phys. stat. sol. (c) **0**, No. 7, 2589–2592 (2003) / **DOI** 10.1002/pssc.200303336

Direct growth of cubic AlN and GaN on Si (001) with plasma-assisted MBE

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Received 28 May 2003, revised 23 June 2003, accepted 30 June 2003

PACS 81.07.Bc, 81.15.Hi, 81.15.Kk

Highly lattice mismatched (HM^2) heteroepitaxial growth of cubic zincblende c-AlN and c-GaN on Si (001) was performed by MBE using plasma excited nitrogen sources without using a low temperature buffer layer. The early stage of the direct nucleation of AlN and GaN on a Si substrate using microwave and radio frequency plasma-assisted MBE was studied. The islands of a zincblende structured material (c-SiN_x [a = 0.43 nm]), effectively worked as a seed for successive coherent growth of c-AlN and c-GaN oriented ⟨001⟩. The growth of c-AlN and c-GaN was analyzed by reflection high energy electron diffraction, X-ray diffraction, and photoluminescence.

1 Introduction Hybrid application of group III nitride semiconductors with silicon technology is a promising one for optical and electronic applications. The growth method of molecular beam epitaxy (MBE) is the most suitable one for interface flatness control and composition control of alloy crystals for optical and electronic applications. Although the hexagonal wurzite (W) phase (h-) of AlN and GaN is currently used for various applications, the cubic zincblende (ZB) (c-) phase is more attractive, because of the doping property and the similarity of the cubic system of Si technology for hybrid application. The growth of ZB group III nitrides by MBE was reported by using a low temperature buffer layer or surface pre-treatments of carbonization or nitridation for a Si substrate [1–12] and for other substrates[13–20]. To overcome the problem of highly lattice mismatched (HM^2) hetero-epitaxial growth [21] is important for hybrid application. No direct growth of GaN from single crystal islands of silicon nitride (SiN_x) on Si(001) was reported before, except for the formation of amorphous SiN_x at the GaN/Si interface [6–8]. The amorphous SiN_x substrate operated as nucleation cores of h-GaN [7]. Single crystal islands work as coherent multi nuclei for the direct growth, which has merits to reduce the interface electric resistance for vertical devices and to reduce the process steps of device preparation. In this report the hetero-epitaxial growth of ZB c-AlN and c-GaN on Si (001) will be performed by MBE without a low temperature buffer layer using nitrogen plasmas of microwave (μ-) and radiofrequency (rf-) discharges. Coherent growth for the single phase of cubic nitrides depending on plasma sources will be discussed.

2 Experimental A VG80H MBE system, which was used to grow GaAs, was converted to a new group III–N system by installing a μ- and a rf plasma-cell for N atom radicals. Substrates, which were mirror polished 2 inch wafers of n-type Si(001) with 0.02 Ω cm, were chemically etched with a solution of $HF(5\%):H_2O_2(5\%):H_2O$ (2 : 1 : 7 by volume) for 1 min, rinsed in deionized water and dried by N_2 gas. Nitrogen μ-plasma of 2.45 GHz in a SiO_2 discharge chamber with magnetic field, EMIS-211, and

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(a) 0 min (b) 5 min (c) 10 min

Fig. 1 RHEED patterns for Si (001) from $\langle 110 \rangle$ azimuth after exposing N plasma.

rf-plasma of 13.56 MHz with a PBN discharge chamber, IRFS, by Arios Co. Ltd. were used. The optical emission of the plasma was monitored through a CCD camera spectrometer (S-2000, Ocean Optics, Inc.). Emission spectra of N atoms are important to maintain necessary active nitrogen atoms to react with Ga or Al [22–24]. The bright discharge for rf-plasma [24] with additional ion-elimination magnetic field was used for our MBE growth. Substrate temperatures were between 500 and 850 °C measured by a VG80H temperature monitor. Refrection high energy electron difraction (RHEED) patters were used to monitor the initial nucleation and growth processes. X-ray diffraction (XRD), photoluminessence (PL), atomic force microscopy (AFM) measurements were performed. The flux of Ga or Al from solid source was fixed at BEP $6.0-8.0 \times 10^{-6}$ Pa (ion guage current 5 to 10 nA, about 0.02 μm/h) with the maximum discharge power 200 W for EMIS and at BEP 2×10^{-5} Pa (about 0.1 μm/h) with the maximum discharge power 500W for IRFS. X-ray photoelectron spectroscopy (XPS) measurement was performed using monochromatized Al K α radiation from an Al anode operated at 200 W by Quantum 2000 (ULVAC phi). All XPS spectra were calibrated using the Au 4f7/2 peak at 84.0 eV. Curve fitting was performed using the Gaussian-Lorentzian sum function after a Shirley background subtraction.

3 Results and discussion RHEED patterns of Fig. 1 show the formation of the ZB structured islands by irradiation of the N plasma. Figure 1a shows a bare Si (001) surface with (2 × 1) reconstruction obtained by thermal cleaning in the growth chamber up to 850 °C at 1.0×10^{-6} Pa. For nitride formation on Si, an N radical shutter was opened at 850 °C at 1.0×10^{-3} Pa toward the Si substrate. The transition from the Si (2 × 1) pattern to a ZB one was monitored by the RHEED pattern as shown in Fig. 1b for 5 min and (b) for 10 min. From the spot pattern of Fig. 1c the lattice constant of 0.43 nm, which was close to the one for 3C-SiC (a = 0.436 nm), was obtained. Possibility of the formation of thin 3C-SiC [3] by the residual CO gas in the growth chamber could be considered. There is no report for ZB structure SiN_x, but the XPS signal for Si 2p (99.5 eV) as shown in Fig. 2 showed the chemical shift due to nitrogen bonding (101.8 eV), not carbon bonding (100.2 eV). Single crystal islands of ZB structure were formed only after plasma-enhanced nitrogen irradiation. The ZB structure islands could be SiN_x. HM^2 hetero-epitaxial growth of under about 20% lattice mismatch was successful through the epitaxial multi nucleation because of the coincidence of 5 times the lattice constant of ZB SiN_x and 4 times the Si lattice constant of $\langle 001 \rangle$ orientation.

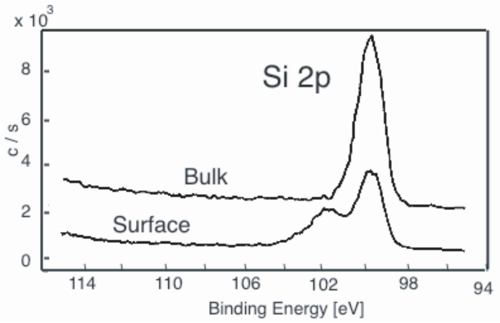
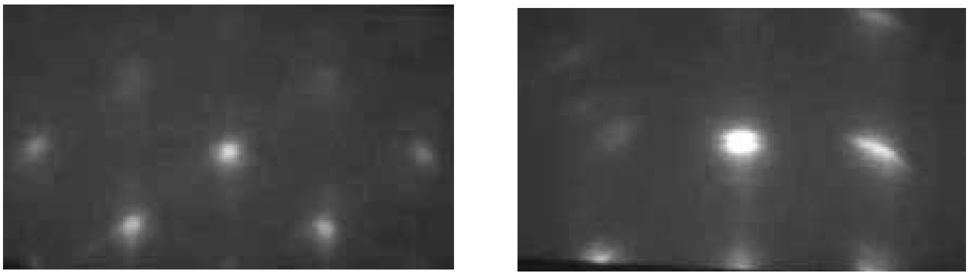
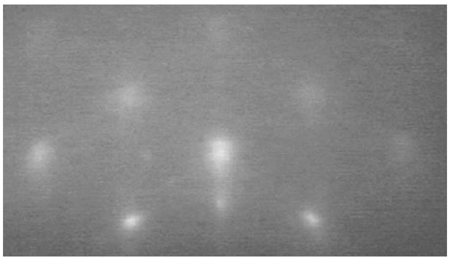


Fig. 2 XPS signal for Si 2p (99.5 eV) showing the chemical shift due to the nitrogen bonding (101.8 eV), not carbon bonding (100.2 eV). The peak values were obtained by curve fitting.



(a) c-GaN along azimuth ⟨110⟩ (b) c-GaN along azimuth ⟨100⟩

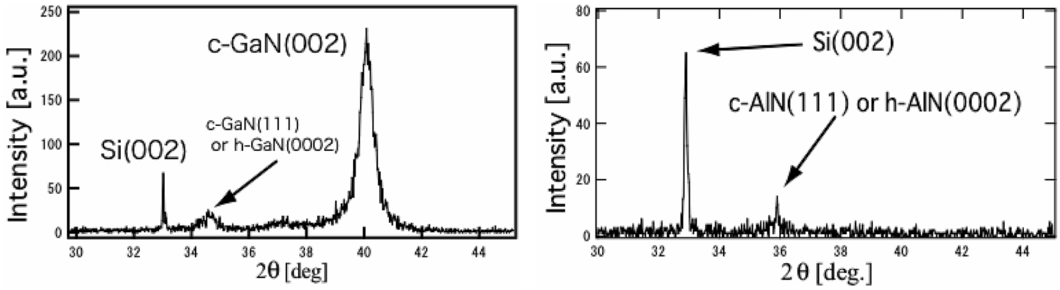


(c) c-AlN along azimuth ⟨110⟩

Fig. 3 a), b) and c) show the ZB c-GaN RHEED patterns observed along azimuth ⟨110⟩ and ⟨001⟩ and c-AlN pattern along azimuth ⟨110⟩, respectively.

After the formation of a spot pattern of the ZB structure of Fig. 1c using μ- or ion eliminated rf- bright plasma, the c-AlN and c-GaN layers were grown at 850 °C and 700 °C, respectively. Figures 3a, b and c, which show the ZB c-GaN RHEED patterns observed along azimuth ⟨110⟩ and ⟨001⟩ and c-AlN pattern along azimuth ⟨110⟩ respectively, indicates the direct growth of c-GaN and c-AlN on Si (001).

Figure 4a shows a 2θ scanning XRD pattern of brown color c-GaN on Si(001) for successive growth from Figs. 3a and b. The peak at 40.5° is assigned as (002) of c-GaN, of which FWHM is 38.4 [arcmin]. A small c-GaN(111) or h-GaN(0002) peak at 34.5° was also observed in Fig. 4a due to the influence of ion species from rf-IRFS. The bright discharge mode of rf-plasma, of which spectra are mainly at 747 nm for atomic nitrogen and at around 660 nm for N_2^+ ions, has the effect of active ion species. The elimination of the effect of ion species using a magnetic field was successful to grow c-GaN. When the rf- nitrogen beam contained more ion species of lower less magnetic field, the h-GaN(0002) peak at 34.5° was more dominant. If we use the effect of ion species, we grew (0002) oriented polycrystalline h-GaN, which was the same structure grown on amorphous substrates [7, 20]. It shows the W structure which is due to the influence of active ion species. The N-rich growth condition is also the other factor to form the W phase [18, 19]. Zincblende c-GaN was grown coherently with the same orientation of substrate Si (001) by atomic nitrogen of the 747 nm peak spectrum. To grow thicker and flat films of ⟨100⟩ oriented single phase c-GaN a larger nitrogen flux without ion species is required.



(a) c-GaN on Si(001) (b) c-AIN or h-AIN on Si(001)

Fig. 4 XRD results of c-GaN and c-AlN on Si(001).

Figure 4b shows a XRD pattern of thiker blue color AlN on Si (001) than that of Fig. 3c. The line from 36.3° corresponds the peak for h-AlN(0002) which was grown at higher substrate temperature compared to the GaN growth. Only the epitaxial growth of thin c-AlN was proved by RHEED. To grow thicker and flat films of ⟨100⟩ oriented single phase c-AlN on inprovement of the nitrogen source to produce a large flux of atomic nitrogen is also requierd.

The photoluminescence peak from thicker c-GaN at 20 K with He–Cd laser of 1.2 mW shows the formation of a mixture of ZB and W phases. After the curve fitting procedure, donor-accepter pair peak and cubic structure plus hexagonal peaks were obtained. Inclusion of the W phase could be eliminated by controlling the V/III flux ratio or the contribution of ion species.

4 Conclusion As a new approach to realize a hybrid nano system between Si and group III-nitrides compound semiconductors for a new electronic material, the direct growth of ZB c-AlN and c-GaN was proposed. The early stage of the direct nucleation of GaN on a Si substrate using microwave and radio frequency plasma-assisted MBE was presented. The islands of a ZB structured material (c-SiN_x [a = 0.43 nm]) worked as a seed for successive coherent growth of c-AlN and c-GaN oriented ⟨001⟩ because of the coincidence of 4 times the Si lattice constant and 5 times the c- SiN_x lattice constant.

Acknowledgements This work was supported by the project, "Hybrid Nanostructured Materials and Its Application" at the Research Centre for Advanced Science and Technology (RCAST) of Doshisha University and was supported with the Aid of Doshisha University's Research Promotion Fund.

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