

PAPER

Systematic oxygen impurity reduction in smooth N-polar GaN by chemical potential control

To cite this article: Dennis Szymanski *et al* 2022 *Semicond. Sci. Technol.* **37** 015005

View the [article online](#) for updates and enhancements.

You may also like

- [A study on the nucleation and MPCVD growth of thin, dense, and contiguous nanocrystalline diamond films on bare and Si₃N₄-coated N-polar GaN](#)
Matthew A Laurent, Mohamadali Malakoutian and Srabanti Chowdhury
- [N-polar GaN/AlGaIn/GaN metal-insulator-semiconductor high-electron-mobility transistor formed on sapphire substrate with minimal step bunching](#)
Kiattiwut Prasertsuk, Tomoyuki Tanikawa, Takeshi Kimura et al.
- [N-polar GaN epitaxy and high electron mobility transistors](#)
Man Hoi Wong, Stacia Keller, Nidhi, Sansaptak Dasgupta et al.



The Electrochemical Society
Advancing solid state & electrochemical science & technology

242nd ECS Meeting

Oct 9 – 13, 2022 • Atlanta, GA, US

Abstract submission deadline: **April 8, 2022**

Connect. Engage. Champion. Empower. Accelerate.

MOVE SCIENCE FORWARD



Submit your abstract



Systematic oxygen impurity reduction in smooth N-polar GaN by chemical potential control

Dennis Szymanski^{1,*} , Ke Wang¹, Felix Kaess¹, Ronny Kirste², Seiji Mita², Pramod Reddy², Zlatko Sitar^{1,2} and Ramon Collazo¹

¹ Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, 27695, United States of America

² Adroit Materials, Inc., Apex, NC 27539, United States of America

E-mail: deszyman@ncsu.edu

Received 13 July 2021, revised 12 October 2021

Accepted for publication 3 November 2021

Published 29 November 2021



Abstract

Process chemical potential control and dislocation reduction were implemented to control oxygen concentration in N-polar GaN layers grown on sapphire substrates via metal organic chemical vapor deposition (MOCVD). As process supersaturation was changed from ~ 30 to 3400, the formation energy of the oxygen point defect increased, which resulted in a 25-fold decrease in oxygen incorporation. Reducing dislocations by approximately a factor of 4 (to $\sim 10^9 \text{ cm}^{-3}$) allowed for further reduction of oxygen incorporation to the low- 10^{17} cm^{-3} range. Smooth N-polar GaN layers with low oxygen content were achieved by a two-step process, whereas first a $1 \mu\text{m}$ thick smooth N-polar layer with high oxygen concentration was grown, followed by low oxygen concentration layer grown at high supersaturation.

Keywords: oxygen, impurity, semiconductor, nitride, chemical potential, defect

(Some figures may appear in colour only in the online journal)

Gallium nitride is a wide bandgap semiconductor that has generated great interest in the field of rf and high-power electronics [1, 2]. Being non-centrosymmetric, c-oriented films can be grown in two different polar orientations, gallium-polar (0001) or nitrogen-polar (000-1). The GaN wurtzite crystal structure shows a deviation from the ideal wurtzite crystal structure, giving rise to a spontaneous lattice polarization. It is the direction of this dipole which defines the polar orientation of the film [3]. Traditionally, smooth epitaxial films with low impurity incorporation were grown in the Ga-polar orientation while N-polar films inherently grew with a rough surface morphology and high unintentional impurity levels. Despite these drawbacks, N-polar epitaxial films have recently attracted interest due to their applications in HEMTs with better 2DEG confinement and scaling [4], and many challenges of the N-polar epitaxy, including inversion domains (IDs),

rough, hexagonal-hillock surface morphology, and unintentional incorporation of oxygen as a shallow donor have been mitigated or overcome [2]. Various studies have shown the dependence of growth conditions, such as V/III ratio and H_2/N_2 diluent gas ratio (F-ratio) on the surface morphology and unintentional impurity incorporation for both polarities of GaN [5–9]. These efforts highlight a paradox in the pathway toward achieving N-polar GaN films with a smooth surface morphology and low unintentional oxygen incorporation. The growth conditions that are required to mitigate oxygen incorporation lead to a rough surface morphology, and those that lead to a smooth surface result in high oxygen incorporation [2, 5, 6, 8–15]. The reduction of background impurities has largely been addressed via empirical approaches for each impurity being considered.

This work successfully addresses both challenges simultaneously: smooth N-polar GaN with low oxygen incorporation. In order to achieve this, a morphology control layer

* Author to whom any correspondence should be addressed.

is implemented in conjunction with chemical potential control (CPC) of the process that mitigates unintentional oxygen incorporation. The CPC approach relates chemical potentials of the growth species and point defects, providing a pathway to maximize the formation energy of unwanted point defects, and thus minimize their incorporation into the GaN film [16]. This model was first developed to control carbon incorporation in Ga-polar GaN and further demonstrated for compensation control in Si-doped AlGaIn [17]. The results of this work demonstrate the generality of the CPC framework and its applicability across different materials systems and point defects.

Control of the supersaturation (and thus chemical potential of O_N) can be achieved by the choice of growth temperature, diluent gas, V/III ratio, as well as growth pressure. The relationship between these growth parameters and supersaturation for the case of GaN and AlGaIn has been previously described by Mita *et al* and Washiyama *et al* [5, 6, 18]. N-Polar GaN films were grown on sapphire substrates with a miscut of 2° along the m -direction in a vertical, cold-walled, rf-heated, low pressure MOCVD reactor. A pressure of 20 Torr, growth temperature of 1100°C , and a metalorganic flow (triethylgallium) of $18\ \mu\text{mol min}^{-1}$, with a total flow of 7.5 slm were maintained as constants. The growth process was performed as follows: the substrate was treated first with an H_2 etch for 7 min at 1100°C , followed by a 4 min nitridation step at 945°C . This nitridation step is essential for obtaining a N-polar film [3, 19–24]. A 20 nm-thick low temperature GaN buffer is then deposited and annealed under N_2 and NH_3 at 1100°C for 6 min. Finally, $1\ \mu\text{m}$ thick N-polar GaN films were grown with V/III ratios varying from 100 to 2000 by adjusting the NH_3 flow within the range of 0.3 slm to 6 slm under both H_2 and N_2 diluent gases.

Since oxygen acts as a shallow donor in N-polar GaN, the oxygen concentration was estimated from the free carrier concentration obtained by Hall measurements [2], using an Ecopia-3000 Hall Effect Measurement System. The measurements were done at room temperature in the van der Pauw geometry using indium contacts. The carbon concentration in the N-polar GaN films was about two orders of magnitude lower than the oxygen concentration [9], thus, the compensation was assumed to be negligible.

Screw and edge dislocation densities were estimated from the full width at half maxima (FWHM) of the x-ray (002) and (302) omega rocking curves, respectively, using the equation $\rho = \frac{\beta^2}{4.35b^2}$ [25], where β is the FWHM in angular units, and b is the Burgers vector of the dislocation. The measurement was performed with a Philips X'Pert MRD with a Cu K_α x-ray source in a double crystal configuration. The surface morphology and roughness of the films were analyzed using an Asylum Research MFP-3D atomic force microscope (AFM) in tapping mode. The RMS roughness values were obtained from a $90 \times 90\ \mu\text{m}^2$ scan area.

As previously described, the reduction of oxygen in the film is achieved by implementing CPC. The model provides a relationship between the change in supersaturation and the equilibrium partial pressures of Ga and N in the gas phase, as well as the formation energy of point defects in the film

[16]. The point defect of interest in this work is oxygen as a nitrogen substitutional impurity. First, it is necessary to relate the partial pressures of the limiting reactant species that affect supersaturation during MOCVD growth. In this case, this is considered for gallium, thus the supersaturation is given by:

$$\sigma_{\text{Ga}} = \frac{P_{\text{Ga}}^o - P_{\text{Ga}}}{P_{\text{Ga}}} = \frac{\Delta P_{\text{Ga}}}{P_{\text{Ga}}}, \quad (1)$$

where P_{Ga}^o is the input partial pressure of the Ga species, and P_{Ga} is the equilibrium vapor pressure of Ga over GaN at growth temperature. The chemical potential of gallium relative to its standard state is then related to the supersaturation as

$$\mu_{\text{Ga}} \sim -kT \ln(1 + \sigma). \quad (2)$$

At equilibrium, the change in chemical potentials of gallium and nitrogen for a binary alloy are related by

$$\Delta\mu_{\text{Ga}} + \Delta\mu_{\text{N}} = 0, \quad (3)$$

thus,

$$\Delta\mu_{\text{N}} = -\Delta\mu_{\text{Ga}}. \quad (4)$$

By calculating the change in chemical potential of gallium, the change in chemical potential of nitrogen is known via equation (4). For the case of oxygen as a nitrogen substitutional impurity, the chemical potentials relate to the energy of formation of the point defect through

$$E^f(O_N) = E_{\text{ref}}(O_N) + \mu_{\text{N}} - \mu_{\text{O}} + [E_F + E_V], \quad (5)$$

where $E_{\text{ref}}(O_N)$ is the free energy of the crystal with a single oxygen point defect compared to the free energy of an ideal crystal, E_F is the Fermi energy with respect to the valence band maximum, and E_V is the valence band energy. The boundary phase of oxygen is not known and is assumed to be either O_2 or Ga_2O_3 .

From equations (5) and (4), considering a change in the nitrogen chemical potential through change in the growth conditions,

$$\Delta E^f(O_N) = (\Delta\mu_{\text{N}}) \text{ assuming } O_2 \text{ boundary phase } (\mu_{\text{O}} = 0) \quad (6)$$

Or,

$$\Delta E^f(O_N) = \left(\frac{1}{3} \Delta\mu_{\text{O}}\right) \text{ assuming } Ga_2O_3 \text{ boundary phase} \\ \times (3\Delta\mu_{\text{N}} + 2\Delta\mu_{\text{Ga}} = 0). \quad (7)$$

It is clear that in either case, the formation energy increases with increase in nitrogen chemical potential. Using the relationship in equation (2), the change in the formation energy is hence proportional to:

$$\Delta E^f(O_N) \propto T \ln\left(\frac{\sigma_{\text{exp}}}{\sigma_0}\right), \quad (8)$$

where σ_{exp} is the input supersaturation and σ_0 is the supersaturation at a reference growth condition. It is important to note that the formation energy of oxygen point defect depends also on E_F , which is assumed to be pinned and constant at the surface of GaN. This relationship illustrates the available process ‘knobs’ to achieve the desired suppression of oxygen incorporation.

The thermodynamic supersaturation in the gas phase was calculated from growth temperature, partial pressures of gas species, choice of diluent gas, total flow rate, and reactor pressure, using a previously established framework [6, 16, 18, 26]. In addition to these input parameters, calculating the supersaturation requires an estimate of the ammonia decomposition efficiency, usually referred to as the α parameter. This parameter is reactor, pressure, flow rate, and temperature dependent and is estimated by thermodynamic analysis and fitting of experimental data as described by Washiyama *et al* [16, 18]

The change in the chemical potential of nitrogen ($\Delta\mu_N$) was calculated relative to a reference state with a low supersaturation value of 30, achieved under H_2 diluent and a V/III ratio of 100. For this reference state, the oxygen incorporation into the film was mid- 10^{19} cm^{-3} . Higher supersaturations and μ_N , needed to increase the formation energy of the oxygen point defect according to equation (6), were achieved by increasing the V/III ratio under H_2 diluent or by replacing H_2 diluent for N_2 .

Figure 1 shows the measured oxygen concentration as a function of supersaturation and $\Delta\mu_N$ for $1 \mu\text{m}$ thick N-polar GaN films with a dislocation density of $\sim 4 \times 10^9 \text{ cm}^{-2}$. As the V/III ratio was changed from 100 to 2000 under H_2 diluent (supersaturation increased from ~ 30 to 1800), the oxygen incorporation in the film decreased by more than one order of magnitude, to mid- 10^{18} cm^{-3} . A further increase of supersaturation to ~ 3400 was achieved at a V/III ratio of 2000 by swapping the diluent gas for N_2 , which further reduced the oxygen concentration to $2 \times 10^{18} \text{ cm}^{-3}$, as shown by the green data point in figure 1

In addition to the process conditions, it was found dislocations played an important role in unintentional oxygen incorporation into the N-polar GaN films [27]. As illustrated in figure 2, the oxygen concentration decreases by one order of magnitude as the dislocation density decreased by about a factor of four. The dislocation density was reduced first by increasing the thickness of the N-polar GaN films under high supersaturation (3400) from $1 \mu\text{m}$ to $2.6 \mu\text{m}$, which resulted in a $1.5\times$ edge dislocation density reduction [28–32]. A further reduction by a factor of two was achieved by increasing the miscut of the sapphire substrate from 2° to 4° . A similar dependence of dislocation density on wafer miscut in N-polar GaN films was observed by Shen *et al* [33] and Keller *et al* [28]. It is interesting to note that previous work by Fichtenbaum *et al* showed no correlation between the sapphire wafer miscut and oxygen concentration in the N-polar GaN films [9].

For Al-rich AlGaIn, it has been shown that dislocations impacted both impurity incorporation as well as compensation, which was reflected in a simultaneous decrease in the free carrier concentration and their mobility [27]. As can be

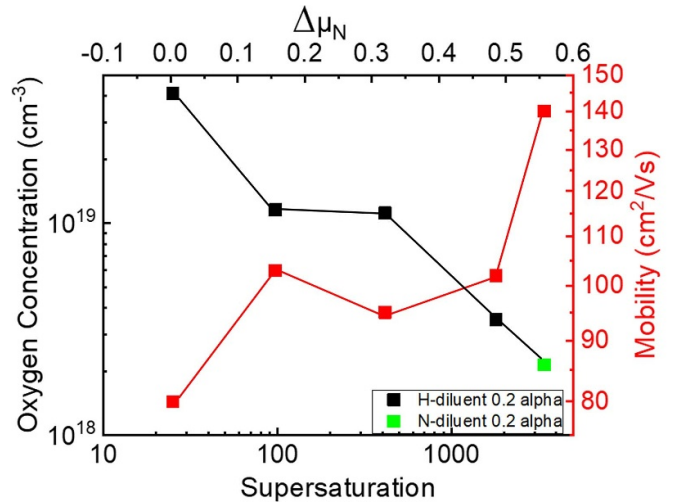


Figure 1. Measured oxygen concentration—corresponding to the carrier concentration, and mobility as a function of σ_{Ga} and $\Delta\mu_N$. The connecting lines are a to guide the eye only.

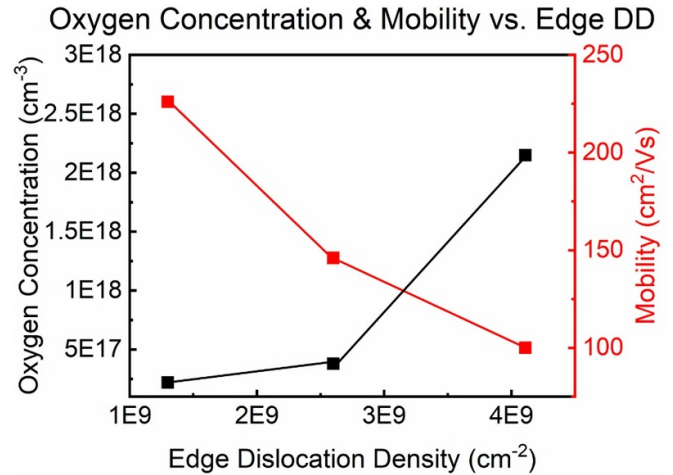


Figure 2. Oxygen concentration and mobility as a function of edge dislocation density. The connecting lines are a to guide the eye only.

seen in both figures 1 and 2, as the n-type carrier concentration decreases, mobility increases, indicating insignificant compensation. As expected for an uncompensated semiconductor and seen in figure 2, as the impurity concentration decreases by an order of magnitude, the mobility more than doubles to $225 \text{ cm}^2 \text{ V s}^{-1}$. Thus, through the reduction of the dislocation density, the oxygen concentration in the N-polar GaN was further reduced by one order of magnitude to $2 \times 10^{17} \text{ cm}^{-3}$.

In addition to low oxygen concentration, a smooth surface morphology is desired for the realization of N-polar GaN based devices. However, this presents a challenge due to the fact that a smooth N-polar surface requires growth under low supersaturation and, as shown by this work, a low unintentional oxygen incorporation requires a high supersaturation [5]. This conflicting requirement was solved by an engineered structure, as shown in figure 3-left. First, a $1 \mu\text{m}$ thick surface morphology control layer (SMCL) was grown under a low supersaturation, followed by a $1 \mu\text{m}$ thick layer grown at high

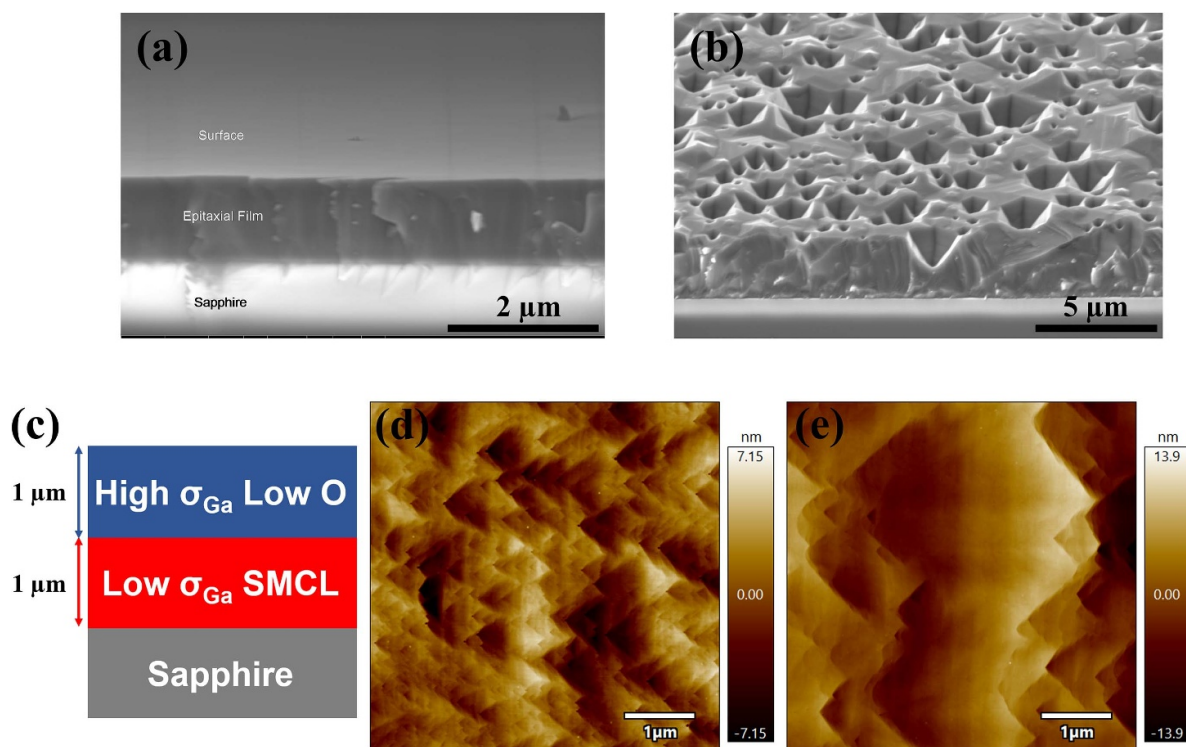


Figure 3. (left) Engineered growth structure for smooth N-polar GaN, (center) surface morphology of the SMCL (RMS roughness 3 nm), (right) step-bunched morphology of the low oxygen layer: RMS roughness = 7 nm, $[O] = 2 \times 10^{17} \text{ cm}^{-3}$.

supersaturation. The unintentional oxygen incorporation in the SMCL was high, however, the surface was relatively smooth, with an RMS roughness value of 3 nm (from $90 \times 90 \mu\text{m}^2$ scan), as shown in figure 3-center. The second layer, grown under high supersaturation, retained the step-bunched morphology of the SMCL layer with an RMS roughness of 7 nm (figure 3-right) and low unintentional oxygen incorporation. It is interesting to note that if this low oxygen concentration layer were grown directly on a sapphire substrate, it would be characterized by a high density of hexagonal hillocks and an RMS roughness of a few hundred nm [5].

A CPC framework, relating the supersaturation to the formation energy of the oxygen point defect, and dislocation reduction processes were implemented to mitigate unintentional oxygen incorporation in N-polar GaN films. CPC reduced the oxygen incorporation from mid- 10^{19} cm^{-3} to low- 10^{18} cm^{-3} . Decreasing the dislocation density by about a factor of four resulted in further reduction of oxygen incorporation and values as low as $2 \times 10^{17} \text{ cm}^{-3}$ were demonstrated. N-Polar GaN layers featuring a smooth surface and low oxygen concentration were achieved through the implementation of a surface morphology control layer.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Acknowledgments

The authors acknowledge funding in part from NSF (ECCS-1610992, ECCS-1653383, ECCS-1916800,) and ARL (W911QX-21-C-0005).

ORCID iD

Dennis Szymanski  <https://orcid.org/0000-0002-9365-8893>

References

- [1] Tsao J Y et al 2018 *Adv. Electron. Mater.* **4** 1600501
- [2] Keller S et al 2014 *Semicond. Sci. Technol.* **29** 113001
- [3] Stutzmann M, Ambacher O, Eickhoff M, Karrer U, Lima Pimenta A, Neuberger R, Schalwig J, Dimitrov R, Schuck P J and Grober R D 2001 *Phys. Status Solidi b* **228** 505
- [4] Lu J, Zheng X, Guidry M, Denninghoff D, Ahmadi E, Lal S, Keller S, DenBaars S P and Mishra U K 2014 *Appl. Phys. Lett.* **104** 092107
- [5] Mita S, Collazo R, Rice A, Tweedie J, Xie J, Dalmau R and Sitar Z 2011 *Phys. Status Solidi c* **8** 2078
- [6] Mita S, Collazo R, Rice A, Dalmau R F and Sitar Z 2008 *J. Appl. Phys.* **104** 013521
- [7] Bryan I, Bryan Z, Mita S, Rice A, Tweedie J, Collazo R and Sitar Z 2016 *J. Cryst. Growth* **438** 81
- [8] Tanikawa T, Kuboya S and Matsuoka T 2017 *Phys. Status Solidi c* **254** 1600751

- [9] Fichtenbaum N A, Mates T E, Keller S, DenBaars S P and Mishra U K 2008 *J. Cryst. Growth* **310** 1124
- [10] Zywiets T K, Neugebauer J and Scheffler M 1999 *Appl. Phys. Lett.* **74** 1695
- [11] Yang F-W, Chen Y-Y, Feng S-W, Sun Q and Han J 2016 *Nanoscale Res. Lett.* **11** 1931–7573, 1556–276X
- [12] Xu S R, Hao Y, Zhang J C, Cao Y R, Zhou X W, Yang L A, Ou X X, Chen K and Mao W 2010 *J. Cryst. Growth* **312** 3521
- [13] Tuomisto F, Saarinen K, Lucznik B, Grzegory I, Teisseyre H, Suski T, Porowski S, Hageman P R and Likonen J 2005 *Appl. Phys. Lett.* **86** 031915
- [14] Sun Q, Cho Y S, Lee I-H, Han J, Kong B H and Cho H K 2008 *Appl. Phys. Lett.* **93** 131912
- [15] Sumiya M, Yoshimura K, Ohtsuka K and Fuke S 2000 *Appl. Phys. Lett.* **76** 2098
- [16] Reddy P, Washiyama S, Kaess F, Kirste R, Mita S, Collazo R and Sitar Z 2017 *J. Appl. Phys.* **122** 245702
- [17] Washiyama S et al 2020 *J. Appl. Phys.* **127** 105702
- [18] Washiyama S, Reddy P, Kaess F, Kirste R, Mita S, Collazo R and Sitar Z 2018 *J. Appl. Phys.* **124** 115304
- [19] Mohn S et al 2016 *Phys. Rev. Appl.* **5** 2331–7019
- [20] Mita S 2007 *Polarity Control in Gallium Nitride Epilayers Grown by Metalorganic Chemical Vapor Deposition* (Cambridge: ProQuest)
- [21] Mita S, Collazo R, Schlessner R and Sitar Z 2004 *MRS Online Proc. Libr.* **831** 0272–9172, 1946–4274
- [22] Mita S, Collazo R, Schlessner R and Sitar Z 2005 *MRS Online Proc. Libr.* **892** 1946–4274
- [23] Collazo R, Mita S, Aleksov A, Schlessner R and Sitar Z 2006 *J. Cryst. Growth* **287** 586
- [24] Liu F, Collazo R, Mita S, Sitar Z, Duscher G and Pennycook S J 2007 *Appl. Phys. Lett.* **91** 203115
- [25] Metzger T et al 1998 *Philos. Mag. A* **77** 1013
- [26] Koukitu A and Kumagai Y 2001 *J. Phys. Condens. Matter* **13** 6907
- [27] Bryan I et al 2018 *Appl. Phys. Lett.* **112** 062102
- [28] Keller S, Fichtenbaum N A, Wu F, Brown D, Rosales A, DenBaars S P, Speck J S and Mishra U K 2007 *J. Appl. Phys.* **102** 083546
- [29] Wang G, Loo R, Simoen E, Souriau L, Caymax M, Heyns M M and Blanpain B 2009 *Appl. Phys. Lett.* **94** 102115
- [30] Tachikawa M and Yamaguchi M 1990 *Appl. Phys. Lett.* **56** 484
- [31] Ayers J E 1995 *J. Appl. Phys.* **78** 3724
- [32] Speck J S, Brewer M A, Beltz G, Romanov A E and Pompe W 1996 *J. Appl. Phys.* **80** 3808
- [33] Shen X Q, Matsuhata H and Okumura H 2005 *Appl. Phys. Lett.* **86** 021912