Supplementary Information:

Graphene oxide monolayers as atomically thin seeding layers for atomic layer deposition of metal oxides

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Experimental methods:

Graphene synthesis was carried out via CVD on Cu (foils and thin films) using methane as the carbon source. Graphene sheets were transferred to SiO_2/Si substrates by etching Cu with $FeCl_3$ solution to release graphene. Poly(methyl methacrylate) (PMMA) was used to support and transfer graphene to the target substrates. The PMMA layer was then removed by acetone followed by heating in a hydrogen/argon atmosphere at 350 ^oC. Repeated transfers were done to obtain double layer graphene stacks.

O_2 plasma treatment was done in a parallel-plate 13.57 MHz rf plasma chamber. A plasma pulse was defined as a linear increase of the power from 0 to 100 W in 3.3 s followed by 1 s at 100 W (O_2 pressure in the chamber at 20 mTorr). To avoid the physical impact of the plasma due to the direct collision of charged particles and the graphene surface, samples were placed upside down in the afterglow discharge, 1 cm above the lower plate and ~2 cm below the center of discharge. The samples were annealed in an inert atmosphere at 200 °C for 2 h after each plasma exposure to desorb weakly bonded oxygen species.

SRPES was performed using soft x-ray photons with photon energies of hν= 450 and 640 eV for C 1s and O 1s, respectively, at the U49-2/PGM-2 beamline at the BESSY II synchrotron facility within the Helmholtz-Zentrum Berlin.

ALD Al_2O_3 was carried out with a Cambridge NanoTech ALD system using trimethylaluminum (TMA) and H_2O vapor at 150 ^oC with TMA being the first pulse. A single ALD cycle consisted of a 30 ms TMA exposure, 15 s N_2 purge, a 30 ms H_2O exposure, and another 15 s purge. The growth rate on GO was 0.95 Å/cycle, no significant difference was observed between different degrees of oxidation of GO.

DFT calculations were carried out using the self-consistent pseudopotential method as implemented in the SIESTA code[1,2] with the generalized gradient approximation and the Perdew–Burke–Ernzerhof exchange–correlation functional. Atomic geometries are relaxed with forces <0.02 eV/ Å and stresses <0.05 GPa. We employed a 3D unit cell in which SLG is isolated by a 15 Å vacuum, large enough to ensure negligible interaction between functionalized graphene and its periodic images.

Leakage current characteristics:

Figure S1(a) compares the leakage currents of the two graphene-Al_2O_3-metal (GIM) capacitors described in Figure 4(a) where one has a GO ALD seeding layer (as explained in the main text), and the other is non-oxidized (pristine) graphene. A 10-nm layer of Al_2O_3 was deposited by ALD on both samples. The GO/Al_2O_3 devices showed low leakage currents with an oxide breakdown voltage $V_{br} \approx 5$ V. As expected for the case of graphene/Al_2O_3, the leakage current was many orders of magnitudes larger indicating the very poor quality of the deposited Al_2O_3 dielectric. This can be attributed to the relatively inert pristine graphene surface that prevents nucleation during ALD. Nucleation can only occur at defect sites, rather than over the whole graphene surface. This can be seen in the AFM image of Figure S1(b), which shows the non-uniform deposition of the Al_2O_3 film and a large number of pinholes. Some of these pinholes penetrate the whole film creating leakage paths. These results are similar to those previously reported by Wang et al.[3]

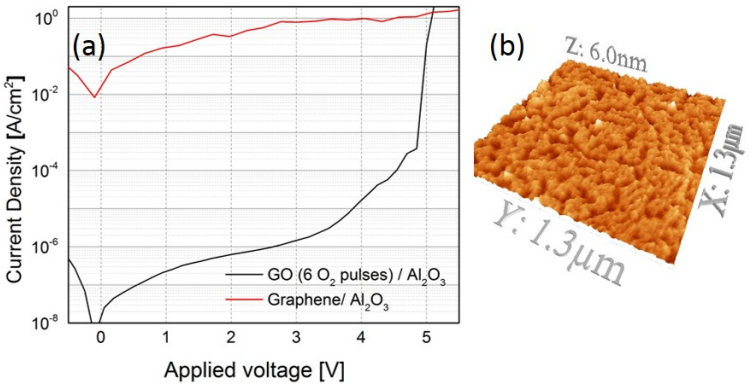

Figure S1. (a) Leakage current characteristics of GIM capacitors with GO/Al_2O_3 and graphene/Al_2O_3. (b) AFM images of ~10 nm thick Al_2O_3 deposited on graphene.

In this work ALD of Al_2O_3, which has a very efficient and self-limiting surface reaction, was developed as a representative model for the family of commonly used dielectric metal oxides MO_x, (e.g., M = Al, Hf, Zr). The main driving force for efficient reaction of the metal precursor with the surface is the formation of a strong metal–oxygen bond. The oxygen functionalized graphene surface can be expected to allow seeding of other metal oxides by the same ALD chemistry. An interesting example is HfO_2 which has higher dielectric constant than Al_2O_3 and is widely used in CMOS technology. Figure S2(a) shows an AFM image of a HfO_2 film deposited on GO (6 O_2 pulse), using 100 ALD cycles at 250 °C, where each cycle consisted of a 100 ms tetrakis(ethylmethylamino)hafnium (TEMAH) exposure, 15 s N_2 purge, a 20 ms H_2O exposure, and another 15 s purge. Figure S2(a) compares leakage current characteristics of GIM capacitors with Al_2O_3 and HfO_2 dielectric films. The HfO_2 GIM has a relatively high leakage current at voltages greater than 1 V and smaller V_{br} than the Al_2O_3 GIM (3.9 vs 5 V). The AFM image in Figure S2(b) shows that a HfO_2 film was uniformly deposited on GO to form a closed film. These results are in agreement with reports on conventional Al_2O_3 and HfO_2 metal-insulator-metal (MIM) capacitors.[4] The higher leakage current in the HfO_2 device can be attributed to the relatively smaller band gap of HfO_2 as compared to Al_2O_3 which results in smaller band offset energies between the graphene electrode and dielectric.

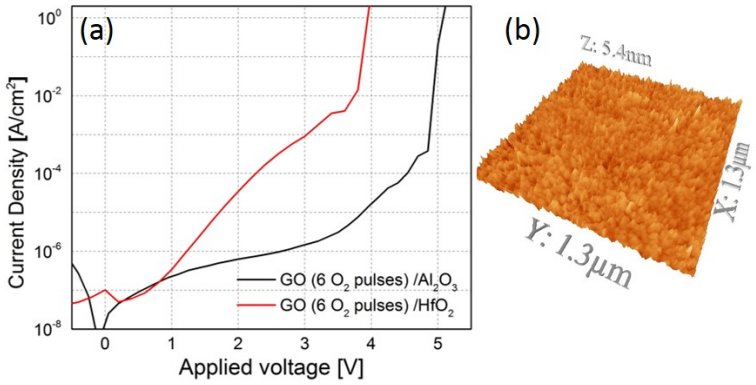

Figure S2. (a) Leakage current characteristics of GIM capacitors with GO/Al_2O_3 and GO/HfO_2. (b) AFM images of ~10 nm thick HfO_2 deposited on fully oxidized GO (6 O_2 plasma pulses).

References:

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