

論文の内容の要旨

論文題目 Structural control of nitride semiconductors and its application
to light emitting devices
(窒化物半導体成長における構造制御と発光素子への応用)

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Group III nitride semiconductors are promising materials for high efficiency light emitting devices because of their excellent optical properties. To date, most of the GaN-based devices have been fabricated on single crystalline sapphire substrates because of the high thermal stability and the high crystalline quality. However, the use of sapphire substrates often restrict applications of GaN-based devices because of their problems such as unavailability of large crystals and high fabrication cost. Many researchers have worked on development of new substrates such as amorphous SiO₂, metal foils, and other oxide crystals. Among these candidates, flat glass is an ideal substrate material for future LEDs because of its scalability and low cost. Despite these advantages of glass, GaN films on glass have not been put into practical use due to two serious problems. One problem is the amorphous nature of glass which causes poor crystalline quality of GaN films grown on glass. To overcome this problem, introduction of crystalline buffer layers is required before the growth of GaN films. Graphene is a suitable material as the buffer layers for the GaN growth, because large-area graphene films with highly c-axis oriented structures are available and can be transferred easily to glass substrates. The other problem is the low softening temperature of glass. Since the substrate temperature for GaN growth is usually above 1000°C in a conventional metalorganic chemical vapor deposition (MOCVD), it is not possible to use glass as the substrates for the growth of GaN with MOCVD. Fortunately, recent progress in the epitaxial growth techniques based on pulsed sputtering deposition (PSD) enables us to grow group III nitrides even at room temperatures. It is believed that this successful reduction in the growth temperatures is attributed to the high kinetic energies and the pulsed supply of the group III atoms, which assists the surface migration of the film precursors at the substrate surfaces. This striking nature of PSD may possibly allow us to fabricate nitride devices even below the softening temperature of flat glass in future. This study assessed the feasibility of nitride crystal growth on SiO₂ with graphene buffer layers grown by PSD as well as the application of this structure to the fabrication of LEDs.

In chapter 1, I provide a brief introduction to the concepts relevant to the study of the heteroepitaxial growth of group III-nitrides. In this chapter the growth of group III- nitride films on

several substrates is briefly discussed.

In chapter 2, the results for group III-nitrides grown on amorphous SiO₂ substrates with graphene buffer layers by PSD are presented. Firstly, effect of graphene buffer layers on the structural properties of the GaN films was investigated. In an SEM image of the GaN films grown without graphene buffer layers, the random and rough features were observed on the surfaces. On the other hand, GaN films with graphene buffer layers have a smooth surface morphology. Crystal orientations of the GaN films were evaluated by EBSD measurements. The GaN films without graphene buffer layers showed broad spots in the {0001} pole figures and ring shape patterns in the {10 $\bar{1}$ 2} pole figure, which indicates the poor crystalline quality with the random orientation in the in-plane directions. In contrast, the {0001} spot for the GaN films with graphene buffer layers was sharp and the {10 $\bar{1}$ 2} pole figure showed a clear six-fold rotational symmetry. This indicates that the crystalline quality of the GaN films is drastically improved by the use of graphene buffer layers. This improvement can probably be attributed to the epitaxial growth of GaN on the highly oriented graphene layers with the epitaxial relationship of (0001)_{GaN} // (0001)_{graphite} and [11 $\bar{2}$ 0]_{GaN} // [10 $\bar{1}$ 0]_{graphite}. However, an EBSD phase mapping revealed that both wurtzite (59%) and zincblende (39%) GaN coexist in the films. The poor phase purity of GaN may cause high-density crystalline defects such as stacking mismatch boundaries and degrade the device performance. Since the inclusion of zincblende phase in the GaN films is probably due to the interfacial reactions between GaN and graphene, 50-nm-thick AlN interlayers were introduced at the heterointerfaces in order to improve the GaN phase purity. An EBSD phase mapping revealed that the zincblende inclusion in the GaN films was drastically suppressed by the use of AlN interlayers. In the room-temperature PL measurements, the GaN films without AlN interlayers exhibited clear luminescence from zincblende phase at the peak wavelength at around 380 nm together with the dominant luminescence at 360 nm from wurtzite phase. On the other hand, the GaN films grown with AlN interlayers showed strong near-band-edge emission from the wurtzite phase with a negligible emission from zincblende phase. This result is quite consistent with the EBSD data. It was also found that the full width at half maximum (FWHM) values of x-ray rocking curves for the 0002 diffractions of the GaN films grown with and without AlN interlayers were 37 and 144 arcmin, respectively. These results indicate that the use of graphene buffer layers and the insertion of AlN interlayers allow us to grow high quality GaN films even on amorphous SiO₂. The polarity of the GaN films on graphene buffer layers was investigated, since polarity of wurtzite GaN: N- or Ga-polarity along its <0001> direction, gives serious impact on the device performance. The surfaces of the GaN films grown on AlN/graphene/SiO₂ were roughened seriously after KOH etching. This chemical vulnerability is the typical feature of the N-polar GaN. It is well known that N-polar GaN is not suitable for the device fabrications because N-polar GaN usually contains high densities of residual impurities. To obtain Ga-polar GaN films, the surfaces of the AlN interlayers were oxidized prior to the GaN growth. The

surface morphology of the GaN films with the surface-oxidized AlN interlayers remained unchanged after KOH etching, which indicate the formation of Ga-polar GaN films.

In chapter 3, the strain generation in the GaN films during the PSD growth is discussed. Heteroepitaxial films often suffers from the strain generation due to the mismatches in the lattice constants and the thermal expansion coefficients between the films and the substrates, since large strain cause crystalline defects such as cracks and dislocations. Therefore, strain control is quite important to grow high quality epitaxial films. Nevertheless, the *in-situ* measurement system of the strain was not been developed in the growth of group III nitride films by PSD. In this study, we developed an *in situ* measurement system of the wafer curvature to investigate the strain evolution during the growth by PSD. The wafer curvature measurement system uses a multibeam optical sensor to precisely measure the laser-beam deflection produced by strain-induced curved wafers. In this technique, it is also possible to measure the curvature of the samples along two axes perpendicular to each other, which enables us to investigate the anisotropic strain in the films, e.g., *a*-plane GaN films grown on *r*-plane sapphire. In the measurements, negative and positive changes in the beam separation mean the compressive and tensile strain, respectively. The beam separation during the GaN growth on sapphire showed a rapid change toward negative values, which indicates the generation of compressive strain in the GaN films. This large compressive strain in the GaN films on sapphire is most likely caused by the lattice mismatch between GaN and sapphire. On the other hand, it was found that the change in the beam separation during the GaN growth on SiO₂ with graphite buffer layers was quite small, indicating the small strain in the GaN films. We also investigated the strain with *ex-situ* XRD measurements. The *c*-axis lattice parameter of the GaN films was determined from the 2 θ / ω diffraction peaks detected in a Bragg symmetrical set-up. The thickness dependence of the strain in *c*-direction of the GaN films revealed that the strain in the GaN films grown on sapphire was as large as 1%, while that on SiO₂ with graphite buffer layers showed small strain values less than 0.4 %. The small strain in the GaN films grown with graphite buffer layers is probably attributed to the weak interaction in the graphite layers.

Chapter 4 covers the fabrication of the LED structure on amorphous SiO₂ substrates with graphene buffer layers. To investigate the feasibility of InGaN based display on amorphous materials, we fabricated LEDs on SiO₂ with graphite buffer layer by PSD. The LED structures on surface-oxidized AlN/graphite/SiO₂ were composed of a 1- μ m-thick n-GaN layer, 5-period InGaN/GaN MQWs, and a 500-nm-thick p-GaN layer. Existence of clear satellite peaks around the GaN 0002 diffraction in the XRD curve indicates the smooth and abrupt interfaces of the MQWs. The curve fitting of the experimental data revealed that the MQWs consist of 3.1-nm-thick In_{0.21}Ga_{0.79}N wells and 8.6-nm-thick GaN barriers. Green luminescence was clearly observed at the peak wavelength of 520 nm in RT-PL measurements. It was also found that the PL integrated intensity of the LED on SiO₂ with graphite buffer layers was approximately 14 % when compared

with a blue luminescence from a commercially available blue LED whose internal quantum efficiency (IQE) was approximately 50 %. The IQE of the LED structure on SiO₂ with graphite buffer layers was also estimated by taking the ratio of the integrated PL intensities at 13 and 300 K (I_{300K}/I_{13K}), assuming that nonradiative recombination processes are negligible at 13K. Temperature dependence of the integrated PL intensity revealed that the ratio of I_{300K}/I_{13K} was 7.4 %, which is comparable to the values of green LEDs on conventional sapphire substrates. After the deposition of Pd/Au and In ohmic electrodes on p- and n-type GaN surfaces, operation of the LED was tested. The EL intensity increases with the injection current varied from 2.1 to 10.8 mA. We have also succeeded in the operation of blue and red LEDs by changing the In compositions in the InGaN wells. These results indicate the present technique possibly allow us to fabricate full color displays on large-area amorphous substrates.

In chapter 5, I summarize this study and discuss future prospects. By demonstrating that full-color LEDs can be fabricated on amorphous substrates, we suggest that since sputtering is very frequently used in the liquid crystal display industry, it is an established process that could be adapted to fabricate large-area inorganic LED displays on glass substrates. It should also be noted that state-of-the-art technology in the glass industry can offer roll-to-roll processing of flexible glass foils. The combination of these techniques can lead to the development of large-area flexible inorganic devices in the future.