Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Control of Hexagonal Boron Nitride Dielectric Thickness by Single Layer Etching

Zichao Ma, Clarissa Prawoto, Zubair Ahmed*, Ying Xiao, Lining Zhang, Changjian Zhou, Mansun Chan*

Email: zmaaa@connect.ust.hk, zahmed@connect.ust.hk.

SI-1. Nitrogen plasma effect on h-BN film

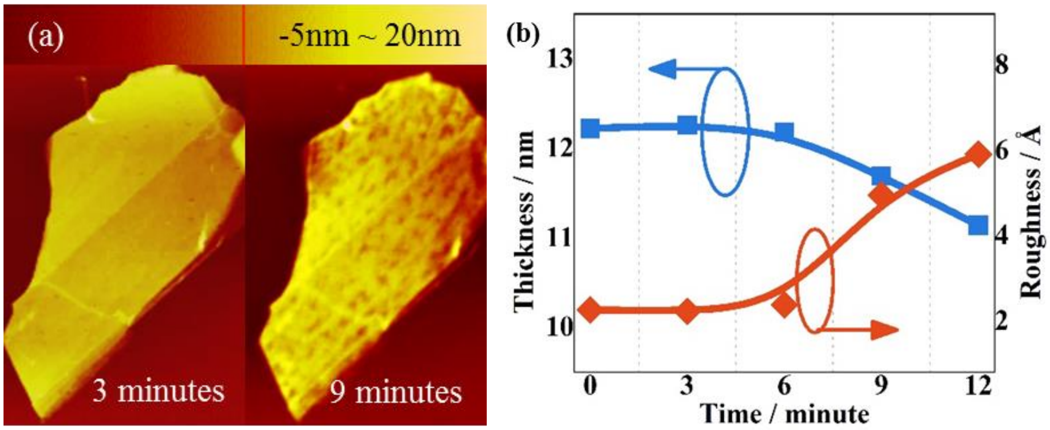

Figure S1. (a) AFM image on the h-BN film that exposed to 100 W nitrogen plasma for 3 minutes and 9 minutes. The scale bar for height is shown at the top. (b) Summarized h-BN film thickness and surface roughness (the same film as in (a)) that measured by AFM.

The long-term effect of 100 W nitrogen plasma on h-BN film is shown in Figure S3(a) and (b). A pristine h-BN flake was put under test for 12 minutes. The AFM characterizations show that the thickness and surface roughness of h-BN film were preserved within the first 6 minutes of processing. After that, surface damaging effect appeared as the surface becomes rougher, indicate the nitrogen plasma starts to etch h-BN film non-uniformly. As an inertia gas of nitrogen, this etching can be regarded as a physical bombardment and defect accumulation process, which may be caused by the minority high energy nitrogen ion bombardments. The slow progress of defect accumulation indicated low concentration of high energy nitrogen ions in the used nitrogen plasma. Therefore, to minimize the h-BN film damage caused by the high energy branch of nitrogen ion, we can simply limit the duration of nitrogen plasma processing to 2 minutes. The AFM topology images were plotted using the XEI (Park System), extracted film thickness and surface roughness were plotted with Origin Pro 9.0.

SI-2. O-radical modification on monolayer h-BN by First principle molecular dynamic simulations

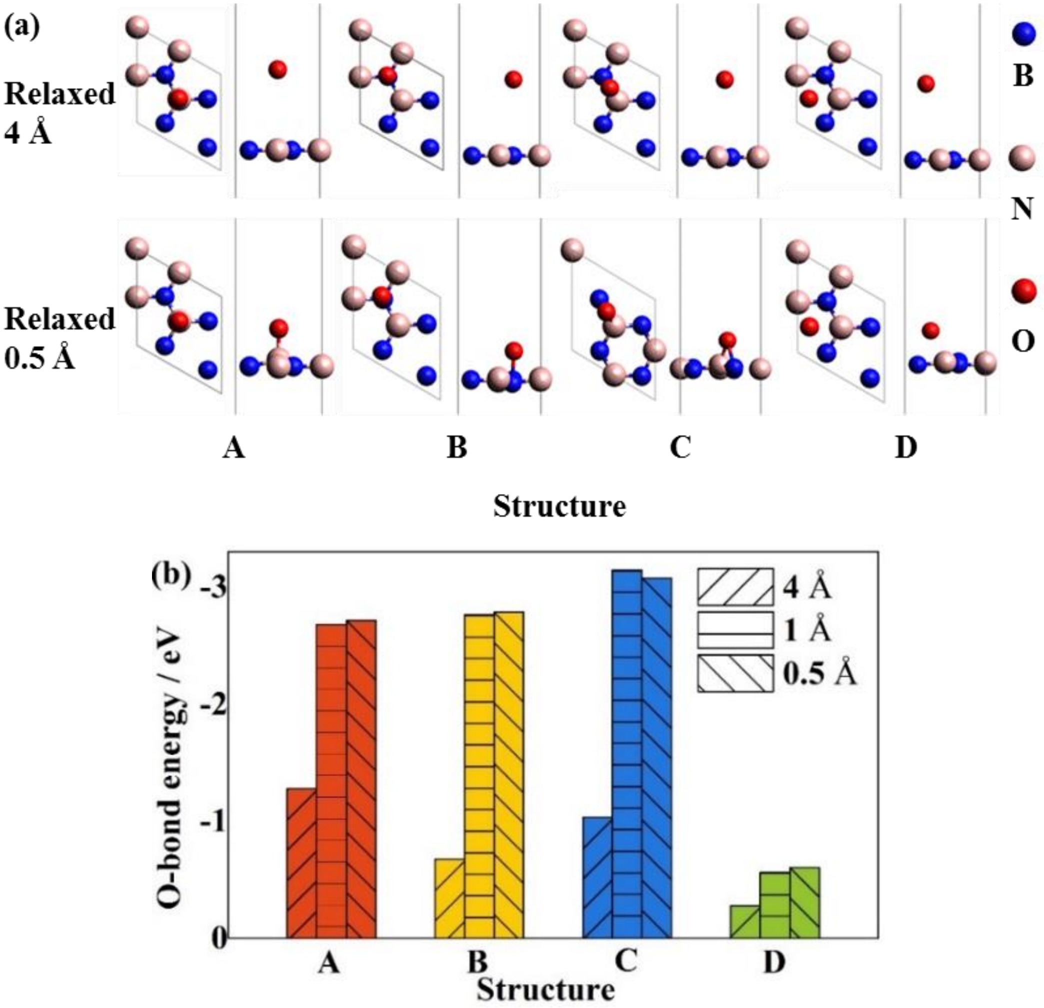

Figure S2. (a) Relaxed atom configurations. The upper row shows the relaxed structure with initial distance of 4 Å between O-radical and h-BN layer. The bottom row shows the relaxed structure with initial distance of 0.5 Å between O-radical and h-BN layer. The configurations with the same O-radical initial locations are placed in the same column. (b) Summarized O-bond energy in relaxed structures. Different patterns are used in bars that show O-bond energy in an atomic structure that with initial distances of 4 Å, 1 Å and 0.5 Å from O-radical to h-BN layer, to show contrast.

Structures with initial distance of 0.5 Å show similar relaxed atom structures and Oxygen bond energy to the results of structures with initial distance of 1 Å (shown in main article), which validates our results that chemisorption of O-radical on h-BN top monolayer. The relaxed structures with initial distance of 4 Å show weaker O-bond energy at around 1 eV, which suggests O-radical is prone to react with h-BN layer.

The first principle molecular dynamic simulations were performed using the Nanodcal package (Hongzhiwei Technology (Shanghai) Co., LTD.). The lattice parameter of the h-BN unit cell was calculated as 4.99648 Å, the B-N lattice is placed in x-y plane with the B-N bond length as 1.44 Å, vacuum layer of 25 Å is left in z-direction to avoid interaction between the h-BN monolayer and screened ones. The free energy calculation was performed by spin un-polarized density function theory with the Perdew−Burke−Ernzerhof generalized gradient approximation (PBE-GGA) in real-space numerical atomic orbital method. [S1] The molecular dynamic simulations were performed with 3-dimensional periodical boundary conditions. The simulation calculates 500 steps with step movement of 0.1 Å. The convergence threshold for the energy is set at 10−5 eV, under the real-space-grid cutoff energy at 1000 eV and Monkhorst−Pack k-point mesh of 8 × 8 × 1. The 3-dimensional atomic structures were visualized with Avogadro code. [S2]

The system free-energy difference (ΔG) was calculated using $\Delta G = E'_{\mathrm{BN}} - E_{\mathrm{BN}}$. The E'_{BN} refer to the total energy of the h-BN layer in the relaxed O-radical on h-BN configurations. E_{BN} is the energy of a pristine monolayer h-BN. The Oxygen bond energy ($E_{\mathrm{O\text{-}BN}}$) was calculated by $E_{\mathrm{O\text{-}BN}} = E_{\mathrm{BNO}} - E'_{\mathrm{BN}} - E_{\mathrm{O}}$. The $\mathrm{E}_{\mathrm{BNO}}$

represents total energy of the relaxed O-radical on h-BN structure and E_O represents the total energy of an isolated Oxygen atom. The extracted energy values were plotted with Origin Pro 9.0.

SI-3. Electrical characterizations

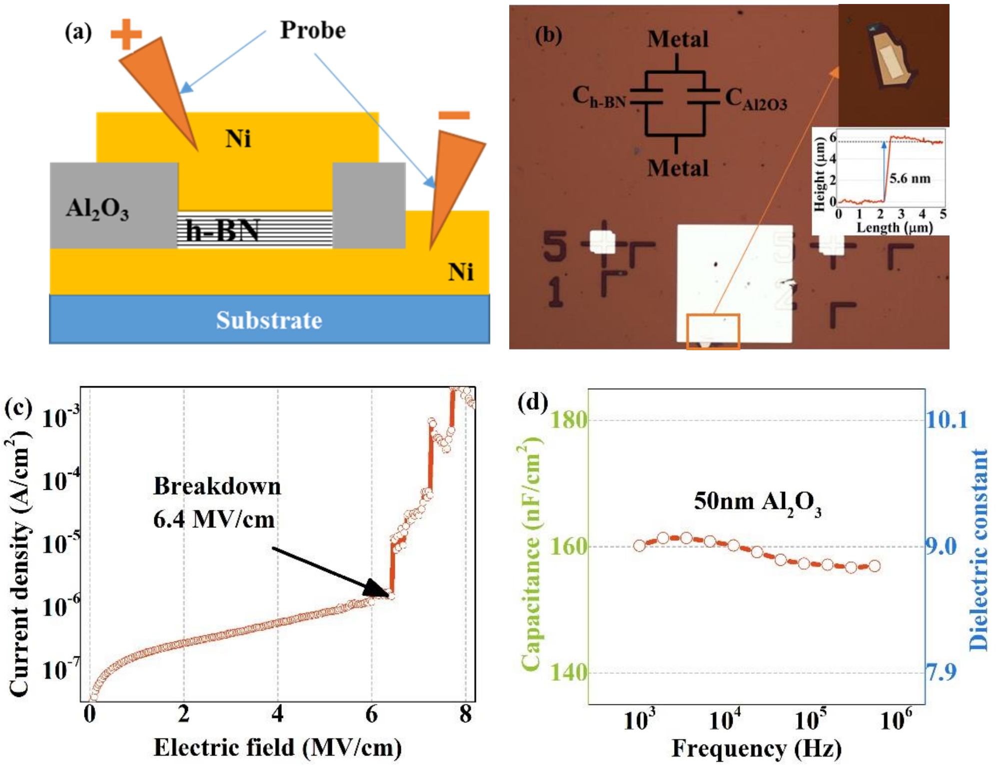

Figure S3. (a) Schematic of device structure. (b) Optical image captures the top metal pad. Sub-image shows the metal h-BN metal structure before top metallization. Two capacitors in this structure is also illustrated. (c) Current – voltage relation of the atomic layer deposited Al_2O_3 film. (d) Capacitance – frequency relation of the atomic layer deposited Al_2O_3 film.

As shown in Figure S3(a), this metal h-BN metal capacitor structure has two capacitors in parallel, namely the $C_{h\text{-}BN}$ and the C_{Al2O3}. The atomic layer deposited Al_2O_3 is 50 nm thick, which can be ignored when characterizing the current – voltage relation of h-BN films that thinner than 20 nm. However, the Al_2O_3

film still contributes a considerable amount to the capacitance of the device. Therefore, $C_{\text{h-BN}} = C_{\text{total}} - C_{\text{Al2O3}}$. C_{Al2O3} is characterized separately and shows dielectric constant around 9. To simplify the calculation, C_{Al2O3} is assumed to be a constant and calculated using equation $C = \frac{\varepsilon_{\text{Al2O3}}\varepsilon_0 Area}{Thickness}$, where the $\varepsilon_{\text{Al2O3}}$ is set to be 9. For the ease of comparison, current density – electric field relations of h-BN films instead of current – voltage relations are plotted in the main content. The current data of h-BN films are unified by the top contact area of the test device, the voltage data are unified by their specific h-BN film thickness. The electrical measurement data is processed by Origin Pro 9.0.

Supplementary References

[S1] V. Michaud-Rioux, L. Zhang, H. Guo, "RESCU: A real space electronic structure method", J. Comput. Phys., 2016, 307, 15, 593-613, DOI: 10.1016/j.jcp.2015.12.014.

[S2] M. D. Hanwell, D. E. Curtis, et al., "Avogadro: An advanced semantic chemical editor, visualization, and analysis platform", J Cheminform., 2012, 13;4(1),17. DOI: 10.1186/1758-2946-4-17.