

Comparative Investigation of Interfacial Characteristics between HfO₂/Al₂O₃ and Al₂O₃/HfO₂ Dielectrics on AlN/p-Ge Structure

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(Received June 17, 2019 : Revised July 12, 2019 : Accepted August 6, 2019)

Abstract The electrical and interfacial properties of HfO₂/Al₂O₃ and Al₂O₃/HfO₂ dielectrics on AlN/p-Ge interface prepared by thermal atomic layer deposition are investigated by capacitance-voltage(C-V) and current-voltage(I-V) measurements. In the C-V measurements, humps related to mid-gap states are observed when the ac frequency is below 100 kHz, revealing lower mid-gap states for the HfO₂/Al₂O₃ sample. Higher frequency dispersion in the inversion region is observed for the Al₂O₃/HfO₂ sample, indicating the presence of slow interface states. A higher interface trap density calculated from the high-low frequency method is observed for the Al₂O₃/HfO₂ sample. The parallel conductance method, applied to the accumulation region, shows border traps at 0.3–0.32 eV for the Al₂O₃/HfO₂ sample, which are not observed for the HfO₂/Al₂O₃ sample. I-V measurements show a reduction of leakage current of about three orders of magnitude for the HfO₂/Al₂O₃ sample. Using the Fowler-Nordheim emission, the barrier height is calculated and found to be about 1.08 eV for the HfO₂/Al₂O₃ sample. Based on these results, it is suggested that HfO₂/Al₂O₃ is a better dielectric stack than Al₂O₃/HfO₂ on AlN/p-Ge interface.

Key words HfO₂/Al₂O₃, mid-gap states, leakage current.

1. Introduction

Germanium(Ge) has attracted significant attention as a channel material for the next generation nanoelectronics due to its high carrier mobility.¹⁾ One big obstacle for realizing high performance Ge n-channel metal-oxide-semiconductor field-effect transistors(MOSFETs) is the thermodynamically unstable germanium oxide(GeO) on the Ge substrate,²⁾ which is easily desorbed from the GeO₂/Ge substrate during the thermal process. The GeO volatilization to the air generates large amount of defects and traps at the GeO₂/Ge interface.^{3,4)} Numerous approaches such as nitridation, sulfur passivation, GeO₂ passivation have been employed to passivate the Ge surface and thus, to improve the interfacial quality.⁵⁾ Among them, GeO₂ showed a promising result as a passivation layer with very low interface state density of $\sim 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$.⁶⁾ However, GeO₂ has low conduction band offset of $\sim 0.6 \text{ eV}$,⁷⁾ which is very low to prevent the

electron injection over the barrier and the direct tunneling through the GeO₂ layer.⁸⁾

The high-k dielectrics can be used as an effective GeO₂ capping layer that prevents GeO desorption from the GeO₂/Ge interface.⁹⁾ High quality of GeO₂/Ge interface can be obtained when the inward diffusion of oxygen vacancy is suppressed,¹⁰⁾ if not, can introduce defect states and degrade the device performance. According to the comparison of HfO₂, LaGeO_x, HfGeO_x, GeN_x, and Al₂O₃ as passivating gate dielectrics for Ge substrates, Li et al. also showed that a key role is to block oxygen vacancy diffusion through the GeO₂.¹¹⁾ They suggested that Al₂O₃ is most proper material for this role, being a diffusion barrier and having large band offsets. Based on the calculation, it was demonstrated that AlN has fewer vacancy states in the Ge bandgap than Al₂O₃ and was suggested that AlN is a better choice for Ge MOSFET from the view of border trap properties, oxygen vacancy diffusion barrier, and band offset.¹²⁾ Ge surface nitridation

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has also been found to successfully reduce the interface defect density.^{13,14} Therefore, AlN might passivate Ge or GeO₂ surface better than Al₂O₃.

It was shown that combination of excellent thermal stability and large bandgap of Al₂O₃ and high dielectric constant of HfO₂ produced better equivalent oxide thickness scalability with low interface state density on Ge than single HfO₂ layer.¹⁵ In this respect, we employed a thin AlN as passivation layer on Ge and comparatively investigated the electrical properties of both HfO₂/Al₂O₃ and Al₂O₃/HfO₂ capping layers.

2. Experimental

Ga-doped, single side polished, Ge(100) wafers (thickness: 500 nm, resistivity: 0.01~0.1 ohm.cm) grown by Czochralski method were used in this work. The Ge wafer was first cut into small pieces and the samples were loaded into an thermal ALD chamber after cleaning process in a HCl:H₂O (1:1) solution. The temperature was ramped up to 350 °C to deposit 2.0 nm thick AlN layer using Trimethylaluminum(TMA) and NH₃ as precursors. Then the temperature was lowered down to 250 °C to deposit AlN protection layers with two different methods, (i) 1.0 nm thick Al₂O₃ was deposited first and then 2.0 nm thick HfO₂ was deposited(denoted as HfO₂/Al₂O₃) and (ii) 2.0 nm thick HfO₂ was deposited first and then 1.3 nm thick Al₂O₃ was deposited(denoted as Al₂O₃/HfO₂). Al₂O₃ and HfO₂ films were grown by using the precursors of TMA and Tetrakis(ethylmethylamino)hafnium (TEMA-

Hf), respectively, and H₂O vapor was used as the oxidant. The thicknesses of the deposited films were measured using a FS-1 multi-wavelength ellipsometer. Metal-oxide semiconductor (MOS) capacitors were fabricated with an Al Schottky electrode(diameter: 500 nm, thickness: 50 nm) and a Pt back contact(thickness: 100 nm) in order to examine the electrical characteristics of the AlN/Ge interface. Capacitance–voltage(C–V) measurements were performed using a HP 4284A LCR meter and current–voltage(I–V) measurements were carried out with a Keithley 238 current source.

3. Results and Discussion

Fig. 1 shows the C–V curves measured at various frequencies. Below 100 kHz, the weak inversion humps are observed for two samples. The inset in Fig. 1(b) shows the normalized C–V data obtained from 500 kHz and 5 kHz. It is known that the hump area is proportional to the amount of mid-gap states.¹⁶ The C–V hump area was obtained by integrating the region bounded by two C–V curves measured at 500 kHz and 5 kHz. The C–V hump areas(i.e., Q_{hump}) were estimated to be 3.41×10^{-7} and 5.41×10^{-7} C/cm², respectively, for the Al₂O₃/HfO₂ and HfO₂/Al₂O₃ samples. This indicates that the HfO₂/Al₂O₃ sample reduced the mid-gap states compared to the Al₂O₃/HfO₂ sample. In addition, higher frequency dispersion in the inversion region was observed for the Al₂O₃/HfO₂ sample. Strong dispersion in the inversion region observed for the nitrided Ge sample was associated with the presence

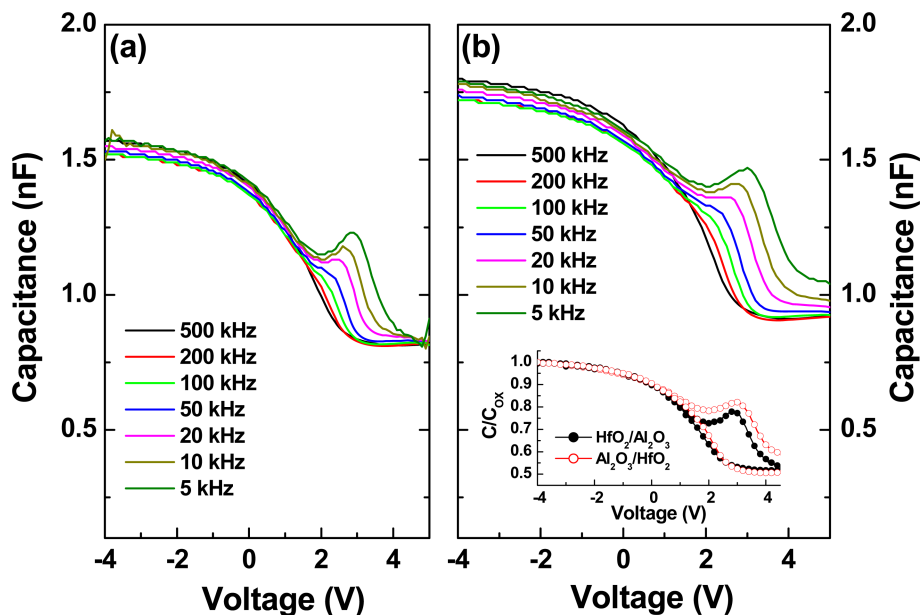


Fig. 1 Capacitance–voltage (C–V) data measured at various frequencies for the (a) HfO₂/Al₂O₃ and (b) Al₂O₃/HfO₂ samples. The inset in (b) shows the normalized capacitance values measured at 500 and 5 kHz.

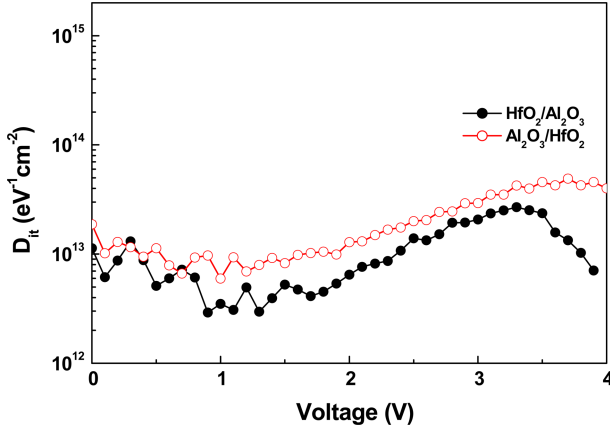


Fig. 2 Interface state density vs. voltage obtained from the high-low frequency method.

of slow interface states,¹⁷⁾ indicating the higher density of slow interface states for the Al₂O₃/HfO₂ sample.

Fig. 1 also shows that the accumulation capacitances are a little higher for the Al₂O₃/HfO₂ sample as compared to the HfO₂/Al₂O₃ sample. Al₂O₃ and HfO₂ have large bandgaps (7.0 and 5.7 eV, respectively) and high dielectric constants (~9 and ~20, respectively).¹⁸⁾ It was reported that the formation of Hf–Al–O by the intermixture of Al₂O₃ and HfO₂ layers provided the dielectric constant between 9 and 20.¹⁹⁾ The bonding energies of Al–O and Hf–O are known to be 501.9(± 10.6) and 801 (± 13) kJ/mol, respectively.²⁰⁾ Hence, Al–O bonding would be dissolved more easily than Hf–O bonding. For the HfO₂/Al₂O₃ sample, the outdiffusion of Al atoms from the first-deposited Al₂O₃ layer might occur during the HfO₂ deposition, leading to the formation of Hf–Al–O and decreasing the effective dielectric constant of dielectric layers. For the Al₂O₃/HfO₂ sample, the outdiffusion of Hf atoms from the first-deposited HfO₂ layer might not occur well during the Al₂O₃ deposition due to the higher bonding energy of Hf–O, suppressing the formation Hf–Al–O and producing the relatively higher effective dielectric constant of dielectric layers. Due to the difference in the effective dielectric constant, the different capacitance values were obtained. However, further investigation using x-ray photoelectron spectroscopy measurements is required in order to confirm this explanation.

Based on high–low frequency method, the interface state density (D_{it}) across the band gap was extracted using the following equation²¹⁾

$$D_{it} = \frac{C_{OX}}{q} \left[\frac{C_{Hf}/C_{OX}}{1 - C_{Lf}/C_{OX}} - \frac{C_{Lf}/C_{OX}}{1 - C_{Hf}/C_{OX}} \right] \quad (1)$$

where C_{OX} is the oxide capacitance at the accumulation,

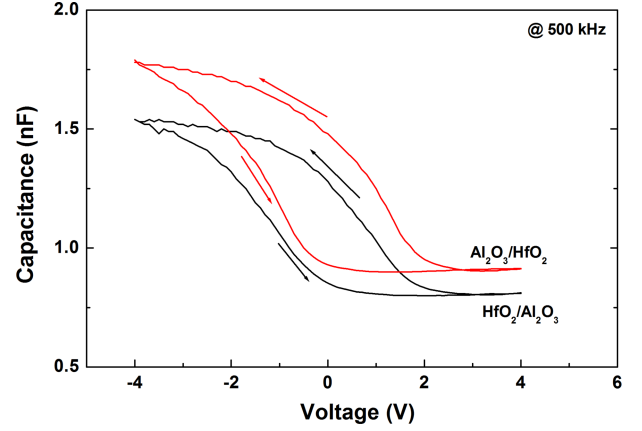


Fig. 3 C–V hysteresis plots measured at 500 kHz.

C_{Hf} and C_{Lf} are the capacitances at high and low frequencies. Here, C_{OX} values were obtained experimentally at 500 kHz from the accumulation region. In the calculation, 500 kHz and 1 kHz were selected as the high and low frequencies, respectively. Fig. 2 shows the D_{it} as a function of the gate voltage. Note that high–low frequency method can underestimate the D_{it} values because neither the 500 KHz nor the 1 kHz C–V data would be true high and low frequency curves, respectively. Nevertheless, this clearly shows that the HfO₂/Al₂O₃ sample has lower interface state density than the Al₂O₃/HfO₂ sample.

Fig. 3 shows the C–V hysteresis characteristics measured at 500 kHz. For both samples, a very large hysteresis was observed at the flat-band voltage (V_{FB}), indicating the presence of high density of bulk oxide traps.²²⁾ The C–V hysteresis was also associated with the GeO volatilization,²⁰⁾ which could produce large amount of defects and traps in the high-k film.³⁾ It is seen that the hysteresis C–V traces of both samples revealed the negative V_{FB} shift, implying the positive charge trapping. Hole injection from p-type Ge substrate and trapping under the negative gate bias occurred higher than electron trapping under the positive gate bias during C–V hysteresis measurements.²⁴⁾ The average oxide trap densities (Q_T) along the Ge bandgap (E_g) were obtained through the relation $Q_T = (C_{OX}\Delta V_{FB})/qE_g$, where ΔV_{FB} is the flatband voltage shift. The Q_T values were calculated to be 1.39×10^{13} and 1.86×10^{13} cm⁻²eV⁻¹, respectively, for the Al₂O₃/HfO₂ and HfO₂/Al₂O₃ samples.

Further investigation was performed by obtaining the parallel conductance values (G_p/ω) from the accumulation region.²⁵⁾ G_p/ω values as a function of radial frequency ($\omega = 2\pi f$) were derived by $G_p/\omega = [\omega G_m (C_{OX})^2] / [(G_m)^2 + \omega^2 (C_{OX} - C_m)^2]$, where C_m and G_m are the measured capacitance and conductance, respectively. These G_p/ω values can be connected with the following equation²⁶⁾

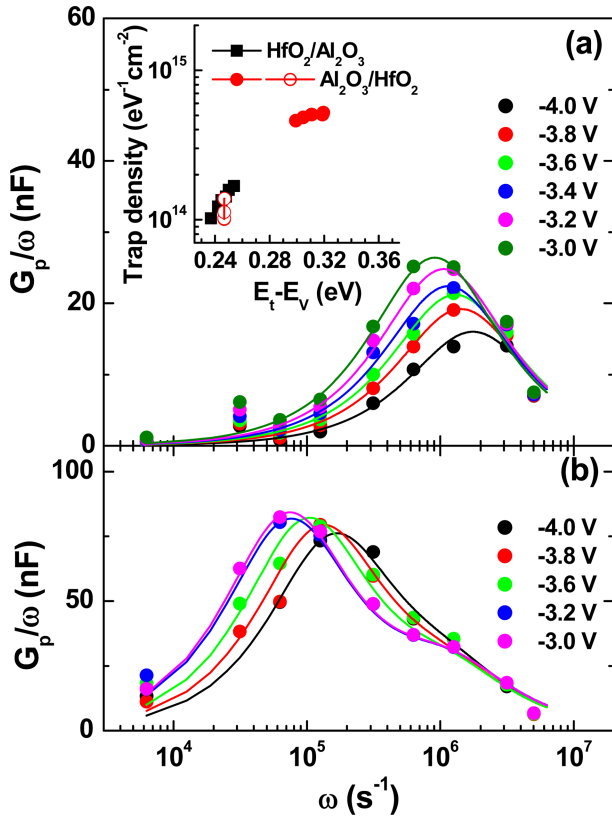


Fig. 4 Frequency dependent parallel conductance for the (a) HfO₂/Al₂O₃ and (b) Al₂O₃/HfO₂ samples. The inset in (a) shows the obtained trap densities from the conductance method.

$$\frac{G_p}{\omega} = \frac{q\omega\tau_T D_T}{1 + (\omega\tau_T)^2} \quad (2)$$

where D_T is the trap density and τ_T is the trap response time. The experimental and fitting data are shown in Fig. 4. The measured curves for the HfO₂/Al₂O₃ and Al₂O₃/HfO₂ samples were resolved into one and two fitting curves, respectively. The energy level of traps above the Ge valence band, $E_t - E_V$ were determined from τ_T according to the Shockley-Read-Hall statistics²⁷⁾

$$E_t - E_V = kT \ln \left(\frac{\sigma_p v_{th} N_V}{\tau_T} \right) \quad (3)$$

where v_{th} is the thermal velocity, σ_p is the hole capture cross section ($\sim 1 \times 10^{-16} \text{ cm}^2$),²⁸⁾ and N_V is the effective density of states in the Ge valence band. As shown in the inset in Fig. 4(a), the traps located at $\sim 0.25 \text{ eV}$ with the time constants between 0.5 and $1 \mu\text{s}$ were observed for both samples. These traps are likely to be located near the AlN/Ge interface. Meanwhile, the traps located at

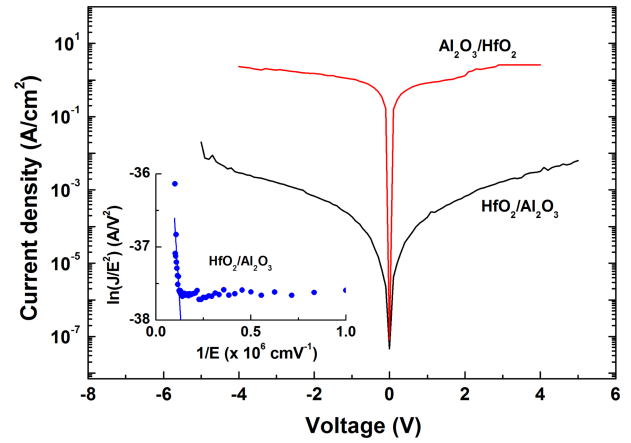


Fig. 5 Current density–voltage (J – V) characteristics at room temperature. The inset shows the Fowler–Nordheim (FN) tunneling plot of $\ln(J/E^2)$ versus $1/E$ for the HfO₂/Al₂O₃ sample.

$0.3\text{--}0.32 \text{ eV}$ observed for the Al₂O₃/HfO₂ sample, which is not observed for the HfO₂/Al₂O₃ sample. Because the time constants for these traps are $6\text{--}15 \mu\text{s}$, they may be regarded as slow states. Border traps show a slower conductance response due to the time needed for the carriers to reach the traps within the AlN layer from the AlN/Ge interface. That is, these traps might be located within the AlN layer, which were generated during the HfO₂ deposition.

The leakage current density as a function of the voltage is shown in Fig. 5. At accumulation region, the gate leakage recorded the values of 3×10^{-3} and 2.3 A/cm^2 at -4.0 V for the HfO₂/Al₂O₃ and Al₂O₃/HfO₂ samples, respectively. This figure demonstrates a reduction of leakage current for the HfO₂/Al₂O₃ sample by about three orders of magnitude, indicating again the better insulator quality. HfO₂ is known to suffer from poor thermal stability and low crystallization temperature (500°C), which produces large leakage current flowing along the grain boundary.²⁹⁾ Thermal stability experiments using the HfO₂/Al₂O₃ bilayer in the AlGaN/GaN device have shown that improved device performance was due to the formation of the Hf–Al–O structure and the amorphous nature of the Al₂O₃ layer.³⁰⁾ Miyazaki et al. observed the larger leakage current using the HfO₂ than that using the Al₂O₃ in the AlGaN/GaN device and they attributed this to the grain boundaries of the microcrystal in the HfO₂ acting as the leakage path.³¹⁾ The larger leakage current was also associated with a lower conduction band offset of 1.1 eV between HfO₂ and GaN than that of 2.3 eV between Al₂O₃ and GaN.^{31,32)} In addition, analysis of C – V characteristics of the HfO₂/AlN stacks on GaN confirmed the dielectric constant of the HfO₂ to be ~ 20 , which is a typical value of ALD HfO₂.³³⁾ This indicates

that the outdiffusion of Al atoms from the AlN layer into the HfO₂ layer was insignificant. As explained previously, the HfO₂/Al₂O₃ sample might form the Hf–Al–O bonding more easily than the Al₂O₃/HfO₂ sample. Based on these results, we can assume that the HfO₂ layer in the Al₂O₃/HfO₂ sample did not undergo significant intermixing. Hence, the grain boundaries of the microcrystal in the HfO₂ would not be affected in the Al₂O₃/HfO₂ sample, which caused a larger leakage current. Consequently, Al₂O₃ is a better choice than HfO₂ as the first deposition layer on AlN/p-Ge. As shown in the inset in Fig. 5, the forward bias current for the HfO₂/Al₂O₃ sample was analyzed using the Fowler-Nordheim (FN) emission, given by $J \propto E^2 \exp(-\beta/E)$.³⁴ From the slope, the barrier height was calculated to be about 1.08 eV.

4. Conclusion

Using C–V and I–V measurements, we investigated the electrical and interfacial properties of HfO₂/Al₂O₃ and Al₂O₃/HfO₂ dielectrics on AlN/p-Ge interface. The inversion humps related to mid-gap states were observed for both samples, which was found to have lower mid-gap states for the HfO₂/Al₂O₃ sample. High-low frequency method revealed the lower interface trap density for the HfO₂/Al₂O₃ sample. According to the parallel conductance method applied to the accumulation region, the border traps at 0.3 ~ 0.32 eV were observed for the Al₂O₃/HfO₂ sample, which was not observed for the HfO₂/Al₂O₃ sample. Therefore, it would be reasonable to assume that these traps were generated during the HfO₂ deposition. The reduction of leakage current by about three orders of magnitude was observed for the HfO₂/Al₂O₃ sample. These results clearly indicate the better insulator quality with an HfO₂/Al₂O₃ dielectric stack.

Acknowledgments

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2017R1D1A1B03030400).

References

1. P. Lim, D. Chi, X. Wang and Y. Yeo, *Appl. Phys. Lett.*, **101**, 172103 (2012).
2. K. Prabhakaran, F. Maeda, Y. Watanabe and T. Ogino, *Appl. Phys. Lett.*, **76**, 2244 (2000).
3. F. Bin, L. Xia, F. Xi, M. Fei, F. Jiao and H. Yue, *Chin. Phys. B*, **22**, 037702 (2013).
4. Y. Seo, C. Kim, T. Lee, W. Hwang, H. Yu, Y. Choi and B. Cho, *IEEE Trans. Electron Dev.*, **64**, 3998 (2017).
5. Q. Xie, S. Deng, M. Schaeckers, D. Lin, M. Caymax, A. Delabie, X. Qu, Y. Jiang, D. Deduytsche and C. Detavernier, *Semicond. Sci. Technol.*, **27**, 074012 (2012).
6. Y. Fukuda, T. Ueno, S. Hirono and S. Hashimoto, *Jpn. J. Appl. Phys.*, **44**, 6981 (2005).
7. M. Perego, G. Scarel, M. Fanciulli, I. Fedushkin and A. Skatova, *Appl. Phys. Lett.*, **90**, 162115 (2007).
8. D. Kuzum, T. Krishnamohan, A. Nainani, Y. Sun, P. Pianetta, H. Wong and K. Saraswat, *IEEE Trans. Electron Dev.*, **58**, 59 (2011).
9. R. Zhang, P.-C. Huang, J.-C. Lin, N. Taoka, M. Takenaka and S. Takagi, *IEEE Trans. Electron Dev.*, **60**, 927 (2013).
10. D. Kuzum, T. Krishnamohan, A. Pethe, A. Okyay, Y. Oshima, Y. Sun, J. McVittie, P. Pianetta, P. McIntyre and K. Saraswat, *IEEE Electron Dev. Lett.*, **29**, 328 (2008).
11. H. Li, L. Lin and J. Robertson, *Appl. Phys. Lett.*, **101**, 052903 (2012).
12. H. Li, Y. Guo and J. Robertson, *Microelectron. Eng.*, **147**, 168 (2015).
13. R. Zhang, T. Iwasaki, N. Taoka, M. Takenaka and S. Takagi, *J. Electrochem. Soc.*, **158**, G178 (2011).
14. H. Kim, P. McIntyre, C. Chui, K. Saraswat and M. Cho, *Appl. Phys. Lett.*, **85**, 2902 (2004).
15. X. Li, Y. Cao, A. Li, H. Li and D. Wu, *ECS Solid State Lett.*, **1**, N10 (2012).
16. I. Krylov, L. Kornblum, A. Gavrilo, D. Ritter and M. Eizenberg, *Appl. Phys. Lett.*, **100**, 173508 (2012).
17. D. Misra, *Electrochem. Soc. Interface*, **20**, 47 (2011).
18. M. Usman, C. Henkel and A. Hall'én, *ECS J. Solid State Sci. Technol.*, **2**, N3087 (2013).
19. G. Wilk, M. Green, M. Ho, B. Busch, T. Sorsch, F. Klemens, B. Brijs, R. van Dover, A. Kornblit, T. Gustafsson, E. Garfunkel, S. Hillenius, D. Monroe, P. Kalavade and M. Hergenrother, *Tech. Dig. VLSI Symp.*, p. 88 (2002).
20. J. Kerr, Strengths of Chemical bonds, in *CRC Handbook of Chemistry and Physics*, p. 9-54, ed. D. R. Lide, CRC Press, Boca Raton, FL (2005).
21. R. Engel-Herbert, Y. Hwang and S. Stemmer, *J. Appl. Phys.*, **108**, 124101 (2010).
22. F. Bellenger, M. Houssa, A. Delabie, V. Afanasiev, T. Conard, M. Caymax, M. Meuris, K. Meyer and M. Heyns, *J. Electrochem. Soc.*, **155**, G33 (2008).
23. Y. Choi, H. Lim, S. Lee, S. Suh, J. Kim, H. Jung, S. Park, J. Lee, S. Kim, C. Hwang and H. Kim, *ACS Appl. Mater. Interfaces*, **4**, 7885 (2014).
24. H. Seo, F. Bellenger, K. Chung, M. Houssa, M. Meuris, M. Heyns and G. Lucovsky, *J. Appl. Phys.*, **106**, 044909 (2009).
25. Y. Yuan, L. Wang, B. Yu, B. Shin, J. Ahn, P. McIntyre, P. Asbeck, M. Rodwell and Y. Taur, *IEEE Electron Dev. Lett.*, **32**, 485 (2011).
26. D. Schroder, *Semiconductor Material and Device Characterization*, p. 1, Wiley, New York, USA (2005).

27. S. Gupta, E. Simoen, R. Loo, O. Madia, D. Lin, C. Merckling, Y. Shimura, T. Conard, J. Lauwaert, H. Vrielinck and M. Heyns, *ACS Appl. Mater. Interfaces*, **8**, 13181 (2016).
28. D. Wang, S. Kojima, K. Sakamoto, K. Yamamoto and H. Nakashima, *J. Appl. Phys.*, **112**, 083707 (2012).
29. G. He, L. Zhang, G. Meng, G. Li, Q. Fang and J. Zhang, *J. Appl. Phys.*, **102**, 094103 (2007).
30. F. Tian and E. Chor, *J. Electrochem. Soc.*, **157**, H557 (2010).
31. E. Miyazaki, Y. Goda, S. Kishimoto and T. Mizutani, *Solid-State Electron.*, **62**, 152 (2011).
32. J. Robertson and B. Falabretti, *J. Appl. Phys.*, **100**, 014111 (2006).
33. D. Deen, S. Binari, D. Storm, D. Katzer, J. Roussos, J. Hackley and T. Gougousi, *Electron. Lett.*, **45**, 423 (2009).
34. G. Dutta, N. DasGupta and A. DasGupta, *IEEE Trans. Electron Dev.*, **64**, 3609 (2017).