A Diamond:H/WO3 Metal–Oxide–Semiconductor Field-Effect Transistor

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

| Citation          | Yin, Zongyou et al. "A Diamond:H/WO3 Metal–Oxide–Semiconductor Field-Effect Transistor." IEEE Electron Device Letters 39, 4 (February 2018): 540 - 543 © 2018 IEEE |
|-------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| As Published      | http://dx.doi.org/10.1109/led.2018.2808463                                                                                                                                                        |
| Publisher         | Institute of Electrical and Electronics Engineers (IEEE)                                                                                                                                           |
| Version           | Author’s final manuscript                                                                                                                                                                         |
| Citable link      | https://hdl.handle.net/1721.1/126179                                                                                                                                                             |
| Terms of Use      | Creative Commons Attribution-Noncommercial-Share Alike                                                                                                                                             |
| Detailed Terms    | http://creativecommons.org/licenses/by-nc-sa/4.0/                                                                                                                                                 |
A Diamond:H/WO₃ Metal-Oxide-Semiconductor Field-Effect Transistor

Zongyou Yin*, Moshe Tordjman*, Alon Vardi, Rafi Kalish, and Jesús A. del Alamo, Fellow, IEEE

Abstract—A p-type Diamond:H/WO₃ MOSFET based on surface transfer doping is demonstrated. Using a low-temperature ALD-grown HfO₂ as gate insulator, the Diamond:H/WO₃ MOSFETs show excellent output characteristics, gate-controllable 2-D hole gas and low gate leakage current. Long-channel FETs exhibit improved subthreshold behavior but reduced transconductance with respect to short-channel devices. An observed WO₃-thickness dependent threshold voltage is consistent with enhanced surface transfer doping as the WO₃ layer is thinned down. Low-temperature measurements suggest a significantly lower mobility than expected in this material system. This illustrates the challenge of maintaining high TMO quality during device fabrication.

Index Terms—Diamond:H, gate length, surface transfer doping, temperature, WO₃ thickness.

I. INTRODUCTION

Diamond is an ultra-stable material with a wide band gap of 5.47 eV. Recently developed surface transfer doping (STD) has opened a new avenue to exploit the excellent electrical and thermal properties of diamond [1]. The negative electron affinity that results after diamond surface hydrogenation (Diamond:H or, simply, D:H) enables the transfer of electrons from Diamond:H to high work-function acceptors located at its surface. This results in the formation of a two-dimensional hole gas (2DHG) at the Diamond:H surface.

Up to this date, water [2], fullerenes (C₆₀) [3], fluorinated Fullerenes (C₆₀F₅₉, x ≈ 18, 36, 48) [4], zinc-tetrphenylporphyrin (ZnTPP) coupled C₆₀F₅₃ [5], Tetrafluoro-tetracyanoquinodimethane (F₄TCNQ) [6], and more recently transition-metal oxides (TMOs) [7]–[10], have been investigated as surface acceptors for D:H. Among these, TMOs such as MoO₃, WO₃, ReO₃ and V₂O₅ stand out with their unique properties of wide-band gap and high electron affinity. As a typical TMO, MoO₃ was first used as acceptor on Diamond:H and metal-oxide-semiconductor field-effect transistors (MOSFETs) have been demonstrated [11]. Separately, MoO₃ has also been used as a gate dielectric for Diamond:H MOSFETs [12]. D:H/V₂O₅ MISFETs have also been reported [13].

Most recently, D:H/WO₃ has been found to have enhanced charge-transfer robustness and efficiency [14], as compared to the D:H/MoO₃ and D:H/V₂O₃ systems. A Hall-effect study of thermally-evaporated WO₃ on D:H measured a record areal hole carrier concentration of $4.8 \times 10^{14}$ cm⁻² at a temperature up to 150°C [14]. The hole mobility reached over 100 cm²/Vs for temperatures up to 300°C. In an effort to take advantage of the outstanding charge-transfer properties of this system, in this work we demonstrate the first implementation of a MOSFET in the D:H/WO₃ system. Moreover, we investigate the impact of WO₃ thickness, gate length and low temperature operation in the device characteristics.

II. DEVICE FABRICATION

Figure 1 shows a schematic cross section of the starting heterostructure and the fabricated MOSFET. Three 3×3×0.5 mm² type IIa (001)-oriented single-crystal diamond substrates supplied from Element6, with nitrogen concentration < 1 ppm were used. Surface hydrogenation was performed by exposure to pure hydrogen plasma in a CVD reactor at 600°C for 40 minutes. Subsequently, the samples were heated at 350°C to desorb H₂O molecules and contaminants from the diamond surface in vacuum [11]. This was immediately followed by low-rate (0.1 Å/min) thermal evaporation of different thicknesses (2.4, 3.4 and 4.8 nm) of WO₃ in each sample A surface roughness of Ra ~ 0.6 nm over an area of 1 μm×1 μm was measured by AFM, and a WO₃ thickness uniformity of 10% was evaluated by ellipsometry. The stoichiometry and thickness of WO₃ was characterized by X-ray photoelectron spectroscopy and ellipsometry and results similar to those reported in Ref. 14 were obtained.

The process continues with electron-beam evaporation of Ti/Au (20/200 nm), as source and drain electrodes, through a shadow mask. Following this, 20 nm of HfO₂ as gate dielectric layer was grown by atomic layer deposition (ALD) at 150°C. The use of a gate oxide was deemed essential to obtain a working FET since WO₃ is expected to become highly conductive after the surface transfer process [14]. After that, flowable oxide (FOX) was spin coated on the sample surface and exposed by electron-beam lithography (EBL). This forms a hard mask that is used to define the active channel. Reactive-ion etching based on a BCl₃/Cl₂/Ar chemistry was performed to etch the exposed HfO₂ and WO₃ and to desorb the Hydrogen from the diamond surface. FOX was then striped with a buffered oxide etchant. Subsequently, a standard photolithographic liftoff step was used to create a Ti/Au (10/100 nm) gate electrode at the center of the channel of the FETs. Devices with gate lengths (Lₘ) ranging from 0.7 to 5 μm and a constant gate width (Wₘ) of 20 μm were fabricated. The source-drain distance gradually increased from 29 μm to 58 μm.
as the gate length changed from 0.7 µm to 5 µm.

In this first demonstration, no effort was given to bringing the source and drain ohmic contacts directly onto the D:H surface. Rather, the goal of this work was to demonstrate the viability of the D:H/WO as a MOSFET system.

### III. RESULTS

Fig. 2 shows electrical characteristics of typical MOSFETs with \( L_g = 4 \) µm and different WO₃ thickness. All devices show well saturated drain current behavior with sharp pinchoff and low output conductance (Figs. 2a and 2b). The 2.4 nm WO₃ MOSFETs show greater drain current, \( I_d \), and transconductance, \( g_m \) (Fig. 2b), and a more positive threshold voltage, \( V_t \). These results are consistent with recent Hall effect observations of decreased surface transfer efficiency and a reduced sheet hole concentration (from \( 2.5 \times 10^{14} \) cm² to \( 1.3 \times 10^{14} \) cm²) of D:H with increasing WO₃ thicknesses (from 1.2 nm to 4.8 nm) [14].

The thinner WO₃ devices also show greater gate leakage current, \( I_g \), (Fig. 2b). This also results in worse drain current saturation (Figs. 2a and 2b). A more effective electron transfer into the 2.4 nm thick WO₃ layer is a plausible explanation for the larger gate current.

![Fig. 2. Output (a) and transfer (b) characteristics for \( L_g = 4 \) µm Diamond:H/WO₃ FETs with WO₃ thickness ranging from 2.4 nm to 4.8 nm.](image)

Device operation at 77 K was further studied by carrying out capacitance-voltage (\( C_{g-V_{GS}} \)) and I-V transfer (\( I_g-V_{GS} \)) characteristics in a device with 4.8 nm of WO₃ and \( L_g = 5 \) µm. The C-V characteristics were measured at 1 MHz with \( V_{DS} = 0 \) V. \( I_g-V_{GS} \) measurements were performed at \( V_{DS} = -2 \) V. A typical \( C_{g-V_{GS}} \) result is shown in Fig. 5. From these data, we extract the gate voltage dependence of the sheet hole concentration (\( \mu_p \)) and hole mobility (\( \mu_h \)) [16],[17]. For this, we used a dielectric constant of 13 for HfO₂ (in consideration of the low ALD temperature of 150°C [18]) and 5 for WO₃. Also, in order to correct for parasitic resistance, the source/drain access resistance at 77 K, was estimated as \( R_{sd.77K} \approx 908 \) k\( \Omega \)-\( \mu \)m from its RT value by using \( R_{sd.RT} = R_{sd.77K} \times [1+\alpha(T_{RT}-T_{77K})] \), where \( \alpha \) is the temperature coefficient of the resistance. A value of \( \alpha = 0.004 \) was estimated from the slope (resistance of \( R_{RT} \) and \( R_{77K} \) of the \( I_g-V_{DS} \) curve under \( V_{DS} = 0.1 \) V and \( V_{GS} = 0 \) at RT for \( R_{RT} \) and 77K for \( R_{77K} \), using an identical equation: \( R_{RT} = R_{77K} \times [1+\alpha(T_{RT}-T_{77K})] \). The inset of Fig. 5 graphs the sheet mobility (\( \mu_s \)) vs. sheet hole concentration (\( \mu_p \)). Over most of its range, the mobility increases with hole concentration.

We have studied the impact of gate length, \( L_g \), on the electrical characteristics of 4.8 nm-thick WO₃ devices. This is graphed in Fig. 3. Fig. 3a shows that the subthreshold behavior rapidly improves as \( L_g \) increases. This probably stems from a combination of short-channel effects and reduced \( I_g \). In addition, we observe that the peak transconductance, \( g_{m_{\max}} \) for short \( L_g \) (≤1 µm) devices is about 3X that of long \( L_g \) (≥2 µm) devices (Fig. 3b). The threshold voltage, \( V_t \), shifts positively as gate length shortens. This could be explained by severe short-channel effects that arise from the use of a relatively thick gate dielectric coupled with the absence of body doping [15].

In addition, we extracted the ON resistance of 4.8 nm-thick WO₃ transistors with different \( L_g \) at \( V_{GS} = 1 \) V and \( V_{DS} = 0.1 \) V (Fig. 3c). From extrapolation of these data to \( L_g = 0 \), we estimated a total source/drain access resistance of ~ 1700 k\( \Omega \)-\( \mu \)m.

We have also studied the effect of temperature on the electrical characteristics of a \( L_g = 5 \) µm, WO₃=4.8 nm FET at 77 K. The results are presented in Fig. 4. At 77 K, we observe a large increase in \( I_g \) and \( g_m \) with \( g_{m_{\max}} \) scaling up by 3.5 times. We also see that \( I_g \) was reduced by about two orders of magnitude (Fig. 4b). This results in significantly improved subthreshold behavior with the minimum subthreshold swing (\( S_{\min} \)) scaling down from ~ 1225 mV/dec to ~ 190 mV/dec and the ON-OFF ratio improving from ~ 10⁸ to ~ 10⁶, as the temperature is reduced from RT to 77K.

![Fig. 4. Output (a) and transfer (b) characteristics for \( L_g = 5 \) µm, WO₃=4.8 nm Diamond:H/WO₃ FETs measured at 77 K and RT.](image)

The inset of Fig. 5 graphs the sheet mobility (\( \mu_s \)) vs. sheet hole concentration (\( \mu_p \)). Over most of its range, the mobility increases with hole concentration.
lower than results obtained from Hall measurements at room temperature of similar unprocessed samples [14]. This is also consistent with Coulomb scattering that could be due to gap states introduced as a result of $WO_3$s reduction during the device fabrication process [19]. The reduction in resistance that is observed as the temperature drops could be due to a insulator-to-metal transport transition recently reported by Mattoni et al. in $WO_3$s [20]. This would also result in a reduced work function and degraded surface transfer doping efficiency at room temperature [19].

Our results reveal the potential of the D:H/$WO_3$ system for future transistor applications but also illustrate the challenge of maintaining high TMO quality during device fabrication, an issue already noted in [11]. To exploit the advantageous properties of the D:H/TMO system, transistor fabrication processes will need to be developed that maintain the integrity of the TMO layer.

IV. CONCLUSIONS

We demonstrate for the first time p-type Diamond:H/$WO_3$ FETs. Long-channel devices display well behaved transistor characteristics with $10^7$ ON-OFF ratio at room temperature. An anomalous threshold voltage dependence on $WO_3$ thickness is observed which is consistent with enhanced surface transfer doping as the $WO_3$ layer is thinned down. Low-temperature mobility measurements suggest strong Coulomb scattering perhaps due to $WO_3$ degradation during the fabrication process.

ACKNOWLEDGMENT

Device fabrication was carried out at the Microsystems Technology Laboratories and the Electron Beam Lithography Facility at MIT.

REFERENCES

[1] O. A. Williams and R. B. Jackman, “Surface conductivity on hydrogen terminated diamond,” *Semicond. Sci. Technol.*, vol. 18, no. 3, pp. S34–S40, 2003. DOI: stacks.iop.org/SST/18/S34.

[2] F. Maier, M. Riedel, B. Mantel, J. Ristein, and L. Ley, “Origin of surface conductivity in diamond,” *Phys. Rev. Lett.*, vol. 85, no. 16, pp. 3472–3475, 2000. DOI: https://doi.org/10.1103/PhysRevLett.85.3472.

[3] P. Strobel, J. Ristein, L. Ley, K. Seppelt, I. V. Goldt, and O. Böttalina, “Surface conductivity induced by fullerences on diamond: Passivation and thermal stability,” *Diam. Relat. Mater.*, vol. 15, no. 4–8, pp. 720–724, 2006. DOI: https://doi.org/10.1016/j.diamond.2005.10.034.

[4] M. T. Edmonds, M. Wanke, A. Tadich, H. M. Vulling, K. J. Rietwyk, P. L. Sharp, C. B. Stark, Y. Smets, A. Schenk, Q. H. Wu, L. Ley, and C. I. Pakes, “Surface transfer doping of hydrogen-terminated diamond by C 60F 48: Energy level scheme and doping efficiency,” *J. Chem. Phys.*, vol. 136, no. 12, 2012. DOI: https://doi.org/10.1063/1.3695643.

[5] D. P. Langley, Y. Smets, C. B. Stark, M. T. Edmonds, A. Tadich, K. J. Rietwyk, A. Schenk, M. Wanke, Q. H. Wu, P. J. Barnard, L. Ley, and C. I. Pakes, “Surface transfer doping of diamond with a molecular heterojunction,” *Appl. Phys. Lett.*, vol. 100, no. 3, pp. 032103, 2012. DOI: https://doi.org/10.1063/1.3676445.

[6] D. Qi, W. Chen, X. Gao, L. Wang, S. Chen, P. L. Kian, and A. T. S. Wee, “Surface transfer doping of diamond (100) by tetrafluoro-tetracyanoquinodimethane,” *J. Am. Chem. Soc.*, vol. 129, no. 26, pp. 8084–8085, 2007. DOI: 10.1021/ja072133r.

[7] S. A. O. Russell, L. Cao, D. Qi, A. Tallaire, K. G. Crawford, A. T. S. Wee, and D. A. J. Moran, “Surface transfer doping of diamond by MoO3: A combined spectroscopic and Hall measurement study,” *Appl. Phys. Lett.*, vol. 103, no. 20, pp. 202112, 2013. DOI: https://doi.org/10.1063/1.4832455.

[8] M. Tordjman, C. Saguy, A. Bolker, and R. Kalish, “Superior Surface Transfer Doping of Diamond with MoO3,” *Adv. Mater. Interfaces*, vol. 1, no. 3, pp. 1–6, 2014. DOI: 10.1002/admi.201300155.

[9] K. G. Crawford, L. Cao, D. Qi, A. Tallaire, E. Limiti, C. Verona, A. T. S. Wee, and D. A. J. Moran, “Enhanced surface transfer doping of diamond by V2O5 with improved thermal stability,” *Appl. Phys. Lett.*, vol. 108, no. 4, pp. 042103, 2016. DOI: https://doi.org/10.1063/1.4940749.

[10] C. Verona, W. Ciccognani, S. Colangeli, E. Limiti, M. Marinelli, and G. Verona-Rinati, “Comparative investigation of surface transfer doping of hydrogen terminated diamond by high electron affinity insulators,” *J. Appl. Phys.*, vol. 120, no. 2, pp. 025104, 2016. DOI: https://doi.org/10.1063/1.4955469.

[11] A. Vardi, M. Tordjman, J. A. Alamo, and R. Kalish, “A Diamond : H/MoO3 MOSFET,” *IEEE Electron Device Lett.*, vol. 35, no. 12, pp. 1320–1322, 2014. DOI: 10.1109/LED.2014.2364832.

[12] Z. Ren, J. Zhang, J. Zhang, C. Zhang, S. Xu, Y. Li, and Y. Hao, “Diamond Field Effect Transisotors With MoO3 Gate Dielectric,” *IEEE Electron Device Lett.*, vol. 38, no. 6, pp. 786–789, 2017. DOI: 10.1109/LED.2017.2695495.

[13] C. Verona, W. Ciccognani, S. Colangeli, E. Limiti, M. Marinelli, G. Verona-Rinati, D. Cannatà, M. Benetti, and F. P. Pietrantonio, “V2O3 MISFETs on H-Terminated Diamond,” *IEEE Electron Device Lett.*, vol. 36, no. 12, pp. 4647–4653, 2016. DOI: 10.1109/LED.2016.2617362.

[14] M. Tordjman, K. Weinfeld, and R. Kalish, “Boosting Surface Charge-Transfer Doping Efficiency and Robustness of Diamond with WO 3 and ReO3,” *Appl. Phys. Lett.*, 111, pp. 111601, 2017. DOI: 10.1063/1.4986339.

[15] J. A. del Alamo, Integrated Microelectronic Devices: Physics and Modeling, 1st Edition, Pearson Publication., Sec 10.2, 2017.

[16] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, “Single-layer MoS2 transistors,” *Nat. Nanotechnol.*, vol. 6, no. 3, pp. 147–150, 2011. DOI: 10.1038/nnano.2010.279.
[17] S. Balendhran, J. Deng, J. Z. Ou, S. Walia, J. Scott, J. Tang, K. L. Wang, M. R. Field, S. Russo, S. Zhuiykov, M. S. Strano, N. Medhekar, S. Sriram, and M. Bhaskaran, “Enhanced Charge Carrier Mobility in Two-Dimensional High Dielectric Molybdenum Oxide,” Adv. Mater., vol. 25, pp. 109–114, 2013. DOI: 10.1002/adma.201203346.

[18] H. Jung, H. Jeon, K. Kim, I. Yu, Y. Lee, J. Lee, J. Chung, D. Cho, N. Lee, J. Park, J. Choi, S. Han, and C. Seong, “The Impact of Carbon Concentration on the Crystalline Phase and Dielectric Constant of Atomic Layer Deposited HfO$_2$ Films on Ge Substrate,” ECS J. Solid State Sci. Technol., vol. 1, no. 2, pp. 33–37, 2012. DOI: 10.1149/2.020202jss.

[19] M. Greiner, L. Chai, M. Helander, W. Tang, and Z. Lu, “Transition Metal Oxide Work Functions: The Influence of Cation Oxidation State and Oxygen Vacancies,” Adv. Funct. Mater., vol. 22, pp. 4557-4568, 2012. DOI: 10.1002/adfm.201200615.

[20] G. Mattoni, A. Filippetti, N. Manca, P. Zubko, and A. D. Caviglia, “Charge doping and large lattice expansion in oxygen-deficient heteroepitaxial WO$_3$,” arXiv:1711.05106v1, 2017.