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Valence band offsets of $Sc_xGa_{1-x}N$/AlN and $Sc_xGa_{1-x}N$/GaN heterojunctions

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Abstract

The valence band offsets of $Sc_xGa_{1-x}N$/AlN heterojunction were measured by X-ray photoelectron spectroscopy (XPS) and were found to increase from 0.42 eV to 0.95 eV as the Sc content x increased from 0 to 0.15. The increase in valence band offset with increasing x is attributed to the corresponding increase in spontaneous polarisation of the wurtzite structure. The $Sc_xGa_{1-x}N$/AlN heterojunction is type I, similar to other III-nitride-based heterojunctions. The results also indicated that a type II staggered heterojunction, which can enhance spatial charge separation, could be formed if $Sc_xGa_{1-x}N$ is grown on GaN.

Keywords: ScGaN, heterojunction, molecular beam epitaxy, X-ray photoelectron spectroscopy, valence band offset

PACS codes: 78.66.Fd, 79.60.Jv, 81.15.Hi

Introduction

Wurtzite structure III-nitrides and their alloys are used widely in optoelectronics, especially in light emitting diodes (LEDs). By controlling the composition of the nitride alloys, the band gap can be adjusted from 6.2 eV to 0.9 eV, covering the ultraviolet (UV) to infrared wavelength range[1–4]. However, although LEDs emitting in the blue wavelength range have internal quantum efficiencies as high as 90 %, improved device designs are needed in the deep-UV range used for germicidal applications (260 – 280 nm) because the internal quantum efficiencies in this range are currently only 30%[5–9]. The low efficiencies are due in part to the extended defects which appear within the active light-emitting regions of device heterostructures due to the lattice constant mismatch between layers. The high tensile stresses which typically develop due to the lattice constant and thermal expansion coefficient mismatches between layers within a UV-LED device structure also limit the total device thickness and the variety of structures which can be grown successfully[10–12]. Therefore, alternative wurtzite nitrides such as $Sc_xGa_{1-x}N$ with different lattice parameter – band gap relationships[13] are of interest to control internal stresses and open up new routes to device design. In this regard, $Sc_xGa_{1-x}N$/AlN heterojunctions are of interest for the active regions of UV light emitters, however the band offsets and the heterojunction type must first be established and confirmed experimentally.

$Sc_xGa_{1-x}N$ is an alloy between wurtzite GaN and rock-salt ScN, therefore a structural phase transition is expected to occur as the Sc content x increases. $Sc_xGa_{1-x}N$ films grown using molecular beam epitaxy (MBE) under nitrogen-rich conditions showed a transition from the wurtzite to the cubic structure at approximately $x = 0.17$[14] whereas the films grown under metal-rich conditions remained in the wurtzite structure up to $x = 0.26$, consistent with a recent high quality theoretical calculation[13,15]. Recent data from high quality wurtzite Sc_xGa_{1-}

$_x$N films showed that the optical band gap increases with increasing Sc content, consistent with recent theoretical calculations[13,16]; a decrease in the band gap of $Sc_xGa_{1-x}N$ with increasing x (as reported previously[14,17]) only occurs with increasing Sc content in the presence of nanoscale inclusions[16].

The valence band offset (ΔE_v) at a semiconductor interface is an important parameter in designing and modelling quantum well structures and devices[18–22]. It can be measured by optical spectroscopy (e.g. optical absorption and photoluminescence), electron spectroscopy (e.g. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS)) and electrical measurement (e.g. I-V and C-V measurements of a device)[21,22]. Among them, XPS is the most commonly used technique as it allows direct measurement of the valence band edge relative to the Fermi level along with the core level binding energy, whereas simulation and fitting are needed for other techniques[21–23]. Since the $Sc_xGa_{1-x}N$ films grown on MOVPE AlN have better crystal quality, the ΔE_v for $Sc_xGa_{1-x}N$/AlN heterojunction is of interest for its potential devices[16]. Therefore, this study aims to investigate the influence of Sc to the valence band offsets of the $Sc_xGa_{1-x}N$/AlN heterojunction using XPS.

Experimental

Epitaxial (0001)-oriented $Sc_xGa_{1-x}N$ thin films were deposited on (0001)-sapphire under metal-rich conditions using molecular beam epitaxy with an RF nitrogen plasma source. The composition of the film was controlled by varying the Sc flux by controlling the effusion cell temperature, while the Ga flux was kept constant. The Sc flux varied between 0 nA and 2 nA, which corresponds to a Sc content x of 0 and 0.15 according to previous Rutherford backscattering measurements[16]. The film thicknesses (~ 5 nm and ~100 nm) were estimated from the growth rate reported in Ref. 15. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific Kα instrument with monochromated Al Kα X-ray source~~s~~ (1486.6 eV).

Results and discussions

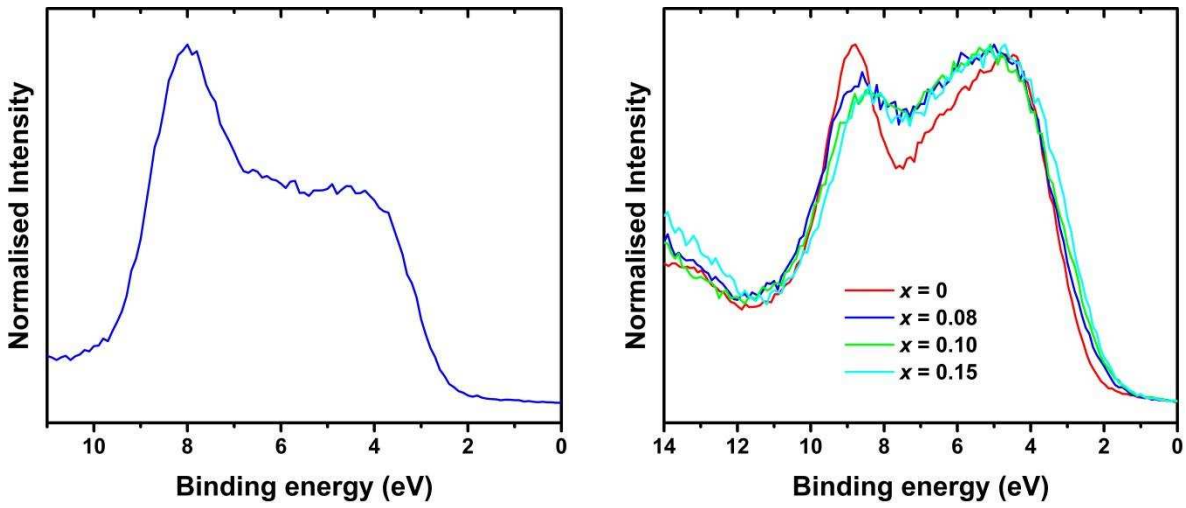

Fig. 1. Valence band spectra for (a) AlN and (b) $Sc_xGa_{1-x}N$.

The valence band spectra for AlN, GaN and $Sc_xGa_{1-x}N$ are shown in Fig. 1, where the shape of the spectra of GaN and $Sc_xGa_{1-x}N$ is similar, with the features at 5 eV and 9 eV corresponding to the p states of Ga[24–26]. The valence band maximum (VBM) was determined by linearly extrapolating the low binding energy onset of the valence band the spectral

baseline[27] and the VBM and the core level energy of the samples are listed in Table I. The valence band offsets of the $Sc_xGa_{1-x}N$/AlN heterojunction were measured by taking separate photoemission spectra from thick films of AlN and $Sc_xGa_{1-x}N$ and also from a thin film (< 5 nm) of $Sc_xGa_{1-x}N$ on top of AlN. From the thick films of AlN and $Sc_xGa_{1-x}N$, the binding energies of the VBM (denoted E_{VBM}^{AlN} and E_{VBM}^{ScGaN}) and a core line ($E_{Al\ 2p}^{AlN}$ and $E_{Ga\ 3d}^{ScGaN}$ respectively) were determined. In the thin film, $E_{Al\ 2p}^{ScGaN/AlN}$ and $E_{Ga\ 3d}^{ScGaN/AlN}$, being the binding energies of the Al 2p and Ga 3d core lines, were measured. These were input in Eq. (1), to yield the valence band offsets.

$$\Delta E_v = \left(E_{Ga\ 3d}^{ScGaN} - E_{VBM}^{ScGaN}\right) - \left(E_{Al\ 2p}^{AlN} - E_{VBM}^{AlN}\right) + \left(E_{Al\ 2p}^{ScGaN/AlN} - E_{Ga\ 3d}^{ScGaN/AlN}\right) \quad (1)$$

The valence band offset for GaN/AlN in this experiment was 0.42 ± 0.05 eV, which is consistent with the experimental value of 0.4 eV reported by Rizzi et al. and the theoretical value of 0.44 eV from Nardelli et al.[28,29]. However, a wide range of valence band offset values have been reported for III-nitride based heterostructures, especially for GaN/AlN where the values range from 0.4 – 1.36 eV[30–36]. The measured valence band maximum is influenced by the surface stoichiometry and defect levels in the GaN, leading to a large range of the measured energy difference between the core level and the valence band maximum. Therefore, the measured valence band offset depends on the growth method, polarity and defect densities of the films[21,37]. Moreover, the use of different valence band maximum determination methods may contribute to the wide range of reported values[27,37].

Sample	Region	Binding energy (eV) ($\pm$ 0.05)	FWHM
AlN	Al 2p	73.11	1.16
	VBM	2.42	–
		GaN	
GaN/AlN	Ga 3d	20.00	1.61
	Al 2p	73.30	1.22
GaN	Ga 3d	20.00	1.34
	VBM	2.20	–
		$Sc_xGa_{1-x}N$ (x = 0.08)	
$Sc_xGa_{1-x}N$/AlN	Ga 3d	19.87	1.67
	Al 2p	73.57	1.21
$Sc_xGa_{1-x}N$	Ga 3d	19.82	1.68
	VBM	2.07	–
		$Sc_xGa_{1-x}N$ (x = 0.10)	
$Sc_xGa_{1-x}N$/AlN	Ga 3d	19.77	1.73
	Al 2p	73.54	1.23
$Sc_xGa_{1-x}N$	Ga 3d	19.73	1.71
	VBM	1.92	–
		$Sc_xGa_{1-x}N$ (x = 0.15)	
$Sc_xGa_{1-x}N$/AlN	Ga 3d	19.52	1.77
	Al 2p	73.33	1.25
$Sc_xGa_{1-x}N$	Ga 3d	19.66	1.69
	VBM	1.83	–

Table I. Binding energy of the core level and valence band maxima (VBM) of $Sc_xGa_{1-x}N$ and AlN.

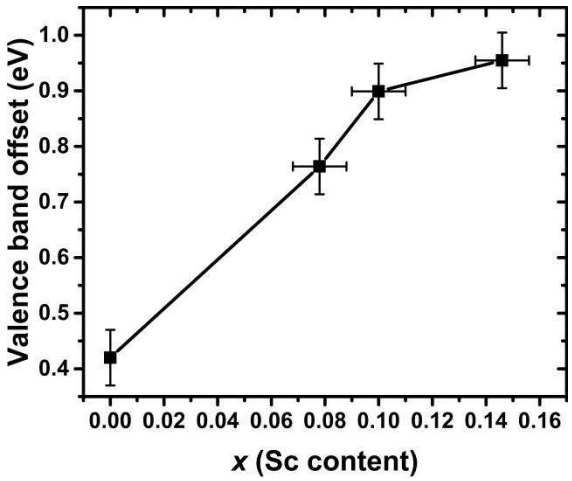

Fig. 2. The valence band offsets of $Sc_xGa_{1-x}N$/AlN heterojunction as a function of Sc content x.

As the Sc content x increased from 0 to 0.15, the valence band offset of the $Sc_xGa_{1-x}N$/AlN heterojunction increased from 0.42 eV to 0.95 eV (Fig. 2). The increase in valence band offsets with increasing x for (0001)-oriented $In_xGa_{1-x}N$/GaN and $Al_xGa_{1-x}N$/GaN heterostructures has been attributed to a strain-induced piezoelectric field oriented along [0001][30]. However, as the films grown for this experiment were thicker than the critical thickness suggested by theoretical calculations[38], the films appeared to be fully relaxed and thus no strain-induced piezoelectric field contributed to the increase in the valence band offset. On the other hand, the spontaneous polarisation of the wurtzite structure is enhanced by the addition of Sc because of the higher ionicity of the Sc-N bond and the decrease in the c/a lattice parameter ratio with increasing Sc content, as well as the possible contributions from a local internal distortion at the Sc atom site[38–40]. The difference in spontaneous polarisation between $Sc_xGa_{1-x}N$ and AlN leads to charge redistribution at the interface, which is responsible for the increase in valence band offset. It is possible that the doping level would affect the Fermi energy level and thus the measurement of valence band maximum[41], however, since all the GaN and $Sc_xGa_{1-x}N$ films were grown in the same MBE reactor and under the same conditions, it can be assumed that the doping level for the films were similar.

$$\Delta E_c = \left(E_g^{AlN} - E_g^{ScGaN}\right) - \Delta E_v \quad (2)$$

The conduction band offset of the heterojunction can be calculated using Eq. (2), where the band gaps of $Sc_xGa_{1-x}N$ films have been presented in Ref. 16 and the band gap of AlN have been known as 6.2 eV[13,42]. Therefore, a band alignment diagram can be constructed, as shown in Figure 3. As the band gap of $Sc_xGa_{1-x}N$ is lower than the band gap of AlN, a type I heterojunction is formed, similar to other III-nitride heterojuntions[30]. However, Fig. 3 indicates that a type II staggered heterojunction would be formed if $Sc_xGa_{1-x}N$ is grown on GaN. Type I heterojunction, which is used for light emitting and laser applications, confines electrons and holes on one side of the semiconductor interface leading to greater charge recombination. On the other hand, charges favour separation naturally in type II heterojunction due to the band alignment[43–45], therefore this is an advantage for solar cell[46–49] and water splitting applications[50,51]. The solar cells that used III-nitrides as the active layer have been using the p-i-n structure[52–54], where carrier recombination could lower the efficiency of the solar cell, the formation of $Sc_xGa_{1-x}N$/GaN type II heterojunction may be one solution to this problem.

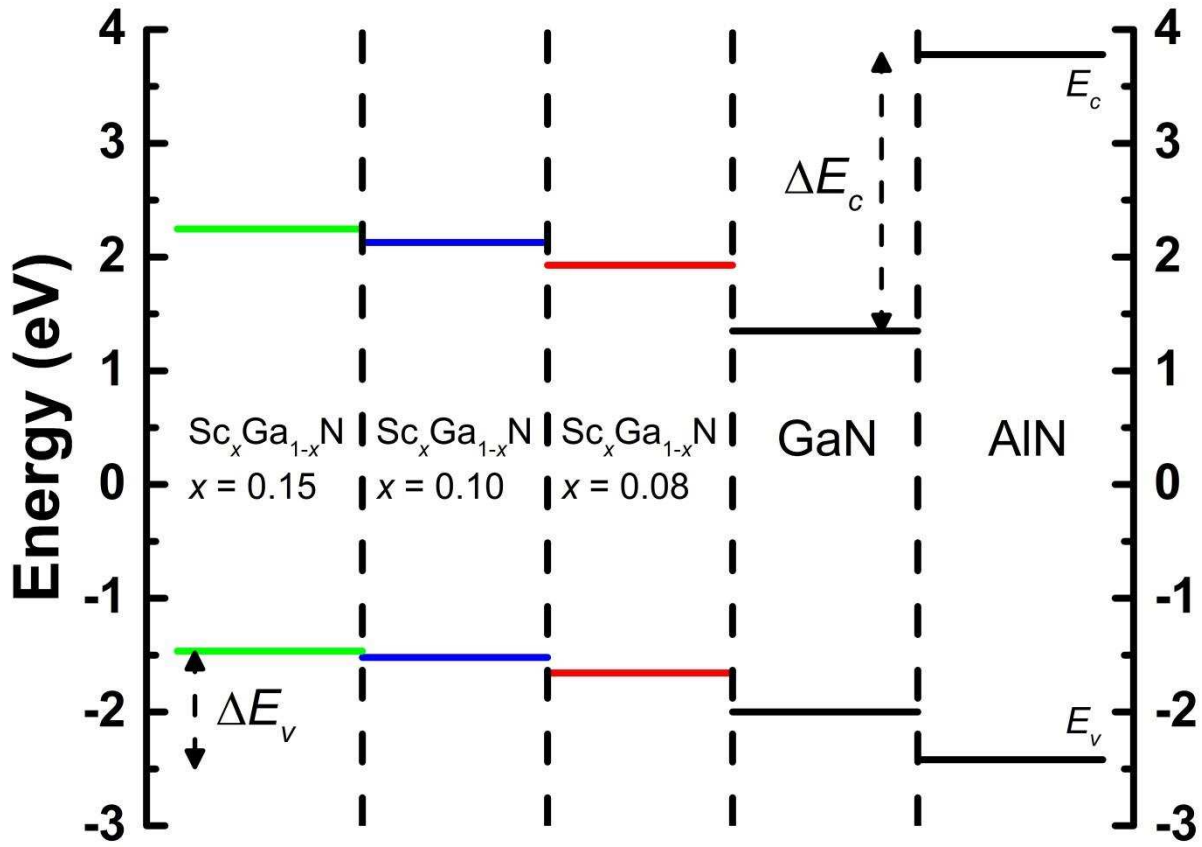

Fig. 3. Band alignments for $Sc_xGa_{1-x}N$/AlN heterojunctions.

Conclusions

In conclusion, the valence band offset of $Sc_xGa_{1-x}N$/AlN heterojunction was found to increase as the Sc content increases. This is attributed to the increase in spontaneous polarisation of the wurtzite structure with increasing x. The $Sc_xGa_{1-x}N$/AlN heterojunction was determined as type I whereas $Sc_xGa_{1-x}N$/GaN was determined as type II.

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