Applied Surface Science 345 (2015) 440–447

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Surface chemistry and electronic structure of nonpolar and polar GaN films

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ARTICLE INFO

Article history:
Received 25 February 2015
Received in revised form 24 March 2015
Accepted 25 March 2015
Available online 1 April 2015

Keywords:
GaN
Photoemission
Polarization
Surface states

ABSTRACT

Photoemission and microscopic analysis of nonpolar (a-GaN/r-Sapphire) and polar (c-GaN/c-Sapphire) epitaxial gallium nitride (GaN) films grown via RF-Molecular Beam Epitaxy is reported. The effect of polarization on surface properties like surface states, electronic structure, chemical bonding and morphology has been investigated and correlated. It was observed that polarization lead to shifts in core level (CL) as well as valence band (VB) spectra. Angle dependent X-ray Photoelectron Spectroscopic analysis revealed higher surface oxide in polar GaN film compared to nonpolar GaN film. On varying the take off angle (TOA) from 0° to 60°, the Ga—O/Ga—N ratio varied from 0.11–0.23 for nonpolar and 0.17–0.36 for polar GaN film. The nonpolar film exhibited N-face polarity while Ga-face polarity was perceived in polar GaN film due to the inherent polarization effect. Polarization charge compensated surface states were observed on the polar GaN film and resulted in downward band bending. Ultraviolet photoelectron spectroscopic measurements revealed electron affinity and ionization energy of 3.4 ± 0.1 eV and 6.8 ± 0.1 eV for nonpolar GaN film and 3.8 ± 0.1 eV and 7.2 ± 0.1 eV for polar GaN film respectively. Field Emission Scanning Electron Microscopy measurements divulged smooth morphology with pits on polar GaN film. The nonpolar film on the other hand showed pyramidal structures having facets all over the surface.

1. Introduction

The unique optical and electrical properties (e.g. wide and direct bandgap, high mobility and thermal conductivity, etc.) of III-nitride materials have demonstrated an attractive potential in the technology of modern electronic components like visible and UV lasers, light emitting diodes, high temperature and frequency detectors, transistors and photovoltaic devices [1–4]. GaN based semiconductors with superior material properties are promising candidate revealing several advantages over competing Si, SiC, GaAs, etc. based technologies [5]. GaN is well recognized for power transistors with high breakdown voltage, power per unit width, operation at higher voltages and impedance with easy manufacturing [6]. The group III-Nitride semiconductors with wurtzite crystal structure are pyroelectric materials exhibiting a large spontaneous and piezoelectric polarization [7,8], where the piezoelectric constant factors are found to be 5–20 times larger than those of III-As [9]. It is well reported that the III-nitride based quantum well structures suffer from quantum-confined stark effect (spatially separating the electron and holes wave function within the quantum well) due to the piezoelectric and spontaneous polarization when grown along conventional c-axis ((0 0 0 1) direction) [10]. The macroscopic polarization (P) which arises from material properties is the sum of spontaneous polarization (P_{SP}) inherent to equilibrium lattice and the piezoelectric polarization (P_{PE}) created by strain. The piezoelectric polarization along c-axis (as defined via ab initio calculations) is given via the following equation:

$$P_{PE} = 2\frac{a - a_o}{a_o}\left(e_{31} - \frac{C_{13}}{C_{33}}e_{33}\right)c \qquad (1)$$

where C_{13} and C_{33} are elastic constants, e_{31} and e_{33} are piezoelectric coefficients, and a_o and a are lattice constants [11,12]. However, the piezoelectric polarization is observed to be negligible for relaxed layers (grown above critical thickness ~10 nm) [12,13]. Polarization induces strong electrostatic electric field (up to 3 MV/cm), interface charge densities (>10^{13} cm^{-2}) and reduces the internal quantum efficiency. This produces a strong impact on the performance of InGaN/GaN based light emitting diodes as well as on AlGaN/GaN based microelectronic devices [14,15]. Although the resulting macroscopic polarization engenders high drift carrier velocity and lead to the formation of high density two dimensional electron gas (2DEG) at the heterostructure interface without

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http://dx.doi.org/10.1016/j.apsusc.2015.03.166
0169-4332/

doping [16], it also reduces the radiative efficiency in quantum well light emitters [17]. Hence, in order to elucidate this inherent property for the fabrication of efficient optoelectronic and electronic devices, growth along *a*-axis ((1 1 $\bar{2}$ 0) direction having a zero normal component of the polarization field) has attracted considerable attention in recent years [18]. The nonpolar GaN based devices offer significant applications in light emitters with multiple quantum wells (MQW) active regions which alleviate the aforementioned quantum-confined stark effect and 2DEG [18].

For the fabrication of III-Nitride based noble devices, thorough understanding of surface properties is of key importance. The surface properties related exotic phenomenon play significant role in governing the overall performance of the device [19]. It is reported that the performance of III–V based devices are plagued by a large number of surface states resulting in leakage current, current collapse, formation of virtual gate, high contact resistance that implicates device reliability [6,19]. The GaN films grown along different crystal orientations are expected to exhibit significant variation in the surface properties and interface charges [20,21]. These charges on compensation (to avoid the large electric field and charge neutrality mechanism) lead to the changes in electronic structure, surface chemistry, morphology and development of new surface states. The generated surface states may act as pinning states, defect states or trap centres which can affect the Schottky barrier height and would assist to thermionic emission electron tunnelling that causes current collapse and failure mechanism [22–24]. However, the polarization also has a strong impact on III-nitride heterojunction band offsets (interfaces), and laterally large discontinuities in the measurements of Valence Band Offsets (VBO) related to polarization effect are reported [25–27]. Since the determination of VBO is correlated with the core level (CL) and valence band maximum (VBM) positions, the discontinuities in the measurement of VBO refer to alteration/modification in the CL as well as in the VBM positions due to shift in the spectra. Hence, the analysis of growth direction and corresponding polarization charge compensated states on surface structure, morphology and electronic properties of the grown films becomes essential. To the best of our knowledge, no such report is available in literature to the date. This report presents a comprehensive angle dependent photoemission (XPS & UPS) and microscopic (FE-SEM) analysis of nonpolar (i.e. (1 1 $\bar{2}$ 0) GaN/r-Sapphire interface) and polar (i.e. (0 0 0 1) GaN/c-Sapphire interface) undoped GaN films grown under identical conditions via RF-Plasma Assisted Molecular Beam Epitaxy. The correlation of the surface polarity, morphology, band structure, electron affinity and photo-threshold energy of the nonpolar and polar GaN films due to polarization effect has been discussed.

2. Experimental

The growth of undoped crystalline polar (c-plane) and nonpolar (a-plane) GaN films were carried out on c- and r-plane sapphire substrates respectively, via RIBER RF-Plasma Assisted Molecular Beam Epitaxy (PAMBE). To eliminate the influence of growth kinetics, both films were grown to be 600 nm thick under identical Ga/N flux ratio and RF power of 500 W. Photoemission (XPS & UPS) experiments were performed in ultra-high vacuum (UHV) based system (OMICRON Multiprobe Surface Analysis System) operating at a base pressure of 5×10^{-11} Torr. The field emission scanning electron microscopic (FE-SEM) measurements were done via ZEISS AURIGA Field Emission Scanning Electron Microscope. Samples were ultrasonicated in acetone for 10 min and chemically etched in 20% HCl solution for 60 s to remove excess gallium or Ga_xO_y prior to introduction in UHV chamber. The samples were mounted on a stainless steel plate using conductive tape with silver contacts on the edges to avoid charging; however the system was also equipped with a charge neutralization facility to eliminate the additional build-up charge during the measurement. For XPS

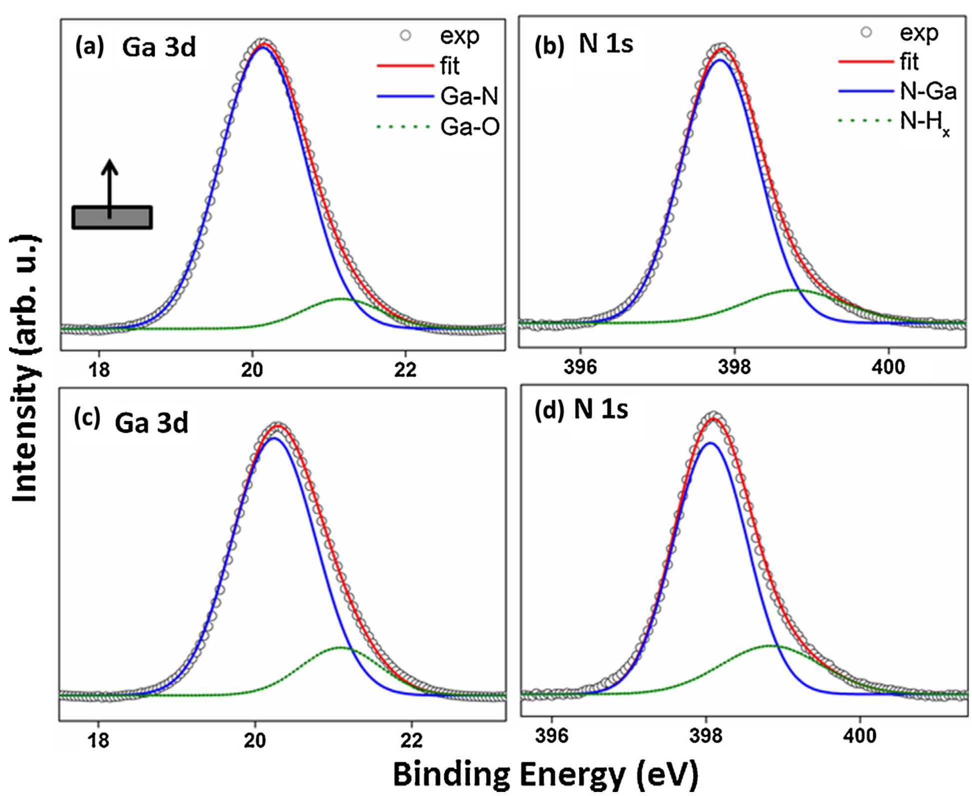

Fig. 1. De-convoluted XPS spectra of Ga (3d) core levels of (a) nonpolar and (c) polar GaN film, and N (1s) core level of (b) nonpolar and (d) polar GaN films at TOA = 0°. Open circles showing experimental data while solid lines are fitted curves.