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Improved electrical properties of NO-nitrided SiC/SiO_2 interface after electron irradiation*

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Effective improvement in electrical properties of NO passivated SiC/SiO_2 interface after being irradiated by electrons is demonstrated. The density of interface traps after being irradiated by 100-kGy electrons decreases by about one order of magnitude, specifically, from 3×10^{12} $cm^{-2}\cdot eV^{-1}$ to 4×10^{11} $cm^{-2}\cdot eV^{-1}$ at 0.2 eV below the conduction band of 4H-SiC without any degradation of electric breakdown field. Particularly, the results of x-ray photoelectron spectroscopy measurement show that the C–N bonds are generated near the interface after electron irradiation, indicating that the carbon-related defects are further reduced.

Keywords: SiC, electron irradiation, interface traps, MOS

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1. Introduction

4H-type silicon carbide (4H-SiC) is almost unanimously regarded as the best material for the next generation of power electronic devices. In fact, in some specific application fields (energy conversion, power supply, consumer electronics, *etc*.), 4H-SiC metal–oxide–semiconductor field-effect transistors (MOSFETs) can be excellent candidate to replace silicon insulated gate bipolar transistors (IGBTs) in power modules, enabling a lower power consumption at high switching frequencies and junction temperatures above 200 °C.[1–3] However, the potential of MOSFETs on 4H-SiC has not been fully tapped because of the low channel mobility resulting from an unacceptable high density of interface traps (D_{it}) near the conduction band edge of 4H-SiC.[4,5] Electrons trapped by these interface states will lead the free carriers density to decrease in the inversion layer, which reduces the channel conductivity. Additionally, the electron mobility in the inversion layer is lowered due to coulomb scattering by the trapped charges at the interface states. In this sense, a significant improvement of the SiO_2/SiC interface quality has been obtained by introducing annealing steps of the gate oxide in NO or N_2O, which enables channel mobility to reach a value in a range of 20 $cm^2\cdot V^{-1}\cdot s^{-1}$–50 $cm^2\cdot V^{-1}\cdot s^{-1}$.[6–8] The further increase of the channel mobility (up to 89 $cm^2\cdot V^{-1}\cdot s^{-1}$) in 4H-SiC lateral MOSFETs has been demonstrated by employing post-deposition-annealing (PDA) of the gate oxide in $POCl_3$.[9,10] Besides, combined NO and forming gas annealing (FGA) treatment and high temperature (over 800 °C) annealing in diluted H_2 were reported to be efficient for SiC/SiO_2 interface passivation.[11,12] During the annealing treatment, NO, N_2O, H_2 or $POCl_3$ molecules decompose. Atoms of N (H/P) diffuse through the silicon–dioxide layer into the 4H-SiC/SiO_2 interface, and react with carbon-related defects there. As a result, the energy position of the interface states shifts into the conduction band of SiC,[13] which reduces the efficiency of carrier capture at traps. Although some improvements have been achieved in channel mobility, it is still far from the ideal one. It is thought that electrons injected into the interface will be captured by the traps, reducing the effective D_{it}, or will change the stoichiometry of the interface, improving the interface quality.[14] Therefore, we present the electrical properties and x-ray photoelectron spectroscopy (XPS) results of the nitrided SiC MOS capacitor after being irradiated by electrons, indicating that electron irradiation can lead the NO-nitrided passivation to be improved.

2. Experiment and measurement

The starting substrate was an n-type 4H-SiC (0001) wafer covered by a 12-μm epilayer ($N_D \sim 1\times10^{16}$ cm^{-3}). Before dry oxidation, the SiC wafers were cleaned by the standard Radio Corporation of America (RCA) cleaning procedure. Thermal oxides were grown by dry oxidation at 1300 °C

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for 30 min in pure oxygen atmosphere in HT-RTP4000 cold wall furnace. Afterwards, samples were annealed in NO ambient for 2 h at 1350 °C. The samples were finally pulled out from the furnace in 100% N_2 ambient in 30 min. The final thickness of SiO_2 was measured by UVISEL spectroscopic ellipsometry to be 60 nm. Circular gate electrode and backside ohmic contact were formed by aluminum evaporation and the diameters of the electrode were 100 μm and 300 μm respectively. The electron irradiation of the devices was carried out at Shanghai SN Irradiation Technology Co., Ltd., China at 10-MeV energy with using four different absorbed doses: 0 kGy, 2 kGy, 20 kGy, and 100 kGy. During the irradiation, no bias was applied to the MOS capacitors. XPS analyses were performed using a PHI Quantera scanning x-ray microprobe with a monochromatic Al x-ray source ($h\nu = 1486.7$ eV) with an energy resolution of 0.1 eV. Ar sputtering was used to slowly remove the SiO_2 layer. It has been shown that preferential sputtering did not occur on SiC surfaces under Ar bombardment. After each Ar sputtering step, the XPS spectra were recorded by performing multiple scans in each binding energy range of interest with a pass energy of 55 eV. Specified analyzed area was about 100 μm in diameter. The Si 2p, O 1s, C 1s, and N 1s core-level spectra were recorded. Interface state density (D_{it}) was estimated by the high (1 MHz)–low (quasi-static) method at room temperature through using a computer-controlled Agilent B1500A LCR meter under dark condition. The dielectric breakdown properties were also investigated.

3. Results and discussion

The measured high-frequency C–V curves of SiC MOS capacitors irradiated by electrons at doses of 0 kGy, 2 kGy, 20 kGy, and 100 kGy are shown in Fig. 1(a). The 0-kGy sample corresponds to the non-irradiated reference sample. There is no large flatband voltage (V_{FB}) shift in the samples subjected to electron irradiation at doses of 2 kGy and 20 kGy compared with the non-irradiated reference sample; however, a positive shift of ~ 0.6 V is found in the 100-kGy irradiated sample, which indicates a considerable increase on the negative charges generated in the oxide during irradiation. The contribution of oxide-trap charges and interface-trap charges to the V_{FB} shift are estimated to be ΔV_{ot} and ΔV_{it}, respectively. As shown in Fig. 1(a), V_{FB} and V_{ot} are determined from the flatband capacitance ($C_{FB} = 3.7$ pF) and midgap capacitance ($C_{mg} = 1.5$ pF@$E_C - E = 1$ eV) by the standard formula.[15,16] V_{it} indicates the stretch-out between V_{FB} and V_{ot} along the gate voltage axis, commonly referred to $|V_{FB}–V_{ot}|$. Figure 1(b) shows the calculated values of ΔV_{ot} and ΔV_{it} for the irradiated samples in contrast to the non-irradiated reference. The values of ΔV_{ot} are quite close to ΔV_{FB}, and all the samples show quite small ΔV_{it} values of ~ 0 V, which suggests that the V_{FB} shift mainly results from the increase in oxide trap charge density. It could also be concluded that no interface state is generated by electron irradiation in the studied dose range. However, the oxide layer is changed to negatively charged after 100-kGy irradiation. Mobile and fixed oxide charges are positive, whereas the polarities of interface traps may be positive or negative due to holes or electrons trapped depending on their relative positions to the Fermi level. It has been proposed that the interface traps in the lower half of bandgap be negatively charged and the interface traps between midgap and the Fermi level be neutral for the n-type SiC MOS capacitor. Only the traps above the Fermi level are positively charged.[17] Therefore, the increase in negative charge density is probably attributed to deep interface trap buildup and the reduction of shallow interface traps. Storasta *et al.*[14] have reported that low energy electron irradiation can induce the hole trap (HS2 ($E_v - 0.39$ eV)) in SiC layer, which may be one of the reasons for the negative charges.

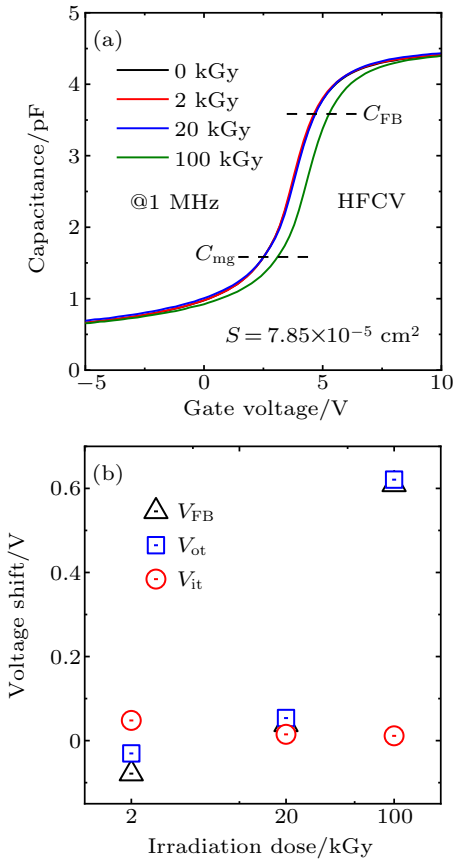


Fig. 1. (a) Typical high-frequency C–V curves of these SiC MOS capacitors irradiated by electrons at different doses. High frequency here refers to 1 MHz. Gate area is 7.85×10^{-5} cm^2.

Quasi-static C–V (QSCV) measurement is carried out for D_{it} estimation. The results are shown in Fig. 2(a). There is no significant V_{FB} shift until an irradiation dose rises up to 100 kGy as happened to C–V curves measured at high frequency illustrated in Fig. 1(a). A frequency dispersion is obtained at the onset of depletion in QSCV measurement, which indicates a reduction in deep D_{it}. This behavior was not observed in the high frequency C–V results. Thereafter, the D_{it}

value is calculated using high–low method with the expression below

$$D_{\rm it} = \frac{1}{q}\left[\left(\frac{1}{C_{\rm QS}} - \frac{1}{C_{\rm ox}}\right)^{-1} - \left(\frac{1}{C_{\rm HF}} - \frac{1}{C_{\rm ox}}\right)^{-1}\right], \quad (1)$$

where $C_{\rm ox}$ is the oxide capacitance and q is the electron charge. Figure 2(b) shows the extracted $D_{\rm it}$ value as a function of energy position in the band gap measured from the 4H-SiC conduction band ($E_{\rm C} - E$) for MOS capacitors subjected to electron irradiation at different doses. The $E_{\rm C} - E$ is calculated from

$$E_{\rm C} - E = e\,(0.19\ {\rm V} - \psi_{\rm s}) \quad (2)$$

by taking into account the Fermi level of the SiC epilayer ($E_{\rm C} - 0.19$ eV). The surface potential ($\psi_{\rm s}$) can be calculated from quasi-static capacitance and high frequency depletion capacitance.[18] It is found that $D_{\rm it}$ decreases with increasing irradiation dose, especially at deep energy level ($E_{\rm C} - E \geq 0.4$ eV). The $D_{\rm it}$ value at $E_{\rm C} - E = 0.2$ eV decreases by about one order of magnitude, specifically, from $\sim 3 \times 10^{12}$ cm^{-2}·eV^{-1} to 4×10^{11} cm^{-2}·eV^{-1} after 100-kGy electron irradiation. It is even lower at $E_{\rm C} - E = 0.4$ eV (2×10^{11} cm^{-2}·eV^{-1}). The result is attributed to the fact that interface states at deep energy level are occupied by the injected electrons, making them invariant to charge trapping during C–V sweep, as a consequence, reducing the $D_{\rm it}$ To investigate the validity of our data, the statistical plot of $D_{\rm it}$ values at energy level $E_{\rm C} - E = 0.2$ eV is shown in Fig. 2(c) with a box chart. Although there is some fluctuation in the $D_{\rm it}$ values, the tendency is identical with that in Fig. 2(b), indicating that the electron irradiation indeed helps reduce the value of $D_{\rm it}$.

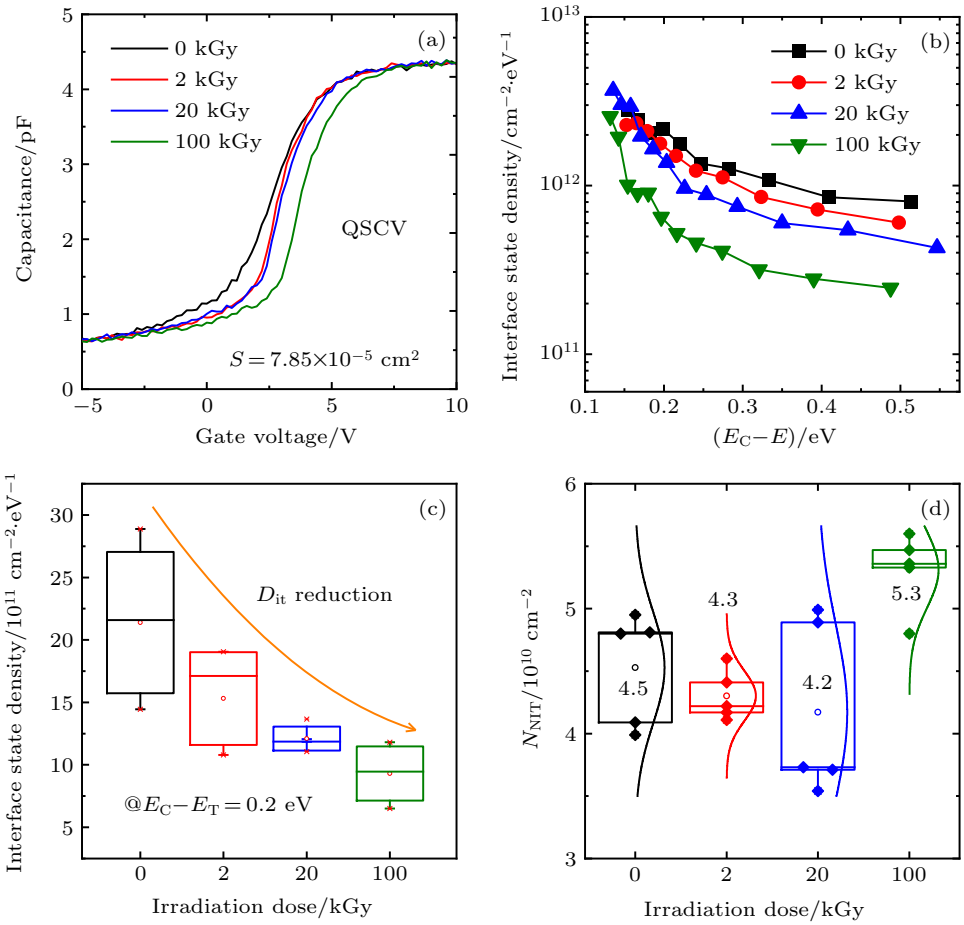


Fig. 2. (a) Quasi-static C–V results of SiC MOS capacitors after 10-MeV electron irradiation; (b) $D_{\rm it}$ distribution *versus* energy level below conduction band of 4H-SiC; (c) box chart statistics of $D_{\rm it}$ values *versus* irradiation dose at energy level $E_{\rm C} - E = 0.2$ eV of five samples; (d) Box chart of the density of near interface traps (NIT) estimated from the C–V hysteresis characteristics of these studied samples.

Furthermore, the effect of electron irradiation on near interface trap is evaluated statistically through the hysteresis of high frequency C–V data from the following expression:

$$N_{\rm NIT} = \frac{|\Delta V_{\rm Hys}|\,C_{\rm ox}}{qS}, \quad (3)$$

where $C_{\rm ox}$ is the oxide capacitance, S is the gate area, is the hysteresis voltage extracted from the bidirectional C–V curve at 1 MHz, and q is the electron charge. Figure 2(d) shows the box plot of $N_{\rm NIT}$ *versus* irradiation dose of the investigated samples, revealsing that a mean $N_{\rm NIT}$ value is $\sim 4.5 \times 10^{10}$ cm^{-2} in the samples after being irradiated by electrons at doses of 0, 2, and 20 kGy. And the $N_{\rm NIT}$ value experiences a slight increase from 4.5×10^{10} cm^{-2} to 5.3×10^{10} cm^{-2} after 100-kGy electron irradiation. When electrons pass through

the oxide, the already presented positively charged traps becomes neutralized, hence not acting as trapping centers. And the electrons trapped in the oxide will also capture the injected electrons, which increases the density of oxide trap charge, leading V_{FB} to positively shift, which is in good agreement with the high frequency and QSCV results.

Figures 3(a) and 3(c) show the Si 2p core-level spectra of the SiO_2/SiC interfaces at sputtering time of 612 s for the NO annealed sample and the electron irradiated samples with NO annealing, respectively. The Si 2p spectrum of the NO annealed sample can be fitted with three Gaussian peaks which are marked as Si-1 [100.1 eV, full width at half maxima (FWHM) = 2 eV], Si-2 (101.8 eV, FWHM = 2 eV), and Si-4 (103.2 eV, FWHM = 2 eV), which relate to SiC from the substrate, Si≡N bond and SiO_2, respectively.[19] After 100-kGy electron irradiation, the energy position of the peak of Si-4 shifted to the 102.8 eV (Si-3, FWHM = 2 eV), indicating that silicon oxide states exist in the interface region.[19] It has been reported that O–Si–N defects exist in the crystalline lattice in the NO-annealing treated SiC/SiO_2 interface.[20] Additionally, it has been shown that the O–Si–N defects are efficient electron trap centers.[21] Therefore, when a neutral O–Si–N molecule near an interface defect is electrically activated, a negative SiO-charge is created at the SiC/SiO_2 interface. This N-depassivation reaction can be described with the following diffusion-limited electrochemical reaction:[21]

$$\mathrm{O–Si–N} + \mathrm{e}- \longleftrightarrow \mathrm{O–Si} - + \mathrm{N}^{\circ}.$$

The N atoms are bonded to some other Si atoms in the SiO_xN_y transition layer. The weakening of Si–N bond by the injected electron will make the N atoms more susceptible to diffuse than the other species. The N atoms, to a minor extent, are forced to diffuse more deeply towards the epilayer during electron irradiation. And the residual N atoms are currently located at the interface. Figures 3(b) and 3(d) show the C 1s spectra obtained from samples after sputtering for 756 s. The C 1s spectrum of the NO annealed sample can be fitted with two Gaussian peaks which are marked as C-1 (282.8 eV, FWHM = 1.8 eV) and C-2 (284.0 eV, FWHM = 1.8 eV). It can be seen from Figs. 3(b) and 3(d) that C 1s spectra of NO annealed samples before and after being irradiated by electrons all have the spectra of C-1 and C-2 species which relate to SiC from the substrate and intermediate oxide/carbon compound,[19] while the C-3 (285.3 eV, FWHM = 1.8 eV) peak only appears after the electron irradiation, indicating the existence of C–N bonds near the interface.[19] This is further supported by the observation of the peak in the corresponding N 1s spectrum of the electron irradiated sample. The binding energy of 398 eV of N suggests the existence of C–N bonds near the interface as shown in Fig. A2 (in Appendix A). Therefore, after irradiated by electrons, new bonds between N and C are created, leading the passivation to be improved, and thus, explaining the absence of carbon related defects. As a result, the interface quality is improved. The slight increase in N_{NIT} possibly originates from the formation of Si interstitials by Si–O structure reconstruction[22] where N atom is released.

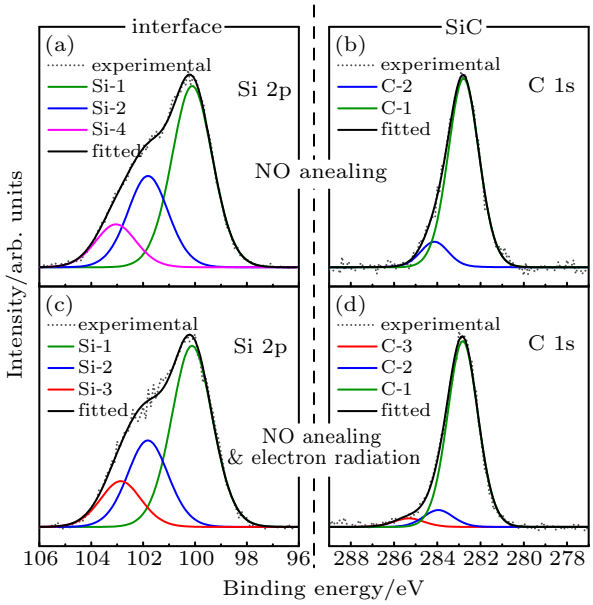


Fig. 3. Si 2p XPS spectra of the SiO_2/SiC interfaces after (a) being annealed in NO atmosphere and (c) electrons irradiated NO annealing at sputtering time of 612 s. C 1s XPS spectra of (b) NO-annealed sample and (d) electron-irradiated NO annealed sample at sputtering time of 756 s.

The electrical breakdown properties of the dielectrics are also studied for all MOS structures after being irradiated by electrons. Figure 4(a) shows the typical current–electric field (I–E) characteristics of samples investigated for each set. The current begins to increase exponentially at electric field above 6 MV/cm, which indicates that the current conduction follows the Fowler–Nordheim (FN) mechanism given by the following equation, which does not consider the Frenkel-pool emission:

$$J = \frac{q^3(m/m^*)}{8\pi h \Phi_{\mathrm{B}}} E^2 \exp\left(\frac{-8\pi(2m^*)^{1/2}\Phi_B^{3/2}}{3hqE}\right), \tag{4}$$

where h is the Planck constant, q is the electronic charge, E is the electric field, is the barrier height, and m^* is the electron effective mass inside the oxide, and m is the free electron mass. Based on the I–E curves in Fig. 4(a), the breakdown electric field (E_{BD}) is determined as shown in Fig. 4(b). The mean values of E_{BD} are 8.83, 8.64, and 9.07 MV/cm for the MOS capacitors after irradiation. Comparing with E_{BD} value of the reference (8.97 MV/cm), no apparent degradation is caused by irradiation. Besides, the effective barrier heights are also calculated from the slope of $\ln(J/E^2)$ *versus* $(1/E)$ curves with $m^* = 0.42m$.[23] The results are shown in Fig. 4(c). The barrier height shows a slight increase from 2.24 eV to 2.27 eV after

2-kGy electron irradiation due to the effective passivation of interface states. It seems that the increase saturates at doses higher than 20 kGy. The samples subjected to 20-kGy and 100-kGy irradiations show a barrier height of 2.29 eV. Moreover, the standard deviations among the E_{BD} and barrier height values decrease also with irradiation dose increasing, which suggests that uniformity is greatly improved by electron irradiation.

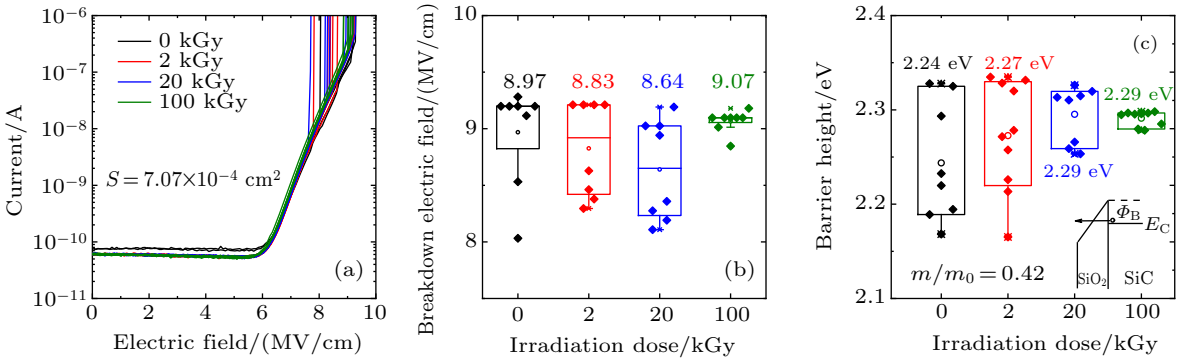


Fig. 4. (a) Typical current–electric field characteristics of these irradiated SiC MOS capacitors; (b) box chart plot of breakdown electric field determined from *I*–*E* curves and (c) barrier height calculated from FN part of the current with $m = 0.42m_0$. Several samples are investigated and the number marked in the figure is the mean values of E_{BD} and barrier height. The diameter of circular gate electrode is 300 μm.

4. Conclusions and perspectives

In summary, we find that the electron irradiation with a dose of 100 kGy further improves the electrical properties of NO Passivated SiC/SiO$_2$ interface. The D_{it} value decreases by about one order of magnitude, specifically, from 3×10^{12} eV^{-1} to 4×10^{11} cm^{-2}·eV^{-1} at an energy level $E_C - E = 0.2$ eV despite N_{NIT} slightly increasing from 4.5×10^{10} cm^{-2} to 5.3×10^{10} cm^{-2}. In the case of current-voltage characteristic, electron irradiation helps increase the barrier height and statistical uniformity, however, makes no contribution to E_{BD} degradation ($\sim$ 9 MV/cm).

Appendix A: Supplementary material

The XPS spectra of the NO-annealed sample and the electron-irradiated NO annealed sample for a sputtering time of 756 s are shown in Figs. A1 and A2, respectively.

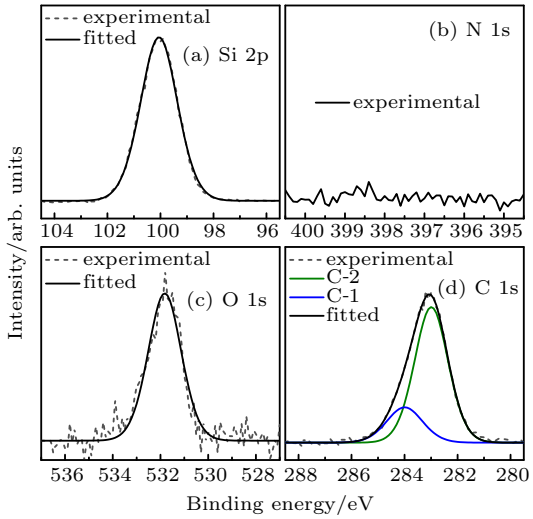


Fig. A1. (a) Si 2p, (b) N 1s, (c) O 1s, and (d) C 1s XPS spectrums of NO-annealed sample at sputtering time of 756 s.

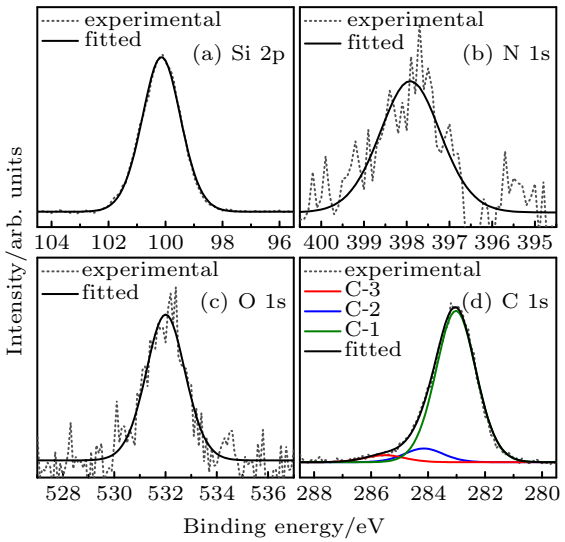


Fig. A2. (a) Si 2p, (b) N 1s, (c) O 1s, and (d) C 1s XPS spectrums of electron-irradiated NO annealed sample for sputtering time of 756 s.

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