Effects of ultraviolet-assisted photo-electrochemical etching current densities on structural and optical characteristics of porous quaternary AlInGaN alloys

Hock Jin Quah a,b, Way Foong Lim a,b,* Zainuriah Hassan a,b, Rosfariza Radzali a,c, Norzaini Zainal a, Fong Kwong Yam a

a Institute of Nano-Optoelectronics Research and Technology (INOR), School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia
b Centre for Research Initiatives (CRI) Natural Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia
c Faculty of Electrical Engineering, Universiti Teknologi MARA, Jalan Permatang Pauh, 13500 Permatang Pauh, Penang, Malaysia

Received 27 June 2015; accepted 3 October 2015

Abstract Effects of ultraviolet-assisted photo-electrochemical (PEC) etching current densities (J = 20, 40, 80, and 160 mA/cm²) towards structural, physical, and optical properties of aluminium indium gallium nitride (AlInGaN) semiconductors as well as corresponding schematized mechanism were studied and discussed. Formation of porous AlInGaN semiconductors at J lower than 80 mA/cm² has led to the acquisition of larger lattice parameters c and a, out-of-plane strain, in-plane strain, and hydrostatic strain as compared to the non-porous semiconductor, owing to the generation of more vacancy-type defects in the porous AlInGaN semiconductors. For the porous semiconductor formed at J greater than 80 mA/cm², the etching was affected by a limited mass transport of electrons and holes for anodic oxidation and cathodic reduction. According to the band gap (Eg) and Urbach energy (UE) determined from photoluminescence (PL) shift and UV–Vis absorption measurement, the vacancy-type defects were revealed as the radiative localized states that led to the enhancement in PL peak intensity. The acquisition of a lower density of...
dislocation-type defects in the porous semiconductors in contrast to the non-porous one on the other hand indicated that the dislocations were the non-radiative recombination centres, in which much of the density has been eliminated after PEC etching in the 1% potassium hydroxide electrolyte.

© 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

To date, the quaternary III-nitride aluminium indium gallium nitride (\(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\)) semiconductors have come to light as a prospective candidate for application in GaN-based light-emitting diodes (LEDs). This is owing to an ability of the manipulation between the aluminium (Al) and indium (In) compositions for the attainment of a desired band gap and lattice constant of the quaternary \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) (Aumer et al., 1999; Cao and Yang, 2010; Wang et al., 2007). Moreover, the utilization of \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) in GaN-based LEDs would circumvent shortcomings encountered by the ternary aluminium gallium nitride (\(\text{Al}_x\text{Ga}_{1-x}\text{N}\)) alloys, wherein the incorporation of indium (In) into \(\text{Al}_x\text{Ga}_{1-x}\text{N}\) would induce additional localized sites as the radiative recombination centres (Cao and Yang, 2010; Hirayama et al., 2002). It was noteworthy that the localization would promote a radiative recombination between the excited carriers at the In sites, rather than a non-radiative recombination at the defect sites of the \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) (Hirayama et al., 2002; Cao et al., 2006; Cao and LeBoeuf, 2007). Hence, an enhancement in photoluminescence intensity was perceived in the \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\)-based structure as compared to the \(\text{Al}_x\text{Ga}_{1-x}\text{N}\)-based structure (Hirayama et al., 2002).

Nevertheless, the growth of a high quality \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) layer has been confronted with numerous setbacks, which included the formation of nanocluster, phase separation, and poor crystalline quality during the growth of \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) layer at 810 °C as well as the formation of \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) layer containing high In and/or Al content (Cao and Yang, 2010; Marques et al., 2004; Wu et al., 2006). The concern in regard to the above-mentioned matters that would degrade structural and optical properties of the grown \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) layer could be counteracted through the growth of \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) layer at a higher growth temperature of 900 °C (Wu et al., 2006). However, heteroepitaxial growth of either \(\text{Al}_x\text{Ga}_{1-x}\text{N}\) or indium gallium nitride (\(\text{In}_x\text{Ga}_{1-x}\text{N}\)) layer on the \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) would induce the formation of defects and strains in the investigated layer as a result of a discrepancy in thermal expansion coefficient and lattice mismatch of the materials. This would ultimately influence optical, structural, and electrical characteristics of the investigated layer (Fu et al., 2014; Shatalov et al., 2002; Fareed et al., 2004; Zhou et al., 2006).

In order to solve the abovementioned issues, there is a need to exploit the formation of porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\), which was foreseen to effectively minimize the formation of defects and relaxation of strains during the growth of \(\text{Al}_x\text{Ga}_{1-x}\text{N}\) and/or \(\text{In}_x\text{Ga}_{1-x}\text{N}\) on the porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\). With this effort, a relatively thick with lower defect and relaxed \(\text{Al}_x\text{Ga}_{1-x}\text{N}\) and/or indium gallium nitride (\(\text{In}_x\text{Ga}_{1-x}\text{N}\)) film with high Al and In contents could be realized on the porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\). Keeping pace with the beneficial effects acquired through the formation of porous GaN (Fareed et al., 2004; Hartono et al., 2007; Mynbaeva et al., 2000; Vajpeyi et al., 2005b; Najar et al., 2012), it was anticipated that the formation of porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) would alter optical properties of the \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) in the aspects of band gap enlargement, shifting of emission to smaller wavelength, and improvement in luminescence efficiency. Successful fabrication of the porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) could be a substrate to grow III-nitrides LED structures.

Thus far, research studies on the formation of porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) are meagre. A recent study on the formation of porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) semiconductors has been carried out by Radzali et al. (2015) using photo-electrochemical (PEC) etching under Xenon illumination in 1% potassium hydroxide (KOH) electrolyte. Different etching duration (1–30 min) has been performed at a constant etching current density \((J)\) of 10 mA/cm² to investigate structural and optical properties of the resulting porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) semiconductors. Subsequent effort was continued by Lim et al. (2015) by exposing the \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) semiconductor to an ultraviolet (UV) lamp source. The reported work was dissimilar from the previous work, whereby the PEC etching was performed at various KOH electrolyte concentration (1–4%) on a weight basis) for a duration of 20 min under a constant supply of etching \(J\) of 80 mA/cm². Apart from the aforementioned etching duration and electrolyte concentration, etching behaviour of the \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) semiconductors could be also influenced by the etching \(J\). It has been reported that pore diameter would change with respect to the etching \(J\) (Wang et al., 2012) and an enhancement in PL intensity was attained with the porosity (Kasra et al., 2012) for porous silicon (Si) while a higher PL intensity, a better crystalline quality, and a compressive stress relaxation could be obtained in the porous GaN (Al-Heuseen et al., 2010; Vajpeyi et al., 2005a) as compared to the non-porous GaN.

Nonetheless, to the best of our knowledge, the exploration in the aspect of etching \(J\) effect on \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) semiconductor remains null. Therefore, it is of interest in present work to investigate the influence of various etching \(J\) (20, 40, 80, and 160 mA/cm²) in a fixed 1% KOH concentration for 20 min towards structural, physical, and optical properties of the porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) semiconductors. An etching duration of 20 min was selected following the recent study on the formation of porous \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) semiconductors, which has reported that the highest pore density was obtained in the \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) semiconductor subjected to etching at \(J\) of 10 mA/cm² in 1% KOH electrolyte for a duration of 20 min (Radzali et al., 2015). For the etching time lesser and greater than 20 min, the shorter time might not be sufficient to yield porosity in the \(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}\) semiconductor while the longer time might slow down the etching process as a result.
of the formation of thick oxide layer that caused a degradation in dissolution of the semiconductor.

2. Experimental procedures

N-type un-intentionally doped Al\textsubscript{0.1}In\textsubscript{0.1}Ga\textsubscript{0.8}N epilayer with thickness of approximately 100 nm grown on sapphire substrate using plasma-assisted molecular beam epitaxy was commercially purchased from SVT Associates Inc., USA. The wafer was diced into a smaller dimension prior to the PEC etching process. In order to carry out the PEC etching process, a Teflon cell was used to hold the Al\textsubscript{0.1}In\textsubscript{0.1}Ga\textsubscript{0.8}N sample as the anode while platinum (Pt) wire was utilized as a cathode. A diluted potassium hydroxide (KOH) solution with 1% concentration on a weight basis was used as the electrolyte. The PEC etching was carried out under illumination of ultraviolet (UV) (240 W; 477.5 W/cm\textsuperscript{2}) for 20 min at different etching current densities, \(J\) (20, 40, 80, and 160 mA/cm\textsuperscript{2}) with a positive polarity supplied from a 2612B Keithley source meter. Subsequently, the etched samples were rinsed using deionized water and dried under the flow of nitrogen gas. Surface morphology and topography of the porous samples were characterized using field emission scanning electron microscopy (FESEM; FEI Nova NanoSEM 450) and atomic force microscopy (AFM; Dimension Edge, Bruker), respectively. High resolution (0.0001\()\)-X-ray diffraction (HR-XRD; Panalytical X’Pert PRO MRD PW3040) was used to investigate the presence of crystalline phases and orientation of the non-porous and porous Al\textsubscript{0.1}In\textsubscript{0.1}Ga\textsubscript{0.8}N samples using line focus mode in a scan range of \(20 = 25–80^\circ\) using a step time of 2.0 s and a step size of 0.05°. The Cu K\textsubscript{\alpha} radiation (\(\lambda = 1.5406\ \text{Å}\)) was run under a voltage of 40 kV and a current of 30 mA. For rocking curve (RC) measurement of symmetric (0002) and asymmetric (10–12) \(ω\)-scans, point focus mode was performed at a voltage of 40 kV and a current of 35 mA. Optical properties of the investigated samples were measured using Raman spectroscopy (argon ion laser; \(\lambda = 514.5\ \text{nm}\)) and photoluminescence (PL; helium-cadmium laser; \(\lambda = 325.0\ \text{nm}\)) at room temperature. The Raman and PL measurements were performed using a Horiba Jobin Yvon HR800UV system. Optical transmittance properties of the investigated samples were measured using a computerized UV–visible spectrophotometer (Cary 5000).

3. Results and discussion

Fig. 1 shows high resolution X-ray diffraction (HR-XRD) patterns of the non-porous and porous AllnGaN samples, which have been subjected to different etching current densities (\(J = 20–160\ \text{mA/cm}^2\)). Noticeable peaks located at 34.3593–34.3786° ascribed to (0002) plane of AllnGaN phase were detected in all the investigated samples. The (0002)-oriented AllnGaN peaks were shifted to lower diffraction angles when compared with those of hexagonal GaN phase detected in (0002) plane (International Centre of Diffraction Data, ICDD file No. 00-050-0792). A vertical red dashed line has been included in Fig. 1 to indicate the (0002) plane obtained from a standard reference pattern of the hexagonal GaN phase. The shift of the AllnGaN (0002) peak to lower diffraction angle symbolized an increase in lattice parameter \(c\) of the samples.

This observation was plausible, owing to an incorporation of Al\textsuperscript{3+} (0.039 nm) and In\textsuperscript{3+} (0.079 nm) with dissimilar ionic radius into the GaN structure, whereby the Ga\textsuperscript{3+} was having an ionic radius of 0.047 nm (Ambacher, 1998). Due to a charge similitude of the Al, Ga, and In, the trivalent Al\textsuperscript{3+} and In\textsuperscript{3+} would substitute Ga\textsuperscript{3+} in the lattice in order to form the quaternary alloy composition. The substitution of Al\textsuperscript{3+} with a smaller ionic radius into the GaN structure would contract the lattice while incorporation of In\textsuperscript{3+} with a larger ionic radius would contribute to a lattice expansion. Since the composition of Al and In incorporated into the GaN was of the same ratio (1:1) in this work, an increase in overall lattice parameter of the AllnGaN would happen due to a larger variation between the ionic radius of In\textsuperscript{3+} and Ga\textsuperscript{3+} when compared with that of Al\textsuperscript{3+} and Ga\textsuperscript{3+}.

Rocking curve (RC) measurement was performed for symmetric (0002) of the investigated samples in order to justify accurately the XRD peak shift and the corresponding lattice parameter \(c\). Typical symmetric (0002) \(ω\)-scan of the AllnGaN sample subjected to etching \(J\) of 80 mA/cm\textsuperscript{2} is presented in inset (a) of Fig. 1. The resulting \(θ\) angle for (0002) plane (Table 1) was substituted into Eqs. (1) and (2) for the calculation of lattice parameter \(c\) of all the investigated samples.

\[
\frac{1}{d_{hk0}}^2 = \frac{4}{\lambda^2} \left( \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right)
\]
the AlInGaN sample subjected to etching $J$ of 80 mA/cm$^2$ is depicted in inset (b) of Fig. 1.

Prior to an explanation on the changes in lattice parameters $c$ and $a$ in the porous AlInGaN samples with respect to the $J$ in this work, a simple etching mechanism was proposed and is illustrated in Fig. 3 in order to understand pore formation in the AlInGaN layers. The process was initiated with an irradiation of the UV light on the AlInGaN samples (Fig. 3a). Absorption of photons by the samples would stimulate generation of electron–hole pairs typically near the semiconductor surface (Seo et al., 2002; Hwang et al., 2007; Tamboli et al., 2009). The upward band bending at the interface between the AlInGaN semiconductor and KOH electrolyte (Tamboli et al., 2009; Youtsey et al., 1998) would favor interfacial charge transfer across the interface, whereby the photo-generated holes were drifted to the AlInGaN semiconductor surface (Hwang et al., 2007; Grenko et al., 2004) while the electrons were drifted to an opposite direction, which was away from the interface to the electrolyte. The application of etching $J$ would enhance the accumulation of photo-generated holes at the AlInGaN semiconductor surface and extraction of electrons from the semiconductor to the electrolyte. An excess of positive charges at the AlInGaN surface as a result of the hole accumulation as well as a loss of electrons from the semiconductor would weaken chemical bonding of the AlInGaN and thus promoting anodic oxidation (decomposition) (Seo et al., 2002; Hwang et al., 2004; Rotter et al., 2000; Youtsey et al., 1997) of the AlInGaN semiconductor, according to the following expression (Lim et al., 2015):

$$2\text{AlInGaN} + 6h^+ \rightarrow 2\text{AlInGa}^{3+} + \text{N}_2$$

The anodic oxidation would result in the formation of trivalent aluminium indium gallium ($\text{AlInGa}^{3+}$) dangling bonds on the AlInGaN semiconductor surface due to the presence of the unpaired electrons, following the loss of electrons from the AlInGaN via the formation of nitrogen (N$_2$) gas bubbles (Fig. 3b) (Trichas et al., 2009). The AlInGaN could be Al$^{3+}$, In$^{3+}$, and/or Ga$^{1+}$ while the dissipation of N$_2$ gas bubbles would leave anion nitrogen (N) vacancies in the lattice (Fig. 3b). Meanwhile, the electrons that were drifted to the electrolyte were responsible for cathodic reaction at the platinum (Pt) counter electrode, whereby the diluted KOH electrolyte would be dissociated to aqueous hydroxyl ions ($\text{OH}^-$), according to Eqs. (4) and (5):

$$\text{KOH} + e^- \rightarrow \text{K}^{+}_{\text{aq}} + \text{OH}^-_{\text{aq}}$$

$$2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^-_{\text{aq}} + \text{H}_2$$

The generation of negatively charged OH$^-$ species in the electrolyte would create a higher tendency for the ions to diffuse to the region nearer to the AlInGaN semiconductor surface (Fig. 3c). Simultaneous occurrence of the anodic and cathodic reactions would improve etching tendency via oxidation and dissolution of the AlInGaN semiconductor surface, in which

<table>
<thead>
<tr>
<th>Symmetry rocking curve (0002)</th>
<th>Asymmetry rocking curve (10–12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{0002}$ (°)</td>
<td>$\theta_{10–12}$ (°)</td>
</tr>
<tr>
<td>$d_{hkl}$ (nm)</td>
<td>$d_{hkl}$ (nm)</td>
</tr>
<tr>
<td>FWHM (°)</td>
<td>FWHM (°)</td>
</tr>
<tr>
<td>Non-porous</td>
<td>17.165</td>
</tr>
<tr>
<td>20 mA/cm$^2$</td>
<td>16.523</td>
</tr>
<tr>
<td>40 mA/cm$^2$</td>
<td>16.222</td>
</tr>
<tr>
<td>80 mA/cm$^2$</td>
<td>16.103</td>
</tr>
<tr>
<td>160 mA/cm$^2$</td>
<td>17.055</td>
</tr>
</tbody>
</table>

Figure 2 Lattice parameters $c$ and $a$ for non-porous and porous AlInGaN samples.
the formation of anion N vacancies as well as the positively charged anodic oxidized AlInGaN surface (AlInGa\textsuperscript{3+}) would serve as favourable sites for molecular and/or dissociative adsorption of the hydroxyl (OH\textsuperscript{-}) species from the electrolyte.

The dissociative adsorption of OH\textsuperscript{-} would form atomic oxygen (O) (Takashi, 2012). The reaction occurring between the O and AlInGa\textsuperscript{3+} that led to the formation of oxides (Al\textsubscript{2}O\textsubscript{3}, Ga\textsubscript{2}O\textsubscript{3}, and In\textsubscript{2}O\textsubscript{3}) (Fig. 3d) can be represented in Eq. (6). Meanwhile, the reaction between the molecular OH\textsuperscript{-} species with the AlInGa\textsuperscript{3+} would form hydroxides [Al(OH)\textsubscript{3}, Ga(OH)\textsubscript{3}, In(OH)\textsubscript{3}] (Fig. 3d) (Eq. (7)). In comparison, due to the relatively high energy required for the dissociation of OH\textsuperscript{-} species (4.77 eV) (Blanksby and Ellison, 2003), molecular adsorption would be more feasible.

\[
\begin{align*}
2\text{Al}^{3+} + 2\text{Ga}^{3+} + 2\text{In}^{3+} + 9\text{O} & \rightarrow \text{Al}_{2}\text{O}_{3} + \text{Ga}_{2}\text{O}_{3} + \text{In}_{2}\text{O}_{3} \quad (6) \\
\text{Al}^{3+} + 2\text{Ga}^{3+} + 2\text{In}^{3+} + 9\text{OH}^- & \rightarrow \text{Al(OH)}_3 + \text{Ga(OH)}_3 + \text{In(OH)}_3 \quad (7)
\end{align*}
\]

It has been reported that the oxides and hydroxides were insoluble (Lim et al., 2015), except that soluble species were formed via subsequent adsorption of the molecular OH\textsuperscript{-} species on the dangling bond sites that have been initially adsorbed by other OH\textsuperscript{-} species as compared to other sites without dangling bonds. There might exist a possibility for the adsorbed OH\textsuperscript{-} species to bridge with neighbouring lattice atoms to form chemical bonding (Masel, 1996), provided that there were half-filled orbitals for bonding in the AlInGaN lattice. Nevertheless, in the AlInGaN semiconductor surface, the evolution of N\textsubscript{2} would cause the flow of electrons from the dangling bonds on the Al/Ga/In sites to the dangling bonds on other N sites to equalize electronegativity of the AlInGaN surface (Masel, 1996). With these, half-filled orbitals were absent in the AlInGaN semiconductor surface, and thus the formation of a bridging bond between the OH\textsuperscript{-} species and dangling bonds would be difficult. Therefore, the resulting oxides/hydroxides were unstable and subsequent attack of the oxides/hydroxides by the OH\textsuperscript{-} species would lead to the formation of soluble oxides/hydroxides (Fig. 3e), which eventually led to the dissolution of the AlInGaN surface by dissolving in the electrolyte. Representative reactions showing the formation of soluble oxides/hydroxides are shown below.

\[
\begin{align*}
\text{Al}_2\text{O}_3 + \text{Ga}_2\text{O}_3 + \text{In}_2\text{O}_3 + 18\text{OH}^- & \rightarrow 2(\text{Al(OH)}_3)^3^- + 2(\text{Ga(OH)}_3)^3^- + 2(\text{In(OH)}_3)^3^- + 9\text{H}_2\text{O} \quad (8) \\
\text{Al(OH)}_3 + \text{Ga(OH)}_3 + \text{In(OH)}_3 + 3\text{OH}^- & \rightarrow [\text{Al(OH)}_4]^3^- + [\text{Ga(OH)}_4]^3^- + [\text{In(OH)}_4]^3^- \quad (9)
\end{align*}
\]

The dissolution of the AlInGaN surface would leave cation (Al,Ga,In) and anion (O/N) vacancy sites (Fig. 3f) in the lattice position initially occupied by the cations and anions, in which chemically the cation and anion vacancies were created while physically pores were formed.

Figure 3  Schematic diagram of etching mechanism of the porous AlInGaN sample, which initiates with (a) absorption of UV, (b) anodic oxidation of AlInGaN and liberation of nitrogen gas bubbles, (c) adsorption of hydroxyl (OH\textsuperscript{-}) species on the AlInGa\textsuperscript{3+} dangling bonds, (d) formation of insoluble oxides and hydroxides, (e) formation of soluble oxides and hydroxides, (f) formation of vacancies, and (g) new exposed AlInGaN surface.
The increasing trend of lattice parameters $c$ and $a$ in the porous AlInGaN samples as the etching $J$ was increased from 20 mA/cm$^2$ to 80 mA/cm$^2$ which might be owing to the increasing amount of vacancies that might have induced tensile strains in the samples. For justification, out-of-plane and in-plane strains could be conveniently calculated using the following equations:

$$e_{zz} = \frac{c - c_0}{c_0}$$

(10)

$$e_{xx,yy} = \frac{a - a_0}{a_0}$$

(11)

where $e_{zz}$ is the out-of-plane strain, $e_{xx}$ is the in-plane strain, $c$ and $a$ are the lattice parameters of the porous and non-porous AlInGaN (Figs. 2) while $c_0$ and $a_0$ are the lattice parameter of strain free AlInGaN. The $c_0$ and $a_0$ of AlInGaN layer were determined using Vegard’s law (Zhou et al., 2006), which was represented by the subsequent equation:

$$c_0 = x_{AIn}c_{AIn} + x_{InN}c_{InN} + x_{GaN}c_{GaN}$$

(12)

$$a_0 = x_{AIn}a_{AIn} + x_{InN}a_{InN} + x_{GaN}a_{GaN}$$

(13)

where $x_{AIn}$, $x_{InN}$, and $x_{GaN}$ are the mole fractions of AIN, InN, and GaN, respectively, while ($a_{AIn}$, $c_{AIn}$), ($a_{InN}$, $c_{InN}$), and ($a_{GaN}$, $c_{GaN}$) are the lattice parameters of AIN ($a_{AIn} = 0.31094$ nm, $c_{AIn} = 0.49790$ nm) (ICDD file No. 03-065-0831), InN ($a_{InN} = 0.35400$ nm, $c_{InN} = 0.57040$ nm) (ICDD file No. 03-065-3412), and GaN ($a_{GaN} = 0.31891$ nm, $c_{GaN} = 0.51855$ nm) (ICDD file No. 00-050-0792), respectively. In comparison, the porous AlInGaN samples demonstrated larger out-of-plane and in-plane strains (Fig. 4) than the non-porous sample. Besides, an increasing trend in the out-of-plane and in-plane strains (Fig. 4) as a function of etching $J$ up to 80 mA/cm$^2$ was observed and this was in agreement with the proposed fact that the formation of more vacancies would increase the tensile strains.

Whilst for the sample subjected to the highest etching $J$ (160 mA/cm$^2$), the lattice parameters $c$ and $a$ as well as out-of-plane and in-plane strains were decreased to a value, which was slightly larger than that of the non-porous sample (Fig. 4). This occurrence might be associated with the decrease in the amount of vacancies that were formed during the PEC etching at 160 mA/cm$^2$. It has been noteworthy that formation of vacancies would lead to a lattice expansion due to the existence of electrostatic repulsion between the cations that were located closest to the vacancy (Li et al., 2009). Therefore, the lattice parameters kept increasing and the corresponding strains were tensile for the porous AlInGaN samples etched at $J$ below 80 mA/cm$^2$. On the other hand, for the sample etched at 160 mA/cm$^2$, the decrease in the amount of vacancies might be due to a degradation in etching tendency of the AlInGaN semiconductor surface as a result of degraded cathodic reduction at the Pt electrode. It was postulated that the degradation of cathodic reduction at the Pt electrode might lead to an excess of electrons in the electrolyte, which might inhibit further transfer of electrons from the AlInGaN semiconductor surface. Eventually, the electrons would recombine with the existing holes in the AlInGaN semiconductor (Lim et al., 2015). This mass-transport limited etching would inhibit etching ability of the AlInGaN semiconductor surface. Furthermore, besides the mass-transport limited effect, additional effect due to the oxidation of the OH$^-$ ions that have been reduced from the KOH electrolyte would also limit etching tendency of the AlInGaN semiconductor. The oxidation of OH$^-$ ions would result in the generation of H$_2$ gas bubbles at the Pt counter electrode while O$_2$ gas bubbles on the AlInGaN semiconductor surface. A representative reaction can be described as follows:

$$2\text{OH}^- + 2\text{H}^+ \rightarrow \text{H}_2 + \text{O}_2$$

(14)

The hydrostatic strain originated from vacancies present in the investigated samples has been calculated using the following expression:

$$e_h = \frac{1 - \nu}{1 + \nu} \left( e_{zz} + \frac{2\nu}{1 - \nu} e_{xx,yy} \right)$$

(15)

where $e_h$ and $\nu$ are the hydrostatic strain and Poisson’s ratio, respectively. The $\nu$ value of Al$_{0.10}$In$_{0.10}$Ga$_{0.80}$N films was determined as 0.228 by taking into account $\nu$ values reported for GaN (0.210) (Polian et al., 1996) and AlN (0.203) (Shur and Davis, 2004; McNeil et al., 1993), and InN (0.399) (Shur and Davis, 2004; Sheleg and Savastenko, 1995).

![Figure 4](image-url) A relationship between the out-of-plane strain, in-plane strain, and hydrostatic strain as a function of etching current density.
Fig. 4 presents a relationship of the $e_h$ values with respect to the non-porous and porous samples. In comparison, the AlInGaN samples that have been subjected to PEC etching at different etching $J$ demonstrated larger $e_h$ values than the non-porous sample. This finding supported that the amount of vacancies was increased after the etching process. It was postulated that the enhancement in the number of vacancies as a function of etching $J$ was related to the increase in the number of holes accumulated at the interface between the AlInGaN semiconductor and the KOH electrolyte for anodic oxidation as well as the increase in the number of electrons being transferred to the electrolyte for cathodic reduction. Eventually, higher possibility for dissolution of AlInGaN semiconductor occurs and results in higher number of vacancies. On the other hand, the acquisition of the lowest $e_h$ value at 160 mA/cm$^2$ when compared to other porous AlInGaN samples supported the aforementioned anticipation that the PEC etching process was inhibited at the etching current density of 160 mA/cm$^2$.

Field emission scanning electron microscopy (FESEM) analysis was performed to examine surface morphology of the AlInGaN semiconductors after the PEC etching process performed at different etching $J$ in comparison with the non-porous AlInGaN sample (Fig. 5a). In the non-porous sample, the surface was relatively smooth without the formation of void. In the sample subjected to PEC etching at etching $J$ of 20 mA/cm$^2$, surface morphology change was observed through the emergence of small spots distributing on the sample (Fig. 5b). As the etching $J$ was increased to 40 mA/cm$^2$ (Fig. 5c) and 80 mA/cm$^2$ (Fig. 5d), the spots became obviously seen as shallow round-shaped pores on the samples’ surface, in which the pores were growing into bigger size at 80 mA/cm$^2$. In the sample being etched at 160 mA/cm$^2$ (Fig. 5e), a dissimilar surface morphology (no pore-like structure) was observed. It was hypothesized that the etching $J$ of 160 mA/cm$^2$ might be too high that either promoted excessive etching on the sample or restricted subsequent etching of the sample due to the mass-transport limited etching.

Further investigation was performed using atomic force microscopy (AFM) analysis to investigate changes in surface topography and root-mean-square (RMS) roughness of the samples after the PEC etching process. AFM analysis would be appropriate for determination of porosity in the investigated samples because any chemical or geometric heterogeneity of the solid surface would provide different contact angles of the AFM probe tip on the sample surface, whereby the contact angle was larger on a rough or porous surface when compared with that on a microscopically smooth surface of the same composition. It was postulated that the formation of pores with different sizes and shapes on the AlInGaN semiconductor surface after the PEC etching process would induce different contact angles onto the AFM probe top during the AFM scanning. As being observed in the non-porous sample (Fig. 6a), the hillocks (peaks) appeared to be tall and sharp in the tip when compared to other samples that have been etched at different etching $J$. As the etching $J$ was increase to 20 (Fig. 6b), 40 (Fig. 6c), and 80 mA/cm$^2$ (Fig. 6d), the tip of the hillocks seemed to be shortened and was no longer sharp. This was an indication of the PEC etching effect on the sample surface. While approaching 160 mA/cm$^2$ (Fig. 6e), the tip of the hillocks became sharp and tall again, mimicking the non-porous AlInGaN sample. Apart from these, it could be estimated from the $z$-scale of the AFM images, which indicated the degree of AFM probe tip deflection with respect to topography of the samples. In the non-porous sample, the deflection was approximately 4.8 nm. In the AlInGaN samples subjected to etching $J$ of 20–80 mA/cm$^2$, the degree of deflection was increased to 8.7–12.9 nm. The increase of deflection in the porous samples as compared to the non-porous sample might be due to the coarse topography of the samples as a consequence of formation of pores after the PEC etching process. Nonetheless, in the

Figure 5  FESEM images of (a) nonporous sample and porous samples subjected to etching current density of (b) 20, (c) 40, (d) 80, and (e) 160 mA/cm$^2$. 

Please cite this article in press as: Quah, H.J. et al., Effects of ultraviolet-assisted electrochemical etching current densities on structural and optical characteristics of porous quaternary AlInGaN alloys. Arabian Journal of Chemistry (2015), http://dx.doi.org/10.1016/j.arabjc.2015.10.003
AlInGaN sample etched at 160 mA/cm², the degree of deflection was decreased to 5.7 nm, signifying improved smoothness of the sample surface though after the etching process. With these, the corresponding RMS surface roughness (Fig. 6f) for this sample (1.69 nm) was comparable to the RMS roughness obtained for the non-porous sample (1.40 nm), while larger values were obtained for the samples subjected to lower etching (2.32–3.60 nm). The findings suggested that the high etching J (160 mA/cm²) might have limited the etching process, rather than an excessive etching on the surface because later might have yielded rougher surface than the other porous AlInGaN semiconductors etched at lower J.

Optical phonon characteristics of the non-porous and porous samples were investigated using Raman spectroscopy conducted at room temperature in $\sigma(x\chi)\sigma$ scattering geometry, where the $\sigma$ was parallel to $c$-axis of the samples. According to the selection rule of Raman, $E_2$(high) and $A_1$(LO) are the two phonon modes that could be detected under the $\sigma(x\chi)\sigma$ configuration (Kuball, 2001). Raman spectra in the range of 490–900 cm⁻¹ of the non-porous and porous samples are

![3-dimensional AFM surface topographies of (a) non-porous and (b)-(e) porous samples subjected to etching at different current densities ((b) 20, (c) 40, (d) 80, and (e) 160 mA/cm²). RMS roughnesses of the investigated samples are shown in (f).](image)

![Raman spectra of non-porous and porous samples.](image)
elucidated in Fig. 7. De-convolution using Gaussian fitting was performed on the Raman peaks detected at a lower energy side in order to distinguish between the peaks related to InGaN-like $E_2$(high) and sapphire. Inset of Fig. 8 shows the de-convoluted peaks associated with the InGaN-like $E_2$(high) and sapphire for the investigated samples. The peak detected in the range of 566.2–569.1 cm$^{-1}$ was assigned to the InGaN-like $E_2$(high) phonon mode (Davydov et al., 1998) due to the existence of the peak in the range of $E_2$(high) of GaN (569 cm$^{-1}$) and $E_2$(high) of InN (488 cm$^{-1}$) (Hernandez et al., 2005). Besides, sapphire peak that was located in the range of 577.3–579.8 cm$^{-1}$ (Fig. 7) was also determined for the investigated samples.

It was observed from the inset of Fig. 8 that the peak of InGaN-like $E_2$(high) phonon was shifted to a lower energy for the porous samples relative to the non-porous sample. The peak shift to lower energy proposed that the porous samples have experienced tensile stresses (Liu et al., 2011). As the $E_2$(high) phonon was sensitive towards in-plane strain (Liu et al., 2011; Zhang et al., 2014), it was utilized to calculate in-plane stress relaxation in the porous samples relative to the non-porous sample using Eq. (16), as follows (Tripathy et al., 2002; Vajpeyi et al., 2005b):

$$\Delta \nu E_2(\text{high}) = K_R \sigma$$  \hspace{1cm} (16)$$

where $\Delta \nu$, $E_2(\text{high})$, $K_R$, and $\sigma$ is energy shift with respect to the non-porous sample, InGaN-like $E_2(\text{high})$ phonon mode, proportionality factor, and in-plane stress relaxation, respectively (Tripathy et al., 2002; Vajpeyi et al., 2005a). The $K_R$ values in the range of 4.227–4.231 were determined using a linear interpolation method by taking into consideration the $c$ (Fig. 2) and band gap (Fig. 9) calculated from XRD and photoluminescence (PL), respectively, for the porous samples. The acquired $K_R$ values of the porous AlInGaN layers formed at different $J$ were within the ranges reported for GaN (4.2) (Kisielowski et al., 1996), InN (9.0) (Wang et al., 2006), and AlN (4.0) (Yang et al., 2011). It could be observed from Fig. 8 that larger in-plane stress relaxation was achieved by the porous AlInGaN samples obtained by etching at different $J$. The attainment of a larger stress relaxation in the porous samples was attributed to the existence of vacancies after the PEC etching process that have induced tensile strains to the samples as compared to the non-porous sample. Besides, as the $J$ was increased from 20 to 80 mA/cm$^2$, the in-plane stress relaxation was increased, except for the sample subjected to etching at 40 mA/cm$^2$ (Fig. 8). The increasing trend was in agreement with the increase in lattice parameters $c$ and $a$, out-of-plane and in-plane strains, as well as the hydrostatic strain. Nevertheless, the out-of-trend exhibited by the porous sample subjected to etching at 40 mA/cm$^2$, which showed an acquisition of a smaller in-plane stress relaxation than the samples etched at 20 mA/cm$^2$ remained unknown. The acquisition of a decreased stress relaxation for the sample subjected to 160 mA/cm$^2$, which showed a comparable value with that of the non-porous AlInGaN sample, could be related to the mass transport limited etching that has decreased the amount of vacancies and thus decreasing the lattice parameters and strains. Besides, the emergence of peak positioned at a higher energy side was attributed to the AlGaN-like $A_1$(LO) phonon mode (Hu et al., 2012; Cros et al., 2006; Chen et al., 2004), wherein the range of energy for $A_1$(LO) of GaN and $A_1$(LO) of AlN was 734 cm$^{-1}$ and 890 cm$^{-1}$, respectively.

Room temperature PL spectra of the non-porous and porous AlInGaN samples subjected to different $J$ are shown in the inset of Fig. 9. It was noteworthy from the PL spectra that the porous samples demonstrated higher PL intensities when compared with the non-porous sample. The reason contributing to the acquisition of significantly higher PL intensities in the porous samples might be due to the increased RMS roughness values of the samples after the etching process. It has been reported elsewhere (Kang et al., 2007) that the absence of multiple PL emission peaks would be an indicator of the occurrence of surface roughening, owing to the suppression of total internal reflection and interference effects. In fact, apart from the aforementioned impacts brought by the surface roughening condition on the porous samples in contrast to the non-porous sample, which would passivate total internal reflection effect and caused scattering of the photons off the sidewalls of the pores, the increase in the PL intensity obtained for the porous samples in comparison with the non-porous sample could be also attributed to

![Figure 8](image1.png)  
**Figure 8** The calculated in-plane stress relaxation as a function of etching current densities. Inset of this figure shows the de-convoluted Raman spectra for the investigated samples.

![Figure 9](image2.png)  
**Figure 9** The calculated band gap based on PL emission wavelength and PL spectra (inset) of non-porous and porous samples.
the presence of either radiative or non-radiative localized states that caused an alteration of the PL intensity.

As the J was increased from 20 to 80 mA/cm², an increasing trend in the PL intensities was observed. Nevertheless, a lower intensity was obtained in the sample etched at 160 mA/cm², which was comparable to that of non-porous sample. A plausible explanation for this observation might be attributed to the presence of surface states that might have served as radiative recombination centres. The surface states were possibly originated from the vacancies that were formed after the PEC etching process, in which the increase of PL peak intensity was corroborated with the increasing trend observed for the hydrostatic strain as the etching J was increased from 20 to 80 mA/cm². Previous literature has revealed that a competition between the oxidation and dissolution processes during etching would create either cation or anion vacancy sites at the surface (Slimane et al., 2013). It has been also disclosed from the literature that Ga and N vacancies might be the sources of radiative recombination centres in porous GaN (Yan et al., 2012). In addition, any exciton bound to a vacancy, if recombine radiatively, would also enhance the photoluminescence properties (Tongay et al., 2013).

The higher PL intensity observed for the sample subjected to etching at 160 mA/cm² could either be due to the presence of the least amount of vacancies in the sample or due to the mass-transport limited PEC etching that has not efficiently removed non-radiative surface states on the AlInGaN semiconductor surface (Fukuda, 1999).

AlInGaN samples etched at different J (20, 40, 80, and 160 mA/cm²) were taken and examined after the PEC etching process. As the etching J was increased from 20 mA/cm² to 80 mA/cm², an increase in the \( E_g \) energy was observed (Fig. 9). This was in agreement with the reported blue shift in PL peaks that might be corresponded to an increase in the \( E_g \) (Veal et al., 2005). The increased \( E_g \) might happen when the electrons bound to the vacancy sites have filled conduction band minimum (Sadofyev and Samal, 2010), and the subsequent electrons would be excited to a higher energy level. As a result, Fermi level would be shifted and the \( E_g \) was enlarged (Sadofyev and Samal, 2010; Lee et al., 2012). In addition, it could be noted that the increase in the \( E_g \) energy could be associated with the increase of the porosity, which would induce a higher exposure to the PL excitation light over a higher surface area per unit volume and therefore providing more electrons for the excitation and recombination to take place (Al-Heuseen et al., 2011). In addition, the elimination of any non-radiative localized states initially present in the non-porous AlInGaN sample after the etching process would also enhance the \( E_g \) energy, whereby the localized states would increase absorption of the PL excitation light and thus decreasing propagation of the light over a wider band gap region.

In this work, it was suggested that the non-radiative localized states might be originated from dislocation-type defect present in the samples. Fig. 10 presents the relationship between the screw dislocation density \( (N_{\text{screw}}) \), edge dislocation density \( (N_{\text{edge}}) \), and total dislocation density \( (N_{\text{total}}) \) for the investigated samples, which have been calculated by taking into consideration the full-width-half-maximum (FWHM) values for rocking curves of the (0002) and (10–12) planes (Table 1), as follows:

\[
N_{\text{screw}} = \frac{\beta_{(0002)}}{4.35 \times b_{\text{screw}}^2}
\]

\[
N_{\text{edge}} = \frac{\beta_{(10–12)}}{4.35 \times b_{\text{edge}}^2}
\]

where \( N_{\text{screw}}, N_{\text{edge}}, \beta_{(0002)\text{type}} \), \( \beta_{(10–12)\text{edge}} \), \( b_{\text{screw}} \), and \( b_{\text{edge}} \) are the screw dislocation density, edge dislocation density, θ-scan full-width-half-maximum (FWHM) of (0002) plane, θ-scan FWHM of (10–12) plane, c-type Burger’s vector, and a-type Burger’s vector, respectively. As the etching current density was increased from 20 mA/cm² to 80 mA/cm², a decrease in \( N_{\text{total}}, N_{\text{edge}}, \) and \( N_{\text{screw}} \) was observed (Fig. 10). This was in corroboration with the aforementioned anticipation that the increasing trend obtained for the \( E_g \) energy could be due to the decrease in the localized states originating from the dislocation-type defects. For the porous AlInGaN sample obtained by etching at 160 mA/cm², the acquisition of increased \( N_{\text{total}}, N_{\text{edge}}, \) and \( N_{\text{screw}} \) values with respect to other porous samples further supported the suggestion that a mass-transport limited PEC etching process has taken place in the sample, in which decreased vacancy sites and/or many-body effects (Shokhovets et al., 2014; Jiang, 2002) were present in the sample.

In addition, full-width-half-maximum (FWHM) of the PL peaks obtained for all the porous AlInGaN samples subjected to different etching J was larger than the non-porous sample (inset of Fig. 9). As the etching J was increased from 20 mA/cm² to 80 mA/cm², a decrease in the FWHM of the PL peak from 17.1578 nm to 16.9449 nm was obtained, signifying improved quality of the samples after the PEC etching process. However, an increase of the FWHM was observed for the sample etched at 160 mA/cm² to a value (17.7829 nm) similar to that of the non-porous sample. The changes in the FWHM of the PL peaks could be attributed to the alloy disorder (Polimeni et al., 2000) that might happen in the AlInGaN samples after the PEC etching process, in which the composition of AlInGaN might no longer be the...
as-received $\text{Al}_{0.1}\text{In}_{0.1}\text{Ga}_{0.8}\text{N}$. It was believed that the alloy disorder, which contained more vacancy-type defects that served as the radiative recombination centres and lesser dislocation-type defects that served as the non-radiative recombination centres in the samples etched at $J$ lower than $80 \text{ mA/cm}^2$ as compared to the non-porous sample has led to the attainment of smaller FWHM.

UV–Visible absorption spectra of the non-porous and porous AlInGaN samples are presented in Fig. 11b. All of the porous samples have demonstrated higher absorption background (Kim et al., 2010) than the non-porous sample. In comparison, the porous samples etched from 20 to $80 \text{ mA/cm}^2$ were having higher absorption than the sample etched at $160 \text{ mA/cm}^2$. This finding could be correlated with the increased pores in the samples, which would extensively lengthen the path of incident light, and thus enhancing the absorption. Tauc plot (Mahnaz et al., 2012) has been utilized to evaluate optical $E_g$ of the non-porous and porous AlInGaN samples using the following equation:

$$\left(\frac{a}{hv}\right) = A\left(\frac{h}{E_g}\right)^{2/\alpha}$$

where $a$, $h$, and $v$ are absorption coefficient, Planck’s constant, and frequency, respectively. The $s$ value was determined as $(1–7) \times 10^6 \text{ cm}^{-1}$. According to the Tauc law, the $(\frac{a}{hv})^2$–$hv$ plots (Fig. 11a) of the samples would give a linear region with a slope $A$ and the $E_g$ values of the investigated samples were extracted through linear extrapolation of the plots to the $x$-axis of $(\frac{a}{hv})^2$–$hv$ plots where the $(\frac{a}{hv}) = 0$. Inset of Fig. 11b shows the extracted values of $E_g$ for the investigated samples and the obtained values of $E_g$ were comparable to the results obtained from the PL emission band gap energy (Fig. 9).

In addition, a long absorption tail was observed in the absorption spectrum of each sample, which might be an artefact due to the multiple light scattering effect, but it could be also due to defects-induced absorption. Nevertheless, if the multiple light scattering was present, flattening of the spectrum would occur at absorption wavelength greater than 800 nm (Tian and Scheblykin, 2015). Thus, for absorption at wavelength lesser than 800 nm, the long absorption tail would be caused by the defects-induced absorption. In order to determine the defects-induced absorption, Urbach law (Ikhmayies and Bitar, 2013) was applicable for calculation of the localized

Figure 11 (a) Tauc plot determined from (b) UV–visible absorption spectra for the non-porous and porous samples. Inset of (b) presents optical $E_g$ and $U_E$ of the investigated samples.
energy states present in optical band gap of the investigated samples, according to the following equation:

\[ \alpha = \alpha_0 \exp \left( \frac{h\nu}{U_E} \right) \]  

(21)

where \( \alpha \), \( \alpha_0 \), \( h \), \( \nu \), and \( U_E \) denote the absorption coefficient, absorption constant, Planck’s constant, frequency, and Urbach energy, respectively. The \( U_E \) value could be estimated from reciprocal of the linear slope region of the Urbach plot (not shown). It was observed that the \( U_E \) value was slightly increased as the etching \( J \) was increased from 20 mA/cm² to 80 mA/cm², whereby beyond which, the \( U_E \) value was decreased to a value closer to that of the non-porous AlInGaN sample (inset of Fig. 11b). The trend demonstrated by \( U_E \) value was similar to that of the \( E_g \) value determined from the PL peak shift. This was an indication that the increase in \( U_E \) of the localized states did not shrink but increased the \( E_g \) value. It was therefore suggested that the localized states were originated from the vacancy-type defects that served as the radiative recombination centres.

4. Conclusions

Effects of etching current densities (J = 20, 40, 80, and 160 mA/cm²) towards structural, physical, and optical properties of porous quaternary AlInGaN semiconductors prepared by photo-electrochemical (PEC) etching in a diluted potassium hydroxide solution under UV illumination have been studied. The formation of vacancies in the porous AlInGaN samples has led to the acquisition of larger tensile strains and hydrostatic strain as compared to the non-porous sample. Nevertheless, dislocation density present in the porous AlInGaN samples was lower than that of the non-porous sample. It was therefore deduced that the vacancies and dislocations have respectively served as radiative and non-radiative states in the porous samples, which contributed to an increase in the photoluminescence (PL) intensity, band gap (\( E_g \)) energy, and in-plane stress relaxation as a function of etching \( J \). Nevertheless, as the \( J \) was increased beyond 80 mA/cm², a decrease in the PL intensity and \( E_g \) energy as well as the lattice parameters, hydrostatic strain, and root-mean-square surface roughness as compared to other porous samples suggested that the PEC etching in the sample etched by 160 mA/cm² has been inhibited. In conclusion, an improvement in structural and optical properties under the influence of etching \( J \) for the porous AlInGaN samples in contrast to the non-porous sample suggested that the porous AlInGaN samples could be used as the templates for overgrown layers with stress relaxation, in which upon successful would promote greater performance in light-emitting diodes for solid-state lighting.

Acknowledgements

The authors would like to acknowledge Universiti Sains Malaysia, Fundamental Research Grant Scheme (FRGS/203/PFIZIK/6711376), and RU Top-Down Grant (1001/CSS/870019) for their financial support. HJQ and WFL would like to acknowledge the support provided by Universiti Sains Malaysia under post-doctoral fellowship scheme.

References

Effects of ultraviolet-assisted electrochemical etching current densities


