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# Low-voltage pentacene organic field-effect transistors with high-κ $HfO_2$ gate dielectrics and high stability under bias stress

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Low-voltage pentacene organic field-effect transistors are demonstrated (operating voltage of −3 V) with high-κ hafnium dioxide gate dielectrics grown by atomic layer deposition at 200 °C. A high hole mobility of 0.39 $cm^2/V\,s$ with low threshold voltage (<−0.5 V) and low subthreshold slope of 120 mV/dec is achieved with a $HfO_2$ dielectric layer modified with a phosphonic acid based treatment. A high value of 94.8 nF/V s is obtained for the product of mobility and capacitance density. The devices show excellent bias stress stability with or without the phosphonic acid at the $HfO_2$ gate dielectric surface. © *2009 American Institute of Physics*. [doi:10.1063/1.3269577]

Organic field-effect transistors (OFETs) have recently gained attention as building blocks for electronic applications that can greatly benefit from low-cost, large-area fabrication, and flexible form factors, such as radio-frequency identification tag,[1] drivers for electronic paper,[2] and driving circuits for flat panel displays.[3] To realize practical applications with organic-based transistors and circuits, development of suitable gate dielectric materials with high capacitance density in addition to high-mobility organic semiconductors are important. High-κ gate dielectric materials are preferable since they are promising for replacing $SiO_2$ (where continued thickness scaling makes it difficult to control the leakage current). $HfO_2$-based gate dielectrics with a dielectric constant ranging from 15 to 29 play a leading role in the development of high resolution process technology for the fabrication of metal-oxide silicon field-effect transistors (MOSFETs). Techniques for the formation of $HfO_2$ include sol-gel processing,[4] anodic oxidization,[5] chemical vapor deposition (CVD) (Ref. 6), and physical vapor deposition (PVD). Those processing routes often require high temperature for complete chemical conversion of precursors into oxides (e.g., sol-gel), and high chamber vacuum (e.g., CVD and PVD), or yield undesirable film quality (e.g., anodization). On the other hand, atomic layer deposition (ALD) technique allows for the deposition of highly conformal, defect-free dielectric layers at relatively low temperature and low cost.[7,8] Even though the formation of $HfO_2$ by ALD has been reported with different precursors,[9–11] the application in organic-based transistors has not yet been demonstrated. Pentacene OFETs with very low operating voltage of −1.5 V have already been demonstrated with $HfO_2$ gate dielectrics fabricated by sol-gel processing,[12] however, the high processing temperatures (600 °C) that is required is not compatible with the organic flexible substrates commonly used in printed electronics.

Here, we report on the low-voltage pentacene OFETs using $HfO_2$ as a gate insulator formed by ALD at a deposition temperature of 200 °C which is compatible with organic flexible substrates such as polyethersulfone. A high capacitance density of 245 (±1) $nF/cm^2$ was achieved with a film thickness of 50 nm and a high dielectric constant of 14.9. The dielectric surface of $HfO_2$ was modified with phosphonic acid to passivate the polar surface groups and improve the pentacene film morphology for charge transport. The OFET devices could be operated at a low voltage of 3 V with a high mobility of 0.39 $cm^2/V\,s$, a low threshold voltage <−0.5 V, and a low subthreshold slope of ~120 mV/dec. The product of mobility and capacitance density ($\mu C_{OX}$) (94.8 nF/V s), a parameter defining the channel current, is higher than that of pentacene OFETs with sol-gel $HfO_2$ gate dielectric (88.5 nF/V s).[12] In addition to high electrical performance, the pentacene OFETs were also very stable under dc bias stress for 2 h.

OFETs were built on heavily n-doped silicon substrates ($n^+$-Si, $5\times10^{-3}$ Ω cm) with a top-contact bottom-gate device geometry. The wafers were processed with a buffered oxide etchant (1:6 diluted HF in $H_2O$) to remove the native oxide. The $n^+$-Si substrates act as a common gate electrode with the backside metallized with Ti/Au (10 nm/100 nm) to enhance good electrical contact. $HfO_2$ dielectric films were grown by ALD using a Savannah100 ALD system (Cambridge Nanotech Inc.). It has been employed to deposit high quality $Al_2O_3$ gate dielectrics for OFETs as reported in our previous studies.[13] Before loading for deposition, the substrates underwent $O_2$ plasma treatment in a plasma asher for several minutes to remove organic residues and other contaminants from surfaces, as well as to increase the concentration of surface hydroxyl groups. $HfO_2$ films were deposited at 200 °C by alternating exposures of the substrates to tetrakis(dimethylamido)hafnium(IV) and $H_2O$ vapor. With 500 cycles, the thickness of the $HfO_2$ films was around 50 nm, measured by a Woollam V.A.S.E ellisometer.

The dielectric properties of the 50 nm thick $HfO_2$ were characterized using parallel plate capacitors of various plate areas ranging from $3.1\times10^{-3}$ $cm^2$ to $2.4\times10^{-1}$ $cm^2$. The capacitors were fabricated with gold (80 nm) patterned through a shadow mask on top of the $HfO_2$ film. The leakage current density of the $HfO_2$ film was below $10^{-8}$ $A/cm^2$ under an applied field of 2 MV/cm, as shown in Fig. 1. The dielectric constant (κ) at 1 kHz was extracted from the linear dependence of capacitance as a function of device area $C_{OX}=\frac{\varepsilon_o\kappa}{t}$ (where $\varepsilon_o$ is the permittivity in vacuum, $t$ is the thickness, and κ is the dielectric constant) and yielded a

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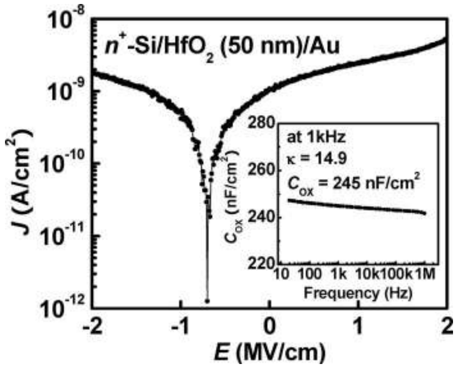


FIG. 1. Leakage current density vs electrical field and capacitance density vs frequency (inset) for $HfO_2$ with a thickness of 50 nm grown by ALD.

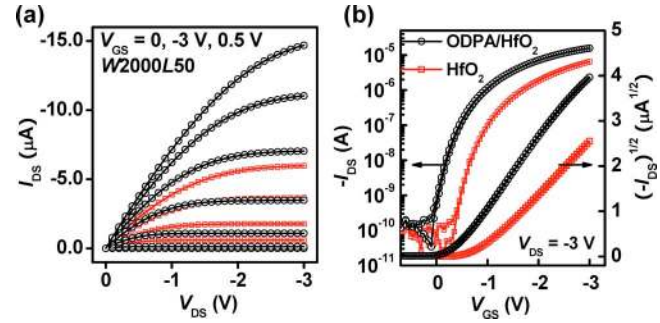


FIG. 2. (Color online) Comparison of output (a) and transfer electrical characteristics (b) of pentacene OFETs with ODPA-treatment $HfO_2$ and untreated $HfO_2$.

value of 14.9. The capacitance density ($C_{OX}$) of 245 $nF/cm^2$ was achieved at a frequency of 1 kHz and was nearly constant up to 1 MHz, as shown in the inset of Fig. 1.

To better control the interfacial properties at the $HfO_2$ and the organic semiconductor and minimize the effect of dielectric polar functional groups and other surface charges on the conducting channel, the $HfO_2$ surface was modified with octadecylphosphonic acid (99.9%, PCI synthesis) (ODPA). To form uniform ODPA surface modification of $HfO_2$, the substrate was first treated with plasma $O_2$ for 3 min, and then immersed in 0.5 mM ODPA in Tetrahydrofuran (THF)/ethanol (1:1 in volume) in a $N_2$-filled glovebox for 16 h. After rinsing with ethanol the samples were dried with $N_2$ with a blower and annealed on a hot plate at 120 °C for 10 min in $N_2$ to enhance the interchain packing of the ODPA on the surface. The substrates were then sonicated for 5 min in THF/ethanol (1:1) to remove the extra physically adsorbed multilayers. The static aqueous contact angle measurement showed that after the treatment, the previously hydrophilic surfaces became hydrophobic with a water contact angle of 95°. Reference samples with untreated $HfO_2$ were also prepared. These substrates were briefly annealed on the hotplate at 150 °C in the $N_2$-filled glovebox to remove adsorbed water molecules. In subsequent experiments, samples with untreated $HfO_2$ and ODPA treated $HfO_2$ underwent the same processing steps and testing procedures.

Sublimed grade pentacene (Sigma-Aldrich), was purified using gradient zone sublimation prior to deposition as a *p*-type active layer. The pentacene film (50 nm) was deposited using a Kurt Lesker Spectros thermal evaporator at a rate of 0.3 Å/s. The top-contact source/drain electrodes with Au (80 nm), patterned with a shadow mask, were deposited at 1 Å/s from the same system without breaking the vacuum. The substrates were held unheated during all the deposition processes with a chamber pressure below $5 \times 10^{-8}$ Torr. The electrical measurements were performed in a $N_2$-filled glovebox ($O_2$, $H_2O < 0.1$ ppm) in the dark using an Agilent E5272A source/monitor unit.

Representative output and hysteretic transfer electrical characteristics of pentacene OFETs with ODPA treated $HfO_2$ and untreated $HfO_2$ are compared in Fig. 2 with the same device geometry (channel length $L = 50$ $\mu$m, channel width $W = 2000$ $\mu$m). The output curves show excellent linearity in the region with low $V_{DS}$, demonstrating good contact between Au and pentacene with low contact resistance, as discussed in previous work.[14] No threshold voltage shift or hysteresis was observed in either type of transistors, demonstrating good electrical stability with $HfO_2$ as gate dielectrics for hole transport. With this excellent operational stability, the electrical parameters of the devices can be justifiably extracted from either the forward bias or the reverse bias. Field-effect mobility values $\mu$ and threshold voltages $V_T$ were calculated in the saturation regime defined by standard MOSFET models by fitting the $\sqrt{|I_{DS}|}$ versus $V_{GS}$ data to a square law model.[15] Also extracted from the transfer characteristics were subthreshold slope ($S$) and on/off current ratio ($I_{on/off}$) values. For each type of transistors, four devices with identical geometry were measured to obtain a mean value and standard deviation (s.d.). The extracted electrical parameters ($\mu$, $V_T$, $S$, and $I_{on/off}$) (calculated from forward bias scans) are summarized and compared in Table I.

Both type of transistors show excellent electrical performance when operated at a low voltage of −3 V. With an ODPA layer on top of $HfO_2$, the capacitance density was slightly reduced from 245 (±1) to 244 (±2) $nF/cm^2$ (at 1 kHz). With the high capacitance density of the gate dielectric, both type of transistors show similar subthreshold slopes of 120 (±10) and 120 (±7) mV/dec, respectively. However, the electrical performance of the pentacene OFETs with ODPA treated $HfO_2$ show significant improvement over those with bare $HfO_2$ as demonstrated in Fig. 2 and Table I. With ODPA at the interface between $HfO_2$ and pentacene, the average mobility was improved from 0.23 to 0.39 $cm^2/V$ s, the average threshold voltage was dropped by more than 50% (from −0.87 to 0.39 V), and accordingly the on/off current ratio was doubled. The results are consistent with the report by Acton *et al.*[12] where sol-gel $HfO_2$ was used for low-voltage pentacene OFETs. The ODPA modification on top of the high-$\kappa$ $HfO_2$ not only provide a good barrier layer from the polar groups on high-$\kappa$ surface, but

TABLE I. Summary of the electrical parameters for pentacene transistors with $L = 50$ $\mu$m and $W = 2000$ $\mu$m. Each data point represents the mean value and the error bars represent the standard deviation (s.d.) calculated from three identical devices for $\mu$, field-effect mobility; $V_T$, threshold voltage; $S$, subthreshold slope; $I_{on/off}$, on/off current ratio. The capacitance density $C_{OX}$ is derived from the slope of capacitance versus area curve with six ($HfO_2$) and seven (ODPA/$HfO_2$) capacitors with varying area.

| | $C_{OX}$ ($nF/cm^2$) | μ ($cm^2/V$ s) | $V_T$ (V) | $S$ (mV/decade) | $I_{on/off}$ ($\times 10^6$) |
|---|---|---|---|---|---|
| $HfO_2$ | $245 \pm 1$ | $0.23 \pm 0.01$ | $-0.87 \pm 0.22$ | $120 \pm 10$ | 0.6 |
| ODPA/$HfO_2$ | $243 \pm 1$ | $0.39 \pm 0.01$ | $-0.39 \pm 0.12$ | $120 \pm 7$ | 1.5 |

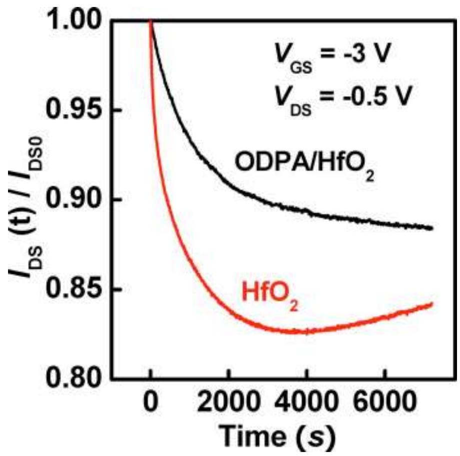


FIG. 3. (Color online) Time-dependent current decay under dc stress for 2 h with applied biases $V_{GS}=-3$ V and $V_{DS}=-0.5$ V.

also improve pentacene morphology for better charge transport.

The bias stress stability of the pentacene transistors was also tested as seen in Fig. 3. The time-dependent decay of channel current $I_D$ was measured under a dc bias stress in the linear operating regime with ($V_{GS}=-3$ V and $V_{DS}=-0.5$ V) for two hours. The pentacene transistors showed excellent operational stability with extremely low $I_{DS}$ decay of ~10% with ODPA and ~15% without ODPA after two hours respectively.

In summary, we fabricated high-performance *p*-channel pentacene-based OFETs operated at a low voltage of 3 V with high-$\kappa$ $HfO_2$ grown by ALD as a gate insulator at a temperature of 200 °C. The total capacitance density of 50 nm thick $HfO_2$ was 245 nF/cm$^2$ at a frequency of 1 kHz. With surface modification of the $HfO_2$ dielectric surface by ODPA, the pentacene OFETs showed good hole mobility of ~0.39 cm$^2$/V s, low threshold voltage ($V_T<-0.5$ V), very low subthreshold slopes ($S\sim 120$ mV/decade). The devices show excellent bias stress stability with or without ODPA at the $HfO_2$ gate dielectric surface.

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[1]V. Subramanian, J. M. J. Frechet, P. C. Chang, D. C. Huang, J. B. Lee, S. E. Molesa, A. R. Murphy, D. R. Redinger, and S. K. Volkman, Proc. IEEE **93**, 1330 (2005).
[2]G. H. Gelinck, H. E. A. Huitema, E. van Veenendaal, E. Cantatore, L. Schrijnemakers, J. B. P. H. van der Putten, T. C. T. Geuns, M. Beenhakkers, J. B. Giesbers, B.-H. Huisman, E. J. Meijer, E. M. Benito, F. J. Touwslager, A. W. Marsman, B. J. E. van Rens, and D. M. de Leeuw, Nature Mater. **3**, 106 (2004).
[3]L. Zhou, A. Wanga, S.-C. Wu, J. Sun, S. Park, and T. N. Jackson, Appl. Phys. Lett. **88**, 083502/1 (2006).
[4]Y. Aoki, T. Kunitake, and A. Nakao, Chem. Mater. **17**, 450 (2005).
[5]J. Tardy, M. Erouel, A. L. Deman, A. Gagnaire, V. Teodorescu, M. G. Blanchin, B. Canut, A. Barau, and M. Zaharescu, Microelectron. Reliab. **47**, 372 (2007).
[6]C. Maunoury, K. Dabertrand, E. Martinez, M. Saadoune, D. Lafond, F. Pierre, O. Renault, S. Lhostis, P. Bailey, T. C. Q. Noakes, and D. Jalabert, J. Appl. Phys. **101**, 034112 (2007).
[7]M. D. Groner, F. H. Fabreguette, J. W. Elam, and S. M. George, Chem. Mater. **16**, 639 (2004).
[8]L. Niinistö, J. Päiväsaari, J. Niinistö, M. Putkonen, and M. Nieminen, Phys. Status Solidi A **201**, 1443 (2004).
[9]M. S. Akbar, J. C. Lee, N. Moumen, and J. Peterson, Appl. Phys. Lett. **88**, 082901 (2006).
[10]E. P. Gusev, C. Cabral, M. Copel, C. D'Emic, and M. Gribelyuk, Microelectron. Eng. **69**, 145 (2003).
[11]J. C. Hackley, J. D. Demaree, and T. Gougousi, J. Vac. Sci. Technol. A **26**, 1235 (2008).
[12]O. Acton, G. Ting, H. Ma, J. W. Ka, H. L. Yip, N. M. Tucker, and A. K. Y. Jen, Adv. Mater. **20**, 3697 (2008).
[13]X.-H. Zhang, B. Domercq, X. Wang, S. Yoo, T. Kondo, Z. L. Wang, and B. Kippelen, Org. Electron. **8**, 718 (2007).
[14]X.-H. Zhang, S. P. Tiwari, and B. Kippelen, Org. Electron. **10**, 1133 (2009).
[15]R. F. Pierret, *Semiconductor Device Fundamentals* (Addison-Wesley, Reading, 1995).