Seeding Atomic Layer Deposition of High-k Dielectrics on Epitaxial Graphene with Organic Self-Assembled Monolayers

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ABSTRACT The development of high-performance graphene-based nanoelectronics requires the integration of ultrathin and pinhole-free high-k dielectric films with graphene at the wafer scale. Here, we demonstrate that self-assembled monolayers of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) act as effective organic seeding layers for atomic layer deposition (ALD) of HfO2 and Al2O3 on epitaxial graphene on Si(0001). The PTCDA is deposited via sublimation in ultrahigh vacuum and shown to be highly ordered with low defect density by molecular-resolution scanning tunneling microscopy. Whereas identical ALD conditions lead to incomplete and rough dielectric deposition on bare graphene, the chemical functionality provided by the PTCDA seeding layer yields highly uniform and conformal films. The morphology and chemistry of the dielectric films are characterized by atomic force microscopy, ellipsometry, cross-sectional scanning electron microscopy, and X-ray photoelectron spectroscopy, while high-resolution X-ray reflectivity measurements indicate that the underlying graphene remains intact following ALD. Using the PTCDA seeding layer, metal-oxide-graphene capacitors fabricated with a 3 nm Al2O3 and 10 nm HfO2 dielectric stack show high capacitance values of ∼700 nF/cm2 and low leakage currents of ∼5 × 10−9 A/cm2 at 1 V applied bias. These results demonstrate the viability of sublimated organic self-assembled monolayers as seeding layers for high-k dielectric films in graphene-based nanoelectronics.

KEYWORDS: graphene · gate insulator · transistor · hafnia · alumina · PTCDA · organic seeding layer

The outstanding electronic transport properties of graphene, including extremely high carrier mobilities, have generated significant interest in graphene-based nanoelectronics. An important step in the development of top-gated graphene-based field-effect transistors (FETs) is the growth of high dielectric constant (high-k) materials to act as the gate insulator. For optimal performance, these dielectric thin films should be ultrathin, conformal, and pinhole-free with minimal disorder or traps at the dielectric–graphene interface. However, due to the chemical inertness and hydrophobicity of graphene, the direct growth or deposition of dielectric layers on bare graphene leads to non-uniform films with sub-optimal electrical performance. Several surface treatment strategies have been pursued by researchers to improve the uniformity of gate dielectric growth on graphene by atomic layer deposition (ALD), including the deposition and oxidation of metal films, functionalization of graphene via ozone and nitrogen dioxide, and the spin-coating of polymer films as seeding layers. Although these methods possess clear advantages compared to ALD dielectric deposition directly on pristine graphene, important issues remain unresolved. For example, graphene surface pretreatments that involve oxidized metal nucleation layers, ozone, or nitrogen dioxide generally lead to surface damage of the graphene and degradation of its electronic properties. Furthermore, polymer seeding layers decrease the overall capacitance of the gate dielectric layer due to increased gate thickness and a reduced effective k value. Additional solution-phase deposited organic seeding layers have also been explored, although the electrical properties of the resulting ALD alumina have not been reported. Consequently, a clear need remains for a graphene chemical functionalization scheme that efficiently and uniformly seeds ALD growth while preserving the underlying graphene structure and achieving desirable dielectric properties such as low leakage current and high capacitance.

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Received for review April 18, 2011 and accepted May 9, 2011.

Published online May 09, 2011 10.1021/nn201414d
Herein, we demonstrate an alternative ALD seeding layer based on organic monolayers of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) that overcomes the aforementioned issues for high-κ dielectric thin films on epitaxial graphene (EG) on SiC(0001). PTCDA is deposited via gas-phase sublimation in ultra-high vacuum (UHV),\textsuperscript{18,19} resulting in a highly uniform and ordered self-assembled monolayer as verified with UHV scanning tunneling microscopy (STM). Subsequent ALD yields homogeneous and conformal thin films of Al₂O₃ and HfO₂ whose structure and chemistry are characterized with atomic force microscopy (AFM), ellipsometry, X-ray photoelectron spectroscopy (XPS), cross-sectional scanning electron microscopy (SEM), and low-angle and high-angle X-ray reflectivity (XRR). As a subsurface probe, XRR also allows verification of the structural integrity of the underlying graphene following ALD dielectric growth. Finally, metal-oxide-graphene capacitors are fabricated via PTCDA-seeded ALD of 3 nm Al₂O₃ and 10 nm HfO₂ dielectric stack, resulting in a measured capacitance of \( \sim 700 \text{ nF/cm}^2 \) and leakage current of \( \sim 5 \times 10^{-10} \text{ A/cm}^2 \) at 1 V gate bias. Overall, this work reveals the effectiveness of sublimated organic monolayers as seeding layers for ALD on EG, thus facilitating the development of graphene-based nanoelectronic devices and circuits.

**RESULTS AND DISCUSSION**

**UHV STM of PTCDA Monolayers.** Graphene was epitaxially grown on n-type 6H-SiC(0001) substrates (Cree, Inc.) by UHV graphitization as described previously,\textsuperscript{18,20,21} resulting in a mixture of monolayer and bilayer graphene. Atomic-scale characterization was accomplished in the same UHV system using a home-built STM at room temperature.\textsuperscript{22} A large-area STM image of the bare epitaxial graphene surface is shown in Figure 1a, and an atomically resolved STM image of bilayer graphene is included in Figure 1b. Following STM confirmation of successful epitaxial graphene growth, the PTCDA monolayer was formed by sublimating PTCDA (97%, Sigma-Aldrich) onto the graphene surface at room temperature in UHV following a previously established protocol.\textsuperscript{18} The molecules self-assemble into a well-ordered monolayer that homogeneously and conformally coats the graphene surface, as shown in the STM image of Figure 1c. The molecular structure of PTCDA is illustrated in Figure 1d. The central perylene core of PTCDA induces the molecule to lay flat on the graphene surface via \( \pi-\pi^* \) stacking, while the oxygenated periphery of the molecule provides relatively strong noncovalent intermolecular bonding that stabilizes the monolayer\textsuperscript{18} and also possesses distinct chemical character from the underlying graphene that holds promise for templating subsequent chemistry such as ALD. In the molecularly resolved STM image of Figure 1e, the monolayer shows a highly ordered herringbone structure. In addition, the ordering of the monolayer is unperturbed by underlying substrate defects such as atomic step edges.\textsuperscript{18} Overall, PTCDA deposition results in a structurally and chemically homogeneous surface with a lower defect density than the original bare graphene.

**Structural and Chemical Characterization of ALD Dielectric Films.** Representative intermittent contact AFM images of EG and PTCDA/EG surfaces are presented in Figure 2a,d, respectively. ALD of Al₂O₃ and HfO₂ was then performed in a custom viscous flow ALD reactor\textsuperscript{23} at a growth temperature of 100 °C. Figure 2b,c shows AFM images of two EG surfaces after depositing 25 cycles of Al₂O₃ and 25 cycles of HfO₂, respectively. The high-κ dielectric films on the bare EG surface are patchy and discontinuous, which confirms previous reports of ALD on nonfunctionalized graphene and HOPG surfaces.\textsuperscript{4,5,10} In contrast, Figure 2e,f shows AFM images of two PTCDA/EG surfaces following the same ALD treatment as EG (i.e., 25 cycles of Al₂O₃ and 25 cycles of HfO₂, respectively). With the PTCDA seeding layer, the resulting ALD dielectric films possess high uniformity, low defect density, and appear to conformally coat the underlying terraces of the EG surface as evidenced by the presence of atomic steps in the post-ALD AFM images. Quantitatively, the measured rms roughness of both films on PTCDA/EG is less than 0.3 nm. This superlative uniformity, conformality, and smoothness...
of the dielectric films persist even following extended ALD treatments that yield thin films with thicknesses above 15 nm.

To probe the adhesion between the deposited ALD films and the underlying substrate, contact-mode conductive AFM imaging was employed. Figure 3a–d shows that after only one AFM scan in contact mode (contact force ~ 20 nN) defects are introduced in the Al₂O₃ (25 cycles ALD) dielectric film on bare EG; while after just two AFM scans, large regions of the dielectric film are removed, exposing the underlying electrically conductive EG/SiC substrate. On the other hand,
Figure 3e,f shows that the Al<sub>2</sub>O<sub>3</sub> (25 cycles ALD) dielectric film on PTCDA/EG is unchanged by contact-mode AFM even following multiple AFM scans at contact forces up to 50 nN. The stability of the Al<sub>2</sub>O<sub>3</sub> film on PTCDA/EG following contact-mode imaging indicates strong adhesion of the dielectric film. In addition, the absence of detectable current in the conductive AFM current map of Figure 3f suggests that the dielectric film on PTCDA/EG is uniformly electrically insulating.

The thickness and chemistry of the ALD dielectric films were determined by ellipsometry and XPS, respectively. In particular, ellipsometric measurements were obtained before and after ALD using a J.A. Woollam Co. M2000 V variable angle spectroscopic ellipsometer (VASE). The thicknesses of the Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> dielectric films were obtained by fitting the ellipsometric data to a model using known optical constants of the dielectric films and the contribution from the substrate obtained preceding ALD. Figure 4a,b contains plots of the ellipsometrically determined dielectric film thickness as a function of ALD growth cycle number for Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>, respectively. Figure 4a shows that the Al<sub>2</sub>O<sub>3</sub> ALD on the bare EG surface is initially inhibited for ∼3–4 ALD cycles, indicating a lack of reactive sites for the ALD precursors compared to growth on the SiO<sub>2</sub> surface, which exhibits no apparent inhibition. On the other hand, nucleation on the PTCDA-functionalized surface is more efficient with growth progressing in a linear fashion following only 1–2 ALD cycles. Similar behavior is seen in Figure 4b, where the HfO<sub>2</sub> ALD on the bare EG is suppressed for ∼7–8 cycles compared to the prompt nucleation on the SiO<sub>2</sub> surface, while the PTCDA functionalization reduces the nucleation period on EG to only 3–4 cycles. Since linear growth is typical of ALD on surfaces with a high concentration of reactive sites, the ellipsometric data provide further evidence that PTCDA chemically functionalizes EG to facilitate chemisorption of the ALD Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> precursors.

To verify the chemical identity of the ALD dielectric films, XPS was performed on both the Al<sub>2</sub>O<sub>3</sub>- and HfO<sub>2</sub>-coated PTCDA/EG samples (Figure 4c,d, respectively). Following survey scans to check for the presence of Al or Hf, high-resolution spectra of the Al 2p peak and the Hf 4f peaks were taken on the respective samples and calibrated relative to the C 1s peak. The Al 2p peak binding energy position at ∼74.2 eV confirms the presence of Al<sub>2</sub>O<sub>3</sub> (Figure 4c), while the Hf 4f<sub>7/2</sub> peak binding energy position at ∼16.5 eV confirms the presence of HfO<sub>2</sub> (Figure 4d).

X-ray Reflectivity of ALD Dielectric Films and Underlying PTCDA/EG. Specular X-ray reflectivity (XRR) was used to confirm the integrity of the buried PTCDA/EG/SiC layers following ALD. This technique, while largely insensitive to the amorphous dielectric overlayer at high incident angles, probes the atomic-scale ordering of periodic surface and interface structures. In particular, synchrotron-based high-resolution XRR has been previously utilized in structurally probing both EG overlayers and PTCDA-functionalized EG. Additional analysis concentrating on the low-angle region of the XRR curves, which is sensitive to the thicker amorphous dielectric overlayers, was used to investigate
the thickness, density, and roughness of the dielectric films.

Figure 5 displays specular XRR curves of three samples: bare EG/SiC, PTCDA/EG/SiC, and HfO2/Al2O3/PTCDA/EG/SiC. Sharp features at \( q \sim 2.49 \) and 4.99 Å\(^{-1}\) correspond to the (0006) and (000 12) bulk SiC Bragg peaks, while the broad peaks at \( q \sim 1.70, 3.60, \) and 5.55 Å\(^{-1}\) correspond to graphene and PTCDA overlayers. In the first region of interest (ROI 1), the PTCDA/EG/SiC data exhibit a greater reflected intensity at \( q \sim 3.60 \) Å\(^{-1}\) compared to that of bare EG/SiC. This feature is a result of the additional PTCDA monolayer and remains in the data after ALD deposition on the PTCDA-functionalized graphene surface (HfO2/Al2O3/PTCDA/EG/SiC), indicating persistent interlayer structure following ALD.

PTCDA—graphene layers, the diffracted signals from these layers appear near the same positions along the XRR curve, at \( q \sim 1.70, 3.60, \) and 5.55 Å\(^{-1}\). These features are present in all three data sets. As PTCDA and graphene layers have been shown to have similar stacking positions, the signal from either graphene or PTCDA/EG layers will be defined in this work as a generalized “interlayer”. In addition to the high-q film signals, a broad thin-film oscillation can be observed in each data set with minima near \( q = 0.40 \) and 1.05 Å\(^{-1}\). The positions of these minima imply an oscillation period \( \Delta q \) of 0.65 Å\(^{-1}\), resulting from the PTCDA/EG interlayer structure of \( \sim 1 \) nm in thickness.

Systematic changes in the XRR data due to the PTCDA functionalization of graphene have been described elsewhere. Here, we note specifically that an increase in the reflected intensity near the interlayer peaks (at \( q \sim 1.70, 3.60, \) and 5.55 Å\(^{-1}\)) indicates the presence of a PTCDA overlayer. For clarity, in Figure 5b, all three data sets have been presented on a linear scale in the first region of interest (ROI 1), the PTCDA/EG/SiC data exhibit a greater reflected intensity at \( q \sim 3.60 \) Å\(^{-1}\) compared to that of bare EG/SiC. This feature is a result of the additional PTCDA monolayer and remains in the data after ALD deposition on the PTCDA-functionalized graphene surface (HfO2/Al2O3/PTCDA/EG/SiC), indicating persistent interlayer structure following ALD.

Figure 6. Low-q XRR is shown for the second region of interest (ROI 2) from Figure 5a. Kiessig fringes are observed, corresponding to a smooth, uniform dielectric film with sharp interfaces. The inset is the best least-squares fit result for the film overlayer strictly from the low-q data, with the electron density normalized to that of the bulk SiC substrate.
relative to the underlying graphene following ALD of the high-$k$ dielectric film.

In Figure 6, we investigate the low-$q$ XRR data, denoted by ROI 2 in Figure 5a. The oscillations in the HfO$_2$/Al$_2$O$_3$/PTCDA/EG/SiC data reveal the presence of a smooth, uniform thin-film overlayer that is attributed to the dielectric thin-film stack. The final $\chi^2$ value was 3.98.\(^{30}\) The results of the fitting are displayed as an electron density profile in the inset of Figure 6.

Least-squares fitting\(^{31}\) of the reflectivity data yielded a total dielectric film overlayer of thickness $t_{\text{tot}} = 13.0 \pm 0.4$ nm, with a HfO$_2$ thickness of $t_{\text{HfO}_2} = 10.0 \pm 0.2$ nm and an Al$_2$O$_3$ thickness of $t_{\text{Al}_2\text{O}_3} = 3.0 \pm 0.2$ nm, which is in close agreement with the thicknesses deduced from the ellipsometric data. The model provides for a low-density PTCDA/EG interface region, which the fit gave to be a 1.5 $\pm$ 0.2 nm thick layer. This thickness is consistent with previous work that indicates the PTCDA/EG layer combined with the underlying ($6\sqrt{3} \times 6\sqrt{3}$)R30$^\circ$ SiC reconstructed layer is $\sim$1.6 nm thick.\(^{28}\) Extracted electron densities (reported with respect to the SiC substrate, $\rho$/$\sigma_{\text{SiC}}$) are found to be $\rho_{\text{HfO}_2}/\sigma_{\text{SiC}} = 2.57 \pm 0.04$ and $\rho_{\text{Al}_2\text{O}_3}/\sigma_{\text{SiC}} = 1.18 \pm 0.04$, in agreement with expected values derived from bulk crystal structures, which are nominally 2.50 for $\rho_{\text{HfO}_2}/\rho_{\text{SiC}}$ and 1.8 for $\rho_{\text{Al}_2\text{O}_3}/\rho_{\text{SiC}}$. Additionally, the PTCDA/EG interlayer electron density ($\rho_{\text{PTCDA}/\text{EG}}/\rho_{\text{SiC}} = 0.71 \pm 0.03$) is close to the nominal value for a graphite crystal ($\rho_{\text{graphite}}/\rho_{\text{SiC}} = 0.65$), reflecting the similarity between the two structures.\(^{28}\) Extracted XRR rms roughnesses, which take into account both topography and density fluctuations, indicate exceptionally smooth surfaces and interfaces ($\sigma_{\text{HfO}_2,\text{Air}} = 0.60 \pm 0.05$ nm, $\sigma_{\text{Al}_2\text{O}_3,\text{HfO}_2} = 0.40 \pm 0.05$ nm, and $\sigma_{\text{PTCDA}/\text{EG},\text{Al}_2\text{O}_3} = 0.2 \pm 0.2$ nm). The $\sigma_{\text{HfO}_2,\text{Air}} = 0.60 \pm 0.05$ nm value obtained from the XRR measurements is in reasonably good agreement with the value $\sigma_{\text{HfO}_2,\text{Air}} = 0.3$ nm measured by AFM given the finite AFM tip size. Overall, the low-$q$ XRR indicates that the HfO$_2$ and Al$_2$O$_3$ dielectric layers grown on PTCDA/EG are smooth, uniform, and highly ordered. Furthermore, the high-angle XRR confirms that the buried PTCDA/EG layer remains structurally intact following ALD deposition.

**Electrical Characterization of Metal-Oxide-Graphene Capacitors.** In field-effect transistors (FETs), it is highly desirable to avoid power losses through gate leakage while maintaining the high capacitance necessary for low-voltage device operation. Since metal-oxide-semiconductor (MOS) capacitors provide a rapid assessment of gate dielectric quality in MOSFET technology,\(^{32}\) we fabricated and characterized metal-oxide-graphene parallel-plate capacitors using ALD dielectrics grown on the PTCDA seeding layer. In particular, after SiC graphitization and deposition of PTCDA, 2 nm of ALD Al$_2$O$_3$ was deposited at a low growth temperature of 100 $^\circ$C to avoid PTCDA desorption. The ALD growth temperature was then increased to 225 $^\circ$C, whereupon another 1 nm of Al$_2$O$_3$ was deposited followed by 10 nm of HfO$_2$. The higher deposition temperature was employed to increase film density and improve dielectric quality.\(^{29,36}\) Figure 7b is an AFM image of the top surface following ALD of the both Al$_2$O$_3$ and HfO$_2$ layers. The underlying terraces of the substrate are still observable even following 13 nm of ALD, showing that the total dielectric film is conformal, smooth, and homogeneous.

Cross-sectional scanning electron microscopy (SEM) images were taken using focused ion beam (FIB) milling in a dual beam FIB/SEM (FEI Helios Nanolab) to cut a trench into the dielectric stack to reveal its
cross-sectional structure. The FIB milling region was first prepared by depositing a thick layer of platinum via ion beam induced deposition (IBID), which allows for uniform cross-sectional FIB milling by minimizing charging effects. In the cross-sectional SEM image of Figure 7c, a bright layer is observed between the platinum IBID layer and the bulk SiC, which corresponds to the dielectric layers. The dielectric layers appear bright due to their electrically insulating properties, which causes negative charging and an increase in the secondary electron yield. Figure 7d was taken at a lower beam current to reduce this charging effect. In both cases, the dielectric layer is clearly visible with a measured thickness of 13 ± 3 nm as expected from the ALD growth conditions.

After ALD of the dielectric stack on PTCD/EG, a Au (75 nm) on Cr (10 nm) top electrode layer was thermally evaporated (Nano38, Leskar) on the substrate through a TEM grid (90 μm hole width, SPI) to form a grid of square electrodes. The heavily doped SiC substrate (resistivity ~0.054 Ω-cm) was used as the global bottom electrode. A schematic of the thin-film capacitor structure is shown in Figure 7a. At 1 V applied bias, low leakage currents of ~5 × 10⁻⁹ A/cm² were recorded for greater than 80% of the capacitors tested. At high biases exceeding 3 V, Fowler–Nordheim (FN) tunneling was observed as expected (Figure 8a). Irreversible dielectric breakdown was not observed up to a bias of 5 V, corresponding to an electric field of ~4 MV/cm.

Capacitance–voltage (CV) measurements were performed over a frequency range of 10 kHz to 1 MHz (Figure 8b). The slight V-shape of the CV curves are similar to CV results obtained on exfoliated graphene on SiO₂ and epitaxial graphene on SiC which has been attributed to the influence from the quantum capacitance of graphene. Capacitance dispersion with frequency is also observed, which likely results from the series substrate resistance and finite leakage current. Using the two-frequency measurement technique to account for this dispersion, a total capacitance of ~700 nF/cm² was calculated across the dielectric stack. Bidirectional bias sweeps revealed minimal hysteresis of 0.1–0.4 V for the range of frequencies tested, which suggests low interface trap density. In addition, no differences were observed in the CV data taken in the light and in the dark. This measured capacitance is significantly higher than reported for previously published top-gated FETs on graphene, while the measured gate leakage is significantly lower than reported values. An exception is a recently published top-gate dielectric capacitance of 1200 nF/cm², although the measured gate leakage of our dielectric stack is at least 4 orders of magnitude lower.

By assuming a parallel-plate capacitor geometry, dielectric constants for the ALD layers can be extracted using \( k = \frac{Cd}{\varepsilon_o} \), where \( C \) is the capacitance per unit area, \( d \) is thickness of the film, and \( \varepsilon_o \) is the permittivity of free space. With this model, our capacitance measurements imply dielectric constants of 13 for HfO₂ (10 nm) and 5.6 for Al₂O₃ (3 nm), which are both consistent with previous reports and similar to our measurements on reference silicon samples. Overall, the metal-oxide-graphene capacitor characteristics demonstrate the superlative dielectric properties of the PTCD-seeded ALD dielectric films.

**CONCLUSIONS**

In summary, we have demonstrated the utility of vacuum sublimated organic monolayers of PTCD as a seeding layer for ALD dielectric growth on epitaxial graphene on SiC(0001). Using a suite of surface science techniques including UHV STM, AFM, ellipsometry, XPS, XRR, and FIB-SEM, thin films of Al₂O₃ and HfO₂ grown on PTCD/EG have been thoroughly characterized and shown to be exceptionally uniform, smooth, and conformal. In particular, with its subsurface sensitivity, XRR verifies that the underlying graphene remains intact and possesses sharp interfaces with the deposited dielectric films following ALD. To verify electrical integrity, metal-oxide-graphene parallel-plate capacitors were fabricated and shown to possess desirable characteristics including high capacitance values of ~700 nF/cm² and low leakage currents of ~5 × 10⁻⁹ A/cm² at 1 V gate bias. This demonstration of high-k dielectric performance
shows the viability of organic self-assembled monolayers as seeding layers for ALD, thus providing a promising pathway for realizing high-performance graphene-based nanoelectronics.

**METHODS**

**Sample Preparation: Epitaxial Graphene.** The epitaxial graphene samples were grown on n-type (nitrogen-doped) 6H-SiC(0001) wafers (Cree, Inc.). The SiC wafer was diced into 9 mm × 6 mm sample pieces (American Precision Dicing), which were ultrasonically cleaned in acetone and isopropl alcohol before being introduced into the UHV chamber (base pressure ~5 × 10⁻¹¹ Torr). The samples were then outgassed at 600 °C overnight and annealed at 1100 °C for several minutes to remove the native oxide and other contaminants. The samples were subsequently graphitized by repeatedly heating to 1350 °C for 1 min cycles to produce a mixture of single-layer and bilayer graphene. The cleanliness of the surfaces and the graphene coverage were verified by room temperature STM imaging in the same UHV system.

**Sample Preparation: PTCD Monolayer.** The PTCD powder (97% purity, Sigma Aldrich) was loaded into an alumina-coated W boat and thoroughly outgassed in vacuum by resistively heating the boat. The PTCD was deposited onto the EG substrates, which were held at room temperature, by thermal evaporation from the boat. The PTCD monolayer coverage was verified by STM imaging and controlled by varying the duration of the molecular flux.

**Sample Preparation: Atomic Layer Deposition.** After deposition of PTCD, the samples were briefly exposed to air, while being transferred to a separate custom viscous flow reactor for ALD. Ultrahigh purity nitrogen was continuously passed through the flow tube at a rate of 360 sccm and a pressure of ∼1 Torr. Al₂O₃ and HfO₂ films were prepared using trimethyl aluminum (TMA, Aldrich, 99%) and tetrakis(diethylamido)hafnium(IV) (TDEAHf, Sigma-Aldrich, 99%), and tetraethylorthotitanate (TEOTi, Aldrich, 99.99%), respectively. Deionized H₂O was used as the oxygen source in both cases. The TDEAHf vapor was delivered by a 60 sccm N₂ flow through a bubbler held at 120 °C.

**Atomic Force Microscopy.** All AFM images were collected utilizing a modified CP Research (Thermomicroscopes) AFM in air. Imaging was performed in intermittent contact mode using a Si probe (μMasch, NSC36A) with a nominal tip radius of curvature of 10 nm. AFM images were rendered using WSxM SPM analysis software.46

**Current mapping was achieved with a conductive diamond-coated Si probe (CDT-FMR, Nanosensors) in contact mode with contact forces of 8–50 nN, scan rate of 0.3 Hz, and sample bias of 0.3 V. Current was collected through the conductive AFM probe using a DL Instruments current preamplifier (model 1212) and a 160 Hz low-pass in-line filter. A limiting resistor (~12 MΩ) was used in series with the current preamplifier to prevent exposure of the conductive AFM tip to potentially damaging high current levels. The conductive AFM probes were tested on Au reference samples, where contact resistances of <5 kΩ were recorded. Contact-mode topography signals were collected concurrently with the current signal.**

**Ellipsometry.** Ellipsometric measurements were performed using a J.A. Woollam Co. M2000 V variable angle spectroscopic ellipsometer (VASE) at an incidence angle of 75°. Measurements were obtained before and after ALD. Nominal thicknesses of Al₂O₃ and HfO₂ dielectric films were found by fitting the spectra to a model using optical constants of the dielectric films and the contribution from the substrate obtained preceding ALD.

**X-ray Photoelectron Spectroscopy.** An Omicron ESCA (Electron Spectroscopy for Chemical Analysis) probe was used for XPS analysis. The measurements were made using Al Kα (1486.6 eV) radiation, which was incident on the sample at a 45° takeoff angle, and a hemispherical electron energy analyzer. A survey scan was initially performed to check for the presence of Al and Hf peaks after Al₂O₃ and HfO₂ ALD, respectively. Subsequently, high-resolution spectra of the Al 2p peak and the Hf 4f peaks were gathered on the respective samples and calibrated relative to the C 1s peak.

**X-ray Reflectivity.** Specular X-ray reflectivity was measured at beamline 33-BM-C of the X-ray Operation and Research Division, Advanced Photon Source (APS), Argonne National Laboratory. The incident photon beam on the sample had an energy of 17.00 keV, beam size of 0.1 mm (vertical) × 2.00 mm (horizontal), and incident flux of ~10¹⁰ photons/s. Samples were mounted within an evacuated (~10⁻³ Torr) beryllium dome sample cell. The scattered X-ray intensity in the region of the specular condition was acquired with either a point detector (low-angle reflectivity; 0 < q < 1.25 Å⁻¹)47 or with a 2D CCD detector (q > 1.00 Å⁻¹).48 Data from these two methods were combined to produce a single XRR curve with overlapping regions between q = 1.00 and 1.25 Å⁻¹. Uncertainties for all data points were determined by counting statistics. For simplification of reflectivity analysis, data points were removed near the sharp quasi-forbidden SiC(0001) Bragg peaks27,48 at q = 2πncosθ/λ, where n is an integer value that is not a multiple of 6 and c₀ = 15.12 Å is the 6H-SiC(0001) out-of-plane lattice parameter.

**FIB/SEM Characterization.** Cross-sectional scanning electron microscopy (SEM) images were taken using focused ion beam (FIB) milling in a dual beam FIB/SEM (FEI Helios Nanolab). The FIB milling region was first prepared by depositing a thick layer of platinum via ion beam induced deposition (IBID). A trench was then FIB milled to allow for SEM access to the cross section of the dielectric film. Finally, SEM images were taken at a 38° angle to the normal of the cross section, causing an apparent contraction of the vertical scale by a factor of 0.788.

**Electrical Characterization.** After ALD, a top electrode layer of Au (75 nm) on Cr (10 nm) was thermally evaporated (Nano38, Leskar) on the substrate through a TEM grid (90 µm hole width, SPI) to form a grid of square electrodes, the size of which was measured by an optical microscope (ME6005, Nikon). The highly doped SiC substrate (resistivity ~0.054 Ω cm) was used as the global bottom electrode. All electrical measurements were performed under ambient conditions. Contact to the top electrode was made with a conductive diamond-coated Si probe (CDT-FMR, Nanosensors) that was actuated by an AFM. Contact forces were held at ~0.3 mN and the integrated electrical contact. Current—voltage measurements were performed with a Keithley 2636A dual source meter, and capacitance—voltage curves were gathered with an HP 4192A impedance analyzer.

**Acknowledgment.** This work was supported by the National Science Foundation (Award Number DMR-0520513), the Office of Naval Research (Award Number N00014-09-1-0180), Argonne National Laboratory (ANL), and ANSER Energy Frontier Research Center (funded by the Department of Energy, Award Number DE-SC0001059). ANL is a U.S. Department of Energy Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago Argonne, LLC. In addition, the FIB-SEM characterization by A.L.L. was funded by the Department of Energy (Award Number DE-AC02-06CH11357 to the CEEES-
EFRC. FIB-SEM and XPS were performed in the NUANCE facility at Northwestern University, which is supported by the NSF-NSEC, NSF-MRSEC, Keck Foundation, and State of Illinois. The authors thank P. Fenter for the development of extraction and analysis routines for the XRR data. Finally, the authors acknowledge J. Lyding for use of his STM control software.

REFERENCES AND NOTES

10. Here, $\chi = (I_{000} - I_{k})/I_{000}(N - N_0)$, where $I_0$ and $I_{k}$ are the measured and calculated reflected intensities, respectively, $I_{000}$ is the measured uncertainty at the kth data point, and $N$ and $N_0$ are the number of data points and parameters used in the fit, respectively.


