論文の内容の要旨

論文題目　Stress and quality engineering of GaN growth on Si with in-situ wafer curvature analysis
（In situウエハ曲率解析によるシリコン上窒化ガリウム成長における応力・結晶品位の制御）

氏　名　劉　才

This work has been devoted to the clarification of basic growth mechanism of GaN on Si employing AlN buffer layer and AlN interlayers, including the stress behavior of both GaN and AlN layers as well as the influence of AlN buffer and interlayers on the quality of GaN, based on the in-situ curvature monitoring and other characterizations. The unique points of this work are as follows.

1. A model of ideal AlN interlayer to induce compressive stress in GaN layers has been proposed, based on systematic in-situ curvature monitoring and morphology observations. This model has pointed out the key features that ideal AlN interlayer should possess, which are small lattice constant close to neutral AlN and high-quality coherent upper interface of it. In most of the cases small lattice constant of the interlayer demands relaxed lower interface of it.
2. A routine of arbitrary wafer bow design has been discovered and a program to realize it has been produced. Prior to applying this routine, the strain and stress states in every individual AlN and GaN layer under certain growth conditions should have been known. After setting the mechanical properties of AlN and GaN layers, arbitrary wafer bow design is available. This routine was put forward for the first time.
3. Prototypes of innovative AlN interlayers have been invented and tested, following the model of ideal AlN interlayer. They are one-step pulse-injection method AlN IL, two-step low-temperature/pulse-injection AlN IL and two-step low-temperature/high-temperature AlN IL. All the interlayers employed in previous studies were one-step conventional AlN. These new AlN ILs grown by special methods or with special structure have proved the reliability of the ideal AlN IL model and are induced larger compressive strain in GaN than normal conventional AlN ILs.

The work flow started with demonstration of successful GaN growth on Si (111) substrate by clearing all obstacles. Following the sample structure, conventional AlN buffer layer and AlN interlayer were investigated successively, including their growth conditions, stress introduction in overlying GaN and influence on GaN quality. Then based on the in-situ curvature monitoring data, strain states in every layer were analyzed and model of ideal AlN interlayer and a routine of arbitrary bow design were proposed. In the end, three prototypes of innovative AlN interlayer were designed and tested.

The most important benefit of GaN-on-Si is cost reduction by using Si substrate and the advantages of combining nitrides and silicon. The basic difficulties of the growth of GaN on Si lie in the large lattice constant mismatch (~ 17%) and thermal expansion coefficient mismatch (~ 54%) between them. This work aimed at understanding and clarifying the stress control mechanism and the roles of AlN buffer layer and AlN interlayers in the growth of GaN on Si.

The most serious difficulties included Si melt-back, Si surface nitridation and the stability of growth environment inside the reactor. There were many factors to facilitate Si melt-back, such as the adsorption of H atoms and cleanliness of Si surface, Ga contamination on Si surface from the parts in the reactor prior to the growth of AlN buffer layer, and most importantly the quality of AlN buffer layer. Ga contamination can be eliminated by using clean liner tube and susceptor parts, or AlN coating of the inner of reactor. Nothing was working to stop Si melt-back if the AlN buffer quality was poor. Finally, after changing for new gas purifiers, AlN buffer quality was improved significantly and Si melt-back was eliminated. Nitridation of Si surface was avoided by pre-flowing TMAl source, 10 s under flow rate of 22 sccm. Proper TMAl pre-flow also improved the GaN quality substantially. The chemical environment inside the reactor should be kept to be constant to yield controllable growth. The most important point was deposited GaN or Ga should be covered since they may cause Ga contamination on Si surface. Therefore, AlN coating or AlN dummy growth should be performed prior to every growth of GaN on Si.

Curvature can be adjusted by tuning the quality of AlN buffer layer which determines the stress in the 1st GaN, changing the growth conditions and the number of AlN interlayers, and tuning the growth mode and thickness of the 1st GaN. AlN buffer layer is important for both of the strain and quality of the 1st GaN. The AlN buffer with higher quality caused more compressive strain in the 1st GaN. It was initially compressively strained. The strain transited from being compressive to tensile as the thickness increased. However, the relaxation speed was depending on the growth conditions and quality of AlN buffer layer. The relaxation was very rapid and the critical thickness from being compressive strain to tensile was only several hundreds of nanometers, if the AlN buffer quality was low, such as grown at 1000 ℃. This was because of high-density defects in AlN buffer propagated into or caused more dislocations in overlying GaN and led to more rapid relaxation in GaN. The best AlN buffer layer which induced most compressive strain was grown at 1250 °C, under V/III ratio of 3005 and with thickness of 110 nm. Growth conditions of conventional one-step AlN interlayers were studied intensively, including thickness from 4.5 nm to 45 nm, growth temperature from 600 °C to 1200 °C and V/III ratio from 115 to 9015. Optimized AlN interlayer which induced the most compressive strain in GaN was grown at 900 °C, under V/III ratio of 1503 and with thickness of 9 nm. If it was too thin, it consisted of neighboring separated grain domains. In too thick AlN IL, cracking occurred. Both lost the capability of inducing compressive strain in GaN. If the growth temperature was too low like 600 °C, although with smaller lattice constant, since it was amorphous and not coalesced, the GaN on it relaxed rapidly. In high-temperature (> 1000 °C) ones, Ga diffusion into the interlayer happened, formed AlGaN with lattice constant more close to GaN and then small compressive strain in GaN. V/III has minimal influence on the performance of AlN IL if it was in the range from 500 to 1500. A model of ideal AlN IL was proposed based on the observations, with relaxed incoherent lower interface and high-quality coherent upper interface.

Based on the review of stress generation mechanisms in heterostructure, methodology of analysis was built. The tensile strain of AlN buffer layer ranged from 0.25% to 0.5% while the ideal misfit strain of AlN on Si is about 23.2%, which indicates that AlN buffer on Si is almost completely relaxed. The tensile strain decreases as the growth temperature is elevated. Such relaxation is favorable to stressing overlying GaN more compressively. Depending on the growth conditions of AlN buffer layer, the relaxation speed from compressive (~ -0.45%) to tensile strain (~ 0.05%) differs in the 1st GaN. The thickness of neutral point is only about 600 nm if the quality of AlN buffer is poor such as grown at 1100 °C. On the best AlN buffer, compressive strain through the large thickness of 1.75 um can be maintained. In spite of smaller lattice constant between AlN and GaN, tensile strain in AlN interlayers is much higher than that in AlN buffer, which ranges from 1.45% to 1.9%. The relaxation was in the range from 22% to 42%, which is about only one third of that in AlN buffer. These results show that the crystal quality of AlN interlayers is better than that of AlN buffer layer. The largest compressive strain in GaN layers is about 0.45% on AlN interlayer grown at 900 °C and with thickness of 9 nm, which is the same of the initial value of the 1st GaN. This leads to compressive stress of about 2 GPa in GaN and is 2~3 times of that in previous publications. Curvature due to thermal stress was also calculated. Based on the strain and stress states in every individual stage, the curvature curve can be recovered and the final curvature and wafer bow can be predicted, using the arbitrary bow design program. The size of Si wafer which the curvature and wafer bow is easiest to be controlled is 6 inch, 150 mm.

Quality elevation of AlN buffer layer and 3D growth mode are the most effective methods to improve the quality of GaN. The same with compressive stress introduction in the 1st GaN, it also demands high-quality AlN buffer layer to produce high-quality GaN, since the defects in the buffer can propagate into overlying GaN and they can also act as defect sources to generate new dislocations in GaN. Using conventional AlN, higher quality is achieved at higher temperature, 1250 ℃ in this work, under mediate V/III ratio of 3005. By alternating growth mode from 2D to 3D, the FWHM of XRD rocking curves of the plane (10-10) reduced from 820 arcsec to 570 arcsec while that of (0002) plane keeps almost constant. Thick AlN interlayer (≥ 22 nm) is favorable to the reduction of dislocations in GaN, but not for stress inducing. Since it doesn't coalesce completely, thin AlN IL (< 13 nm) increase the dislocation density in GaN by introducing new defects at the grain domain boundaries. Blue LEDs has been demonstrated.

Concepts of innovative prototypes of AlN interlayers were designed and tested, including one-step pulse-injection method AlN IL and two-step IL consists of lower low-temperature AlN and upper pulse-injection AlN or high-temperature AlN. In the structure of LT/HT-AlN, the growth temperature of HT-AlN higher is better such as 1200 ℃, with optimal thickness around 6 nm. They confirmed the solidity of ideal AlN model and showed the same performance of the best conventional AlN. For that the growth conditions of them were not optimized, more compressive strain in overlying GaN on them can be expected.