Preparation of GaN Quantum Dots by MOVPE

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Gallium nitride and AlGaN films were grown on on–axis 6H–SiC(0001) substrates by MOVPE (metalorganic vapor phase epitaxy). The 6H–SiC substrates were dipped in a buffered HF solution for 30 min to remove the oxide layer. The RHEED (reflection high energy electron diffraction) pattern of these 6H–SiC substrates indicated the (2×2) surface reconstruction. After that, AlN buffer layer with 3 nm thick was deposited on 6H–SiC substrate at 1080ºC by MOVPE. AlN layer on the 6H–SiC substrate showed the (3×1) surface reconstruction by RHEED observations. $Al_{0.1}Ga_{0.9}N/Al_{0.2}Ga_{0.8}$ /N layer were grown on AlN buffer layer. GaN quantum dots (QDs) were formed by introducing Si on $Al_{0.1}Ga_{0.9}N/Al_{0.2}Ga_{0.8}$ N/AlN (buffer layer)/6H–SiC(0001). The shift of the photoluminescence peak of GaN QDs in the high energy side was observed.

INTRODUCTION

Column III–nitride semiconductors are gathering great interest from the view–point of its application to optical devices, especially blue and ultraviolet light emiting diodes (LEDs) and laser diodes (LDs), as well as electronic devices because of its wide band gap nature[1]. These films and devices are grown epitaxi–ally on sapphire (Al_2O_3) or silicon carbide (SiC) substrates. The large difference in lattice constants and thermal expansion coefficients between the sapphire or silicon carbide substrate and the III–nitride semi–conductor has made it difficult to grow high quality nitride films on these substrates. During the late 1980s, the first highly efficient nitride–based LEDs were realized when researchers discovered a method of pro–ducing high–quality nitride epilayers on sapphire substrates by inserting an initial AlN[2] or GaN buffer layer grown at low temperature[3,4]. Growing this buffer layer on a sapphire substrate greatly improves the morphology of the subsequently grown GaN layer. Shen et.al. have reported that the growth mode can be changed by introucing Si before GaN growth, where the Si is believed to play an important role in the change of the AlGaN surface free energy [5]. In this paper, GaN and AlGaN films were grown on on–axis 6H–SiC(0001) substrates by MOVPE. SiC possesses a lattice constant and a thermal expansion coefficient that are much more compatible with GaN than those of sapphire. Similar to the nitrides, SiC is tetrahedrally coordinated and has a polar surface. Nitride epitaxy is generally performed on the Si–termi–nated growth face rather than the C–terminated one, due to differences in surface stability. GaN quantum–dots (QDs) were formed by introducing Si on $Al_{0.1}Ga_{0.9}N/Al_{0.2}Ga_{0.8}N$/AlN buffer layer/6H–SiC (0001).

EXPERIMENTAL PROCEDURE

The vertical–type MOVPE system used in this study consists of three gas flow channels in the reactor, which are capable to separately introduce N_2, III–metalorganic sources and ammonia (NH_3) onto the susceptor region. The susceptor is SiC–coated graphite and is heated by rf induction. On–axis 6H–SiC(0001) substrates were initially thermal–oxidized for 4 hrs and then cleaned by dipping in a buffered HF solution for 30 min to remove the oxide layer. Substrates were loaded into the reactor and then elevated to 1100 for 10 min in the stream of H_2. After thermal cleaning at 1100 for 10 min in the stream of H_2, AlN buffer layer with 3 nm thick was grown on 6H–SiC substrate at 1100 by MOVPE.

Table 1. Preparation conditions of GaN quantum-dots.

Total pressure (Torr)	700
Growth rate (nm/h)	1600
Growth temperature (℃)	1100
NH_3 flow rate (SLM)	1.5
TMAl flow rate (SCCM)	3 ~ 5
TMGa flow rate (SCCM)	2.6 ~ 4.2
TESi flow rate (nmol/min)	200
V/III ratio	6600 ~ 10194
Al/Ga ratio	0.10 ~ 0.23
Carrier gas H_2 flow rate (SLM)	0.5 ~ 0.9
Carrier gas N_2 flow rate (SLM)	0.4

Fig.1.Growth sequence of GaN/$Al_{0.1}Ga_{0.9}N$/$Al_{0.2}Ga_{0.8}N$/AlN/6H–SiC (0001).

$Al_{0.1}Ga_{0.9}N$ and $Al_{0.2}Ga_{0.8}N$ were grown on AlN buffer of 6H–SiC substrates. Tetraethylsilane (TESi) was introduced at a flow rate of 200 nmol/min with H_2 carrier gas before GaN growth onto $Al_{0.1}Ga_{0.9}N$ surface. When TESi was intrroduced NH_3 supply was stopped. After that,NH_3 was supplied again and GaN was grown. Preparation conditions of GaN QDs are listed in Table 1 and the growth sequence of GaN QDs is shown in Fig.1. Crystalline quality of the films was determined by RHEED, X–ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Cathodoluminescence (CL) measurement was carried out at 30 ~ 300K by using electron beam accelerated at 10 kV. Photoluminesence measurement carried out at 15 ~ 300K.

RESULTS and DISCUSSION

On–axis 6H–SiC(0001) substrates were thermally oxidized for 4 hrs and cleaned by dipping in a buffered HF solution for 30 min to remove the crystalline imperfections of substrate surface and to make the Si–terminated growth face. These surface–treated 6H–SiC substrates indicate the RHEED pattern of the (2×2) surface reconstruction. After thermal cleaning at 1100 for 10 min in the stream of H_2, AlN buffer layer with 3 nm thick was deposited on the Si–terminated growth face at 1100 by MOVPE. The RHEED pattern of AlN buffer layer indicated the (3×1) surface reconstruction. $Al_{0.1}Ga_{0.9}N$/$Al_{0.2}Ga_{0.8}N$ layer were grown on AlN buffer layer. Crystal quality of AlGaN/AlN buffer layer on the surface–treated 6H–SiC substrate was characterized by XRD and RHEED. Fig.2 shows the RHEED pattern and the XRD spectrum of $Al_{0.22}Ga_{0.78}N$ layer were grown on AlN buffer layer. V/III ratio, Al composi–tion and the thickness of AlGaN films were 10200, 0.22 and 800nm, respectively. As shown in Fig.2, the peak associated with (0002) was observed at 2θ=34.9 °with an FWHM of 0.37 degree. Cathodoluminescence spectrum from AlGaN layer on a thin AlN buffer (3nm)/6H–SiC(0001) at 30 K were shown in Fig.3. This AlGaN layer has V/III ratio of 8064, and has a good crystallinity and surface morphology. The FWHM of CL peak was about 7nm peaking at 331nm.

Fig.2. RHEED pattern and X–ray diffraction pattern of AlGaN/AlN films on the surface–treated 6H–SiC(0001)

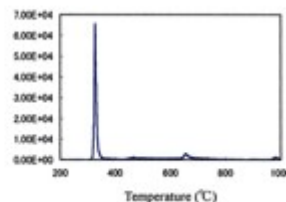
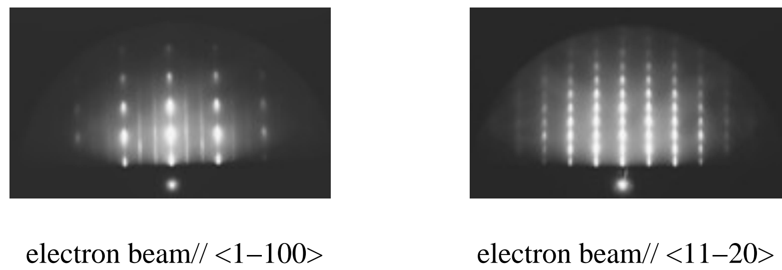


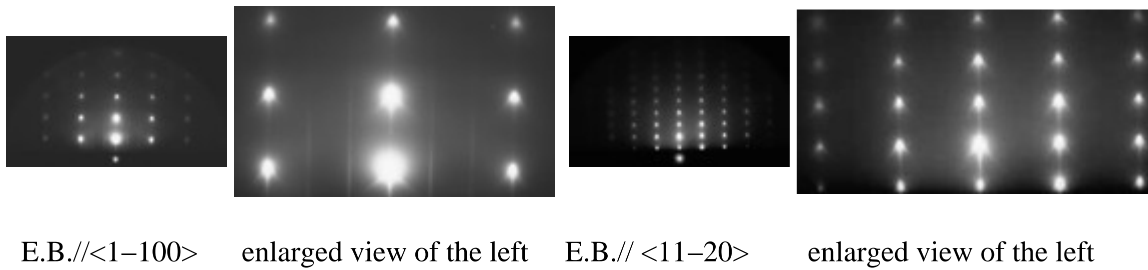
Fig.3 CL spectrum from AlGaN film on 6H–SiC at 30K.

The GaN growth was formed by introducing Si on $Al_{0.1}Ga_{0.9}N/Al_{0.2}Ga_{0.8}N$/6H–SiC. Tetraethylsilane was introduced at a flow rate of 200 nmol/min with H_2 carrier gas before GaN growth onto $Al_{0.1}Ga_{0.9}N$surface. When TESi was introduced, NH_3 supply was stopped. After that, NH_3 was supplied again and GaN was grown. When TESi was introduced, NH_3 supply was stopped. After that, NH_3 was supplied again and GaN was grown. The surface of $Al_{0.1}Ga_{0.9}N$ modified by the introduction of TESi indicates the streak (3×1) surface reconstruction as shown in Fig.4, and is a flat surface. The GaN QDs were grown on the modified $Al_{0.1}Ga_{0.9}N$ surface by supplying TMGa (trimethylgallium) and NH_3 with H_2 carrier gas for 30 sec. The RHEED patterns are shown in Fig.5. As the RHEED patterns indicate the inverted –V– shaped streak pattern, GaN QDs seem to have been formed, although in MOVPE growth. With that the growth time becomes 60 sec, GaN QDs kept the growth more and more, and the RHEED pattern



electron beam// <1–100> electron beam// <11–20>

Fig.4. RHEED patterns of the modified surface of $Al_{0.1}Ga_{0.9}N$ introducing TESi.



E.B.//<1–100> enlarged view of the left E.B.// <11–20> enlarged view of the left

Fig.5. RHEED patterns of GaN QDs grown on the modified surface of $Al_{0.1}Ga_{0.9}N/Al_{0.2}Ga_{0.8}N$/AlN/ 6H–SiC for 30 sec.

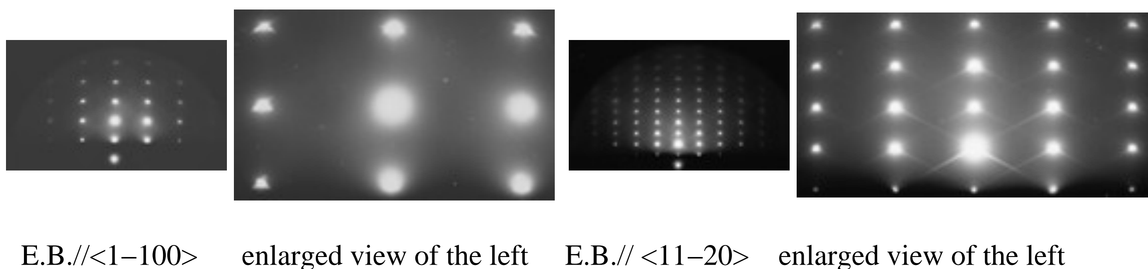


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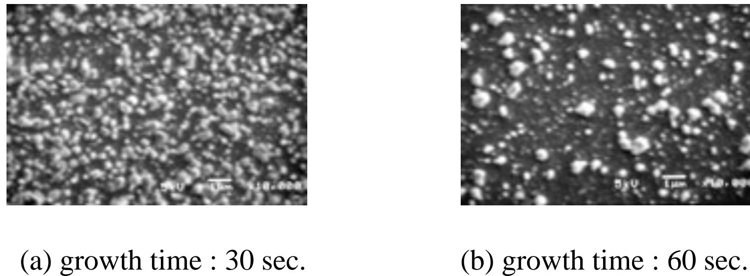
Fig.6. RHEED patterns of GaN QDs grown on the modified surface of $Al_{0.1}Ga_{0.9}N/Al_{0.2}Ga_{0.8}N$/AlN/ 6H–SiC for 60 sec.

changed as shown in Fig.6. These RHEED patterns show that the island structure due to GaN QDs are grown on the modified surface. The GaN QDs are grown on the $Al_{0.1}Ga_{0.9}N$ surface modified by the introduction of TESi by supplying TMGa (trimethylgallium) and NH_3 with H_2 carrier gas for 30 sec and 60 sec. The SEM images of GaN QDs grown on the modified $Al_{0.1}Ga_{0.9}N$ surface are shown in Fig.7. The GaN QDs of several decade nm intermingle with GaN islands of several hundred nm.



(a) growth time : 30 sec. (b) growth time : 60 sec.

Fig.7. SEM images of GaN QDs grown on the modified surface of $Al_{0.1}Ga_{0.9}N/Al_{0.2}Ga_{0.8}N/AlN/6H{-}SiC$ for 30 sec (a) and 60 sec (b).

Photoluminescence spectrum of GaN QDs is shown in Fig. 8. The shift of the peak in the high energy side was observed, but it is small. GaN QDs were formed by introducing Si on $Al_{0.1}Ga_{0.9}N$/ $Al_{0.2}Ga_{0.8}$ N/6H–SiC (0001) by MOVPE process. The GaN QD formation was possible by piling up AlN buffer layer, $Al_{0.2}Ga_{0.8}N$ layer and $Al_{0.1}Ga_{0.9}N$ layer on 6H–SiC (0001) in order and by introducing Si to modify the surface of $Al_{0.1}Ga_{0.9}N$ layer. Si plays an important role in changing the growth mode of GaN.

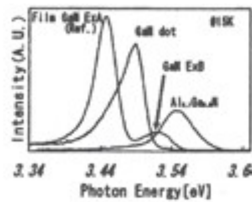


Fig.8. Photoluminescence spectrum of GaN QDs grown on the $Al_{0.1}Ga_{0.9}N$ surface.

CONCLUSIONS

GaN QDs were formed on the modified surface of $Al_{0.1}Ga_{0.9}N/Al_{0.2}Ga_{0.8}N/6H{-}SiC$ (0001) by the introduction of TESi by MOVPE process. The GaN QD formation was possible by piling up AlN buffer layer, $Al_{0.2}Ga_{0.8}N$ layer and $Al_{0.1}Ga_{0.9}N$ layer on 6H–SiC (0001) in order and by introducing Si to modify the surface of $Al_{0.1}Ga_{0.9}N$ layer. Si plays an important role in changing the growth mode of GaN.

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