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Controlling the threshold voltage of β-Ga₂O₃ field-effect transistors *via* remote fluorine plasma treatment

Janghyuk Kim[†], Marko J. Tadjer[‡], Michael A. Mastro[‡] and Jihyun Kim^{†,*}

[†]Department of Chemical and Biological Engineering, Korea University, Seoul 02841 Korea

[‡]US Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375 USA

ABSTRACT

β-phase gallium oxide (β-Ga₂O₃), emerging as an ultra-wide bandgap semiconductor, suffers from negative threshold voltage (V_{th}) characteristics, which only allow depletion-mode (Dmode) operation; however, enhancement-mode (E-mode) operation is preferred to ensure fail-safe operation and simplify circuit topologies. Therefore, in this study, the V_{th} is controlled via remote fluorine plasma treatment in β-Ga₂O₃ metal-insulator-semiconductor field-effect transistors (MISFETs). Under the top-gate modulation, the V_{th} of the fluorinated β-Ga₂O₃ MISFET was positively shifted by +4 V, exhibiting high on/off ratio (~10⁷) and low sub-threshold swing (175 mV/dec). Under the double-gate modulation, the E-mode β-Ga₂O₃ MISFET was demonstrated, where the V_{th} was estimated to be +2.2 V. The obtained results suggest that the fluorine plasma treatment is an effective method to control the V_{th} of the β-Ga₂O₃ FETs from D-mode to E-mode, pointing out monolithic integration of β-Ga₂O₃ transistors for future smart power electronics.

KEYWORDS: gallium oxide; field-effect transistors; enhancement-mode; plasma treatment

*Corresponding Author: E-mail: <u>hyunhyun7@korea.ac.kr</u> (Jihyun Kim)

INTRODUCTION

β-phase gallium oxide (β-Ga₂O₃) is a promising semiconductor material for nextgeneration high-power electronics because of its ultra-large energy bandgap of 4.8 eV (room temperature) and a theoretical critical field strength of approximately 8 MV/cm.^{1–3} The Baliga's figure of merit,⁴ which is the metric of conduction loss in power devices, of β-Ga₂O₃ (at 3214) is considerably higher than those of SiC (at 317) and GaN (at 846). This indicates that β-Ga₂O₃-based power electronics are more efficient than other competing wide bandgap materials. As the proportion of electrical energy passing through power electronics has been increasing considerably, near-future power electronics utilizing β-Ga₂O₃ as an active layer can lead to a considerable reduction in energy consumed. ⁵ Furthermore, another prominent feature of β-Ga₂O₃ compared to other wide-bandgap semiconductors is that high-quality single crystals can be synthesized cost-effectively using melt growth techniques such as the floating zone, Czochralski and edge-defined film-fed growth. Therefore, it can be concluded that β-Ga₂O₃ has an economical advantage over SiC and GaN.

β-Ga₂O₃ device technology has developed rapidly in recent years and various transistors, including MOSFETs, MESFETs, and FinFETs, have been successfully demonstrated. Higashiwaki et al. pioneered single-crystal β-Ga₂O₃-based transistors.⁶ Tadjer et al. demonstrated a β-Ga₂O₃ MOSFET with HfO₂ gate dielectric layer.⁷ Interestingly, a single crystalline β-Ga₂O₃ with a monoclinic structure can be exfoliated into ultra-thin flakes along a (100) plane owing to its strong in-plane force and weak out-of-plane force,⁸⁻¹⁰ demonstrating various β-Ga₂O₃ nano-layer based transistors.^{10–13} β-Ga₂O₃ typically contains oxygen vacancies, and therefore, β-Ga₂O₃ has been considered as an n-type semiconductor.¹⁴ Recently, it is reported that the oxygen vacancy cannot contribute to the conductivity because they are deep donors.¹⁵ Furthermore, n-type dopants including Si and Sn have been incorporated to achieve higher carrier concentrations.² Therefore, most of the fabricated β-

 Ga_2O_3 transistors exhibit n-type characteristics with a negative threshold voltage (V_{th}).^{6,12,16,17} The negative V_{th} of n-type β -Ga₂O₃ transistors allows only depletion mode (D-mode) operation, which limits their implementations in electronic circuits. Enhancement-mode (E-mode) operation is preferred for power transistors, which enables simple circuit designs and fail-safe operation under high voltage conditions.^{18,19}

Various techniques have been suggested to control V_{th}, including forming trench- or Fin-shaped channels,^{20,21} partial Si doping,²² and thickness control of β -Ga₂O₃ channel.²³ In addition, incorporating fluorine close to the channel is an efficient method to modulate the V_{th} of FETs. Fluorine plasma treatment has been previously used to control the V_{th} of AlGaN/GaN high electron mobility transistors (HEMTs) and amorphous InGaZnO (a-IGZO) thin-film transistors.^{24–28} The incorporated fluorine atoms, which have high electronegativity, are negatively charged and increase the potential in the AlGaN or a-IGZO barrier, which results in a positive shift of V_{th}. Yang et al. reported that when the fluorine plasma was exposed, the barrier height of β -Ga₂O₃ Schottky barrier diodes was increased; this was because the Si donors were compensated by fluorine atoms, forming neutral complexes.²⁹ In this work, we demonstrate a facile, efficient, and reproducible method to control the V_{th} of β -Ga₂O₃-based metal insulator field-effect transistors (MISFETs) via remote CF₄ plasma treatment. E-mode operation was achieved under the double gate condition, presenting a potential for β -Ga₂O₃-based smart power integrated circuit (IC) applications.

EXPERIMENTAL DETAILS

Two MISFETs in series were fabricated on a single β -Ga₂O₃ flake. Figures 1(a–d) show optical microscope images that present the fabrication sequence of pristine and fluorinated β -Ga₂O₃ MISFETs on a single flake. β -Ga₂O₃ flakes were obtained from a (-201)

 β -Ga₂O₃ single crystal by a mechanical exfoliation process. The β -Ga₂O₃ single crystal, which is unintentionally n-doped with an effective carrier density (N_d-N_a) of approximately 3x10¹⁷ cm⁻³, was produced by the edge-defined film-fed method (Tamura Corp.). Exfoliated β -Ga₂O₃ flakes were then dry-transferred onto a SiO₂ (300 nm)/p⁺⁺-Si (500 µm) substrate, which was pre-patterned with Ti/Au (20 nm/80 nm) as a bottom-gate electrode (Fig. 1(a)). Source and drain electrodes (Ti/Au 20 nm/80 nm) were defined using an electron-beam (ebeam) lithography and lift-off process (Fig. 1(b)). The channel length and width of β -Ga₂O₃ FETs were 20 µm and 4 µm, respectively. Rapid thermal annealing in an argon atmosphere was performed for 60 sec at 480 °C to form ohmic contact with the exfoliated β-Ga₂O₃ flake. As shown, part of the channel (red box) was opened to the CF₄ plasma treatment by an ebeam lithography after the sample was coated with the electron-beam resist (Fig. 1(c)). The CF_4 plasma was introduced to the surface of the β -Ga₂O₃ flake using a conventional reactive ion etching (RIE) system (RIE 5000, SNTEK). To avoid damage by direct ion bombardment, the sample was placed face-down between the high supports in the RIE chamber, which is similar to the remote plasma configuration. The precursor gas used was CF_4 (50 sccm) at the pressure of 3 mTorr, and the etching power and time were 100 W and 60 sec, respectively. Multilayer h-BN nanosheets were mechanically exfoliated from a bulk powder (Momentive Corp.) and were dry-transferred onto the β -Ga₂O₃ flake. Two h-BN flakes were deposited as a gate dielectric layer. The top gate electrode was defined by depositing Pt/Au (20/80 nm) after e-beam lithography (Fig. 1(d)). A schematic of the fabricated β-Ga₂O₃ MISFETs on a single flake is shown in Fig. 1(e).

The thickness and surface morphology of β -Ga₂O₃ and h-BN were characterized using atomic force microscopy (AFM) (XE100, PSIA). Micro-Raman spectroscopy was conducted with back-scattering geometry using the 532 nm line of a diode-pumped solid-state

laser (Omicron) to analyze the structural properties of the exfoliated β -Ga₂O₃ and h-BN layers. X-ray photoelectron spectroscopy (XPS) (Thermo, K-alpha) using the monochromated Al Ka line as the X-ray source was employed to study changes in the bonding structure of the β -Ga₂O₃ flakes after the CF₄ plasma treatment. The electrical and transport characteristics of the fabricated β -Ga₂O₃ MISFETs were obtained using an Agilent 4155C semiconductor parameter analyzer connected to a probe station.

RESULTS AND DISCUSSION

The morphology and thickness of the β -Ga₂O₃ and h-BN nanosheets in the fabricated FETs were analyzed, as shown in Figs. 2(a–b). The β -Ga₂O₃ and h-BN nanosheets were approximately 250 and 25~28 nm thick, respectively. The thickness of the pristine β -Ga₂O₃ was identical to that of the fluorinated one, as shown in Fig. S1, indicating that there was no significant degradation or etching of β -Ga₂O₃ during the remote CF₄ plasma treatment. The crystal quality of the β -Ga₂O₃ flake and h-BN nanosheets was evaluated using micro-Raman spectroscopy (Fig. 2(c)). Phonon peaks corresponding to the β -Ga₂O₃ flake are observed in the range 60–800 cm⁻¹. The peaks near 200, 347, 416, and 767 cm⁻¹ correspond to the Ag³, Ag⁵, Ag⁶, and Ag¹⁰ vibration modes of β -Ga₂O₃, respectively.^{30,31} The peak at approximately 1350 cm⁻¹ corresponds to the E_{2g} vibration mode of h-BN.³² The Raman spectra also indicate that there was no significant disruption of the sample by remote CF₄ plasma treatment. XPS measurement was performed to investigate the chemical property of the surface of β -Ga₂O₃ flakes after CF₄ plasma treatment. Figure 3(a) shows XPS survey scans of the pristine and CF₄ plasma-treated β -Ga₂O₃, where F1s and F KLL signals appear. A more detailed analysis of the F1s core levels indicates the influence of the CF₄ plasma treatment, where the peak of a

Ga–F bond appears at 684.7 after the CF_4 plasma treatment. This suggests that the remote CF_4 plasma treatment effectively forms a Ga–F bond.^{33,34}

Prior to the deposition of the top-gate electrode, the bottom-gated β-Ga₂O₃ FET was characterized to observe the effects of the CF₄ plasma treatment. The I_{DS}–V_{DS} output and transfer characteristics of a bottom-gated β-Ga₂O₃ MOSFET with a thermally grown SiO₂ dielectric, before and after the CF₄ plasma treatment, are compared in Fig. S2 (a–b). After the CF₄ plasma treatment, the V_{th} shifted positively, indicating the F-induced depletion of the channel. The negatively charged fluorine atoms incorporated into the β-Ga₂O₃ partially deplete carriers in the n-channel. For a more detailed analysis of device performance, two h-BN layers as top-gate dielectrics were deposited on top of each channel, making two topgated MISFETs. Figures 4(a–b) exhibit the I_{DS}–V_{DS} output characteristics of pristine (Fig. 4(a)) and fluorinated (Fig. 4(b)) β-Ga₂O₃-based MISFETs, respectively, both showing good saturation and sharp pinch-off characteristics. The transfer curve for pristine β-Ga₂O₃ topgated MISFET (Fig. 4(c)) shows a V_{th} of -5.1 V with a current on/off ratio ~10⁸ at V_{DS} = +10 V. An estimated field effect carrier mobility (μ_{FE}) and a sub-threshold swing (SS) were about 18.9 cm² V⁻¹ s⁻¹ and 350 mV dec⁻¹, respectively. The μ_{FE} can be obtained from the following equation:

$$\mu_{FE} = \frac{L}{W} \frac{2}{C_g} \left(\frac{\partial \sqrt{I_{DS}}}{\partial V_{TG}} \right)^2$$

, where L and W denote the length and width of the channel, respectively. C_g is the gate dielectric capacitance per unit area, and V_{TG} is the top gate bias. These transfer properties are comparable to previous reports of FETs using unintentionally doped β -Ga₂O₃. For fluorinated β -Ga₂O₃ MISFET, V_{th} of -1.1 V and μ_{FE} of 37.2 cm² V⁻¹ s⁻¹ with a current on/off ratio ~10⁷ were extracted at $V_{DS} = +10$ V, as shown in Fig. 4(c). The SS of fluorinated β -Ga₂O₃ MISFET (~172 mV·dec⁻¹) is lower than that of a pristine β -Ga₂O₃ MISFET, and the gate

leakage currents for both pristine and fluorinated β-Ga₂O₃ MISFETs are almost equivalent, implying nominal plasma-induced damage. The positive shift of V_{th} from -5.1 to -1.1 V is observed in fluorinated β-Ga₂O₃ when compared with pristine β-Ga₂O₃ under the top-gate operation, where V_{th} was extracted from the plot of the square root of drain current versus gate voltage. The F atom adsorbed on the β-Ga₂O₃ has a strong electronegativity (3.98), increasing the depletion region in the β-Ga₂O₃ channel. Figure 4(d) shows the energy band diagram of the interface between β-Ga₂O₃ and h-BN before and after the CF₄ plasma treatment. The fluorine atoms on the surface increased the $V_{th} (= \psi_{bi} - \psi_P)$ by lowering the pinch-off potential ($\psi_P = \frac{qN_D d^2}{2\varepsilon_s}$), where ψ_{bi} , q, N_D, d and ε_s are the built-in potential, electronic charge, carrier concentrations, channel height, and the channel material's permittivity, respectively.³⁵ The edge of the conduction band of fluorinated β-Ga₂O₃ at the interface between β-Ga₂O₃ and h-BN bends upward, and the depletion width extends.

Double gate operation of pristine and fluorinated β -Ga₂O₃ MISFETs was performed, sweeping top-gate bias with varying bottom gate (V_{BG}) bias as shown in Fig. 5. V_{th} of the pristine β -Ga₂O₃ MISFET shifted from -5.1 V to -3.1 V as the V_{BG} varied from 0 to -9 V. Meanwhile, V_{th} of the fluorinated β -Ga₂O₃ MISFET gradually shifted from -1.1 V to +2.2 V, demonstrating an E-mode operation. As shown in Fig. 5(c), the incorporation of F into the top surface facilitated the positive V_{th} under the double gate operation. The formation of an Emode MISFET and a D-mode MISFET in the single β -Ga₂O₃ flake via partial the CF₄ plasma treatment can be utilized to fabricate various circuit designs. Our approach allows the fabrication of E-mode β -Ga₂O₃ FETs as well as the monolithic integration of E/D-mode FETs, both of which are expected to give valuable circuit applications, such as logic inverters.³⁶ These results suggest that the CF₄ plasma treatment, which is controllable and compatible with the CMOS process, provides a simple approach to achieve V_{th} control of β -Ga₂O₃ FETs, proposing β -Ga₂O₃-based logic devices for future miniaturized smart power and harsh environment electronics.

CONCLUSION

The V_{th} of β -Ga₂O₃ FETs was controlled from D-mode to E-mode through the remote CF₄ plasma treatment, demonstrating a β -Ga₂O₃-based E/D-mode FETs in a single β -Ga₂O₃ flake. The V_{th} was positively shifted by +4 V compared with a pristine β -Ga₂O₃ FET owing to the incorporated fluorine atoms with high electronegativity. A Ga–F bond was formed on β -Ga₂O₃ using the remote CF₄ plasma treatment. The fluorinated β -Ga₂O₃ MISFET displayed excellent transistor characteristics with I_{DS} on/off ratio of ~10⁷, μ_{FE} of 37.2 cm²·V⁻¹·s⁻¹ and a subthreshold swing of 175 mV·dec⁻¹. The E-mode operation of the double-gate fluorinated β -Ga₂O₃ grants a facile way to achieve the V_{th} modulation of β -Ga₂O₃ FETs and the realization of β -Ga₂O₃-based smart power electronics.

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Supporting information

Height profile of pristine and fluorinated β -Ga₂O₃ flakes, output characteristics and transfer curves of bottom gated β -Ga₂O₃ MOSFETs before and after the CF₄ plasma treatment (PDF)

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Figure 1 Optical microscope images of each fabrication step of a series of pristine and fluorinated β -Ga₂O₃ MISFETs; (a) β -Ga₂O₃ flake was transferred onto the SiO₂/p⁺⁺–Si substrate pre-patterned with Ti/Au back-gate electrode (b) Source and drain electrodes were defined on a single β -Ga₂O₃ flake. (c) After the sample was coated with ER, part of the β -Ga₂O₃ flake was opened for remote CF₄ plasma treatment. (d) Two h-BN nanosheets were deposited on each channel and Pt/Au gate electrodes were defined on each channel. The scale bars are 10 µm. (e) Schematic of the series of pristine and fluorinated β -Ga₂O₃ MISFETs with the front (Pt/Au) and back (Ti/Au) gate electrodes.



Figure 2 (a) AFM image of the fabricated series of pristine and fluorinated β -Ga₂O₃ MISFETs. The scale bar is 5 µm. (b) Height profile of the β -Ga₂O₃ and multilayer h-BN in both pristine and fluorinated regions. (c) Raman spectra before and after the dry transfer.



Figure 3 (a) XPS survey scans from the pristine and fluorinated β -Ga₂O₃ surfaces. (b) XPS spectrum of F1s for pristine and fluorinated β -Ga₂O₃



Figure 4 (a–b) I_{DS} – V_{DS} output characteristics of pristine and fluorinated β -Ga₂O₃ MISFETs. (c) Transfer curves of pristine and fluorinated β -Ga₂O₃ MISFETs. (d) Energy-band diagram of a h-BN/ β -Ga₂O₃ flake before and after CF₄ plasma treatment .



Figure 5 Transfer curves of the double-gated (a) pristine and (b) fluorinated β -Ga₂O₃ MISFETs with varying the back gate (V_{BG}) and the top gate (V_{TG}) at V_{DS}=+10 V (c) the energy band diagram of the fluorinated β -Ga₂O₃ channel under V_{BG}<0 V (note that V_{TG} is not biased).

