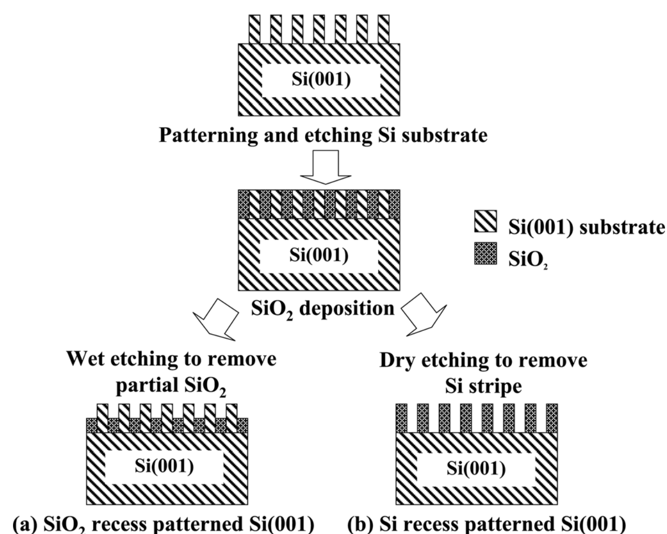

Figure 1. Schematic diagrams of the processing steps used to prepare (a) SiO_2 recess patterned Si(001) substrate and (b) Si recess patterned Si(001) substrate.

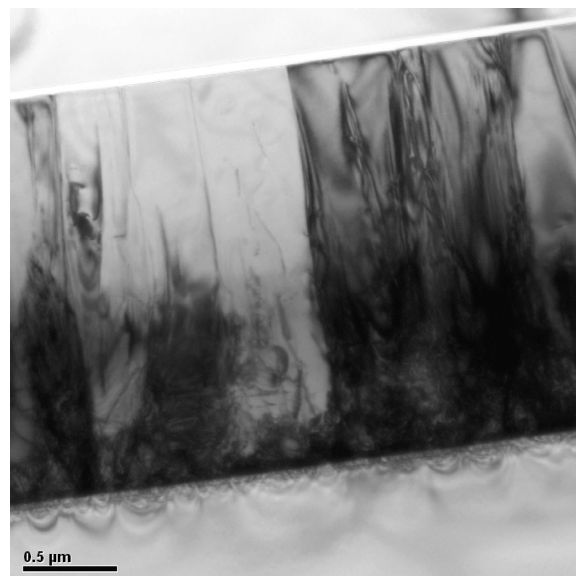

Figure 3. Cross-sectional TEM image for the samples prepare on un-patterned Si(111) substrate.

Results and Discussion

Figure 3 shows cross-sectional TEM image of the sample prepared on un-pattern Si(111) substrate. It can be seen clearly that a significant amount of TDs were generated from the GaN/Si(111) interface due to the large mismatches in lattice constant and thermal expansion coefficient between GaN and Si(111). Similar result has also been reported elsewhere.[8,9] Figures 4a–4d, show cross-sectional TEM images of the samples prepared on 50 nm SiO_2 recess patterned Si(001) substrate, 50 nm Si recess patterned Si(001) substrate, 200 nm SiO_2 recess patterned Si(001) substrate and 200 nm Si recess patterned Si(001) substrate, respectively. For the sample prepared on 50 nm Si recess patterned Si(001) substrate, it was found that LT AlN can not fill the 50 nm trench completely due to the large aspect ratio. As a result, a LT AlN layer was formed, as shown in Fig. 4b. It is possible that the LT AlN was first grown on the SiO_2 nano-stripes and then extended horizontally to form a continuous planar-like layer. Since this LT AlN was initiated on top of the amorphous SiO_2, the subsequently deposited GaN layer will also become amorphous. As we increased the spacing between the neighboring SiO_2 nano-strips to 200 nm, it was found that LT AlN was deposited uniformly on the exposed Si(001) surface. As shown in Fig. 4d, we could thus achieve crystalline GaN epitaxial layer with the LT AlN serving as the nucleation layer. Grown vertically from the exposed Si(001) surface, it should be noted that the subsequently deposited GaN epitaxial layer should contain both hexagonal phase and cubic phase.

Figure 4a shows TEM image of the sample prepared on 50 nm SiO_2 recess patterned Si(001) substrate. With 50 nm spacing between two neighboring Si nano-stripes, it is difficult to initiate the growth vertically from the exposed SiO_2 surface. Thus, the growth should be initiated horizontally from the sidewalls of the Si nano-stripes. Similarly, TDs generated during the initial growth should also be generated from the sidewalls of the Si nano-stripes, propagated horizontally and eventually terminated at the sidewalls of the neighboring Si nano-stripes. As a result, we could achieve single crystalline GaN epitaxial layer with only few TDs. As we increased the spacing between two neighboring Si nano-stripes to 200 nm, vertical growth initiated from the exposed SiO_2 surface should become dominated. As shown in Fig. 4c, the subsequently deposited GaN layer will also become amorphous.

Figure 5 shows micro-Raman spectra measured from samples prepared on un-patterned Si(111) substrate, 200 nm Si recess patterned Si(001) substrate and 50 nm SiO_2 recess patterned Si(001) substrate. For the sample prepared on un-patterned Si(111) substrate, only one Raman peak at 565.0 cm^{-1} was observed. This peak should be attributed to the high frequency E_2 mode of the hexagonal GaN.[17,18] Similar peaks located at 566.3 and 566.9 cm^{-1} were also

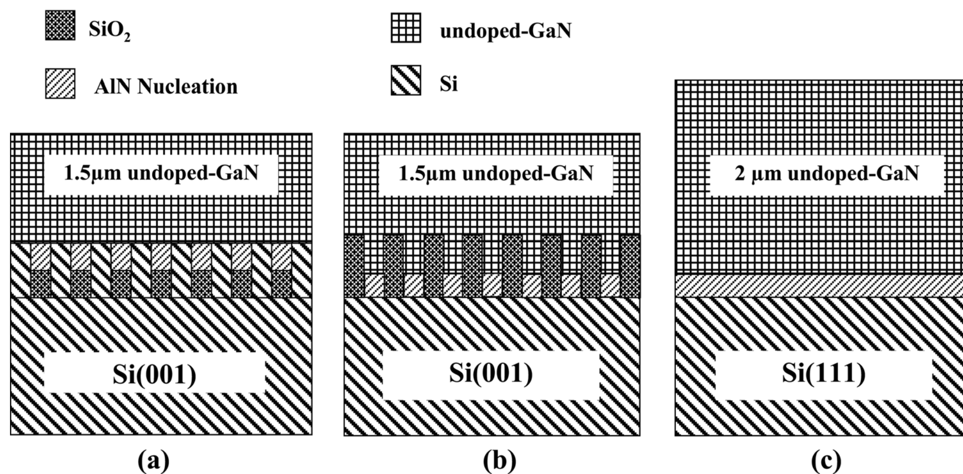

Figure 2. Schematic diagrams of the MOCVD growth steps for (a) samples prepared on SiO_2 recess substrates and Si recess substrates, (b) samples prepared on Si recess patterned Si(001) substrate, and (c) samples prepared on Si(111) substrate.

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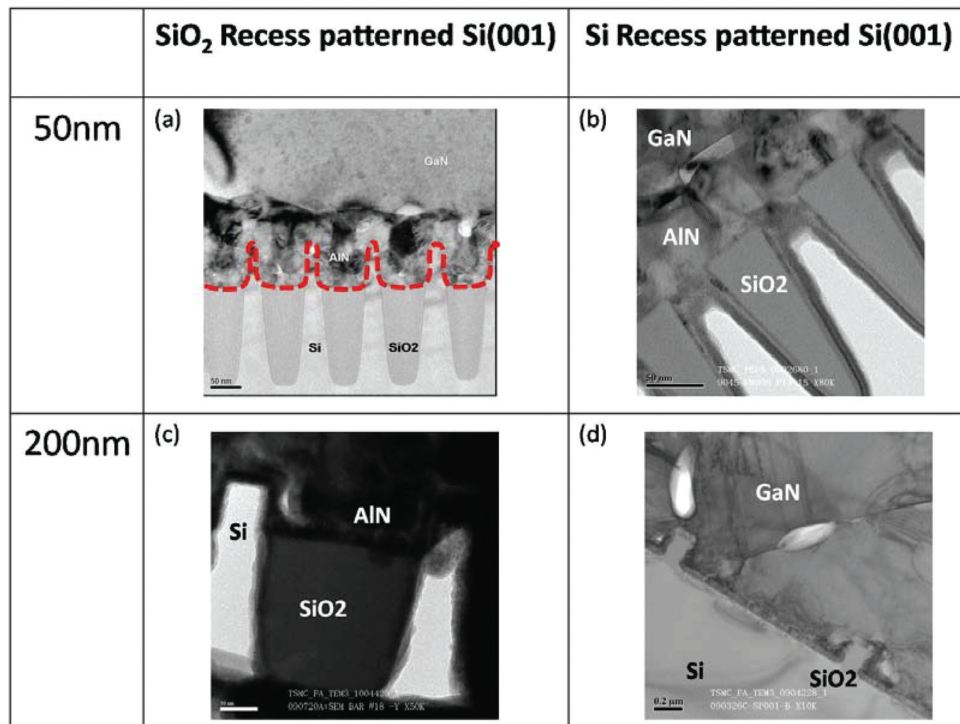

Figure 4. (Color online) Cross-sectional TEM images of the samples on (a) 50 nm SiO_2 recess patterned Si(001) substrate, (b) 50 nm Si recess patterned Si(001) substrate, (c) 200 nm SiO_2 recess patterned Si(001) substrate and (d) 200 nm Si recess patterned Si(001) substrate.

observed from the samples prepared on 200 nm Si recess patterned Si(001) substrate and 50 nm SiO_2 recess patterned Si(001) substrate, respectively. It has been shown previously that the E_2 mode Raman peak of the unstrained hexagonal GaN is located at 567.0 cm^{-1}.[19] In other words, the Raman peak position red-shifted by 2.0, 0.7, and 0.1 cm^{-1} for the samples prepared on un-patterned Si(111) substrate, 200 nm Si recess patterned Si(001) substrate and 50 nm SiO_2 recess patterned Si(001) substrate, respectively. It has also been reported that the relationship between the E_2 mode Raman peak shift ($\Delta\omega$) and the in-plane biaxial stress (σ_{xx}) can be expressed as: $\Delta\omega = 4.3\sigma_{xx}$ cm^{-1} GPa^{-1}.[20] Using the equation, it was found that in-plane biaxial stress in the sample prepared on conventional un-patterned Si(111) substrate was around 0.48 GPa. In contrast, in-plane biaxial stress in the sample prepared on 200 nm Si recess patterned Si(001) substrate was 0.16 GPa while the sample prepared on 50 nm SiO_2 recess patterned Si(001) substrate was only around 0.023 GPa. In other words, we can reduce tensile stress in the GaN epitaxial layer by about 95% using the 50 nm SiO_2 recess patterned Si(001) substrate, as compared to the conventional un-patterned Si(111) substrate. Other than the E_2 mode Raman peak of the hexagonal GaN, an additional peak located at 557 cm^{-1} was also observed from the sample prepared on 200 nm Si recess patterned Si(001) substrate. This peak should be attributed to TO mode of cubic GaN.[21,22] The observation of this peak indicates that GaN epitaxial layer prepared on 200 nm Si recess patterned Si(001) substrate exhibits both cubic and hexagonal phases.

Figure 6 shows micro-PL spectra measured from the samples prepared on un-patterned Si(111) substrate, 200 nm Si recess patterned Si(001) substrate and 50 nm SiO_2 recess patterned Si(001) substrate. As expected, it was found that only one PL peak located at 365 nm was observed from the sample prepared on un-patterned Si(111) substrate. This peak is attributed to band edge emission of the stable hexagonal GaN.[23] In contrast, one extra peak located at

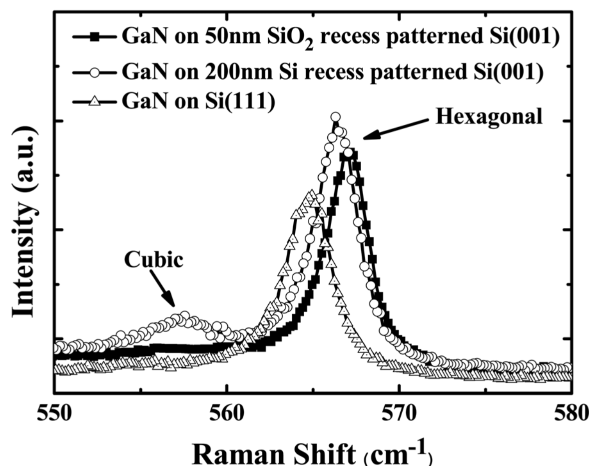

Figure 5. Micro-Raman spectra measured from the samples prepared on un-patterned Si(111) substrate, 200 nm Si recess patterned Si(001) substrate and 50 nm SiO_2 recess patterned Si(001) substrate.

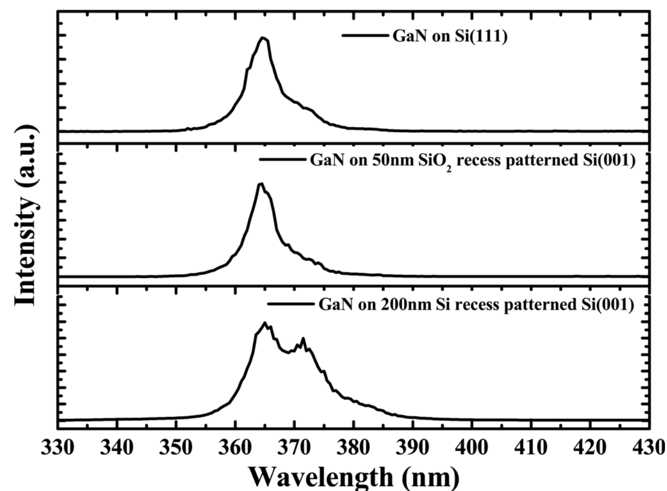

Figure 6. Room-temperature micro-PL spectra measured from the samples prepared on un-patterned Si(111) substrate, 200 nm Si recess patterned Si(001) substrate and 50 nm SiO_2 recess patterned Si(001) substrate.

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375 nm was observed from the sample prepared on 200 nm Si recess patterned Si(001) substrate. This peak is attributed to band edge emission of the metastable cubic GaN.[24,25] The observation of the peak at 375 nm again indicates that some cubic GaN was indeed formed in the epitaxial layer. This suggests that hexagonal phased GaN and cubic phased GaN co-existed in this particular sample. Such an observation also agrees with the micro-Raman result shown in Fig. 5. Similar to the sample prepared on un-patterned Si(111), it was found that only the hexagonal phased GaN peak at 365 nm was observed from the sample prepared on 50 nm SiO_2 recess patterned Si(001) substrate. It should be noted that the 5.5 nm PL full-width-half-maximum (FWHM) observed from the sample prepared on 50 nm SiO_2 recess patterned Si(001) substrate was much smaller than that observed from the sample prepared on un-patterned Si(111) substrate (i.e., 10.2 nm). The significantly smaller FWHM indicates that the GaN epitaxial layers prepared on 50 nm SiO_2 recess patterned Si(001) substrate was single crystalline with good crystal quality. It also suggests that the nano-patterned Si(001) substrate proposed in this study is potentially useful for the performance improvement of GaN-based opto-electronic devices.

Conclusion

In summary, we report the growth of GaN epitaxial layers on nano-patterned Si(001) substrates prepared by the standard facilities used in IC industry. It was found that we could achieve high-quality single crystalline GaN by using the 50 nm SiO_2 recess patterned Si(001) substrate. It was also found that we can reduce the tensile stress in GaN epitaxial layer by about 95% using the nano-patterned Si(001) substrate, as compared to the conventional un-patterned Si(111) substrate.

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