Accepted Manuscript

Growth and Characterization of Nitrogen-Phosphorus Hybrid Passivated Gate Oxide Film on N-type 4H-SiC Epilayer

Yifan Jia, Hongliang Lv, Xiaoyan Tang, Qingwen Song, Yimen Zhang, Yuming Zhang, Sima Dimitrijević, Jisheng Han

PII: S0022-0248(18)30455-X

DOI: <https://doi.org/10.1016/j.jcrysgro.2018.09.029>

Reference: CRYG 24753

To appear in: *Journal of Crystal Growth*

Received Date: 10 August 2018

Accepted Date: 19 September 2018

Please cite this article as: Y. Jia, H. Lv, X. Tang, Q. Song, Y. Zhang, Y. Zhang, S. Dimitrijević, J. Han, Growth and Characterization of Nitrogen-Phosphorus Hybrid Passivated Gate Oxide Film on N-type 4H-SiC Epilayer, *Journal of Crystal Growth* (2018), doi: <https://doi.org/10.1016/j.jcrysgro.2018.09.029>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Growth and Characterization of Nitrogen-Phosphorus Hybrid Passivated Gate Oxide Film on N-type 4H-SiC Epilayer

Yifan Jia¹, Hongliang Lv¹, Xiaoyan Tang^{1,*}, Qingwen Song¹, Yimen Zhang¹, Yuming Zhang¹, Sima Dimitrijević^{2,3} and Jisheng Han³

¹*School of Microelectronics, Xidian University, The State Key Discipline Laboratory of Wide Band Gap Semiconductor Technology, Xi'an 710071, China*

²*Queensland Micro- and Nanotechnology Center, Griffith University, Nathan, Queensland 4111, Australia*

³*Griffith School of Engineering, Griffith University, Nathan, Queensland 4111, Australia*

E-mail: xytang@mail.xidian.edu.cn

A novel nitrogen-phosphorus (N&P) hybrid passivation technique by NO-containing dry oxidation of phosphorus-implanted 4H-SiC epilayer has been proposed to grow high-property gate oxide film. For demonstration and contrast, n-type 4H-SiC MOS capacitors with N&P hybrid and only N passivation have been fabricated and tested. The results from Secondary Ion Mass Spectroscopy (SIMS) reveal that about 60 % of the implanted phosphorus atoms remain in the SiO₂ film after sacrificial oxidation of the implantation layer. And the distribution of phosphorus is approximately uniform throughout the grown SiO₂ film with a concentration about $4 \times 10^{19} \text{ cm}^{-3}$, avoiding the SiO₂ film converting to phosphosilicate glass (PSG). I-V and X-ray Photoelectron Spectroscopy (XPS) data show that the grown SiO₂ film with the appropriate phosphorus passivation can effectively improve the quality of oxide film, leading the gate oxide bandgap and integrity improved and reducing the leakage current above two orders of magnitude. The bias stress measurements with ultraviolet light (UWL) irradiation also show that the N&P hybrid passivation treatment can completely restrain the near-interface electron traps (NIETs) in 4H-SiC MOS devices, indicating

that incorporation an appropriate amount of phosphorus atoms in the grown SiO₂ film also can make the electron trap density reduced effectively.

Keywords: gate oxide film, nitrogen-phosphorus hybrid passivation, gate oxide integrity, energy band alignment

1. Introduction

Due to its superior material properties, silicon carbide (SiC) has attracted great attention as a suitable semiconductor for power device applications. Besides its highly desirable properties, only stable silicon dioxide (SiO₂) insulator on SiC can be formed by conventional thermal oxidation, which makes SiC MOS device fabrication process easier compared with the other wide band gap semiconductors. Thus, SiC metal oxide semiconductor field effect transistors (MOSFETs) have been regarded as a candidate for high-voltage, high-temperature, and high-speed power devices.

However, SiC MOSFETs have some problems to be solved, such as low channel mobility and gate oxide reliability [1,2], which have been mainly ascribed to the high density of near-interface electron traps and low gate oxide integrity. In the last decades, several post-oxidation annealing (POA) treatments such as high-temperature annealing in nitrogen or phosphorus rich containing ambience have been proved to improve electrical characteristics of SiC MOSFETs [3-9]. One widely used nitrogen rich passivation process in SiC technology is the POA in NO or N₂O atmosphere, which could increase the channel mobility up to the range 20~50 cm²/V·s [3-6]. But the channel mobility with nitrogen passivation is still far from theoretical expectation value. More recently, a further increase of the channel mobility (up to the range 80~100 cm²/V·s) has been demonstrated by POA of the gate oxide in POCl₃ and P₂O₅ [5-9], which may due to the phosphorus rich passivation can effectively reduce the electron traps [10]. However, after phosphorus rich passivation, the oxide films are no longer SiO₂ but rather are converted to phosphosilicate glass, in which the phosphorus atoms are uniformly distributed with the concentration range of 2~5×10²¹ cm⁻³ [7-9]. The polar characteristics of PSG decline the gate oxide integrity [6,8], leading to the

problem of gate oxide reliability. Thus, it is necessary to find a method to effectively improve the property of gate oxide film with phosphorus passivation and understand the mechanism.

To overcome these problems, a nitrogen-phosphorus hybrid passivation method is proposed and demonstrated in this paper, in which phosphorus ion implantation is implemented before the NO-containing dry oxidation. The bidirectional capacitance-voltage (C-V) with bias stress and forward current-voltage (I-V) measurements are performed to investigate the property of the grown gate oxide film. SIMS is applied to investigate the components in the N&P hybrid and N passivation samples, so as to reveal the mechanism. Besides, the energy band alignment of the 4H-SiC MOS capacitors with N&P hybrid and N passivation are investigated by XPS measurements.

2. Experimental methods

The starting material used in this study was 4° off-axis 4H-SiC (0001) Si-face wafer with lightly doped n-type epilayer (thickness=5 μm , doping= $1\times 10^{16} \text{ cm}^{-3}$). Two kind of samples were obtained from this wafer. One set of samples (denoted as N&P passivation) was carried out by phosphorus ion implantation with high dose at low energy. After high temperature activation annealing, the SIMS results show that the surface phosphorus concentration is Gaussian-like profile within a nearly 40 nm P+ implantation layer with the peak level of $2.5\times 10^{20} \text{ cm}^{-3}$. And the contrast samples have not suffered from any special treatment (denoted as N passivation). Following the RCA cleaning, a HF dip and water rinsing, all of the samples were oxidized in 98% dry O_2 and 2% NO ambient at 1250 °C, and then, annealed by POA in N_2 at 1175 °C for 1 h. The oxide thicknesses (d_{ox}) measured by J.A.Woollam M2000D spectroscopy ellipsometry (SE) were 80 nm and 58 nm for the samples with N&P and N passivation, respectively. Finally, MOS capacitor structures were fabricated, when evaporating aluminum at the backside and on the oxide surface to form ohmic contact and gate electrodes, respectively. Fig. 1 shows the schematic of the process flow for sample preparation.

Fig. 1. The process flow for the samples with N&P and N passivation.

Electrical characteristics of the samples in this study were measured with a CASCADE probe station, using a Keysight B1505A Semiconductor Parameter Analyzer. Time dependent bias stress (TDBS) measurements with ultraviolet light irradiation ($\lambda=365 \text{ nm}$) have been applied on the samples to induce the near interface charge trapping and releasing. The hysteresis of the bidirectional C-V and the shift of flatband voltage (V_{fb}) are used to characterize the influence of near-interface traps. The density of nitrogen, phosphorus and the relative contents of Si, O and C in the samples were obtained by SIMS measurements in Evans Analytical Group laboratories. In order to determine the energy band alignments of SiO₂/SiC structures, bandgap of the grown SiO₂ films and the valence band offset between SiO₂ and SiC were examined by XPS via ThermoFisher ESCALAB 250Xi surface analysis equipment. XPS measurements were carried out using Al K α excitation ($h\nu=1486.68 \text{ eV}$) on the oxidized samples with a takeoff angle of 90°, in which argon ion sputtering was carried out in the same ultrahigh-vacuum chamber to remove the SiO₂ layer gradually.

3. Results and discussion

3.1. Secondary ion mass spectroscopy measurements

Fig. 2. SIMS profiles of P, N, Si, O, and C atoms near the interface of the samples: (a) N&P hybrid and (b) only N passivation.

Figs. 2(a) and (b) show the SIMS depth profiles of P, N, Si, O, and C atoms near the SiO_2/SiC interfaces of the both samples. In both samples, the nitrogen distribution is almost the same, which makes a Gaussian-like profile near the interface (blue line in Figs. 2), as previously reported [11,12]. It is inferred that the main effect of N passivation treatment is to reduce the NIETs within the transition layer which conforms to the results from Refs. [11,13,14]. However, for the N&P hybrid passivation sample, the distribution of phosphorus is approximately uniform throughout the grown SiO_2 film with the concentration about $4 \times 10^{19} \text{ cm}^{-3}$ to reach the interface (red line in Fig. 2(a)), which is nearly two orders of magnitude lower than post-oxidation annealing in POCl_3 and P_2O_5 , avoiding the SiO_2 film converting to phosphosilicate glass [7-9]. Besides, it is calculated that about 60 % of the implanted phosphorus atoms remain in the SiO_2 film after sacrificial oxidation of the implantation layer, indicating the concentration of phosphorus in the SiO_2 film can be regulated through this passivation treatment.

3.2. Electrical characterization

Figs. 3(a) and (b) show the normalized bidirectional C-V curves swept from depletion to accumulation and then back to depletion for the both samples at the frequency of 10 kHz at room temperature in the dark. The initial (1st) curves were

measured without suffering from bias stress. Subsequently, the 2nd curves were measured after a 600 s bias stress of 1.5 MV/cm in the dark. In the following, the 3rd curves were measured after a 600 s bias stress of -1.5 MV/cm with UVL irradiation. It is considered that the condition of negative bias stress with UVL irradiation can effectively help the trapped electrons release and hole capture by the near-interface traps [15]. At last, the 4th curves were also measured after a 600 s bias stress of 1.5 MV/cm in the dark, as the same measurement condition as the 2nd curves.

Fig. 3. Typical bidirectional C-V curves measured in the dark before and after positive and negative bias stress ($\pm$ BS) for the samples with (a) N&P hybrid and (b) only N passivation.

In Fig. 3(b), large positive hysteresis are clearly observed in the 1st and 3rd bidirectional C-V curves for the samples with N passivation, indicating the existence of electrons injection into the NIETs during the accumulation state. Compared with the N passivation samples, the N&P passivation samples do not show any bidirectional C-V hysteresis in all the measurements (shown in Fig. 3(a)). Besides, the 2nd curves measured after positive bias stress are in coincidence with the initial curve for the samples with N&P passivation. Thus, it is considered that N&P hybrid passivation treatment can completely restrain the NIETs in 4H-SiC MOS devices, indicating that an appropriate amount of phosphorus atoms distributed in the grown SiO_2 film also can make the electron trap density reduced effectively [10]. However, it is considered that the N&P hybrid passivation induces excess positive fixed charge in the grown SiO_2 , leading to a large negative V_{fb} for the N&P passivation MOS capacitor (about

-10 V in the initial curves), which may related to Si-P bond near the interface [16]. Besides, a larger and unrecovered negative shift of V_{fb} was obtained form the N&P passivation samples after the negative bias stress with UVL irradiation, indicating the N&P hybrid passivation also induces excess slow-state hole traps about $5.2 \times 10^{10} \text{ cm}^{-2}$ extracted by the method in Ref.[17].

To evaluate the gate oxide integrity, the forward I-V characteristics were measured at room temperature by sweeping the leakage current up to the oxide films breakdown. Fig. 4 shows the forward current density versus electric field (J-E) for the both samples, and the electric field is approximated by $(V_g - V_{fb})/d_{ox}$, where V_g and d_{ox} are the gate voltage and the oxide thickness. It is apparent that all the curves show typical Fowler-Nordheim (F-N) characteristics.

Fig. 4. Typical J-E curves of 4H-SiC MOS capacitors for the both samples.

It is clear that the leakage current of N&P passivation samples are smaller than that of N passivation samples under the same electric field intensity, reducing the leakage current above two orders of magnitude. The further analysis based on the J-E curves reveals that the conduction band offsets at the SiO_2/SiC interface were 2.63 eV and 2.46 eV for the samples with N&P and N passivation [18], respectively. Thus, it is considered that N&P hybrid passivation treatment can effectively improve the gate oxide integrity and reduce the leakage current, which must be related to the distribution of appropriate phosphorus concentration in the grown SiO_2 film (shown

in Fig. 2(a)).

3.3. X-ray photoelectron spectroscopy measurements

To study the energy band alignments of SiO₂/SiC structures, bandgap of the grown SiO₂ films and valence band offset between SiO₂ and SiC were examined by XPS. The bandgap (E_g) values for the dielectric materials can be determined by the onsets of energy loss obtained from the energy-loss spectra [19,20]. Fig. 5(a) shows O 1s energy loss spectra taken from the both samples. The cross points, which obtained by linearly extrapolating the segment of maximum negative slope to the base line, denote the bandgap for the grown SiO₂ films.

The determination of valence band offset is made by measuring the valence band maximum difference between the grown SiO₂ films and the SiC epilayer [20]. The valence band offset (ΔE_V) can be expressed in Eq. (1).

$$\Delta E_V = E_{VBM}^{SiO_2} - E_{VBM}^{SiC}, \quad (1)$$

where $E_{VBM}^{SiO_2}$ and E_{VBM}^{SiC} are the valence band maximum (VBM) in the grown SiO₂ films and the SiC epilayer, respectively. Figs. 5(b) and (c) show the valence band offset taken from the both samples, in which the VBM of are determined by linearly extrapolating the leading edge of valence band spectrum to the base line.

Fig. 5. (a) O 1s energy loss spectra for the both samples, XPS valence band spectra taken from the samples with (b) N&P hybrid and (c) only N passivation.

By taking the bandgap of 4H-SiC (3.26 eV) into account, the conduction band offset (ΔE_C) for SiO₂/SiC structures can be simply derived by the Eq. (2).

$$\Delta E_C = E_g(\text{SiO}_2) - \Delta E_V - E_g(\text{SiC}), \quad (2)$$

Thus, the energy band alignments obtained from XPS experimental data, Eq. (1) and Eq. (2) for the samples with N&P and N passivation are shown in Fig. (6), in which the values of conduction band offset extracted by F-N fitting also listed in parenthesis.

Fig. 6. Energy band alignments of the SiO₂/4H-SiC structures with different passivation treatment extracted from XPS measurements, and the values of conduction band offset extracted by F-N fitting listed in parenthesis.

Based on the analysis of XPS data above, it is found that the ΔE_C at SiO_2/SiC interface is bigger for the N&P passivation sample, which mainly because the gate oxide bandgap of the N&P passivation sample is much bigger and closer to the ideal value. This trend is consistent with the change of ΔE_C extracted by F-N fitting from the I-V characteristics. Thus, it is further indicated that the SiO_2 film with the appropriate phosphorus passivation can effectively improve the quality of oxide film, as well as reduce the NIETs and leakage current.

4. Conclusions

A novel nitrogen-phosphorus hybrid passivation technique is proposed for improving the properties of gate oxide film by NO-containing dry oxidation of phosphorus-implanted 4H-SiC epilayer in this paper. The potential of such method has been demonstrated by fabricating and contrasting MOS capacitors with N&P hybrid and only N passivation. The results from SIMS have revealed that the nitrogen distribution make Gaussian-like profile near the SiO_2/SiC interface for the both samples. But for the N&P passivation samples, about 60 % of the implanted phosphorus atoms remain in the SiO_2 film after sacrificial oxidation of the implantation layer. Besides, the distribution of phosphorus is approximately uniform with a concentration about $4 \times 10^{19} \text{ cm}^{-3}$ throughout the grown SiO_2 film, which is two orders of magnitude lower than conventional P passivation treatment and avoiding the SiO_2 film converting to phosphosilicate glass. The analysis of I-V and XPS data show that the grown SiO_2 film with the appropriate phosphorus passivation can effectively improve the quality of oxide film, leading the gate oxide bandgap and integrity improved and reducing the leakage current above two orders of magnitude. The bias stress measurements with UVL irradiation show that the N&P hybrid passivation treatment can completely restrain the NIETs in 4H-SiC MOS devices, indicating that an appropriate amount of phosphorus atoms distributed in the grown SiO_2 film also can make the electron trap density reduced effectively. However, the hybrid passivation also induces excess positive fixed charge and slow-state hole traps in the grown SiO_2 . Thus, it is important to optimize N&P hybrid passivation treatment in

order to avoid excess nitrogen and phosphorus contents in the oxide film, reducing the density of positive fixed charge and slow-state hole traps induced in the 4H-SiC MOS devices.

Acknowledgements

This work was partially supported by National Key R&D Program of China (Grant No. 2016YFB0400400), National Science Foundation of China (Grant Nos. 61774117 and 61774119), Natural Science Basic Research Plan in Shaanxi Province of China (Grant No. 2017JM6003) and National 111 Center (Grant No. B12026).

References

- [1] G. Liu, B.R. Tuttle, S. Dhar, Appl. Phys. Reviews 2 (2015) 021307.
- [2] T. Kimoto, Jpn. J. Appl. Phys. 54 (2015) 040103.
- [3] G.Y. Chung, C.C. Tin, J.R. Williams, K. McDonald, R.K. Chanana, R.A. Weller, S.T. Pantelides, L.C. Feldman, O.W. Holland, M.K. Das, J.W. Palmour, IEEE Electron Device Lett. 22 (2001) 176.
- [4] J. Rozen, A.C. Ahyi, X. Zhu, J.R. Williams, L.C. Feldman, IEEE Electron Device Lett. 58 (2011) 3808.
- [5] D. Okamoto, H. Yano, K. Hirata, T. Hatayama, T. Fuyuki, IEEE Electron Device Lett. 31 (2010) 710.
- [6] P. Fiorenza, L.K. Swanson, M. Vivona, F. Giannazzo, C. Bongiorno, A. Frazzetto, F. Roccaforte, Appl. Phys. A 115 (2014) 333.
- [7] D. Okamoto, H. Yano, S. Kotake, K. Hirata, T. Hatayama, T. Fuyuki, MRS Online Proceedings Library Archive 1246 (2010) B06.
- [8] Y.K. Sharma, A.C. Ahyi, T. Isaacs-Smith, X. Shen, S.T. Pantelides, X. Zhu, L.C. Feldman, J. Rozen, J.R. Williams, Solid-State Electronics 68 (2012) 103.
- [9] Y.K. Sharma, A.C. Ahyi, T. Isaacs-Smith, A. Modic, M. Park, Y. Xu, E.L. Garfunkel, S. Dhar, L.C. Feldman, J.R. Williams, IEEE Electron Device Lett. 34 (2013) 175.
- [10] D. Okamoto, H. Yano, T. Hatayama, T. Fuyuki, Appl. Phys. Lett. 96 (2010) 203508.
- [11] Y.F. Jia, H.L. Lv, Q.W. Song, X.Y. Tang, L. Xiao, L.Y. Wang, G.M. Tang, Y.M. Zhang, Y.M. Zhang, Appl. Surf. Sci. 297 (2017) 175.
- [12] J. Rozen, S. Dhar, M.E. Zvanut, J.R. Williams, L.C. Feldman, J. Appl. Phys. 105 (2009) 124506.
- [13] T. Zheleva, A. Lelis, G. Duscher, F. Liu, I. Levin, M. Das, Appl. Phys. Lett. 93 (2008) 022108.
- [14] J.A. Taillon, J.H. Yang, C.A. Ahyi, J. Rozen, J.R. Williams, L.C. Feldman, T.S. Zheleva, A.J. Lelis, L.G. Salamanca-Riba, J. Appl. Phys. 113 (2013) 044517.
- [15] Y. Jia, H. Lv, X. Tang, Q. Song, Y. Zhang, Y. Zhang, Mater. Sci. Forum 924 (2018) 449.
- [16] S. Salemi, A. Akturk, S. Potbhare, A. Lelis, N. Goldsman, Mater. Sci. Forum 717 (2012) 457.
- [17] Y.F. Jia, H.L. Lv, Q.W. Song, X.Y. Tang, Y.M. Zhang, Y.M. Zhang, S. Dimitrijević, J.S. Han, J. Mater. Sci.: Mater. Electron 29 (2018) 14292.
- [18] E.H. Nicollian, J.R. Brews, MOS (Metal Oxide Semiconductor) Physics and Technology, John Wiley & Sons, New York, 1982.
- [19] T. Hosoi, T. Kirino, S. Mitani, Y. Nakano, T. Nakamura, T. Shimura, H. Watanabe, Curr. Appl. Phys. 12 (2012) S79.
- [20] H.Y. Yu, M.F. Li, B.J. Cho, C.C. Yeo, M.S. Joo, D.-L. Kwong, J.S. Pan, C. H. Ang, J.Z. Zheng, S. Ramanathan, Appl. Phys. Lett. 81 (2002) 376.

Graphical abstract