

## Nitrogen and Hydrogen Induced Trap Passivation at the SiO<sub>2</sub>/ 4H-SiC interface

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**Abstract.** Post-oxidation anneals that introduce nitrogen at the SiO<sub>2</sub>/4H-SiC interface have been most effective in reducing the large interface trap density near the 4H-SiC conduction band-edge for (0001) Si face 4H-SiC. Herein, we report the effect of nitridation on interfaces created on the (11 $\bar{2}$ 0) a-face and the (000 $\bar{1}$ ) C-face of 4H-SiC. Significant reductions in trap density (from  $>10^{13}$  cm<sup>-2</sup> eV<sup>-1</sup> to  $\sim 10^{12}$  cm<sup>-2</sup> eV<sup>-1</sup> at E<sub>C</sub>-E  $\sim 0.1$  eV) were observed for these different interfaces, indicating the presence of substantial nitrogen susceptible defects for all crystal faces. Annealing nitridated interfaces in hydrogen results in a further reduction of trap density (from  $\sim 10^{12}$  cm<sup>-2</sup> eV<sup>-1</sup> to  $\sim 5 \times 10^{11}$  cm<sup>-2</sup> eV<sup>-1</sup> at E<sub>C</sub>-E  $\sim 0.1$  eV). Using sequential anneals in NO and H<sub>2</sub>, maximum field effect mobilities of  $\sim 55$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> and  $\sim 100$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> have been obtained for lateral MOSFETs fabricated on the (0001) and (11 $\bar{2}$ 0) faces, respectively. These electronic measurements have been correlated to the interface chemical composition.

### Introduction

Continual improvement in the quality of the SiO<sub>2</sub>/4H-SiC interface is vital for development of efficient SiC metal-oxide-semiconductor (MOS) technologies. Thermal oxidation, used to grow insulating SiO<sub>2</sub> layers on SiC, results in the formation of a defected interface with a large interface state density ( $D_{it}$ ), located energetically in the SiC band-gap. These states trap and scatter inversion channel carriers to produce unacceptably low effective channel mobilities in 4H-SiC MOSFETs (metal-oxide-semiconductor-field-effect-transistor). Systematic use of chemical modification and processing, combined with a careful analysis of interfacial structure have resulted in significant progress in reducing such defects. Post-oxidation anneals that introduce nitrogen at the SiO<sub>2</sub>/4H-SiC interface [1-4] have been most effective in reducing the large interface state density near the 4H-SiC conduction band-edge [5]. For thermal oxides grown on the (0001) Si-face, nitridation via post-oxidation annealing in nitric oxide (NO) reduces the interface state density near the conduction band-edge by an order of magnitude (from  $>10^{13}$  cm<sup>-2</sup> eV<sup>-1</sup> to  $\sim 10^{12}$  cm<sup>-2</sup> eV<sup>-1</sup>), and the effective channel mobility increases correspondingly from single digit values to 40-50 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Herein, we report the effect of NO nitridation on interfaces created on the (11 $\bar{2}$ 0) a-face and the (000 $\bar{1}$ ) C-face of 4H-SiC. The 'order of magnitude' trap passivation effect is consistently observed for all faces studied, indicating the presence of nitrogen susceptible defects for interfaces formed via significantly different oxidation kinetics. Furthermore, we investigate the effect of hydrogenation of the nitridated interface. We find that post-metallization annealing in the presence of a catalytic gate metal like Pt results in a further reduction of trap densities (from  $\sim 10^{12}$  cm<sup>-2</sup> eV<sup>-1</sup> to  $\sim 5 \times 10^{11}$  cm<sup>-2</sup> eV<sup>-1</sup> at E<sub>C</sub>-E  $\sim 0.1$  eV on the Si-face). Trap density measurements performed on MOS capacitors have been supplemented by field-effect mobility measurements on lateral MOSFETs. Correlations between electrical measurements and physical analysis of the interface are presented in this article.

### Test device fabrication and measurement

Si, C (both 8° off axis) and a-face (on-axis) *n*-type 4H-SiC wafers with ~10 μm epitaxial layers doped with nitrogen at ~ 1x10<sup>16</sup> cm<sup>-3</sup> were used to fabricate MOS capacitors for interface state density ( $D_{it}$ ) measurements. After a standard RCA cleaning process, samples underwent dry oxidation at 1150°C for different time durations depending on crystal orientation. For nitridation, samples were subjected to post-oxidation annealing (POA) in flowing NO (~575 sccm) at 1175 °C for 2 h. All samples were loaded and unloaded at 900 °C in flowing Ar. Gate metallization was performed using Al or a Au/Mo stack by either thermal evaporation or sputtering. To evaluate the effect of hydrogen, some nitridated samples were further subjected to a post-metallization anneal (PMA) in flowing H<sub>2</sub> (1000 sccm) at 500 °C for 1 h using Pt (deposited via sputtering) as a gate metal. Pt was used to facilitate hydrogen uptake into the SiO<sub>2</sub>/SiC structure as will be discussed in a later section. Trap density measurements were performed using the simultaneous high frequency-quasistatic CV technique at room temperature and at 300°C.

Lateral test MOSFETs were fabricated on *p*-type epitaxial layers (Al doping ~1 x 10<sup>16</sup> cm<sup>-3</sup>) using similar gate oxidation procedures. The source and drain regions were formed using nitrogen implantation (box profile 500 nm, 10<sup>18</sup> cm<sup>-3</sup>), and Ni was sputtered and annealed to form ohmic source/drain contacts. Room temperature field effect mobility values were extracted from measurements of drain current as a function of gate voltage for a fixed drain voltage.

### Nitrogen assisted trap interface passivation for (0001), (11 $\bar{2}$ 0) and (000 $\bar{1}$ ) crystal faces

The (000 $\bar{1}$ ) C and (0001) Si faces are polar faces containing 100% C atoms and 100% Si atoms, respectively; the (000 $\bar{1}$ ) and (0001) planes being basal planes in the hexagonal lattice. The (11 $\bar{2}$ 0) a-face is a non-polar face comprised of 50% C and 50% Si atoms. In this article, for clarity and simplicity we will refer to the different crystal faces as C-face (000 $\bar{1}$ ), a-face (11 $\bar{2}$ 0) and Si-face (0001). The oxidation rate anisotropy among these faces (oxidation rate of C-face > a-face > Si-face) [6, 7] offers the possibility of using the ‘fast-oxidizing’ crystal faces for device fabrication with a lower thermal budget for MOS processing. For processing on these faces, nitrogen treatment could be vital for obtaining an optimized SiO<sub>2</sub>/SiC interface as the trap densities for all faces are extremely high, exceeding 10<sup>13</sup> cm<sup>-2</sup>eV<sup>-1</sup> near the conduction band-edge ( $E_c$ ) [8-10]. Trap density near  $E_c$  as a function of crystal face follows the order:  $(D_{it})_{C\text{-face}} > (D_{it})_{a\text{-face}} > (D_{it})_{Si\text{-face}}$ . The anisotropy in oxidation kinetics suggests different rate limiting reactions, possibly leading to different interfacial / near-interfacial defects. Physical analysis of the ‘as-grown’ interface by several techniques such as surface enhanced Raman spectroscopy (SERS) [11], electron energy loss spectroscopy (EELS) [12] and x-ray photoelectron spectroscopy (XPS) [13] suggests the presence of higher interfacial ‘free’ carbon and/or a different carbon containing sub-oxide on the C-face compared to the Si-face.

Interface trap profiles after NO post-oxidation annealing (1175 °C, 2 h) for the three faces are shown in Fig. 1a. A typical  $D_{it}$  for unpassivated oxides on the Si-face is also shown for comparison. The passivation effect of NO for the a-face and C-face is comparable to the Si-face close to the conduction band-edge, as  $D_{it}$  is reduced from ~ 10<sup>13</sup> cm<sup>-2</sup> eV<sup>-1</sup> to ~10<sup>12</sup> cm<sup>-2</sup> eV<sup>-1</sup> at  $E_c$ - $E \sim 0.1$  eV for all faces. Deeper into the band-gap ( $E_c$ - $E > 0.25$  eV), however, trap density as a function of crystal face follows the same trend as that of as-oxidized interfaces, with the C-face oxide having the highest  $D_{it}$ . These results indicate the presence of nitrogen susceptible traps for the different crystal faces, suggesting for each at least one kind of electrically active defect with similar chemical behavior. Field-effect mobilities in lateral n-channel MOSFETs fabricated on the different faces with similar gate oxidation and NO passivation procedures are shown in Fig. 1b. The peak mobility values are ~ 45 cm<sup>-2</sup> V<sup>-1</sup> s<sup>-1</sup>, ~ 57 cm<sup>-2</sup> V<sup>-1</sup> s<sup>-1</sup> and ~ 35 cm<sup>-2</sup> V<sup>-1</sup> s<sup>-1</sup> for the Si-, a- and C-face MOSFETs, respectively. The higher peak mobility for the a-face compared to the Si-face can be attributed to the anisotropy in the bulk mobility of 4H-SiC ( $\mu_{(0001)}/\mu_{(11\bar{2}0)} \sim 0.8$ ) [14]. Therefore, it is

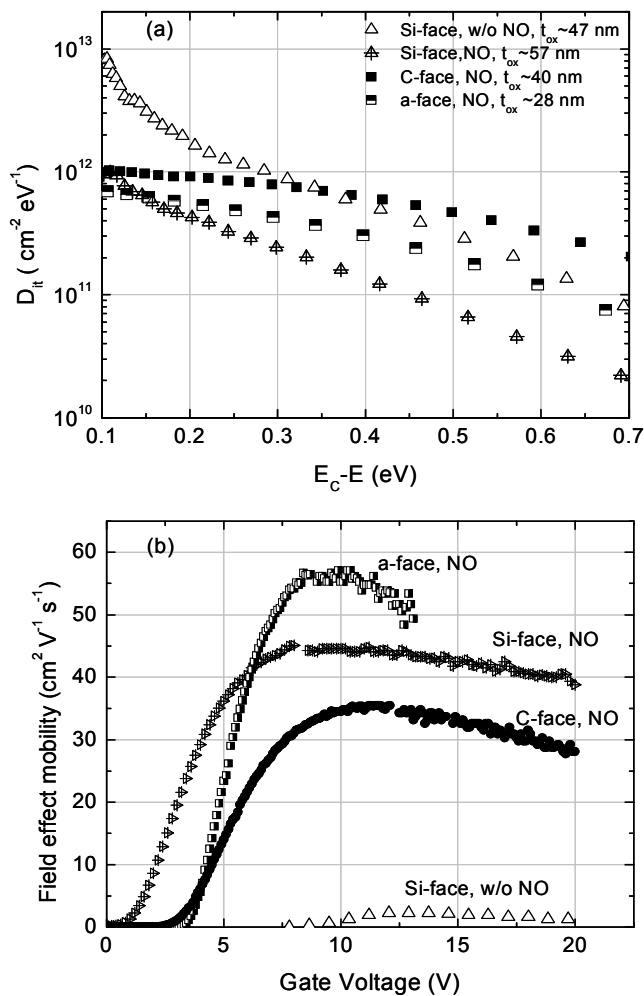


Figure 1. (a)  $D_{it}$  near the conduction band-edge of 4H-SiC for oxides grown on the Si-face, a-face and C-face and subjected to NO POA at  $1175^\circ \text{C}$  for 2h. The data are an average of  $\sim 10$  capacitors.  $D_{it}$  for Si-face oxide without NO POA is also shown for comparison. (b) Field-effect mobilities in n-channel MOSFETs for the corresponding  $\text{SiO}_2/4\text{H-SiC}$  interfaces as in (a).

evident that the field effect mobility (measured for *p*-type material) scales qualitatively with the results of the trap density measurements (measured in *n*-type material).

NO annealing results in nitrogen incorporation exclusively at or near the  $\text{SiO}_2/\text{SiC}$  interface, without any change in stoichiometry of the bulk oxide. This interfacial nitrogen profile is a very sharp distribution located within approximately  $\sim 1$  nm of the interface [12]. In a previous work, it has been shown that the trap density reduction is dependent only on the amount of interfacial N, and not on the anneal time or temperature [15]. In this work, N incorporation was measured using the  $^{15}\text{N}(p,\alpha)^{12}\text{C}$  nuclear reaction for standard oxides that were annealed in  $^{15}\text{NO}$  at  $1175^\circ \text{C}$  and 100 Torr. Interfacial N uptake kinetics for the three crystal faces obtained from these measurements reveal anisotropy in nitridation rates as shown in Fig. 2. The nitridation anisotropy has the same trend as oxidation, i.e. C-face  $\geq$  a-face  $>$  Si-face. All three faces initially show a rapid accumulation of N at the interface before reaching an approximately constant level. This can be explained by identifying the competition between two main processes during NO annealing: N enrichment by NO and N removal by  $\text{O}_2$  formed during the decomposition of NO [16]. It has been shown previously that the N induced trap reduction saturates after a critical amount of interfacial N uptake [15]. The additional oxide growth during NO annealing may be the limitation for further trap passivation, as it may impede the N related defect passivation by generating new defects.

### Hydrogen assisted interface trap passivation

In order to achieve further improvement of nitridated  $\text{SiO}_2(\text{N})/4\text{H-SiC}$  interfaces, additional passivation treatments are mandatory. Hydrogen, which is highly effective for passivating dangling bonds at the  $\text{SiO}_2/\text{Si}$  interface, is relatively ineffective at the  $\text{SiO}_2/\text{SiC}$  interface compared to nitrogen. Theoretical calculations (to be published elsewhere) suggest that possible defects at the  $\text{SiO}_2/\text{SiC}$  interface should bind *atomic hydrogen*, leading to a reduction of the density of interface defect states. We, therefore, pursued hydrogenation following the deposition of a catalytic metal such as Pt, in the expectation that  $\text{H}_2$  molecules would crack as they pass through the metal, leading to monatomic H arriving at the interface. Indeed, the process worked. Using deposition of Pt and a post-metallization anneal at  $500^\circ \text{C}$  for one hour led to a substantial incorporation of H in the oxide

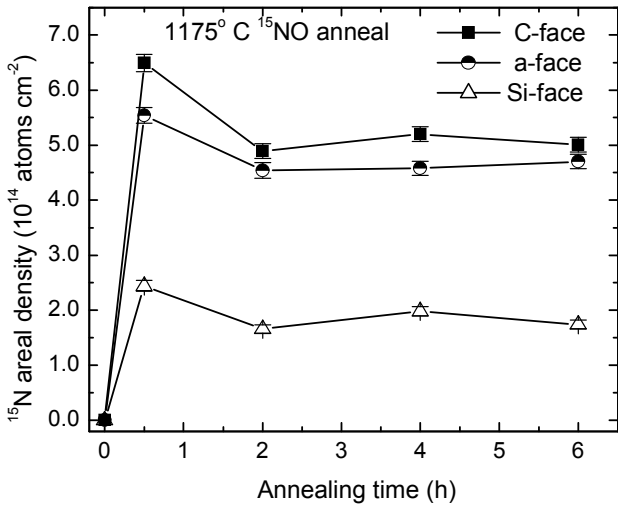


Figure 2. Nitridation kinetics for SiO<sub>2</sub>/4H-SiC interfaces formed on the C-, a- and Si-faces of 4H-SiC. All samples were annealed at 1175°C, in 100 Torr <sup>15</sup>NO. Thickness of oxides prior to annealing was 30-37 nm. See ref. 16 for further details.

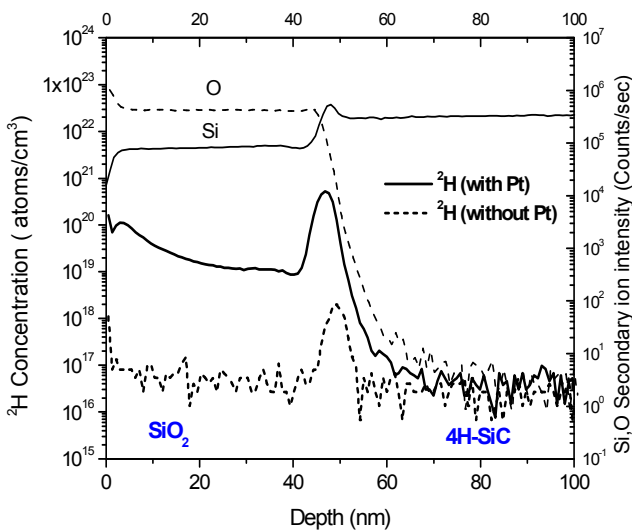


Figure 3. SIMS profiles for SiO<sub>2</sub>(N)/4H-SiC samples with comparable oxide thickness annealed in <sup>2</sup>H (deuterium) at 500°C for 1h with and without a Pt over-layer. (The O and Si profiles are not shown for the ‘with Pt’ sample) About 80% (2.5 x 10<sup>14</sup> atoms cm<sup>-2</sup>) of the <sup>2</sup>H is at or near the SiO<sub>2</sub>/SiC interface with a distribution having FWHM of ~3.5 nm within the depth resolution of SIMS.

and at the interface [17] as shown in the secondary ion mass spectrometry measurements (SIMS) in Fig. 3.

Trap density reduction in Si-face capacitors fabricated with the Pt process without NO treatment is about factor of ~ 2 at E<sub>C</sub>-E ~ 0.1 eV compared to the unpassivated oxides; a relatively small effect compared to the NO effect (Fig. 4). The magnitude of H induced improvement observed in our experiments is comparable to previous reports employing post-oxidation anneals in hydrogen and/or oxidation in H containing ambients [18, 19]. Also shown in Fig. 4 is the typical D<sub>it</sub> profile (denoted NO + H<sub>2</sub>) of an interface processed with Pt / H<sub>2</sub> after undergoing standard NO POA. Comparison with the ‘NO only’ data reveals a ~ 30 % lower D<sub>it</sub> at E<sub>C</sub>-E ~0.1 eV and deeper in the band-gap, i.e. from E<sub>C</sub> – E = 0.6 eV to 1.6 eV. The additional passivation is also observed for the a-face (Fig.5a) and the C-face (not shown). Peak field-effect mobility values obtained from MOSFETs fabricated by the NO+ H<sub>2</sub> process are ~ 55 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and ~ 100 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for the Si-face and a-face, respectively (Fig. 5b ).

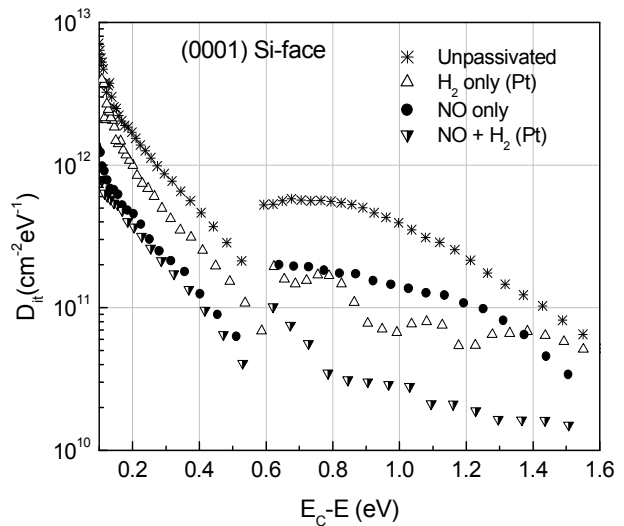


Figure 4. Interface trap densities in the upper half of the 4H-SiC band-gap obtained for the different interface passivation treatments as described in the text. Oxide thicknesses are in the range 45-55 nm. Discontinuities near E<sub>C</sub>-E ~0.6 eV are the result of CV measurements at 23°C and 300°C, respectively, below and above 0.6 eV.

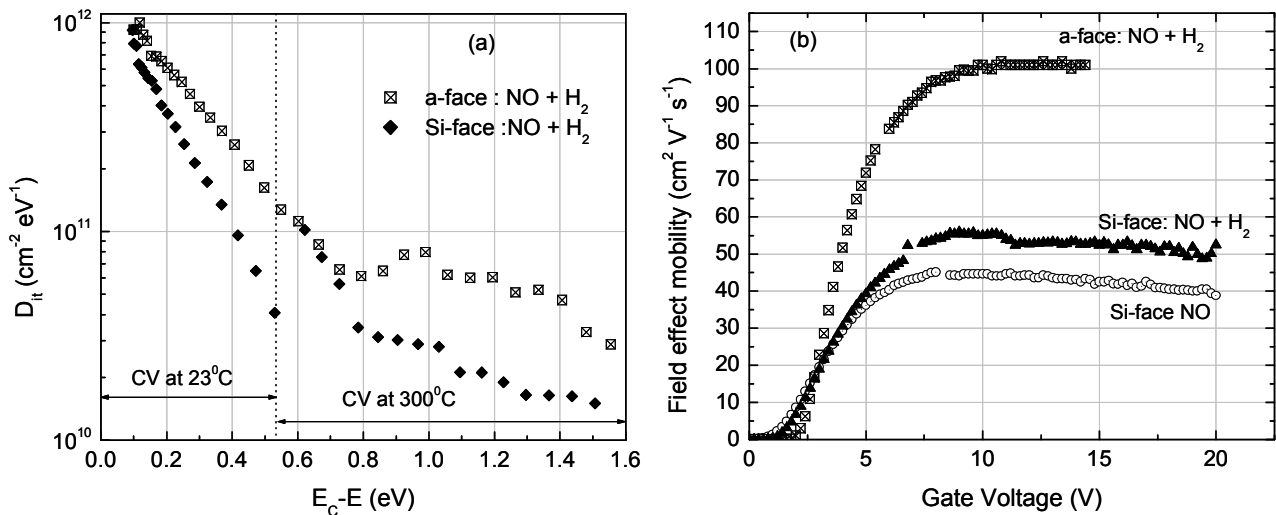


Figure 5. (a)  $D_{it}$  profiles obtained from MOS capacitors fabricated on the Si-face and a-face using sequential annealing in NO and H<sub>2</sub> as described in the text. (b) Field-effect mobilities in n-channel MOSFETs for the corresponding SiO<sub>2</sub>/4H-SiC interfaces, compared to the 'NO only' Si-face.

The improvement of mobility for both faces over passivation with NO only is clearly evident. But the ratio of the peak mobility for these two faces is 0.65, higher than the bulk mobility ratio which indicates a relatively greater improvement for the a-face. This result is intriguing, considering the fact that the a-face has higher  $D_{it}$  than the Si-face throughout the band-gap following (NO + H<sub>2</sub>) treatment (Fig. 5,  $D_{it}$  near valence band not shown). Atomic force microscopy measurements performed following oxide removal at the center of the gate region reveal a rougher surface on the Si-face - a factor that may have a detrimental effect on the Si-face channel mobility. (R.M.S roughness was found to be  $\sim 1.9$  nm and  $\sim 1.3$  nm on the Si- and a- faces, respectively.) The factor that remains a very important question is the accuracy of the trap density measurements for both faces very near the conduction band-edge - i.e., for  $E_C - E \leq 0.1$  eV. The trap density for the a-face may actually be lower over this energy range.

Typical breakdown fields of  $\sim 5$  MV cm<sup>-1</sup> were obtained for oxides that underwent the NO + H<sub>2</sub> process. This value is considerably lower than the breakdown field for 'NO only' oxides ( $\sim 7-8$  MV cm<sup>-1</sup>). To understand the role of hydrogen in this problem, NO passivated oxides with Pt gate contacts were annealed in Ar instead of hydrogen at 500 °C for 1 h in flowing Ar instead of H<sub>2</sub>. The breakdown fields of these samples were found to be similar to the (NO + H<sub>2</sub>) oxides. This result strongly suggests that the lower breakdown strength of the NO + H<sub>2</sub> oxides is associated with the Pt gate metal (possibly sputter deposition damage to the oxide) and not H<sub>2</sub>. To overcome this limitation, Pt deposition methods that induce minimal damage to the SiO<sub>2</sub> surface should be employed.

## Summary

SiO<sub>2</sub>/4H-SiC interface trap passivation can be efficiently achieved in oxides grown on different crystal faces of 4H-SiC by nitridation via NO post-oxidation annealing. In comparison, passivation by atomic hydrogen is still only partially effective, most likely because of the thermodynamic balance between defect passivation and depassivation that occurs at the pertinent temperatures. The best passivated interfaces have been obtained by employing hydrogen in conjunction with nitrogen for all crystal faces. Using sequential anneals in NO and H<sub>2</sub>, maximum field effect mobilities of  $\sim 55$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> and  $\sim 100$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> have been obtained for lateral MOSFETs fabricated on the (0001) Si-face and the (11 $\bar{2}$ 0) a-face, respectively.

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