

Fluorine-based Inductively Coupled Plasma Etching of α -Ga₂O₃ Epitaxy Film

Ji Hun Um¹, Byoung Su Choi², Woo Sik Jang¹, Sungu Hwang¹, Dae-Woo Jeon³,
Jin Kon Kim¹, and Hyun Cho^{1,*}

¹Department of Nanomechatronics Engineering, Pusan National University, Busan 46241, Republic of Korea

²Department of Nano Fusion Technology, Pusan National University, Miryang 50463, Republic of Korea

³Korea Institute of Ceramic Engineering & Technology, JinJu 52851, Republic of Korea

Abstract: α -Ga₂O₃ has the largest bandgap (~5.3 eV) among the five polymorphs of Ga₂O₃ and is a promising candidate for high power electronic and optoelectronic devices. To fabricate various device structures, it is important to establish an effective dry etch process which can provide practical etch rate, smooth surface morphology and low ion-induced damage. Here, the etch characteristics of α -Ga₂O₃ epitaxy film were examined in two fluorine-based (CF₄/Ar and SF₆/Ar) inductively coupled plasmas. Under the same source power, rf chuck power and process pressure, an Ar-rich composition of CF₄/Ar and an SF₆-rich composition of SF₆/Ar produced the highest etch rates. Monotonic increase in the etch rate was observed as the source power and rf chuck power increased in the 2CF₄/13Ar discharges, and a maximum etch rate of ~855 Å/min was obtained at a 500 W source power, 250 W rf chuck power, and 2 mTorr pressure. A smooth surface morphology with normalized roughness of less than ~1.38 was achieved in the 2CF₄/13Ar and 13SF₆/2Ar discharges under most of the conditions examined. The features etched into the α -Ga₂O₃ layer using a 2CF₄/13Ar discharge with 2 mTorr pressure showed good anisotropy with a vertical sidewall profile.

(Received December 15, 2020; Accepted January 14, 2021)

Keywords: α -Ga₂O₃ epitaxy film, SF₆/Ar, CF₄/Ar, inductively coupled plasma, etch characteristics

1. Introduction

Ga₂O₃ is one of the most promising candidates for high power electronic devices due to its large bandgap energy and high breakdown voltage characteristics. Extensive research work has recently been conducted to implement Ga₂O₃-based power electronic devices with higher critical field strength and efficiency compared to their GaN and SiC counterparts [1-3]. As a newly emerging ultra-wide bandgap semiconductor, the most stable β -phase among the five Ga₂O₃ polymorphs [4-6] is preferred, and most of the recent research has been focused on β -Ga₂O₃ field effect transistors (MOSFETs and MESFETs) and Schottky barrier diodes [7-10].

More recently, there has been increasing interest in α -phase Ga₂O₃, given its several advantages over β -Ga₂O₃. α -Ga₂O₃

has a larger bandgap (~5.3 eV) and higher Baliga's figure-of-merit (FOM) compared to β -Ga₂O₃ [11,12]. It has the same corundum crystal structure as a sapphire substrate with the smallest lattice mismatch among the polymorphs of Ga₂O₃, and this allows high quality, large area epitaxial growth using various growth techniques such as Halide Vapor Phase Epitaxy (HVPE), Mist Chemical Vapor Deposition (mist-CVD), and Molecular Beam Epitaxy (MBE) [13-15]. In addition, tuning of the bandgap energy from ~3.7 to ~8.75 eV is possible through alloying with α -In₂O₃ and α -Al₂O₃ [16,17]. For example, a α -Ga₂O₃ Schottky barrier diode showed a lower on-resistance of 0.1 m Ω ·cm² compared a β -Ga₂O₃ Schottky rectifier [18].

When fabricating α -Ga₂O₃-based microelectronic devices such as MOSFETs, Schottky barrier diodes, UV detectors, and UV-LEDs, a patterning process that accurately transfers various features into the α -Ga₂O₃ layer is essential. The pattern transfer can be carried out by either wet etching or dry etching. There have been some reports on the wet etching of β -Ga₂O₃ [19-23], but it is very difficult to produce

- 임지훈: 석사과정, 최병수: 박사과정, 장우식: 학부생, 황승구·김진곤·조현: 교수, 전대우: 연구원

*Corresponding Author: Hyun Cho

[Tel: +82-51-510-6113, E-mail: hyuncho@pusan.ac.kr]

Copyright © The Korean Institute of Metals and Materials

practical etch rates with conventional wet etching at low temperature, because of the high chemical inertness of Ga_2O_3 . Moreover, the isotropic nature of wet etching makes it incapable of performing high resolution pattern transfers of sub-micron device features [24,25]. Dry etching techniques utilizing a high density plasma source, such as inductively coupled plasma (ICP) and electron cyclotron resonance (ECR), have been shown to produce higher etch rates for GaN and SiC compared to conventional reactive ion etching (RIE) and chemically-assisted ion beam etching (CAIBE) [26-30]. In addition, the ion-induced damage can be minimized because of the ability to control ion flux and ion energy separately. Therefore, high density plasma etch techniques are the preferred patterning technique for α - Ga_2O_3 -based microelectronic devices. However, there have been only a few reports on the high density plasma etching of α - Ga_2O_3 epitaxy film [31].

In this work, we report a parametric study on the etch characteristics of α - Ga_2O_3 epitaxy film grown on sapphire in two fluorine-based (CF_4/Ar and SF_6/Ar) inductively coupled plasmas. The effects of plasma composition, ICP source power, rf chuck power and process pressure on the etch rate, surface morphology and etch anisotropy were studied.

2. Experimental

α - Ga_2O_3 epitaxy films were grown on 2 inch diameter c-axis sapphire substrates using the horizontal halide vapor phase epitaxy (HVPE) method. During the growth process, Ga metal, HCl and O_2 gases were used as precursors and the substrate temperature was maintained at 470°C , and the typical thickness of the grown α - Ga_2O_3 epitaxy films were $\sim 1\ \mu\text{m}$ [32,33]. The surface of the grown α - Ga_2O_3 epitaxy film was chemically cleaned and then, the samples were patterned with AZ5214 photoresist and Nickel. The etching of the α - Ga_2O_3 epitaxy film was performed in a planar type inductively coupled plasma (ICP) source operating at 13.56 MHz and power up to 1000 W, and the samples were thermally bonded to a Si carrier wafer that was mechanically clamped to a He backside-cooled, rf-powered (13.56 MHz, up to 450W) chuck. CF_4/Ar and SF_6/Ar ICP discharges with a total gas load of 15 standard cubic centimeters per minute (sccm) were employed to etch the α - Ga_2O_3 , and the process

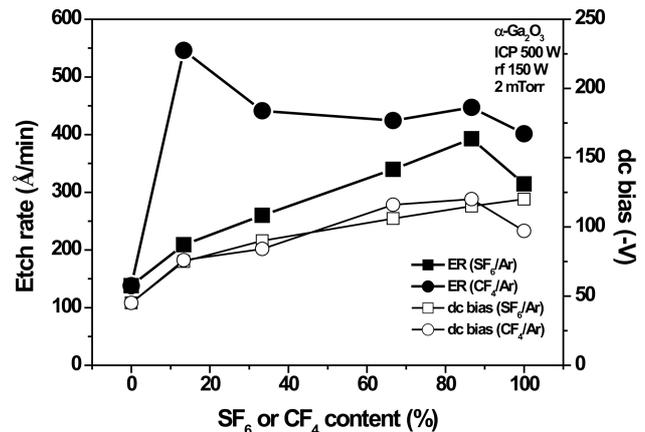


Fig. 1. α - Ga_2O_3 etch rate as a function of plasma composition in CF_4/Ar and SF_6/Ar ICP discharges (500 W source power, 150 W rf chuck power, 2 mTorr pressure).

pressure was varied from 2-20 mTorr during etching. After removal of the mask layer, the etch rate, surface morphology and anisotropy of the etched features were characterized by stylus profilometry, tapping mode atomic force microscopy (AFM) and field-emission scanning electron microscopy (FE-SEM), respectively.

3. Results and Discussion

Figure 1 shows the plasma composition dependence of the α - Ga_2O_3 etch rate in CF_4/Ar and SF_6/Ar ICP discharges under fixed ICP source power (500 W), rf chuck power (150 W) and pressure (2 mTorr) conditions. In the SF_6/Ar discharges, the etch rate initially increases as the SF_6 content increases due to the increase in reactive fluorine radical density in the plasma. After reaching a maximum value of $\sim 392.8\ \text{\AA}/\text{min}$ at 86.7% SF_6 content, the etch rate decreases in pure SF_6 discharge due to the reduced ion-assisted removal of the GaF_x etch products (presumably GaF_3 ; b.p. 1000°C) formed on the surface. In the case of CF_4/Ar discharges, as the CF_4 content increased to 13.3%, the α - Ga_2O_3 etch rate rapidly increased by a factor of ~ 4 compared to the pure Ar discharge. This is attributed to the formation of GaF_x etch products enhanced by the CF_4 addition and balanced with subsequent ion-assisted desorption. However, further increases in the CF_4 content led to a reduction in the etch rate, most likely due to the build-up of a fluorinated selvedge layer with low volatility on the surface.

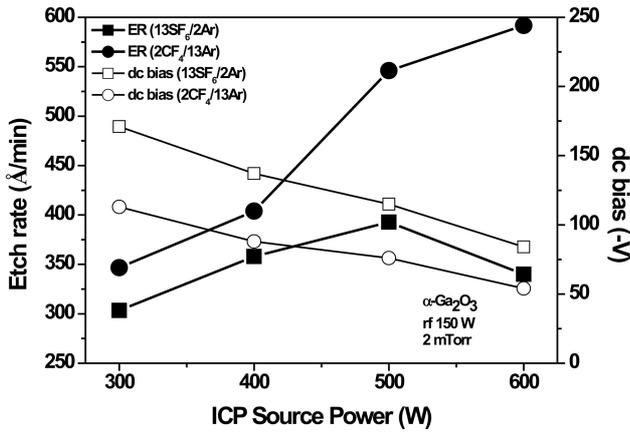


Fig. 2. α -Ga₂O₃ etch rate as a function of ICP source power in 2CF₄/13Ar and 13SF₆/2Ar ICP discharges (150 W rf chuck power, 2 mTorr pressure).

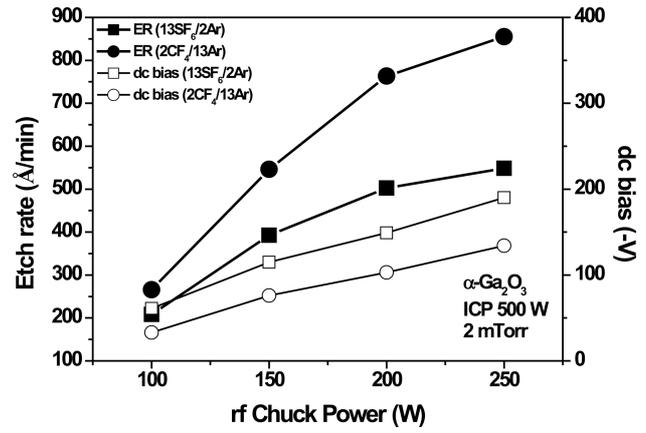


Fig. 3. α -Ga₂O₃ etch rate as a function of rf chuck power in 2CF₄/13Ar and 13SF₆/2Ar ICP discharges (500 W source power, 2 mTorr pressure).

Figure 2 shows the effect of ICP source power on the α -Ga₂O₃ etch rate in the 2CF₄/13Ar and 13SF₆/2Ar discharges, which produced the highest etch rates among the composition conditions presented in Figure 1. In the 2CF₄/13Ar discharges, the etch rate showed a strong dependence on the source power and higher etch rates were obtained compared to the 13SF₆/2Ar discharges. The α -Ga₂O₃ etch rate continuously increased as the source power increased, due to the increased reactive fluorine radical density and ion flux in the discharge. A maximum etch rate of \sim 592 Å/min was obtained at 600 W source power. A similar trend was observed in the 13SF₆/2Ar discharges up to a source power of 500 W. The decrease in

the etch rate at 600 W source power is most likely related to a decrease in ion energy caused by an increase in the source power.

The α -Ga₂O₃ etch rate as a function of the rf chuck power in the 2CF₄/13Ar and 13SF₆/2Ar discharges is shown in Figure 3. During etching, the ICP source power and pressure were maintained at 500 W and 2 mTorr, respectively. In both the 2CF₄/13Ar and 13SF₆/2Ar discharges, the etch rate monotonically increased as the rf chuck power increased, indicating the etch reaction under these conditions is dominated by the physical component of the etching. Increasing the rf chuck power increases the energy of the ions in the

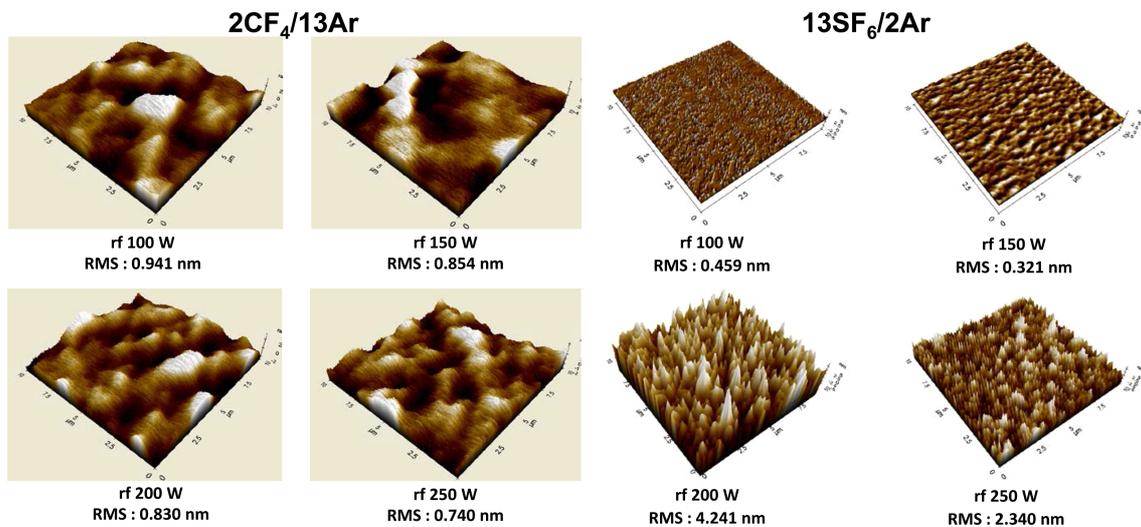


Fig. 4. AFM surface scan images of α -Ga₂O₃ etched in 2CF₄/13Ar and 13SF₆/2Ar ICP discharges with variation of rf chuck power (500 W source power, 2 mTorr pressure).

discharges (Ar^+ and CF_3^+ in the $2\text{CF}_4/13\text{Ar}$, and Ar^+ and SF_5^+ in the $13\text{SF}_6/2\text{Ar}$, respectively) [34-36] and improves the ion-assisted removal of nonvolatile GaF_x etch products. Then this leads to an increase in the etch rate. Maximum etch rates of $\sim 855 \text{ \AA}/\text{min}$ and $\sim 548.3 \text{ \AA}/\text{min}$ were obtained with a moderate rf chuck power (250 W) in the $2\text{CF}_4/13\text{Ar}$ and $13\text{SF}_6/2\text{Ar}$ discharges, respectively.

Figure 4 shows the AFM surface scan images of the $\alpha\text{-Ga}_2\text{O}_3$ epitaxy films etched in the $2\text{CF}_4/13\text{Ar}$ and $13\text{SF}_6/2\text{Ar}$ discharges with variation of rf chuck power at a fixed source power (500 W) and pressure (2 mTorr). The determined normalized roughness is presented in Figure 5. Etch depth in each sample was maintained at $\sim 2000 \text{ \AA}$ and the root-mean-square (RMS) roughness of the unetched $\alpha\text{-Ga}_2\text{O}_3$ control sample was $\sim 0.68 \text{ nm}$. The $\alpha\text{-Ga}_2\text{O}_3$ samples etched in the $2\text{CF}_4/13\text{Ar}$ discharges show almost the same surface roughness as the unetched control sample (normalized roughness in the range of 1.08-1.38) over the entire rf chuck power conditions examined. This is a typical feature of a physically-dominated etch process where the angular dependence of the ion milling removes sharp surface features faster [37].

For the $13\text{SF}_6/2\text{Ar}$ discharge, the $\alpha\text{-Ga}_2\text{O}_3$ samples etched at a low rf chuck power of 150 W or less showed smoother surface morphology than the unetched control sample, while

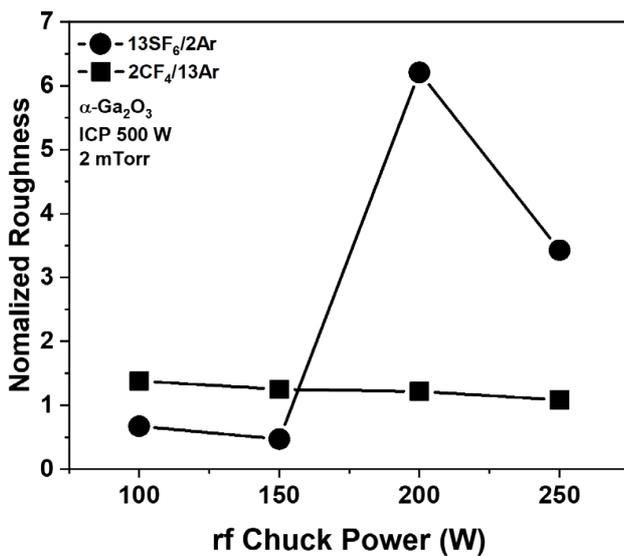


Fig. 5. Dependence of $\alpha\text{-Ga}_2\text{O}_3$ normalized etched surface roughness on rf chuck power in $2\text{CF}_4/13\text{Ar}$ and $13\text{SF}_6/2\text{Ar}$ ICP discharges (500 W source power, 2 mTorr pressure).

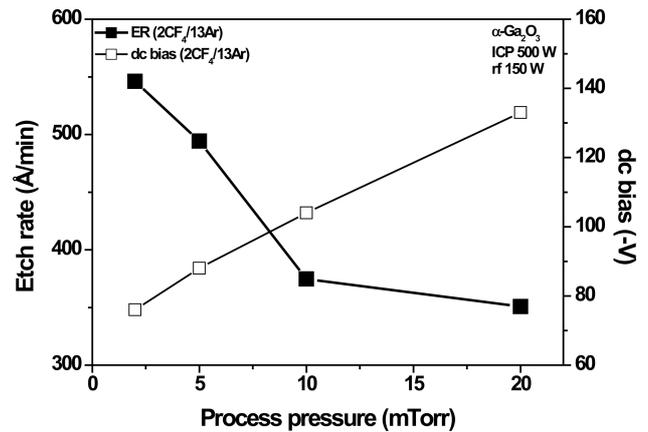


Fig. 6. $\alpha\text{-Ga}_2\text{O}_3$ etch rate as a function of process pressure in $2\text{CF}_4/13\text{Ar}$ ICP discharges (500 W source power, 150 W rf chuck power).

significant surface roughening was observed at rf chuck powers above 200 W, most likely due to the inhomogeneous removal of GaF_x etch products or surface atoms by enhanced ion bombardment.

The effect of process pressure on the $\alpha\text{-Ga}_2\text{O}_3$ etch rate in the $2\text{CF}_4/13\text{Ar}$ discharge is shown in Figure 6. As the process pressure increases, the etch rate continues to decrease due to the reduced physical contribution to the etching. This is because the increase in the process pressure reduces the mean-free-path of ions in the discharge and increases the energy loss of ions impinging on the surface.

Figure 7 shows the SEM cross-sectional images of the

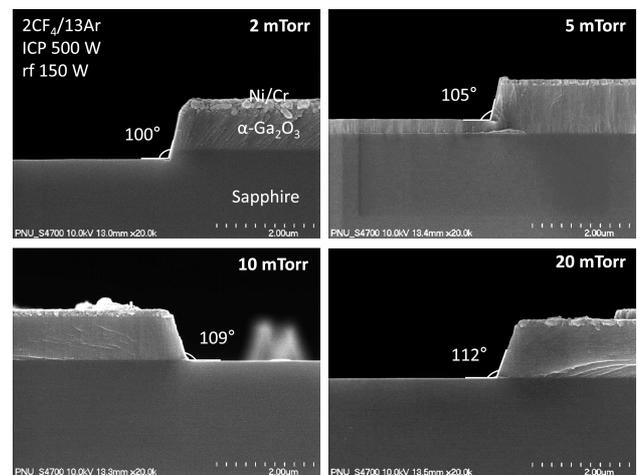


Fig. 7. Cross-sectional SEM micrographs of features etched into $\alpha\text{-Ga}_2\text{O}_3$ using $2\text{CF}_4/13\text{Ar}$ ICP discharges (500 W source power, 150 W rf chuck power).

features etched into the α -Ga₂O₃ layer under the same conditions presented in Fig. 6. Please note that the Ni mask layer is still in place. In the case of the feature etched under the lowest pressure condition of 2 mTorr, it can be seen that a highly anisotropic pattern transfer with a quite vertical sidewall ($\sim 100^\circ$) was achieved due to the ion-assisted nature of the etching. But as the process pressure increased, the frequency of normal incidence of ions was reduced due to the increased collisions with other ions or neutrals in the discharge, resulting in an increased off-angle from the vertical.

4. Summary and Conclusions

High density plasma etching of α -Ga₂O₃ epitaxy film was performed in CF₄/Ar and SF₆/Ar inductively coupled plasmas and the effect of plasma composition, ICP source power, rf chuck power and process pressure on the etch rate, surface morphology and etch profile was examined. In the CF₄/Ar discharges with low CF₄ content, a significant increase in the etch rate was observed due to the synergetic effect between the physical and chemical component of the etching. However, the etch rate generally increased with increasing SF₆ content in the SF₆/Ar. The etch rate showed a stronger dependence on the source power and rf chuck power in the 2CF₄/13Ar discharge compared to the 13SF₆/2Ar discharge. The 2CF₄/13Ar discharge produced higher etch rates under all conditions examined, and maximum etch rates of ~ 855 Å/min and ~ 548.3 Å/min were obtained in the 2CF₄/13Ar and 13SF₆/2Ar discharges, respectively at 500 W source power, 250 W rf chuck power, and 2 mTorr pressure. The α -Ga₂O₃ surfaces etched either in the 2CF₄/13Ar or low rf chuck powered (less than 150 W) 13SF₆/2Ar discharge showed a smooth morphology. Highly anisotropic pattern transfer was performed in the 2CF₄/13Ar discharge with low pressure (2 mTorr) due to the ion-assisted nature of the etching, and the etch rate and etch anisotropy were reduced as process pressure increased. The results of this work show that fluorine-based ICP etching would be a reasonable choice for fabricating a α -Ga₂O₃ device structure with a smooth surface morphology.

REFERENCES

1. S. J. Pearton, F. Ren, M. Tadjer, and J. Kim, *J. Appl. Phys.* **124**, 220901 (2018).
2. K. Konishi, K. Goto, H. Murakami, Y. Kumagai, A. Kuramata, S. Yamakoshi, and M. Higashiwaki, *Appl. Phys. Lett.* **110**, 103506 (2017).
3. M. Higashiwaki, H. Murakami, Y. Kumagai, and A. Kuramata, *Jpn. J. Appl. Phys.* **55**, 1202A1 (2016).
4. S. I. Stepanov, V. I. Nikolaev, V. E. Bougrov, and A. E. Romanov, *Rev. Adv. Mater. Sci.* **44**, 63 (2016).
5. C. Roy, V. G. Hill, and B. F. Osborn, *J. Am. Chem. Soc.* **74**, 719 (1952).
6. H. He, R. Orlando, M. A. Blanco, R. Pandey, E. Amzallag, I. Baraille, and M. Rerat, *Phys. Rev. B* **74**, 195123 (2006).
7. M. Orita, H. Ohta, and M. Hirano, *Appl. Phys. Lett.* **77**, 4166 (2000).
8. A. Kuramata, K. Koshi, S. Watanabe, Y. Yamaoka, T. Masui, and S. Yamakoshi, *Jpn. J. Appl. Phys.* **55**, 1202A2 (2016).
9. J. H. Kim, M. A. Mastro, M. J. Tadjer, and J. H. Kim, *ACS Appl. Mater. Interfaces* **9**, 21322 (2017).
10. A. J. Green, K. D. Chabak, E. R. Heller, R. C. Fitch, M. Baldini, A. Fiedler, K. Irmscher, G. Wagner, Z. Galazka, S. E. Tetlak, A. Crespo, K. Leedy, and G. H. Jessen, *IEEE Electron Device Lett.* **37**, 902 (2016).
11. S. J. Pearton, J. Yang, P. H. Cary, F. Ren, J. H. Kim, M. Tadjer, and M. A. Mastro, *Appl. Phys. Rev.* **5**, 011301 (2018).
12. K. Kaneko, I. Takeya, S. Komori, and S. Fujita, *J. Appl. Phys.* **113**, 233901 (2013).
13. J. H. Park, R. MxClintock, and M. Razeghi, *Semicond. Sci. Technol.* **34**, 08LT01 (2019).
14. Y. Yao, S. Okur, L. A. M. Lyle, G. S. Tompa, T. Salagi, N. Sbrockey, R. F. Davis, and L. M. Porter, *Mater. Res. Lett.* **6**, 268 (2018).
15. M. Oda, R. Tokuda, H. Kambara, T. Tanikawa, T. Sasaki, and T. Hitora, *Appl. Phys. Express* **9**, 021101 (2016).
16. K. Kanaeko, S. Fujita, and T. Hitora, *Jpn. J. Appl. Phys.* **57**, 02CB18 (2018).
17. S.-H. Choe, Y.-J. Park, Y.-S. Kim, B.-C. Cha, S.-B. Heo, S. Yoon, Y.-M. Kong, and D. Kim, *Korean J. Met. Mater.* **58**, 793 (2020).
18. S. Fujita, M. Oda, K. Kaneko, and T. Hitora, *J. Appl. Phys.* **55**, 1202A3 (2016).

19. S. Jang, S. Jung, K. Beers, J. Yang, F. Ren, A. Kuramata, S. J. Pearton, and K. H. Baik, *J. Alloys Compd.* **731**, 118 (2018).
20. T. Oshima, T. Okuno, N. Arai, Y. Kobayashi, and S. Fujuta, *Jpn. J. Appl. Phys.* **48**, 040208 (2009).
21. H. Okumura and T. Tanaka, *Jpn. J. Appl. Phys.* **58**, 120902 (2019).
22. Y. Zhang, A. Mauze, and J. S. Speck, *Appl. Phys. Lett.* **115**, 013501 (2019).
23. S. Ohira and N. Arai, *Phys. Stat. Sol. C* **5**, 3116 (2008).
24. D. Zhuang and J. H. Edgar, *Mater. Sci. Eng. R* **48**, 1(2005).
25. F. Ren, M. Hong, J. P. Mannaerts, J. R. Lothian, and A. Y. Cho, *J. Electrochem. Soc.* **144**, L239 (1997).
26. H. Cho, C. B. Vartuli, S. M. Donovan, J. D. Mackenzie, C. R. Abernathy, S. J. Pearton, R. J. Shul, and C. Constantine, *J. Electr. Mater.* **27**, 166 (1998).
27. H. Cho, K. P. Lee, P. Leerungnawarat, S. N. G. Chu, F. Ren, S. J. Pearton, and C.-M. Zetterling, *J. Vac. Sci. Technol. A* **19**, 1878 (2001).
28. J. M. Lee, K. M. Chang, S. W. Kim, C. Huh, I. H. Lee, and S. J. Park, *J. Appl. Phys.* **87**, 7667 (2000).
29. D. Basak, M. Verdu, M. T. Montojo, M. A. Sanchez-Garcia, F. J. Sanchez, E. Munoz, and E. Calleja, *Semicond. Sci. Technol.* **12**, 1654 (1997).
30. L. Y. Kuritzky, D. L. Becerra, A. S. Abbas, J. Nedy, S. Nakamura, S. P. DenBaars, and D. A. Cohen, *Semicond. Sci. Technol.* **31**, 075008 (2016).
31. Z. Jian, Y. Oshima, S. Wright, K. Owen, and E. Ahmadi, *Semicond. Sci. Technol.* **34**, 03506 (2019).
32. H. Son, Y. J. Choi, Y. J. Lee, M. J. Lee, J. H. Kim, S. W. Kim, Y. H. Ra, T. Y. Lim, J. Hwang, and D. W. Jeon, *J. Korean Cryst. Growth Cryst. Technol.* **28**, 135 (2018).
33. H. Son, Y. J. Choi, Y. J. Lee, J. H. Kim, S. W. Kim, Y. H. Ra, T. Y. Lim, J. Hwang, and D. W. Jeon, *J. Korean Cryst. Growth Cryst. Technol.* **29**, 173 (2019).
34. K. Kim, A. Efremov, J. Lee, K. H. Kwon, and G. Y. Yeom, *J. Vac. Sci. Technol. A* **33**, 031601 (2015).
35. T. Sreenidhi, K. Baskar, A. DasGupta, and N. DasGupta, *Semicond. Sci. Technol.* **23**, 125019 (2008).
36. S. J. Oh, H. C. Lee, and C. W. Chung, *Phys. Plasmas* **24**, 013512 (2017).
37. H. Cho, K. P. Lee, Y. B. Hahn, E. S. Lambers, and S. J. Pearton, *Mater. Sci Eng. B* **67**, 145 (1999).