

Supporting information for “2D-3D integration of hBN and a high- κ dielectric for ultrafast graphene-based electro-absorption modulators”

Hitesh Agarwal^{1,*}, Bernat Terrés^{1,*†}, Lorenzo Orsini^{1,2}, Alberto Montanaro³, Vito Sorianello³, Marianna Pantouvaki⁴, Kenji Watanabe⁵, Takashi Taniguchi⁵, Dries Van Thourhout⁴, Marco Romagnoli³, and Frank H. L. Koppens^{1,6,‡}

¹ICFO - Institut de Ciències Fotòniques, The Barcelona Institute of Science and Technology, 08860 Castelldefels (Barcelona), Spain

²Dipartimento di Fisica E. Fermi, Università di Pisa, Largo Bruno Pontecorvo 3, 56127 Pisa, Italy

³Consorzio Nazionale per le Telecomunicazioni (CNIT), Photonic Networks and Technologies National Laboratory, via Moruzzi 1, 56124 Pisa, Italy

⁴Photonics Research Group, Department of Information Technology, Ghent University-IMEC, Sint-Pietersnieuwstraat 41, Gent, 9000 Belgium

⁵National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

⁶ICREA - Institució Catalana de Recerca i Estudis Avançats, Barcelona, Spain

*These authors contributed equally

†bernat.terres@icfo.eu

‡frank.koppens@icfo.eu

August 10, 2020

I Optical conductivity model for graphene

The optical conductivity (σ) model is based on Kubo's formula [1] [2].

$$\sigma = \sigma_{intra} + \sigma_{inter}, \quad (1)$$

$$\sigma_{intra} = \frac{\sigma_o}{\pi} \frac{4}{\hbar\gamma - i\hbar\omega} \left[E_F + 2k_B T \ln(1 + e^{-E_F/k_B T}) \right], \quad (2)$$

$$\sigma_{inter} = \sigma_o \left[G\left(\frac{\hbar\omega}{2}\right) + i \frac{4\hbar\omega}{\pi} \int_0^\infty dE \frac{G(E) - G(\frac{\hbar\omega}{2})}{(\frac{\hbar\omega}{2})^2 - 4E^2} \right], \quad (3)$$

$$G(x) = \frac{\sinh(x/k_B T)}{\cosh(E_F/k_B T) + \sinh(x/k_B T)}, \quad (4)$$

where $\sigma_o = q^2/(4\hbar)$ is the universal conductivity of graphene [3], ω the frequency, q the elementary charge, $\hbar$ reduced Planck's constant, k_B the Boltzmann constant, $k_B T$ the thermal energy, $\hbar\omega$ the photon energy and $\hbar\gamma$ the electron relaxation energy, with γ being the intra-band scattering rate. The Fermi energy (E_F) is defined as [4]:

$$E_F = \text{sgn}(n_s) \hbar \nu_F \sqrt{\pi |n_s|}, \quad (5)$$

where $\nu_F = 9.5 \times 10^7$ cm/sec is the Fermi velocity, and n_s the free charge carrier density defined as [5]:

$$n_s = \frac{C V_{BT}}{qS}, \quad (6)$$

where V_{BT} is the voltage between the top and bottom graphene electrodes, S the surface of the capacitor and C is the total capacitance. The total capacitance considers the top layer graphene quantum capacitance (C_Q^{top}), the parallel plate capacitance (C_{ox}) (refer to section VII) and the bottom layer graphene quantum capacitance (C_Q^{bottom}) [6]:

$$\frac{1}{C} = \left(\frac{1}{C_Q^{top}} + \frac{1}{C_Q^{bottom}} + \frac{1}{C_{ox}} \right), \quad (7)$$

where:

$$C_Q^{bottom} = C_Q^{top} = \frac{2qk_B T}{\pi(\hbar\nu_F)^2} \log \left[2 \left(1 + \cosh \frac{E_F}{k_B T} \right) \right]. \quad (8)$$

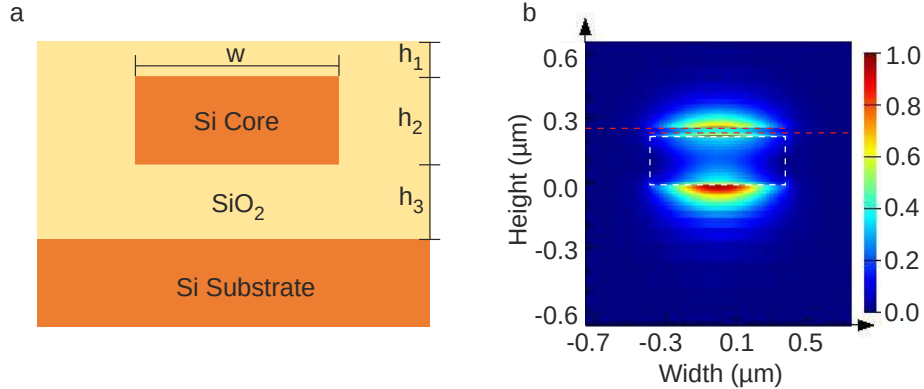
II FDTD simulations of the graphene modulators

To confirm the experimental transmission curves (Fig. 1c and Fig. 3b and c of the main text), we simulated our double-layer (DL) graphene modulator devices with the same geometry as the measured ones. We experimentally determined the values of mobility, intrinsic doping (section III), contact resistance (section IV) and relative permittivity of the hBN, HfO₂ and hBN-HfO₂-hBN (sections V and X). We used commercial FDTD software (Lumerical) and the optical conductivity model of graphene introduced in section I. We treat graphene as an equivalent 3D layer of thickness $h_G=0.34\text{nm}$ [7], with the out-of-plane dielectric constant of graphite and in-plane dielectric constant given by [8]:

$$\epsilon_G(\omega) = 1 + \frac{i\sigma(\omega)}{\omega \epsilon_0 h_G} \quad (9)$$

where ϵ_0 is the vacuum permittivity and $\sigma(\omega)$ is defined in section I. We determine the optical surface conductivity as a function of the Fermi level (E_F) at room temperature for a free-space wavelength $\lambda = 1550 \text{ nm}$ ($\hbar\omega = 0.8 \text{ eV}$). The real part of σ (i.e. the absorption term) decreases significantly for $E_F > 0.4 \text{ eV}$, i.e. when the device reaches Pauli blocking regime due to the lack of inter-band transitions ($E_F > \hbar\omega/2$), which results in a sharp transition (at zero kelvin and for very high mobility of graphene). We thus defined the Pauli blocking as the regime where $E_F > 0.5 \text{ eV}$ (see the orange-shaded region in Fig. 3b and c of the main text or in Fig. S3b) However, at room temperature and for an electronic mobility of $\mu = 33,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (section III) the change of absorption appears more gradual (see solid traces in Fig. 1c and Fig. 3b, c of the main text).

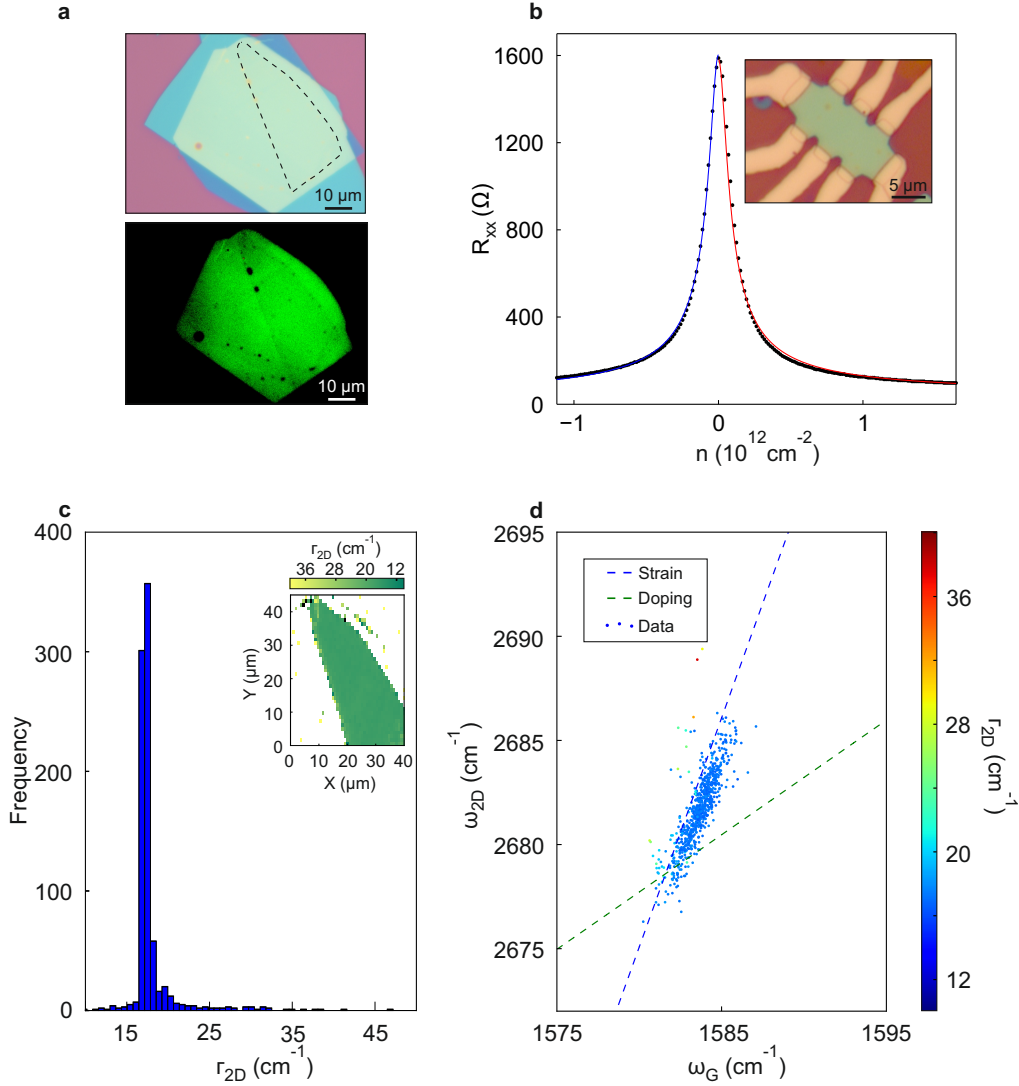
The cross-section of the silicon (Si) waveguide used in Fig. 1c can be seen in Fig. S1a and the obtained mode profile is shown in Fig. S1b, with the modulator structure on top. We repeated the same procedure for each device, where the simulated dimensions and thicknesses of dielectric layers are determined via atomic force microscopy (AFM) inspection. We find very good agreement with the corresponding measurements (compare solid traces with data points in Fig. 1c and Fig. 3b and c of main text).



Supplementary Figure S1. a) Cross-section of the SOI waveguide used for the device in Fig. 1c. The dimensions are as follows: $h_1=10\text{nm}$ (SiO_2 cladding), $h_2=220\text{nm}$, $h_3=2\mu\text{m}$, and $w=750\text{nm}$ (optimized for the TM mode [9]). b) Optical mode profile of the device in Fig. 1c. The device is based on a DL graphene (red dashed lines) modulator separated by a hBN-HfO₂-hBN dielectric on top of a 750nm-wide SOI waveguide (white dashed rectangle, see panel a). The waveguide is optimized for 1550nm wavelength and is designed to carry a single TM mode. The color bar represents the intensity of the electric field $|\vec{E}^2|$ in arbitrary units.

III Quality of the hBN-based graphene modulators

All the modulators of the main manuscript have been fabricated using the hot pickup technique [10] [11]. To characterize the fabrication method, we first analyze the quality of a hBN-graphene-hBN stack fabricated with this technique by means of Raman spectroscopy measurements (Fig. S2c, d). The full-width-half-maximum of the graphene 2D Raman peak (Γ_{2D}) is uniform across the flake surface (see inset of Fig. S2c), with a Γ_{2D} mean value of $\sim 18.1 \text{ cm}^{-1}$ (Fig. S2c), characteristic of high-quality single-layer graphene [12]. The scattering plot indicates low levels of doping and moderate strain (Fig. S2d).

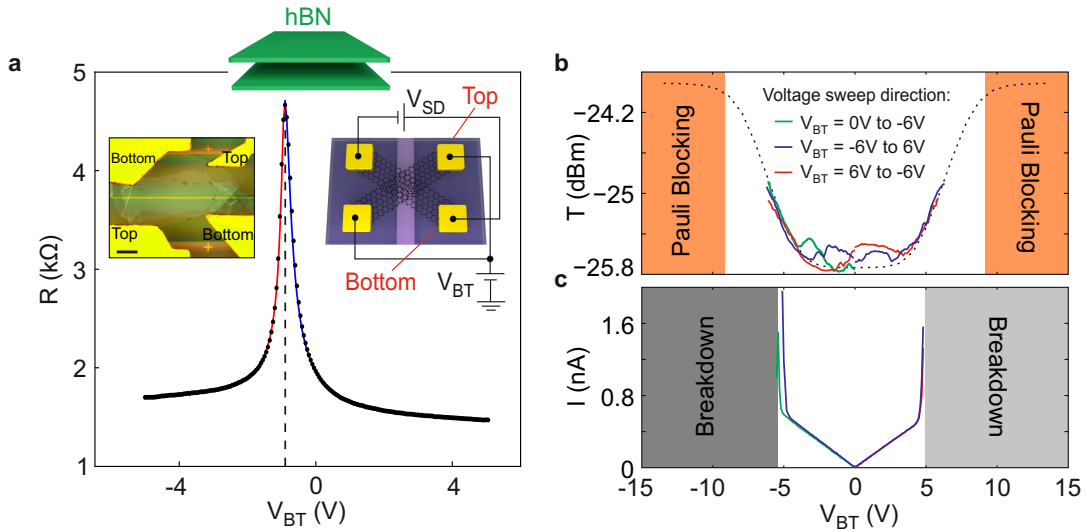


Supplementary Figure S2. a) Optical image of the hBN-graphene-hBN heterostructure fabricated using the hot pick-up technique [10] [11]. The graphene flake (black dashed line in top panel) is optically visible when viewed with enhanced contrast (bottom panel). b) Four-probe longitudinal resistance (R_{xx}) as a function of the charge carrier density (n) of the measured Hall bar device (see inset). c) Histogram plot of the Raman scan (see inset) showing the full-width-half-maximum of the graphene 2D Raman peak (Γ_{2D}). d) Scattering plot of the 2D-peak versus the G-peak frequency (ω_{2D} and ω_G , respectively), where the color bar represents the Γ_{2D} of the recorded spectrum (inset of panel c).

After the Raman inspection, we fabricated a Hall bar device out of the analyzed stack (Fig. S2a, c, d). We extract, considering the conductance model from ref. [13], a residual doping of $n^*=5.94 \times 10^{10} \text{ cm}^{-2}$ and a mobility of 103,000 and 96,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for the electron (red curve) and hole (blue curve) doping, respectively (Fig. S2b).

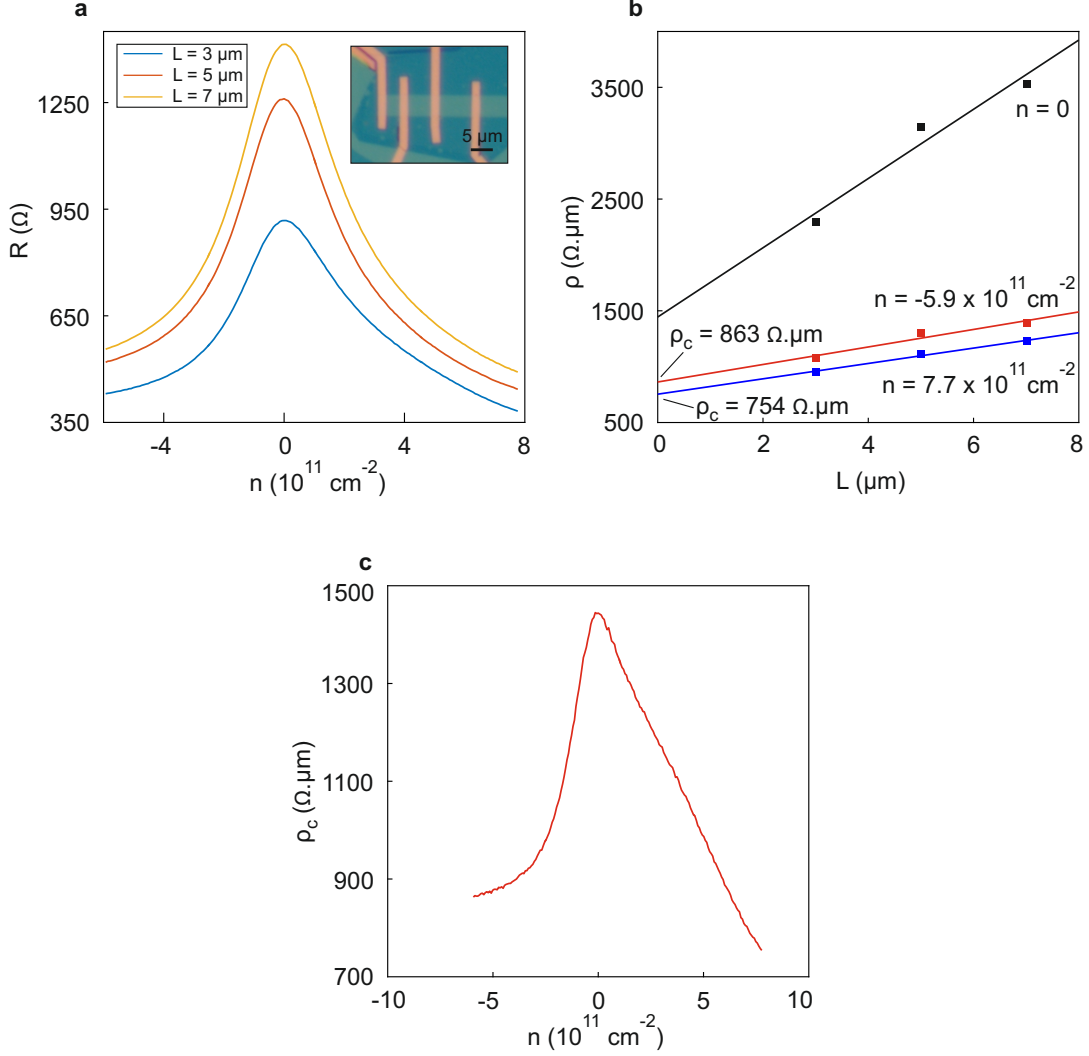
To confirm that the quality of the hBN-encapsulated graphene is conserved when fabricating modulators, we characterized a modulator device fabricated over an optical waveguide substrate (Fig. S3). To obtain the transfer characteristics of the device (Fig. S3a) the top and bottom graphene electrodes were contacted twice (see insets in Fig. S3a for an optical image of the device and its electrical connections). We extracted an electronic mobility as high as 33,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature from the resistance curve in Fig. S3a (see the red and blue fits to the data), considering the conductance model of graphene from ref. [13]. The charge-neutrality point is located at $V_0 = -0.91 \text{ V}$ (dashed vertical line in Fig. S3a), corresponding to a Fermi energy of 0.1722 eV.

To test the electro-optical modulation capabilities of this first device, we measured the transmission as a function of the voltage between the top and bottom graphene electrodes (inset of Fig. S3a). We found a symmetric operation and nearly no hysteresis for multiple sweeps in the forward and backward directions (Fig. S3b), confirming the high quality of the graphene. During the measurements, we continuously monitored the leakage current through the device (Fig. S3c). As observed, the hBN dielectric broke down before reaching the Pauli blocking regime (see grey- and orange-shaded regions in Fig. S3b and c). This is characterized by a sudden increase in current between the top and bottom graphene electrodes (typical breakdown of the dielectric).



Supplementary Figure S3. a) Resistance R of the bottom graphene as a function of the voltage between the top and bottom graphene electrodes (V_{BT}). A source-drain voltage $V_{SD} = 10 \text{ mV}$ is applied between the two terminals of the bottom graphene (see insets for an optical image and the electrical connections, the scale bar is $10 \mu\text{m}$). The blue and red solid lines are fits to the data (black dots). Measurements were taken at room temperature. b) Transmission T through the waveguide as a function of V_{BT} . c) Leakage current I as a function of V_{BT} .

IV Transfer-length-method (TLM) measurements of Cr-Pd-Au 1D edge contacts on hBN-encapsulated graphene



Supplementary Figure S4. a) Two-probe resistance (R) as a function of charge carrier density (n) for different channel length (L). Temperature is 300 K and the source-drain voltage applied is 1 mV. Inset shows an optical image of the TLM device with edge-contacts. b) Two-probe resistivity (ρ) versus L at fixed n . Contact resistivity (ρ_c) is calculated from the least-squares fitting (line) for fixed n [14]. c) ρ_c (calculated as shown in panel b) as a function of n . ρ_c does not saturate here indicating the actual value of ρ_c might be much lower at higher n .

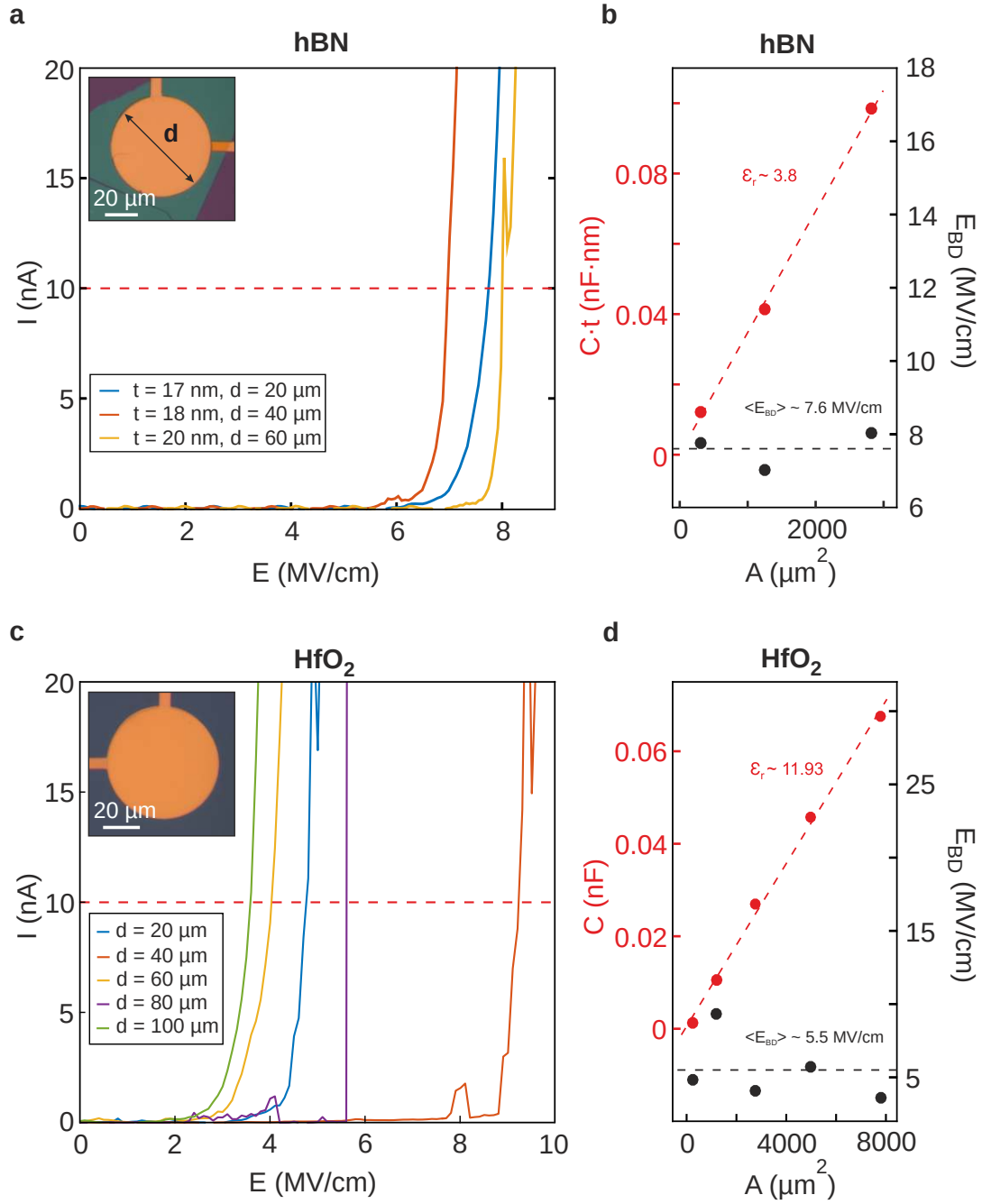
V hBN, HfO₂ and hBN-HfO₂-hBN characterization

To characterize the hBN, HfO₂ and hBN-HfO₂-hBN dielectrics, we fabricated metal-insulator-metal (MIM) capacitors with circular metal electrodes on the top and below the dielectric under study (see insets of Fig. S5). To fabricate the MIM devices, we exfoliated the hBN flakes and dry transferred [10] [11] onto the bottom metal electrodes. The HfO₂ has been grown by atomic layer deposition (ALD) method in a Savannah G1 system from Cambridge Nanotech. The best results were achieved using the recipe E (see table 1). All the HfO₂-based MIM devices analyzed in this section have been fabricated with this ALD recipe E. We measured the leakage current (I) as a function of the applied electric field (E) (Fig. S5a and c) and defined the breakdown field (E_{BD}) as the electric field at a leakage current $I=10\text{nA}$ (see red dashed lines in Fig. S5a and c). As observed in Fig. S5b, d, the extracted E_{BD} values (black data points) do not show any significant dependence on the area of the electrodes (A). We obtain an averaged breakdown field of 7.6 MV/cm and 5.5 MV/cm for the hBN and HfO₂ dielectrics, respectively (Fig. S5b, d).

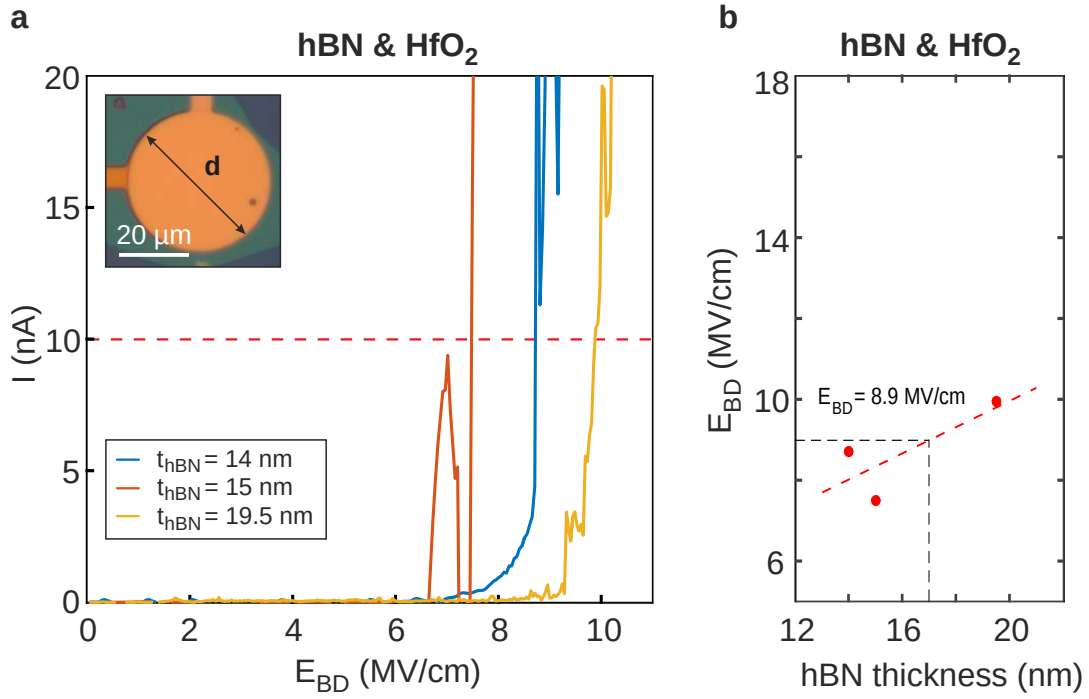
To determine the dielectric constant (ϵ_r), we plotted the capacitance as a function of area and extracted the relative permittivity ϵ_r using a linear fit to the data [15]. For the hBN dielectric, we plot the capacitance scaled by the hBN thickness (Fig. S5b) to account for the different hBN thickness of the devices. We extract a relative permittivity of 3.8 (11.93) for the hBN (HfO₂) dielectric (see red dashed linear fits in Fig. S5b and d). Our results are in good agreement with literature [16] [17] [18].

To characterize the breakdown field of the hBN-HfO₂-hBN dielectric used in the modulators in Fig. 1 and Fig. 3c of the main text and in Fig. S12 in SI, we fabricated three capacitors with a hBN-HfO₂ dielectric. We note that the results of the hBN-HfO₂ MIM capacitor can be directly translated to a hBN-HfO₂-hBN dielectric of the same HfO₂ and total hBN thicknesses. All devices (Fig. S6a) have the same 10nm-thick HfO₂ layer and the total hBN thickness indicated in the inset of Fig. S6a. As expected the breakdown electric field values scale with the hBN thickness (Fig. S6b). We evaluated a breakdown field of $E_{BD} \approx 8.9 \text{ MV/cm}$ (see black dashed lines in Fig. S6b) for the modulator device of the main text (Fig. 1c), i.e. for a 10 nm-thick HfO₂ and a 17 nm total hBN thickness.

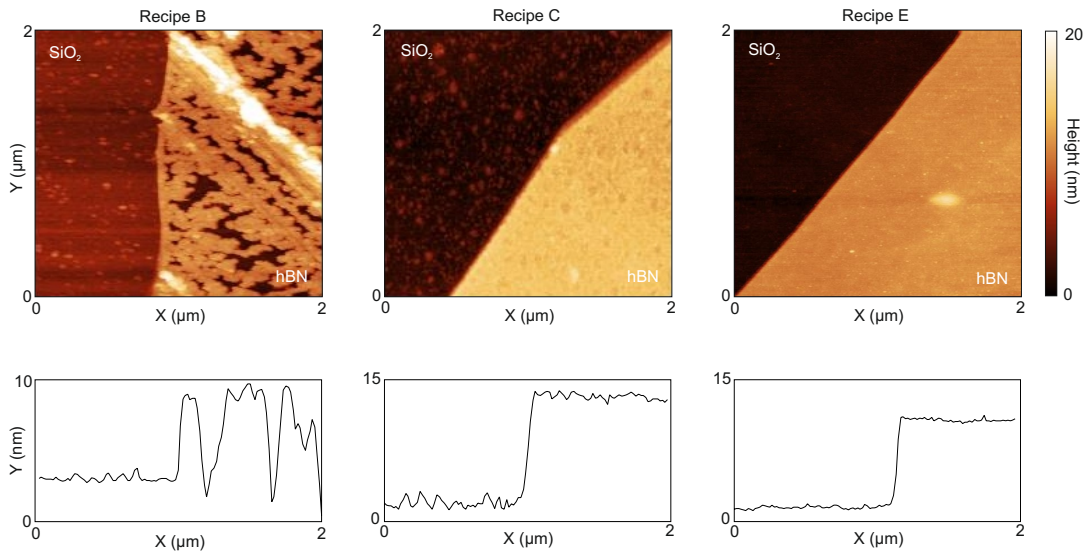
To characterize the quality of the HfO₂ grown over the hBN layer, we analyze the roughness (R_q) extracted by atomic force microscopy (AFM) measurements (see Fig. S7). The roughness indicates how uniform the covering of the HfO₂ layer is, which is crucial for the performance of the dielectric. Furthermore, to confirm that the HfO₂ is suited for Pauli blocking operation (i.e. can withstand Fermi energy $> 0.5 \text{ eV}$ for $\lambda = 1550 \text{ nm}$), we defined the operation field E_o for each HfO₂ growth recipe and compared it with their respective E_{BD} [19]. The comparison of all these parameters (R_q , ϵ_r , E_{BD} and E_o) for the different growth recipes, is summarized in table 1. As observed, the best results are achieved using recipe E (see table 1).



Supplementary Figure S5. a) and c) Leakage current (I) versus electric field (E) between the top and bottom circular metal electrodes (see inset) for hBN (panel a) and HfO₂ (panel c) dielectrics. The dashed red line at $I = 10\ \text{nA}$ represents the current threshold defining the breakdown field E_{BD} (see panels b and d), and d corresponds to the diameter of metal electrodes (see insets). b) and d) Experimentally determined capacitance normalized by the dielectric thickness $C \cdot t$ (panel b), and capacitance C (panel d) (red-colored left axis) as a function of the area $A = \pi(d/2)^2$. The dashed red line are the linear fits used to extract ϵ_r . The black-colored right axis indicates the breakdown field E_{BD} and the black-dashed line the average value of E_{BD} .



Supplementary Figure S6. a) Leakage current (I) versus electric field (E) between the top and bottom circular metal electrodes (see inset) for hBN-HfO₂ dielectrics. The HfO₂ thickness is 10 nm in all three cases. The hBN thicknesses (t_{hBN}) are indicated in the inset. The dashed red line at $I = 10$ nA represents the current threshold defining the breakdown field E_{BD} (see panel b) and d is the metal electrode diameter. b) Breakdown field E_{BD} as a function of the hBN thickness. The red dashed line is a linear fit to the data and the noted breakdown field value of $E_{BD} = 8.9$ MV/cm is the expected E_{BD} for the modulator device in Fig. 1c of the main text (see section X).



Supplementary Figure S7. Atomic force microscopy (AFM) topography scans of 10 nm thick HfO₂ grown over hBN and SiO₂. The root mean square roughness values (R_q) on hBN (analyzed for a 0.4 μ m² area) for recipe B, C and D are 3.33, 0.52 and 0.26 nm respectively. For more details (growth parameters) refer to table 1

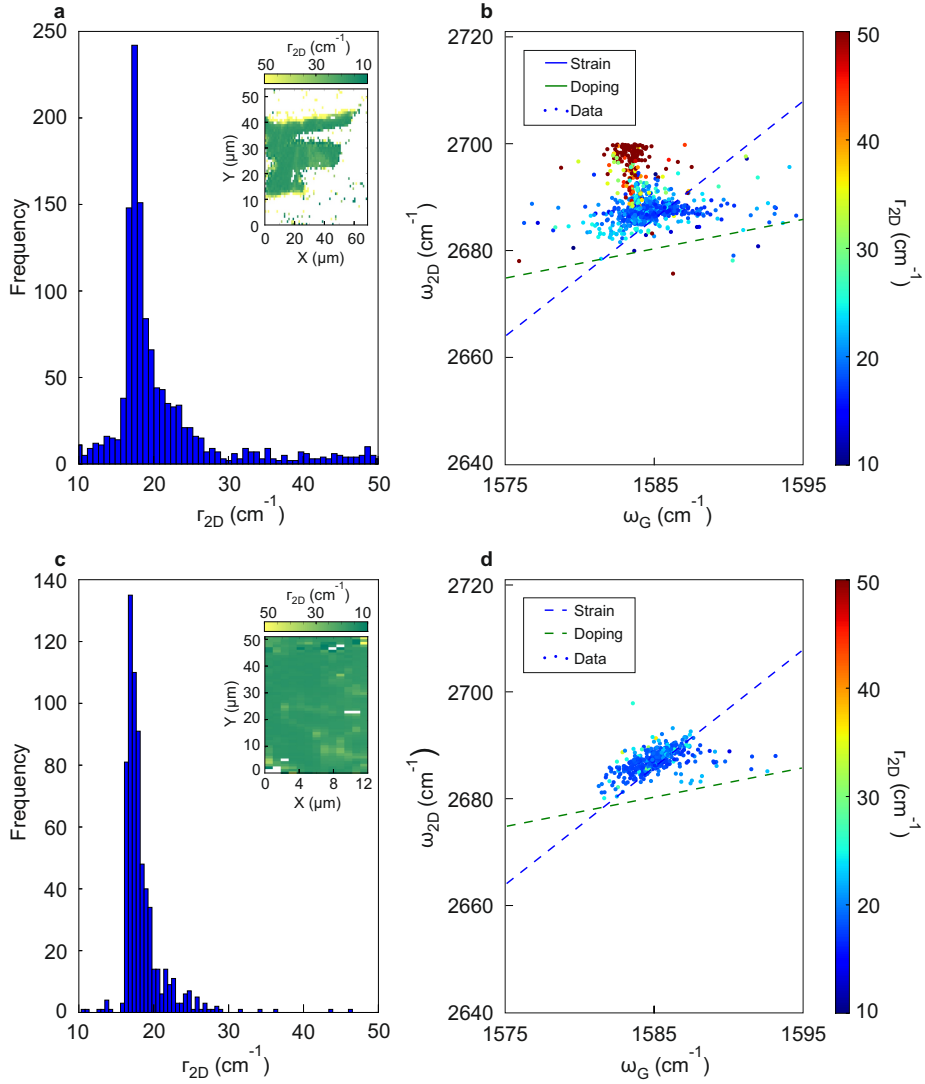
Supplementary Table 1. Optimization growth of HfO₂.

Recipe	T(°C)	Purge time (s)	Seed layer	t (nm)	Rq (nm)	ϵ_r	E _o (MV/cm)	E _{BD} (MV/cm)
A	250	5	-	30	-	12.77	2.8	-
B	250	5	-	10	3.33	10.99	3.28	2.32
C	200	20	-	10	0.52	5.4	6.66	5.71
D	250	5	2nm Si	12	2.98	6.74	5.34	6.76
E	250	5	2nm SiO ₂	12	0.26	11.93	3.02	5.5

- The purge time applies after the treatment with H₂O and Tetrakis(dimethylamido)-hafnium (TDMAH) and t represents the thickness of HfO₂ and the seed layer.
- The root mean square roughness (Rq) is analyzed in a 0.4 μm^2 area for HfO₂ grown over hBN.
- E_o (Operation field) is the field required to withstand Fermi energy larger than 0.5 eV (Pauli blocking regime with $\lambda = 1550$ nm) [19].

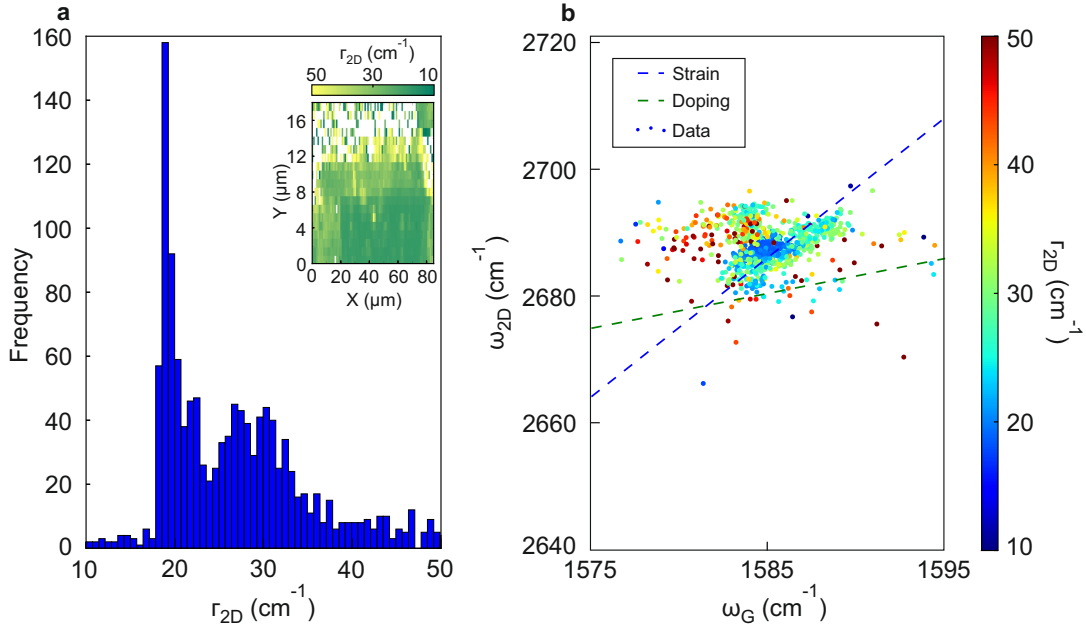
VI Raman characterization

To quantify the degradation in graphene quality due to HfO_2 growth, we compared the Raman spectra of hBN based EA modulators (see Fig. S8a and b) and hBN- HfO_2 -hBN based EA modulators (see Fig. S8c and d). Both devices show very low doping, strain and comparable histograms (see Fig. S8b and d), with mean full-width-half maximum of the graphene 2D Raman peak (Γ_{2D}) ~ 24.1 and 18.4 cm^{-1} , respectively, characteristic of high-quality single-layer graphene [12]. This analysis suggested the quality of DL modulator is independent of the dielectric between two graphene electrodes and hence, HfO_2 layer does not seem to degrade the quality of graphene.



Supplementary Figure S8. a) and c) Histogram plot of the Raman scan (see inset) showing the full-width-half-maximum of the graphene 2D Raman peak (Γ_{2D}) of hBN based EA modulator (panel a) and hBN- HfO_2 -hBN based EA modulator (panel c) over the waveguide. b) and d) Scattering plot of the 2D-peak versus the G-peak frequency (ω_{2D} and ω_G , respectively) of hBN based EA modulator (panel b) and hBN- HfO_2 -hBN based EA modulator (panel d), where the color bar represents the Γ_{2D} of the recorded spectrum (inset of the panel a and c).

To check the quality of our DL graphene EA modulator presented in the main text (see Fig. 1), we measured the Raman spectra of the full modulator (hBN-graphene-hBN-HfO₂-hBN-graphene-hBN) over the silicon waveguide (see Fig. S9a). The analyzed data shows scattering plot and histogram, with average values of the 2D-peak full-width-half-maxima $\Gamma_{2D} = 27.9 \text{ cm}^{-1}$, low doping and moderate levels of strain, characteristic of a high quality graphene (see Fig. S9b) [12]. The high value of Γ_{2D} in this device is due to the very thin bottom hBN (2.9 nm) and highly rough SiO₂ substrate.



Supplementary Figure S9. a) Histogram plot of the Raman scan (see inset) showing the full-width-half-maximum of the graphene 2D Raman peak (Γ_{2D}) of the EA modulator ((hBN-graphene-hBN-HfO₂-hBN-graphene-hBN) over the silicon waveguide presented in the main text (see Fig. 1). b) Scattering plot of the 2D-peak versus the G-peak frequency (ω_{2D} and ω_G , respectively) of the same device, where the color bar represents the Γ_{2D} of the recorded spectrum (inset of the panel a).

VII Relation between E_F and V_{BT}

To compare the breakdown of the different dielectrics, we represent the transmission curve of the modulators as a function of the Fermi energy E_F at the graphene electrodes. Representing the transmission as a function of E_F instead of V_{BT} allows us to rule-out the different thicknesses and relative permittivity of the compared dielectrics. Neglecting the contribution of the quantum capacitance, we define the Fermi energy as:

$$E_F = \text{sgn}(n_s) \hbar \nu_F \sqrt{\pi |n_s|}, \quad (10)$$

where $\hbar$ and ν_F are defined in section I, and the charge carrier density at the graphene electrodes n_s relates to V_{BT} as follows:

$$V_{BT} = \frac{q S n_s}{C_{ox}}. \quad (11)$$

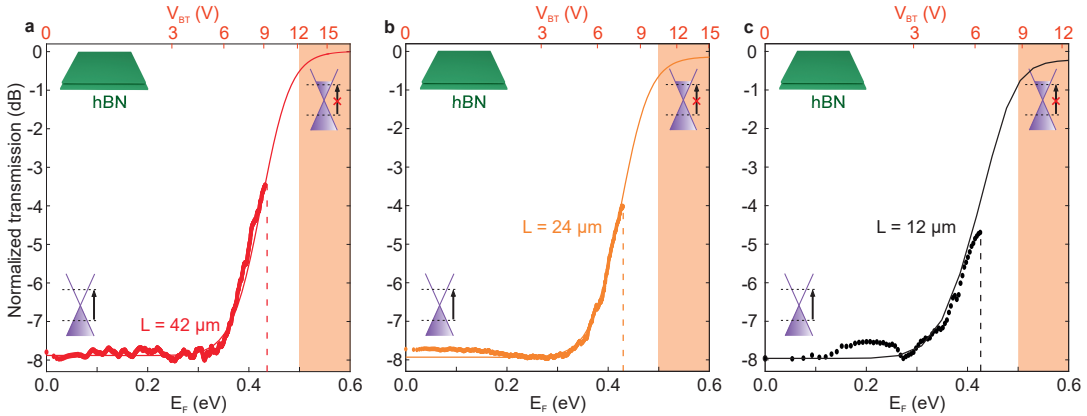
S is the area of the capacitor (defined by the overlap area between the top and bottom graphene electrodes), q the elementary charge and C_{ox} the total capacitance, defined for modulators with a hBN-hBN dielectric as:

$$\frac{1}{C_{ox}} = \frac{1}{C_{hBN_1}} + \frac{1}{C_{hBN_2}} = \frac{d_{hBN_1} + d_{hBN_2}}{S \epsilon_{hBN}}, \quad (12)$$

and for modulators with a hBN-HfO₂-hBN dielectric as:

$$\frac{1}{C_{ox}} = \frac{1}{C_{hBN_1}} + \frac{1}{C_{HfO_2}} + \frac{1}{C_{hBN_2}} = \frac{d_{hBN_1} + d_{hBN_2}}{S \epsilon_{hBN}} + \frac{d_{HfO_2}}{S \epsilon_{HfO_2}}. \quad (13)$$

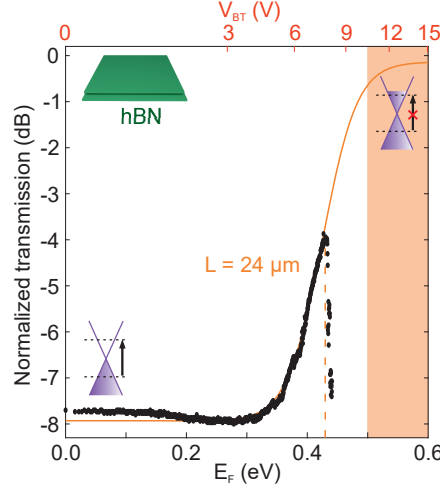
d_{hBN_1} , d_{hBN_2} and d_{HfO_2} are the thicknesses of the hBN layers and the HfO₂ oxide in between the top and bottom graphene electrodes. The relative permittivity $\epsilon_{hBN} = 3.8$ is experimentally obtained (see section V). The relative permittivity for hafnia $\epsilon_{HfO_2} = 9.5$ is extracted from the comparison between simulation and data (see section X). After the conversion from V_{BT} to E_F , we plot the individual traces of Fig. 3b in the main text as a function of both E_F and V_{BT} (see Fig. S10).



Supplementary Figure S10. Individual traces of Fig. 3b of main text plotted with duals axis E_F and V_{BT} .

VIII Dielectric breakdown of a modulator

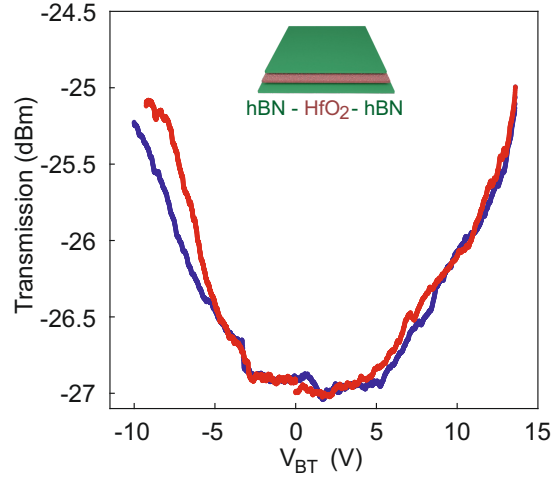
To understand the effect of dielectric breakdown on transmission, we intentionally swept V_{BT} up to high voltages. We found when V_{BT} reaches the breakdown of the dielectric, the transmission drops suddenly, making the device inoperative. As an example, we add below the complete transmission trace of the $L = 24 \mu\text{m}$ long device from Fig. 3b of the main text.



Supplementary Figure S11. Transmission curve of the $L = 24 \mu\text{m}$ long device in Fig. 3b of the main text showing the effect of the dielectric breakdown on the transmission. The data points are measurements and the solid curve is simulation.

IX Hysteresis measurements

Additional to the hBN-HfO₂-hBN based modulators presented in Fig. 1 and Fig. 3c of the main text, we characterize the hysteresis of a third hBN-HfO₂-hBN based modulator (see Fig. S12) to further support the reduced hysteresis and the symmetric operation enabled by this 2D-3D dielectric combination. This third hBN-HfO₂-hBN device shows the lowest modulation efficiency, mainly due to its shorter length ($L=15\mu m$).

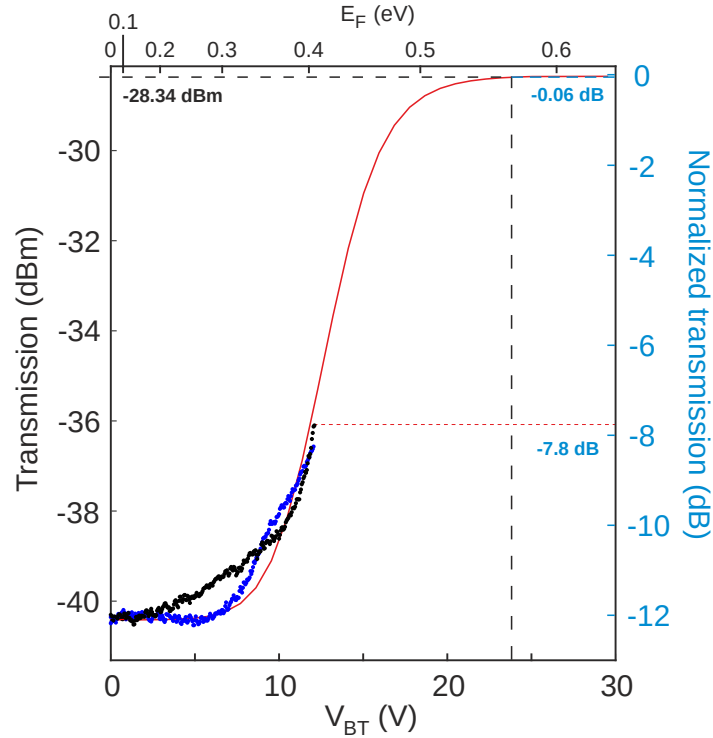


Supplementary Figure S12. Transmission curves as a function of V_{BT} for a DL graphene modulator with a hBN-HfO₂-hBN dielectric and a length $L = 15\mu m$. The forward and backward voltage sweeps (blue and red, respectively) show no major hysteresis.

X Evaluation of the Insertion Loss (IL)

To evaluate the Insertion Loss (IL) of our devices, we compare the measured and the simulated (see section II) transmission curves. Fig. S13 shows the simulated transmission (in red) overlapping the experimental transmission curves of Fig. 1c (shown in black and blue colors for the forward and backward voltage sweeps, respectively). We emphasize that the simulated device has the same geometry as the real device (refer to Fig. 1c), meaning a width of the Si waveguide core of 750 nm , a core height of 220 nm , a cladding thickness of 10 nm , a device length of $60\text{ }\mu\text{m}$, a bottom hBN thickness of 5 nm , a top hBN of 21 nm , a total hBN dielectric of 17 nm , a HfO_2 layer of 10 nm , a metal contact distance of 2680 nm , a metal contact thickness of 48 nm and a 450 nm -wide overlap region between the bottom and top graphene electrodes. We use a hBN relative permittivity of 3.8 (see section V) but the HfO_2 permittivity has been lowered to 9.5 in order to reproduce the experimental transmission curves. The HfO_2 quality is expected to degrade when grown over hBN (see section V). For all the calculations throughout this work, we consider the relative permittivity of HfO_2 over hBN to be $\epsilon_{\text{HfO}_2}=9.5$, as estimated from the comparison between simulations and experimental transmission curves.

To evaluate the IL of our device, we first introduce the intrinsic IL. As widely accepted in literature, the intrinsic IL of a graphene modulator is solely determined by the graphene quality, i.e. the electronic mobility (refer to Fig. 2d and Fig. 3c, d of [20], Fig. 2b and Fig. 4b of [21], Fig. 3b, d of [9] and Fig. 6a of [19]). In our case, we experimentally proved with a functional modulator (see section III) a graphene mobility as high as $33,000\text{ cm}^2/\text{Vs}$ at



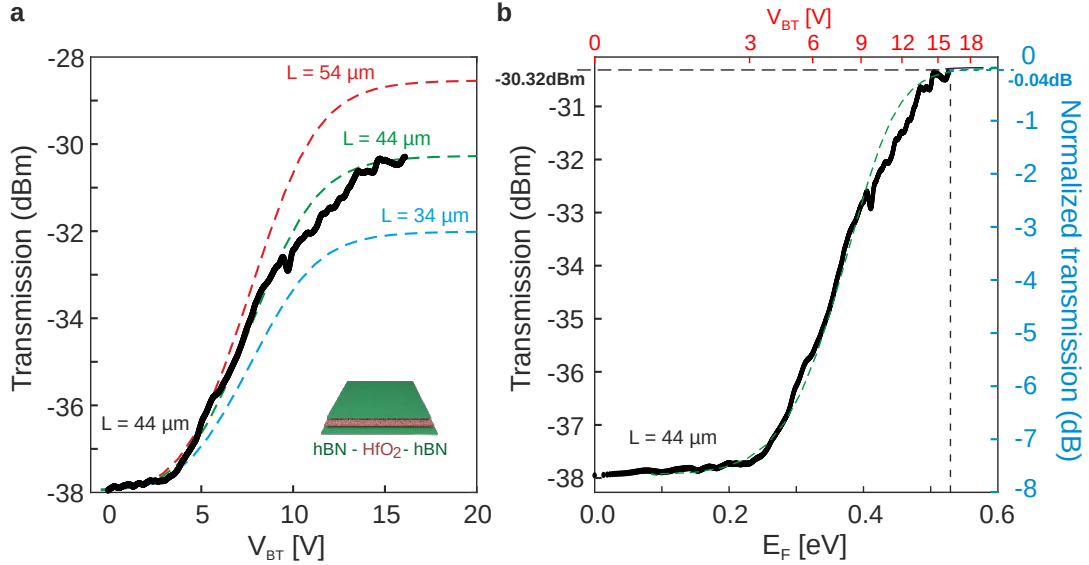
Supplementary Figure S13. Transmission curves as a function of V_{BT} and E_F for the modulator with a hBN- HfO_2 -hBN dielectric in Fig. 1c. The forward and backward voltage sweeps (black and blue, respectively) overlap the simulation trace (in red). We marked in black the IL due to the fabrication residues along the waveguide $IL \approx 28.34\text{ dB}$ and in blue the measured $IL \approx 7.8\text{ dB}$ and the potential $IL \approx 0.06\text{ dB}$.

room temperature. This value of mobility corresponds to a scattering time of $\tau = 1.5 \text{ ps}$, or equivalently, to a scattering rate of $\hbar\Gamma/2 = 0.45 \text{ meV}$ (evaluated at $E_F = 0.4 \text{ eV}$). In that respect, we emphasize that these are the highest reported values for graphene modulators to date, which corresponds to a record low intrinsic $IL \approx 0.024 \text{ dB}$ (estimated from Fig. 2d of [20]).

In practice, however, the effective IL is limited by how far the V_{BT} voltage can be increased. Meaning that the breakdown of the dielectric determines whether the intrinsic IL (dictated by the quality of graphene) can be achieved (refer to Fig. S13). We point out that the maximum voltage applied in Fig. 1c of the main text (or in Fig. S13) is $V_{BT} = 12.1 \text{ V}$, or equivalently $E_F = 0.41 \text{ eV}$ (refer to section VII). This value is far from the breakdown voltage of the hBN-HfO₂-hBN dielectric (see Fig. 3c and section V). To evaluate the E_F^{max} (i.e. the Fermi energy at the dielectric breakdown) for the device in Fig. 1c, we studied the dielectric characteristics of MIM capacitors with a hBN-HfO₂ dielectric combination (see section V). The maximum breakdown field of the hBN-HfO₂ dielectric with a 10 nm thick HfO₂ and a 17 nm total hBN thickness (the same thicknesses as the modulator device in Fig. 1c) is $E_{BD} \approx 8.9 \text{ MV/cm}$ (see black dashed lines in Fig. S6 of section V). This breakdown field corresponds to a maximum Fermi Energy of $E_F^{max} \approx 0.57 \text{ eV}$ (also indicated by a black star in Fig. 3a of the main text), determined through the relation:

$$E_F^{max} = \hbar\nu_F \sqrt{\pi\epsilon_0\epsilon_{rel}E_{BD}/q}, \quad (14)$$

where ϵ_{rel} is the equivalent dielectric constant of a hBN-HfO₂-hBN dielectric with a 10 nm-thick HfO₂ layer and total hBN thickness of 17 nm and considering the relative permittivity for hBN and HfO₂ as $\epsilon_{hBN} = 3.8$ and $\epsilon_{HfO_2} \approx 9.5$, respectively (see section VII for details). This



Supplementary Figure S14. a) Measured transmission (black data points) as a function of V_{BT} for the modulator device in Fig. 3c. The incoming power was set to $P_{in} = 0 \text{ dBm}$. The simulated transmission of a device with the same length as the measured modulator ($L = 44 \mu\text{m}$) is shown by the dashed green trace. The red and blue dashed traces correspond to the simulated transmission of a $L = 54 \mu\text{m}$ and $L = 34 \mu\text{m}$ long devices, respectively. b) Measured transmission (black data points) shown in a) as a function of E_F . The V_{BT} -axis is also indicated (in red). The transmission (black left axis) includes the fiber-to-fiber losses of a pristine waveguide (16 dB) and the fabrication impurities deposited along the waveguide (evaluated as $30.32 \text{ dB} - 16 \text{ dB} = 14.32 \text{ dB}$). The normalized transmission (blue right axis) only considers the losses of the modulator device itself and therefore reflects the true performance of the device.

value of $E_F^{max} \approx 0.57$ eV corresponds to a $V_{BT}^{max} \approx 24$ V (see black vertical dashed line in Fig. S13) and determines a potential IL ≈ 0.06 dB considering the normalized transmission (right-axis in Fig. S13), i.e. neglecting the absorption due to polymer residues deposited along the waveguide during the fabrication processes and the fiber-to-fiber losses of a pristine waveguide. We note that the normalized transmission only considers the losses of the modulator device itself and therefore reflects the true performance of the device.

If we include all the unwanted losses, i.e. we consider the measured raw transmission (left axis in Fig. S13), we obtain a measured IL ≈ 28.34 dB (marked in black in Fig. S13). This value is in agreement with the transmission losses of a device-free Si-based optical waveguide that followed the same fabrication steps as the measured device (27.75 dB). The IL of the modulator device in Fig. 1c is IL ≈ 7.8 dB (marked in blue in Fig. S13, measured ER ≈ 4.4 dB), with a potential IL as low as IL ≈ 0.06 dB (marked also in blue in Fig. S13), meaning a potential ER ≈ 12 dB. We note that this potential IL is achievable experimentally from the quality of our graphene devices and the robustness of the hBN-HfO₂-hBN dielectric.

We repeat the same analysis for the second hBN-HfO₂-hBN device (Fig. 3c). We also compare the measured (black data points in Fig. S14) and simulated (green dashed trace in Fig. S14) transmission curves. To highlight the agreement between simulation and data, we plot in Fig. S14a the simulation curves from a longer ($L = 54 \mu m$, dashed red trace) and a shorter ($L = 34 \mu m$, dashed blue trace) device. Neither the slope nor the saturation region (Pauli blocking at high V_{BT}) of these simulated traces (red and green dashed traces in Fig. S14a) match the measured transmission (black dots in Fig. S14a).

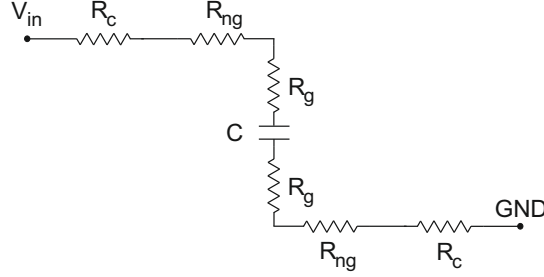
The IL of this second hBN-HfO₂-hBN device is much lower compared to the device in Fig. 1c (compare an IL ≈ 0.04 dB to an IL ≈ 7.8 dB, marked in blue in Fig. S14b and Fig. S13, respectively) since the E_F (alternatively V_{BT}) has been pushed up to the Pauli blocking regime, until the dielectric breakdown ($E_F^{max} = 0.54$ eV, vertical black dashed line in Fig. S14b). We emphasize that the measured IL ≈ 30.32 dB (marked in black in Fig. S14b) includes the fiber-to-fiber losses from the pristine waveguide (16 dB) and the polymer residues deposited along the waveguide during the fabrication processes (evaluated as 30.32 dB - 16 dB = 14.32 dB). This value (14.32 dB) is in agreement with the averaged losses (~ 14 dB) measured in device-free optical waveguides that followed the same fabrication steps.

XI f_{-3dB} bandwidth

The electrical bandwidth f_{-3dB} of the device can be determined as

$$f_{-3dB} = \frac{1}{2\pi RC} \quad (15)$$

where R and C are the total resistance and capacitance of the device.



Supplementary Figure S15. Equivalent RC electronic circuit of DL graphene EA modulator. Here V_{in} is the input voltage, R_c is contact resistance, R_g is gated graphene resistance, R_{ng} is non gated graphene resistance, C is the capacitance of the device, and GND is ground.

In case of a DL graphene EA modulator (see Fig. S15), R can be defined as:

$$R = 2(R_c + R_g + R_{ng}) \quad (16)$$

$$R_c = \frac{\rho_c}{L} \quad (17)$$

where ρ_c is contact resistivity ($808.5 \, \Omega\mu\text{m}$ average contact resistivity of holes and electrons side extracted from TLM measurements, see section IV) and L is the length of the contact ($60 \, \mu\text{m}$ for the device presented in the main text).

$$R_g = \frac{W}{2\sigma_g L} \quad (18)$$

and

$$R_{ng} = \frac{W}{\sigma_{ng} L} \quad (19)$$

with $\sigma = nq\mu$ ($\mu = 33,000 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (see section III), n is evaluated at $E_F = 0.4 \, \text{eV}$ (Pauli blocking) for gated region and $0.1722 \, \text{eV}$ (intrinsic doping evaluated from hBN modulator in supplementary section III) for the non-gated region).

One can further deduce the C of the device by considering three capacitance in series: top layer graphene quantum capacitance (C_Q^{top}), parallel plate capacitance (C_{ox}), and bottom layer graphene quantum capacitance (C_Q^{bottom}) [6] [19].

$$\frac{1}{C} = \frac{1}{C_Q^{top}} + \frac{1}{C_{ox}} + \frac{1}{C_Q^{bottom}} \quad (20)$$

C_Q is defined as

$$C_Q = \frac{2WLqk_B T}{\pi(\hbar\nu_F)^2} \log \left[2 \left(1 + \cosh \frac{E_F}{k_B T} \right) \right] \quad (21)$$

where $E_F = 0.4 \, \text{eV}$ (Pauli blocking), $W = 450 \, \text{nm}$ is overlap between two graphene (capacitor width), $L = 60 \, \mu\text{m}$ and

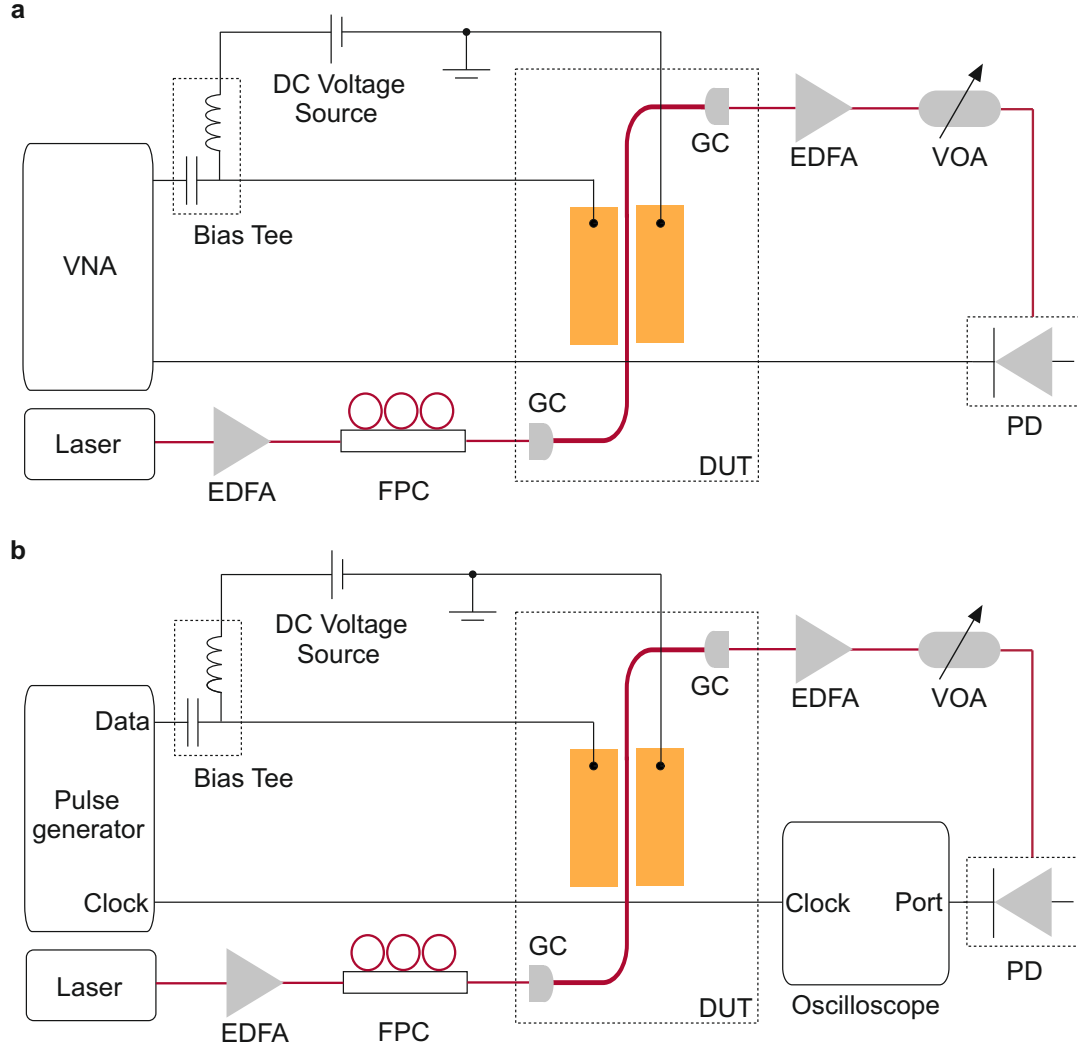
$$C_{ox} = \frac{WL\epsilon_0\epsilon_r}{d} \quad (22)$$

where ϵ_0 is vacuum permittivity, $d = d_{hBN} + d_{HfO_2}$ and ϵ_r is defined as:

$$\epsilon_r = (d_{hBN} + d_{HfO_2}) \cdot \left(\frac{d_{hBN}}{\epsilon_{hBN}} + \frac{d_{HfO_2}}{\epsilon_{HfO_2}} \right)^{-1} \quad (23)$$

where $d_{hBN} = 17$ nm, $d_{HfO_2} = 10$ nm, $\epsilon_{hBN} = 3.8$, $\epsilon_{HfO_2} = 9.5$ for the device presented in the main text (see sections V and X).

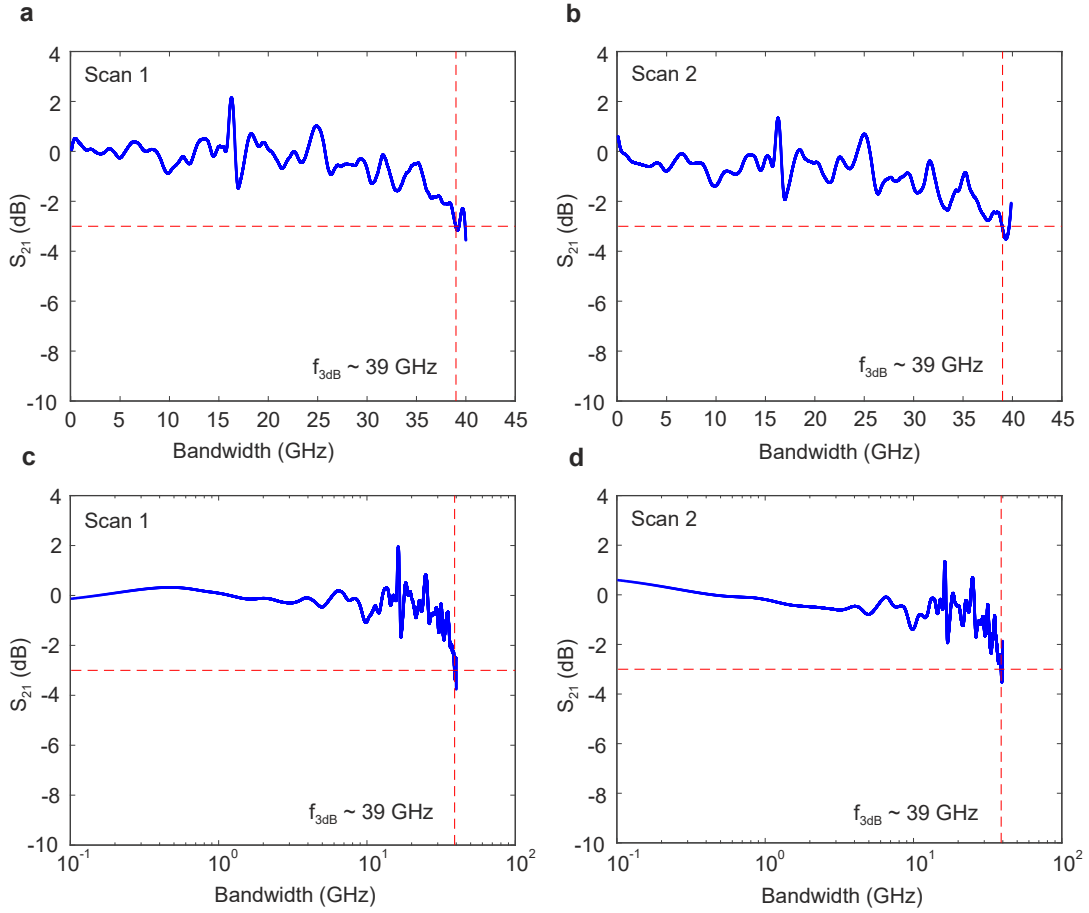
XII High-frequency measurements setup



Supplementary Figure S16. Set-up for measuring the EA modulator electro-optic response of panel b, figure 2 of the main text up to 40 GHz (Vector network analyzer (VNA) limited). The optical path (in red) is composed of a laser source ($\lambda = 1550$ nm), an erbium-doped fiber amplifier (EDFA), a fiber-polarization controller (FPC), a variable optical attenuator (VOA) and a high-speed photodetector (PD). The device under test (DUT) consists of two grating couplers (GC), the optical waveguide and the graphene EAM (refer to figure 1 of the main text). The electronic path (in black) connects VNA, DC voltage source and device through a bias tee.

XIII Frequency response measurements

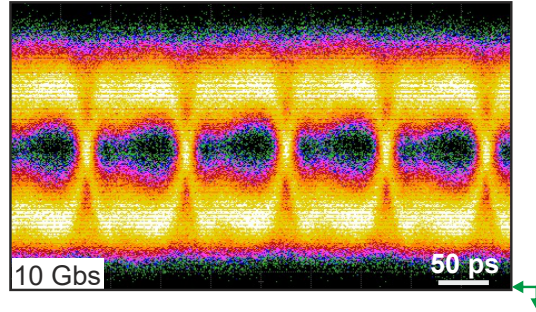
We recorded a second frequency response measurement (scan 2 in Fig. S17) from the device in Fig. 1. Both 1 and 2 scans (scan 1 corresponds to the frequency response in Fig. 2b of the main text) have been measured with no temporal averaging and a low intermediate frequency filtering (IF BW) of 1kHz to 10KHz. Both measurements (Fig. S17) are without de-embedding (i.e. without subtracting the contribution from setup).



Supplementary Figure S17. Two different frequency response measurements (a-c and b-d) of the same device as in Fig. 1 and 2 of the main text, represented in a linear and a log scale (panels a-b and c-d, respectively).

XIV 10 Gbps eye diagram measurement

We also measured our device at lower speeds. Fig. S18 is an eye-diagram measured at 10 Gbps for the device presented in Fig. 1, and 2 of the main text.



Supplementary Figure S18. Eye-diagram measured at 10Gbps (SNR=2.1dB). The green arrow indicates the $0W$ baseline.

XV Comparison of graphene-based EA modulators

Supplementary Table 2. Static characterization comparison for graphene-based EA modulators.

Reference	Wavelength (nm)	Modulation efficiency (dB/V)	Extinction ratio ER (dB)	Insertion Loss IL (dB)	ER/IL
Single-layer graphene					
[22]	1530	1.2 [*]	4	NA	NA
[9]	1550	1.22 [*]	5.2	3.8 †	1.36 †
[23]	1550	1	3.5	NA	NA
[24]	1550	0.44 [*]	1.2	40 ‡	0.03 ‡
Double-layer graphene					
[25]	1537	1.5 [*]	6.5	4 †	1.625 †
[26]	1550	0.13 [*]	2	0.9 ‡	2.22 ‡
[27]	1550	1.42 [*]	16	3.3 †	4.8 †
[28]	1550	0.4 [*]	1.4	NA	NA
[21]	1550	1.37 [*]	3	13 ‡	0.23 ‡
Dev. in Fig. 1c (L.B.)	1550	2.2 [*]	4.4	7.8 ‡	0.57 ‡
Dev. in Fig. 1c (U.B.)	1550	2.2 [*]	12	0.06 ‡	200 ‡
Dev. in Fig. 3c	1550	1.3 [*]	7.8	0.04 ‡	195 ‡

Note:

^{*} These values are extracted from a linear fit in a 0.5V interval.

† The reported IL and ER/IL values include the fabrication impurities deposited along the waveguide as well as non-uniform charge distribution in the graphene and hence, cannot be directly compared to our values.

‡ The reported IL and ER/IL values are attributed to the graphene EA modulator device itself.

- The calculation of the ER/IL lower bound (LB) for device in Fig. 1c considers the measured $ER \approx 4.4 \text{ dB}$ and $IL \approx 7.8 \text{ dB}$. The upper bound (UB) considers the potential $ER \approx 12 \text{ dB}$ and $IL \approx 0.06 \text{ dB}$ (refer to section X for details).

- Both devices in Figs. 1c and 3c are based on a hBN-HfO₂-hBN dielectric.

Supplementary Table 3. Dynamic characterization comparison for graphene-based EA modulators.

Reference	Footprint (μm^2)	EO band-width f_{3dB} (GHz)	Maximum bit rate (Gbps)	Power consumption (fJ/bit)	Dynamic ER (dB)	Normalized dynamic ER (dB/ μm)
Single-layer graphene						
[22]	25	1.2	NA	NA	NA	NA
[9]	37.5	5.9	10	350	2.3 @2.5 V	0.046
[23]	48	5	10	NA	1.4 @1.1 V	0.014
[24]	20	NA	NA	NA	NA	NA
Double-layer graphene						
[25]	40	1	NA	1000	NA	NA
[26]	18	35	NA	1400	NA	NA
[27]	150	0.67	NA	NA	NA	NA
[28]	25	NA	NA	NA	NA	NA
[21]	78	30	50	NA	1.3 @3.5 V	0.011
Dev. in Fig. 1c	27	> 40	40	159.9	5.2 @3.5 V	0.086

XVI Optical power penalty calculations

We calculated the optical power penalty (on-state loss, loss due to on/off and eye-closure penalty) of the modulators in Fig. 1c and Fig. 3c of the main text. The calculations are based on ref. [29, 30] and are summarized in Table 4 together with the comparison with state-of-the-art single- and double-layer graphene modulators.

The upper bound of the optical power penalty (OPP) for the device in Fig. 1c (marked UB in Table 4) has been calculated from the measured ER and IL (see section X). The lower bound has been evaluated considering the potential IL derived in section X ($IL \approx 0.06 \text{ dB}$). We emphasize that the reported lower bound for the OPP value is the lowest reported value so far, amongst all graphene-based modulators (refer to Table 4).

Supplementary Table 4. Penalty calculations for graphene-based EA modulators.

Reference	On-state loss	Loss due to on/off	Eye-closure penalty	OPP* (dB)
Single-layer graphene				
[9]	0.126 †	2.16 †	-0.536 †	8.37 †
[24]	~ 0 ‡	1.16 ‡	-0.137 ‡	49.2 ‡
Double-layer graphene				
[25]	0.089 †	2.73 †	-0.634 †	8.11 †
[26]	0.513 ‡	1.29 ‡	-0.226 ‡	8.24 ‡
[27]	0.012 †	20.4 †	-0.951 †	6.42 †
[21]	0.025 ‡	1.5 ‡	-0.332 ‡	19.0 ‡
Dev. in Fig. 1c (UB)	0.06 ‡	1.89 ‡	-0.47 ‡	12.7 ‡
Dev. in Fig. 1c (LB)	0.062 ‡	8.42 ‡	-0.88 ‡	3.35 ‡
Dev. in Fig. 3c	0.164 ‡	3.51 ‡	-0.72 ‡	3.84 ‡

Note:

* The optical power penalty is defined as $OPP = (P_{\text{out}}(1) - P_{\text{out}}(0)) / (2 \times P_{\text{in}})$, where $P_{\text{out}}(1)$, and $P_{\text{out}}(0)$ are the high and low levels of the optical power output extracted from the ER and IL during static measurements. P_{in} is the input optical power [29, 30].

† The reported IL and ER/IL values include the impurities from the fabrication along the waveguide as well as non-uniform charge distribution in the graphene and hence, cannot be directly compared to our values.

‡ The reported IL and ER/IL values are attributed to the graphene EA modulator device itself.

- The calculation of the upper bound (UB) for the OPP of device in Fig. 1c considers the total measured $IL \approx 7.8 \text{ dB}$, whereas the lower bound (LB) is calculated using the potential $IL \approx 0.06 \text{ dB}$ (section X).

References

- [1] Goncalves, P. A. D. & Peres, N. M. R. An introduction to graphene plasmonics. *World scientific, Singapore* (2016).
- [2] Hanson, G. W. Dyadic Green's functions and guided surface waves for a surface conductivity model of graphene. *J. Appl. Phys.* **103** (2008).
- [3] Sarma, S. D., Adam, S. & Rossi, E. Electronic transport in two-dimensional graphene. *Rev. Mod. Phys.* **83** (2011).
- [4] Yan, J., Zhang, Y., Kim, P. & Pinczuk, A. Electric field effect tuning of electron-phonon coupling in graphene. *Phys. Rev. Lett.* **98**, 166802 (2007).
- [5] Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).
- [6] Xia, J., Chen, F., Li, J. & Tao, N. Measurement of the quantum capacitance of graphene. *Nature Nanotechnology* **4**, 505–509 (2009).
- [7] Yan, J., Zhang, Y., Kim, P. & Pinczuk, A. Electric field effect tuning of electron-phonon coupling in graphene. *Phys. Rev. Lett.* **98** (2007).
- [8] Falkovsky, L. A. Optical properties of graphene and IV–VI semiconductors. *Phys.-Usp.* **51**, 887–897 (2008).
- [9] Hu, Y. *et al.* Broadband 10 Gbps operation of graphene electro-absorption modulator on silicon. *Laser & Photonics Reviews* **10**, 307–316 (2016).
- [10] Pizzocchero, F. *et al.* The hot pick-up technique for batch assembly of van der Waals heterostructures. *Nature Communications* **7**, 11894 (2016).
- [11] Purdie, D. G. *et al.* Cleaning interfaces in layered materials heterostructures. *Nature Communications* **9**, 5387 (2018).
- [12] Lee, J. E., Ahn, G., Shim, J., Lee, Y. S. & Ryu, S. Optical separation of mechanical strain from charge doping in graphene. *Nature Communications* **3**, 1024 (2012).
- [13] Kim, S. *et al.* Realization of a high mobility dual-gated graphene field-effect transistor with Al_2O_3 dielectric. *Applied Physics Letters* **94**, 062107 (2009).
- [14] Wang, L. *et al.* One-dimensional electrical contact to a two-dimensional material. *Science* **342**, 614–617 (2013).
- [15] Yota, J., Shen, H. & Ramanathan, R. Characterization of atomic layer deposition HfO_2 , Al_2O_3 , and plasma-enhanced chemical vapor deposition Si_3N_4 as metal-insulator-metal capacitor dielectric for GaAs HBT technology. *Journal of Vacuum Science & Technology A* **31**, 1–9 (2013).
- [16] Hattori, Y., Taniguchi, T., Watanabe, K. & Nagashio, K. Anisotropic dielectric breakdown strength of single crystal hexagonal boron nitride. *ACS Appl. Mater. Interfaces* **8**, 27877–27884 (2016).
- [17] Hattori, Y., Taniguchi, T., Watanabe, K. & Nagashio, K. Layer-by-layer dielectric breakdown of hexagonal boron nitride. *ACS Nano* **9**, 916–921 (2015).
- [18] Lukosius, M. *et al.* Atomic-vapour-deposited HfO_2 and $\text{Sr}_4\text{Ta}_2\text{O}_9$ layers for metal-insulator-metal applications. *Microelectronic Engineering* **84**, 2165–2168 (2007).
- [19] Soriano, V., Midrio, M. & Romagnoli, M. Design optimization of single and double layer graphene phase modulators in SOI. *Opt. Express* **23**, 6478–6490 (2015).

- [20] Romagnoli, M. *et al.* Graphene-based integrated photonics for next-generation datacom and telecom. *Nature Reviews Materials* **3**, 392–414 (2018).
- [21] Giambra, M. A. *et al.* High-speed double layer graphene electro-absorption modulator on SOI waveguide. *Opt. Express* **27**, 20145–20155 (2019).
- [22] Liu, M. *et al.* A graphene-based broadband optical modulator. *Nature* **474**, 64–67 (2011).
- [23] Sorianello, V. *et al.* Chirp management in silicon-graphene electro absorption modulators. *Opt. Express* **25**, 19371–19381 (2017).
- [24] Kou, R. *et al.* Ultra-fine metal gate operated graphene optical intensity modulator. *Appl. Phys. Lett.* **109**, 1–6 (2016).
- [25] Liu, M., Yin, X. & Zhang, X. Double-layer graphene optical modulator. *Nano Lett.* **12**, 10–13 (2012).
- [26] Dalir, H., Xia, Y., Wang, Y. & Zhang, X. Athermal broadband graphene optical modulator with 35 GHz speed. *ACS Photonics* **3**, 1564–1568 (2016).
- [27] Mohsin, M. *et al.* Graphene based low insertion loss electro-absorption modulator on SOI waveguide. *Optics Express* **22**, 15292–15297 (2014).
- [28] Kleinert, M. *et al.* Graphene-based electro-absorption modulator integrated in a passive polymer waveguide platform. *Optical Materials Express* **6**, 1800–1807 (2016).
- [29] Li, G. *et al.* Ring resonator modulators in silicon for interchip photonic links. *IEEE Journal of Selected Topics in Quantum Electronics* **19**, 95–113 (2013).
- [30] Srinivasan, S. A. *et al.* 56 Gbps germanium waveguide electro-absorption modulator. *Journal of Lightwave Technology* **34**, 419–424 (2016).