

Enhanced Zero-Bias Rectification in 1D Metal-Double-Insulator-Graphene Diodes for RF Energy Harvesting

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Cite This: <https://doi.org/10.1021/acsaelm.5c02741>



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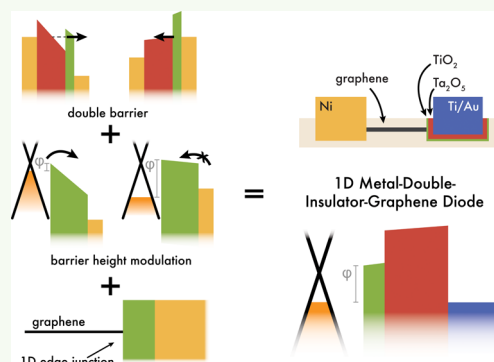
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ABSTRACT: Passive rectifiers in radio frequency (RF) energy-harvesting applications require viable zero-bias responsivities to achieve significant RF-to-DC conversion efficiencies. While conventional metal–insulator–metal (MIM) diodes have been widely studied for high-frequency rectification, they often exhibit suboptimal zero-bias performance. Here, we demonstrate enhanced performance by modifying three key features of MIM diodes. We fabricated diodes with a second insulating layer, used graphene as one of the contacts, and formed a one-dimensional (1D) junction along the edge of graphene. The resulting 1D metal–double-insulator–graphene (MIIG) diode with TiO_2 and Ta_2O_5 insulators shows excellent zero-bias responsivity of up to 9.7 A/W. Our model indicates that this is due to a mix of thermionic emission at the 1D junction, modulation of the graphene work function toward a lower transport barrier, and trap-assisted transport through Ta_2O_5 . These results are essential for the development of high-efficiency rectennas for RF energy-harvesting applications.

KEYWORDS: graphene, metal–insulator–metal diode, double insulator, Ta_2O_5 , TiO_2 , edge contact



INTRODUCTION

Driven by the demand for higher bandwidth and ubiquitous internet-connected devices, future urban wireless networks (e.g., 5G New Radio, 6G) are expected to operate at significantly higher frequencies and power densities in the coming years.^{1–3} In this context, radio frequency (RF) energy harvesting, enabled by rectennas (rectifier + antenna), has the potential to exploit the resulting omnipresent radiation to power-distributed networks of autonomous sensors. The key figure of merit (FOM) in the operation of such rectennas is the power conversion efficiency (PCE), i.e., the ratio of power converted from RF to DC. The PCE depends on the zero-bias responsivity and the impedance mismatch between antenna and diode, determined by the antenna impedance (typically $\approx 100 \Omega$) and the diode zero-bias resistivity. In this regard, Schottky diodes have already demonstrated outstanding conversion efficiencies up to 50% in the low-power regime below -10 dBm .^{4–6} However, they are restricted to low gigahertz (GHz) frequencies, i.e., well below those expected in the forthcoming wireless networks. This limitation could be overcome by metal–insulator–metal (MIM) diodes,^{7,8} which generally have higher cutoff frequencies than Schottky diodes at the cost of a lower zero-bias responsivity and a larger zero-bias resistivity. The improved zero-bias performance of MIM diodes thus becomes essential for their exploitation in low-power autonomous energy-harvesting applications.⁹

MIM diodes consist of a thin insulating layer between two metals with different work functions.¹⁰ The difference in the work functions gives rise to an asymmetry in the insulator/metal potential barriers and thus leads to an asymmetry in the current–voltage diode characteristics. Typically, both tunneling and thermionic currents contribute to the diode current.¹¹ Therefore, the junction resistance of the device can be reduced by thinning the insulator to increase the contribution of the tunneling current, or by lowering the insulator potential barrier to increase the contribution of the thermionic current. However, both approaches also reduce the nonlinear behavior in the current–voltage response and thus lower the responsivity, particularly at zero bias.^{9,12,13}

There are three main strategies to overcome the poor zero-bias characteristics of MIM diodes in literature, which this work combines into a 1D metal–double-insulator–graphene diode (Figure 1a).

The first strategy is the addition of a second insulator layer with a different electron affinity.¹⁴ This forms a MIIM diode, shown as a cross-section in Figure 1b. This can increase

Received: December 31, 2025

Revised: March 21, 2026

Accepted: March 22, 2026

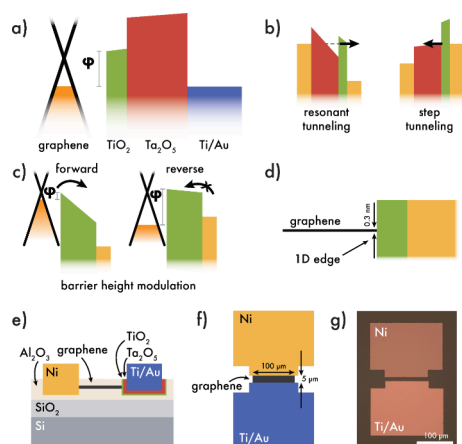


Figure 1. Path beyond MIM diodes. (a) Schematic band diagram of 1D-MIIG diodes (this work) at zero bias. The insulators (shown in red and green) are contacted on the anode side directly by a metal (shown in blue), and on the cathode side by graphene. The Fermi level in graphene is represented by the edge of the orange shaded region. (b) Planar metal–double-insulator–metal diodes show exceptional responsivities. They consist of two different insulators, shown in red and green here. Depending on their relative dielectric constants, thicknesses, and electron affinities, resonant or step tunneling can occur. (c) Replacing the cathode metal in an MIM diode with graphene leads to a metal–insulator–graphene diode, where the graphene work function can be modulated, which lowers the barrier height in the forward bias direction, increasing the on-current. (d) 1D-MIG diodes form an ultrathin, quasi-one-dimensional junction at the graphene edge,^{27,28} resulting in a low capacitance, which is ideal for high-frequency rectification. (e) Schematic cross-section of the 1D-MIIG diode studied in this work. (f) Top-view schematic of the two-terminal diode and (g) the corresponding micrograph of a fabricated device.

responsivity through resonant or step tunneling, which are the two primary transport mechanisms, depending on the insulator thicknesses, dielectric constants, and electron affinities.¹⁵ In the resonant tunneling mode, discrete bound states in the triangular well between the insulators enhance the electron transmission at specific bias voltages. This resonance condition requires stringent band alignment and clean interfaces. Therefore, only a few convincing demonstrations exist in the literature.^{16,17} In the step tunneling mode,¹⁸ the responsivity increases abruptly when the conduction band edge of one insulator drops below the metal work function, suddenly reducing the effective insulator thickness.¹⁹

The second strategy is to replace the cathode metal with graphene,^{11,20} forming a metal–insulator–graphene (MIG) diode, as shown in Figure 1c. Graphene is a two-dimensional semimetal with a linear dispersion relation with a low density of states near the intrinsic Fermi level.²¹ Therefore, the graphene–insulator barrier height can be modulated by the bias voltage.²² When the barrier in the forward direction is lowered in this way, the thermionic diode current increases^{11,20,23,24} and thus the zero-bias performance.

Combining these two approaches into a metal–double-insulator–graphene diode enhances the rectifying performance. Indeed, a semiconductor–double-insulator–graphene (SIIG) junction employed in a hot electron transistor has shown outstanding asymmetries above 1000.²⁵

The third strategy is to use a lateral structure with a small junction capacitance, as shown in Figure 1d. Lateral diodes have been demonstrated with thin metals,²⁶ but perform

particularly well when using two-dimensional materials such as graphene,^{27,28} as their atomic thickness enables quasi one-dimensional (1D) junctions. This graphene “edge” configuration also lowers the contact resistance.²⁹ The reduced junction capacitance and contact resistance enable high-frequency applications since the diode operation speed is limited mainly by the RC time constant.^{23,28} Rectennas based on such 1D-MIG diodes have been shown to rectify at up to 170 GHz in free-space measurements.²⁷

Here, we combine these three strategies to create a 1D metal–double-insulator–graphene (1D-MIIG) diode with 3 nm TiO₂ and 10 nm Ta₂O₅ insulating layers between a monolayer graphene 1D edge and a Ti/Au contact, as seen in a schematic cross section in Figure 1e. The material stack was systematically designed with the goal of optimizing the asymmetry while maintaining reasonable operation current densities. Comprehensive temperature-dependent characterization and numerical simulations suggest that the diode characteristics can be explained by an interplay of thermionic emission, graphene work function modulation, and trap-based transport through the oxide layers. The 1D-MIIG diode FOMs indicate higher efficiency in mmWave and THz rectennas for low-power energy harvesting applications.

Device Design

The experimental design space for a functional MIIG diode is extensive, encompassing the choice of metals and the type, thickness, and composition of each insulating layer. Here, we constrained the experimental design to materials available in our facilities (summarized in the Supporting Information (SI) in Table S1). The metal contacts were chosen based on previous results in the realization of metal–graphene interfaces. In particular, nickel (Ni) was used as the cathode contact due to its ability to form high-quality edge contacts with graphene, achieving contact resistivities³⁰ as low as 130 Ω·μm. For the anode, titanium (Ti) was chosen based on its proven performance as an anode metal in MIG structures.^{20,31–34} We developed a numerical approach (outlined in the Methods section) to predict the electrical performance of MIIG diodes, which allowed us to systematically narrow the design space down to the optimal dielectric layer stack. The Ni–graphene–3 nm TiO₂–10 nm Ta₂O₅–Ti configuration shows maximum current densities for both forward and reverse bias in the range of 10^{−1}–10^{−4} μA/μm and asymmetry factors of 10³–10⁴ within the ±1 V bias window. We then fabricated 50 1D-MIIG diodes with this configuration using the process outlined in the Methods section. A top-view schematic and a micrograph of one of the fabricated devices are shown in Figure 1f and g, respectively. In this device, the channel width is 100 μm and channel length is 5 μm. Due to the edge contact geometry of the diode, the junction area is defined by the channel width and the thickness of monolayer graphene, i.e., 0.3 nm, resulting in a total junction area of only 0.03 μm².

Measurements

We extracted relevant figures of merit from room-temperature DC current–voltage (*I*–*V*) curves obtained by applying a voltage sweep from 0 to 3 V and then to −3 V to avoid charging effects. The Ni/graphene contact was grounded during the measurement, as in previous works on metal–insulator–graphene diodes.^{20,27,28}

We repeated the *I*–*V* measurements at elevated temperatures between 50 and 150 °C to gain further insight into the temperature dependence of electron transport through the

junction. At higher temperatures, the current at positive bias exceeds that at negative bias, in contrast to the behavior observed at room temperature.

RESULTS AND DISCUSSION

Room-Temperature I – V Measurements

The initial I – V curve of a 1D-MIIG diode is shown in Figure 2a on a linear and semilogarithmic scale. It is highly nonlinear:

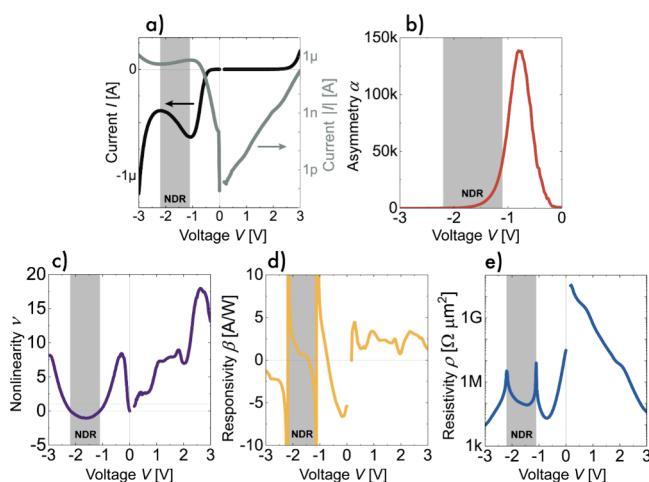


Figure 2. Figures of merit of a typical 1D-MIIG diode at room temperature. (a) Current–voltage characteristics on a linear (black) and semilogarithmic (gray) scale. The negative differential resistance region (NDR) is marked in gray in all subsequent plots. (b) Asymmetry, (c) nonlinearity, (d) responsivity, and (e) differential resistivity of the diode. The derivatives at small positive voltages are dominated by measurement noise and have been omitted for clarity.

the current increases rapidly when a negative voltage bias was applied to the Ti/Au contact, which we refer to here as the reverse direction of the diode. The exponential current rise starts at the turn-on voltage of -0.45 V, which is determined from the extremum of the first-order derivative of the I – V curve.³⁵ At higher reverse voltage biases, the current decreases, causing the differential resistance to become negative between -1.1 and -2.2 V (i.e., a negative differential resistance, NDR). A second exponential current increase starts at -2.6 V. In the forward direction (i.e., with a positive voltage bias applied to the Ti/Au contact), the current increases monotonically.

We derived the key FOMs asymmetry, nonlinearity, and responsivity from this I – V data as well as the differential resistance and responsivity at zero bias, which are of particular interest for rectenna applications.

The diode reaches a peak asymmetry ($\alpha = |I_r/I_f|$) of 138480 at -0.8 V (Figure 2b), which is among the highest values reported for MIM and MIIM diodes in the literature,^{36,37} and decisively higher than our previously reported data on 1D-MIIG diodes.^{27,28} The maximum asymmetry is observed in the negative voltage bias region because the Ni/graphene contact (M1) was grounded during the measurements, in line with the simulations (Figures S2 and S3) and Jenkins et al.³⁸ During subsequent measurements at higher temperatures, the asymmetry decreases, as shown in SI, Figure S4.

The nonlinearity ν of a diode, i.e., the deviation from an ohmic resistor, is defined as

$$\nu = \frac{dI/dV}{I/V} = \frac{R}{R_{\text{diff}}} \quad (1)$$

where $R = V/I$ is the static resistance and $R_{\text{diff}} = dV/dI$ is the differential resistance. The nonlinearity of our 1D-MIIG diode is shown in Figure 2c. ν reaches a maximum of 18 at 2.6 V and 8 at -3 V. There is a notable intermediate peak at the turn-on voltage of -0.45 V, followed by a region where the nonlinearity is negative. The appearance of the NDR region (highlighted in gray in Figure 2a through e) is worth noting because this would be expected only under resonant tunneling conditions, which is not met here because of the band alignment of the insulators (see Figure S3b). An effect resembling that of resonant tunneling has been reported for heterojunctions exposed to humidity.³⁹ Suppose the observed NDR effect was indeed caused by adsorbed humidity at the junction. In that case, we should expect the differential resistance to increase at a voltage bias of -1.23 V, corresponding to the electrochemical potential of the bond in H_2O molecules.³⁹ While we have indeed observed this effect in ambient measurements in previously fabricated, unencapsulated 2D-MIIG diodes (see SI S6), the NDR effect reported in all 50 measured encapsulated 1D-MIIG diodes persists at measurements in vacuum and at elevated temperatures (which would drive out any adsorbed water at the junction). Moreover, the differential resistances in the 1D-MIIG diodes presented here increase from -0.8 V instead of the expected -1.23 V and are therefore not accounted for by a humidity-related mechanism.³⁹ We attribute the NDR effect observed in all 50 devices to more dominant trap-governed conduction in Ta_2O_5 under reverse voltage bias. The conduction through Ta_2O_5 is reduced while oxide trap states are filled until field emission dominates at higher negative voltage biases.

The current responsivity β is defined as

$$\beta = \frac{1}{2} \frac{d^2I/dV^2}{dI/dV} \quad (2)$$

β is relevant in small-signal rectification because it represents the proportionality factor between the input AC voltage and the output DC current. It reaches a maximum of -7.2 A/W at 0 V (Figure 2d) and diverges at the bounds of the NDR region.

The impedance mismatch between the antenna and diode is mainly determined by the diode zero-bias differential resistance ($R_{\text{diff},0} = \left. \frac{dV}{dI} \right|_{V=0}$). The diode in Figure 2e has a $R_{\text{diff},0} = 1.0$ G Ω , or a resistivity ($\rho_0 = R_{\text{diff},0}/A$) of 30.0 M $\Omega \cdot \mu\text{m}^2$, normalized to the 1D edge junction ($A = 0.03 \mu\text{m}^2$), at zero bias.

Temperature-Dependent I – V Measurements

We performed I – V measurements on a fresh device on the same sample at elevated temperatures up to 150 °C in order to identify the charge transport mechanism in the fabricated 1D-MIIG diodes. The current shows a distinct dependence on the applied voltage bias and/or the temperature, depending on the dominant transport mechanisms.

Figure 3a shows the measured diode currents between -3 V and 3 V at temperatures from 21 to 150 °C, along with the proposed band diagrams in the forward and reverse directions as insets. The conduction in each direction is based on a different mechanism with a characteristic scaling law ($I \propto V^m$). We therefore first determine this exponent from the slope m of a logarithmic current–voltage plot at all temperatures. The

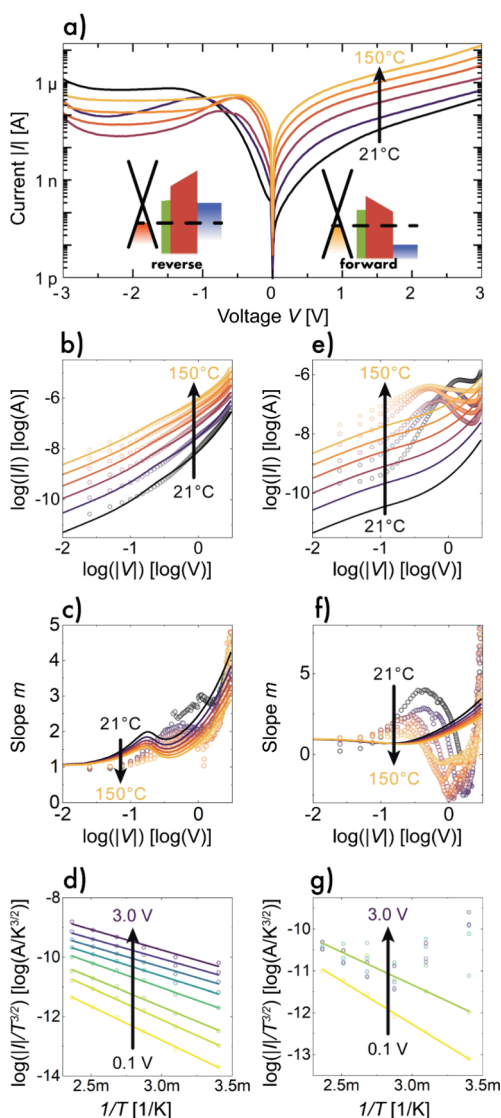


Figure 3. Temperature-dependent characterization of the 1D-MIIG diode. In all the measurements, the graphene was grounded. (a) I – V curves at various temperatures from 21 to 150 °C on a logarithmic scale. The insets show the band diagrams in the forward and reverse directions. In the band diagrams, the blue area represents the Ti/Au contact. The green and red areas represent the TiO_2 and Ta_2O_5 insulating layers, respectively. The doping level of the graphene Dirac cone and the associated graphene– TiO_2 barrier height depend on the voltage bias and are shaded in orange tones. (b) $\log$ – $\log$ I – V curves in the forward direction recorded at different temperatures. The transparent circles correspond to the experimental data points, and the solid lines correspond to the simulated in-plane thermionic transport. (c) Slope m extracted from the forward experimental (circles) and simulated (lines) $\log$ – $\log$ plots. (d) Arrhenius plot of $\log(I/I_0/T^{3/2})$ vs $1/T$, indicating that 1D thermionic emission dominates in the forward direction. (e) $\log$ – $\log$ I – V curves in the reverse direction. The in-plane thermionic model (solid lines) does not describe the experimental data points (circles) in the reverse direction. (f) Slope m extracted from the reverse experimental (circles) and simulated (lines) $\log$ – $\log$ plots. (g) Arrhenius plot of $\log(I/I_0/T^{3/2})$ vs $1/T$. In-plane thermionic emission can only be observed at low reverse voltages.

$\log(I/I_0)$ – $\log(|V|)$ plot in the forward direction is shown in Figure 3b. The in-plane thermionic emission model (solid lines), detailed in the Methods section, describes the

experimental data (hollow circles) well. The slopes in Figure 3c extracted from the modeled and experimental $\log(I/I_0)$ – $\log(|V|)$ plots agree with each other. The peak in the modeled slope occurs at lower voltages than those in the experimental data, which is likely due to the access resistance of the diode. The in-plane thermionic emission model is further corroborated by a linear trend in the Arrhenius plot for edge-contact systems of $\log(I/I_0/T^{3/2})$ with respect to $1/T$ (Figure 3d), where the dimensionality of the interface is expressed⁴⁰ through the exponent 3/2. At voltage biases >1.5 V, the extracted slope is temperature-independent and increases with increasing voltage bias. This indicates a field-dominated process like Fowler–Nordheim tunneling (FNT, see Supporting Information, S7).

In the reverse direction, the behavior at low temperatures is similar to that in the forward case and resembles thermionic conduction (Figure 3e). A clear field-dominated transport regime occurs at higher voltages (Figure 3f), owing to the built-in electric field at zero bias. However, the reverse direction shows a strong influence of traps in the Ta_2O_5 layer. The extracted slope has a maximum, followed by a minimum of $m \approx -2$. The current, in fact, decreases with increasing reverse voltage bias, i.e., it shows a negative differential resistance. Additionally, the Arrhenius plot at higher voltage biases is no longer linear (Figure 3g). This suggests trap-mediated conduction dominating transport in reverse direction. The voltages of the maximum slope and the maximum slope itself decrease with increasing temperature. We attribute this to the filling of traps in Ta_2O_5 , that are likely to form during the physical vapor deposition of the film. A deposition method that yields a stoichiometric Ta_2O_5 film (e.g., atomic layer deposition) may suppress the formation of such traps. At elevated temperatures, the exponential distribution of the thermal energy provided to the carriers makes the transition less abrupt, thus lowering the maximum extracted slope at the transition between thermionic conduction and field-dominated transport regimes. We notice an overall shift toward lower voltage biases at which this maximum occurs, which is due to the work difference between graphene and Ti/Au. In general, a diode with an NDR region can be used to amplify high-frequency signals and can act as a high-frequency oscillator.

The TiO_2 layer ensures that the graphene work function is free to be modulated by the voltage bias. TiO_2 deposited by ALD is a high-quality film, as shown by capacitance–frequency measurements in SI, S8, which revealed a low defect density. Therefore, we do not expect the work function of graphene to be pinned, i.e., it can be readily modulated by the voltage bias. This modulation in turn creates the observed current–voltage characteristics.

Benchmarking

Table 1 compares our device to state-of-the-art devices. At $\alpha_{\text{max}} > 10^5$, our proposed 1D-MIIG diode has one of the highest asymmetry values reported in the literature to date, with a peak at a relatively low voltage bias of -0.8 V. Compared with other types of MIM or MIIM diodes, the planar semiconductor–double-insulator–graphene diode investigated by Vaziri et al. shows an asymmetry above 1000 (at 1.5 or 5 V, depending on the insulator stack), and MIG diodes typically show large asymmetries (up to 520). An exception is the Nb– NbO_x –Pt MIM diode demonstrated by Chin et al.,³⁷ which achieves a large asymmetry of 74000 with a largework function asymmetry between Nb and Pt but at the cost of a high zero

Table 1. Comparison of Key Figures of Merit with Devices Reported in the Literature^a

materials	diode	asymmetry $\alpha_{\max}$	nonlinearity $\nu_{\max}$	zero-bias responsivity β_0 [A/W]	zero-bias resistivity ρ_0 [$\Omega\cdot\mu\text{m}^2$]	reference
Ti/Au-Ta ₂ O ₅ -TiO ₂ -graphene	1D-MIIG	138480	20.6	−9.7	962.2k	this work (best)
Ti/Au-Ta ₂ O ₅ -TiO ₂ -graphene	1D-MIIG	56503 ± 43245	16.9 ± 1.2	−7.2 ± 0.6	11.9M ± 7.0M	this work (median)
Ti-TiO ₂ -graphene	1D-MIG	66	4.5	5*	N/A	28
Ti-TiO ₂ -graphene	1D-MIG	8	3	2.3*	5.6k	27
Ti-TiO ₂ -graphene	MIG	520	15	N/A	N/A	20
Si-TmSiO-Tm ₂ O ₃ -graphene	SIIG	~1000	N/A	N/A	N/A	25
Pt-TiOx-NAlOx-Pt	MIIM	8760	15.8	36.8	83G	36
Nb-NbOx-Pt	MIM	74000	9.5	15	50T	37
Pt-TiOx-NTiOx-Pt	MIIM	28.6	3	13.5	28M	36
Al-AlOx-Ag	MIM	1.2	12.5	9	47.5G	41
Ni-NiO-Cu	MIM	~1*	N/A	3.65	9.6k	54
polysilicon-SiO ₂ -polysilicon	MIM	N/A	N/A	6.25	N/A	55
W-Nb ₂ O ₅ -Ta ₂ O ₅ -W	MIIM	N/A	N/A	5	N/A	15
Ni-NiO-ZnO-Cr	MIIM	16	N/A	2.5	93.6M	56
Cr-Al ₂ O ₃ -HfO ₂ -Cr	MIIM	10	~11*	2.5	196G	57
Ti-TiO ₂ -ZnO-Al	MIIM	~1*	N/A	1.6	15.6k	18
Pt-NTiOx-NAlOx-Al	MIIM	~1*	3.7	1.7	3.6k	36
Ni-NiO-Pt	MIM	N/A	N/A	−1.5	25k	58
Co-Co ₃ O ₄ -TiOx-Ti	MIIM	1.2	N/A	1.2	994	14
Ni-NiO-Al ₂ O ₃ -Cr/Au	MIIM	N/A	N/A	0.5	455	16
Ni-NiO-NbOx-Cr/Au	MIIM	1.15	N/A	0.46	59	59
Ti-TiO ₂ -Al	MIM	~1*	N/A	0.15	3.4k	18
Pt-HfO ₂ -TiO ₂ -Ti	MIIM	N/A	~12*	0.1	40M	60
Cr-Cr ₂ O ₃ -HfO ₂ -Al ₂ O ₃ -Cr	MIIM	>100000	6	N/A	N/A	17

^aThis work's best and median show among the highest reported asymmetries, nonlinearities, and zero-bias responsivities. A negative responsivity value indicates that the peak occurs in the reverse direction. Unavailable literature values are marked with N/A, and values estimated from plots are marked with *. Note that reported responsivity definitions vary in the literature (either $\beta = \frac{1}{2} \frac{d^2I}{dV^2} / \frac{dI}{dV}$ or $\beta = \frac{d^2I}{dV^2} / \frac{dI}{dV}$) and have been brought into agreement for this comparison.

bias resistivity of 50 T $\Omega\cdot\mu\text{m}^2$. We attribute the asymmetry enhancement in our 1D-MIIG diodes to the strong asymmetry in the in-plane thermionic emission from the graphene edge into the double-barrier junction. The asymmetry shows variability across working devices, as seen in the histogram (SI, Figure S8a) and asymmetry curves (Figure S8b) of the 50 measured devices. To minimize the effect of large outliers, we report the median values. The median asymmetry across working devices is 56503 ± 43245, with 90% of measured asymmetries above 1000.

The maximum nonlinearity occurs at approximately 2.8 V in all devices. The best device has a nonlinearity of 20.6; the median of all working devices is 16.9 ± 1.2, a 30% improvement over the state-of-the-art³⁶ of 15.8. A histogram with the cumulative distribution and a plot of all measured nonlinearity values with respect to voltage are shown in Figure S8c and d, respectively.

The zero-bias performance is of special importance for rectenna applications, in which only a relatively weak RF signal from the antenna is coupled directly to the diode input. Efficient rectification of this signal requires: 1) a large current responsivity at zero bias and 2) a small impedance mismatch between the antenna and diode at zero bias. The best zero-bias responsivity of all the measured devices was −9.7 A/W, with a median of −7.2 ± 0.6 A/W (Figure S8e). This responsivity is significantly greater than the zero-bias responsivity of previously reported 1D-MIG diodes.^{27,28} Furthermore, only a

few diodes with larger responsivities at zero bias have been reported in the literature, for example, that of Alshehri et al.³⁶

To compare the zero-bias resistance of the 1D-MIIG diode to those of other diodes in literature, we report here the zero-bias differential resistivity, i.e., the differential resistance normalized to the junction area. The lowest zero-bias resistivity across the chip was 962.2 k $\Omega\cdot\mu\text{m}^2$. It shows relatively large variability across the chip, with a median of 11.9 ± 7.0 M $\Omega\cdot\mu\text{m}^2$, as seen in the histogram in Figure S8f. This outperforms previously reported zero-bias resistivities for MIM or MIIM diodes with comparable zero-bias responsivities,^{36,37,41} yet is still far from the ideal ≈100 Ω required for reflection-less impedance matching to typical antennas. The observed trade-off between zero-bias resistivity and responsivity (dashed line in Figure 4a) is typical for MIM and MIIM diodes.⁹ The resistance of the 1D-MIIG diode could be further reduced by increasing the width of the graphene channel or by using multiple layers of graphene.

We observed a large variability across the devices, which we attribute to the thickness variation of the Ta₂O₅ layer.¹⁷ We presume that Ta₂O₅ deposition by evaporation, in which it is difficult to control the actual film thickness at the vertical 1D edge across the sample, is the main cause of the variability in this edge junction fabrication process.

To assess the potential performance of the 1D-MIIG rectifying technology for RF energy harvesting, we estimate its bandwidth and PCE based on the previously characterized metrics of 1D-MIIG diodes and compare the projected value

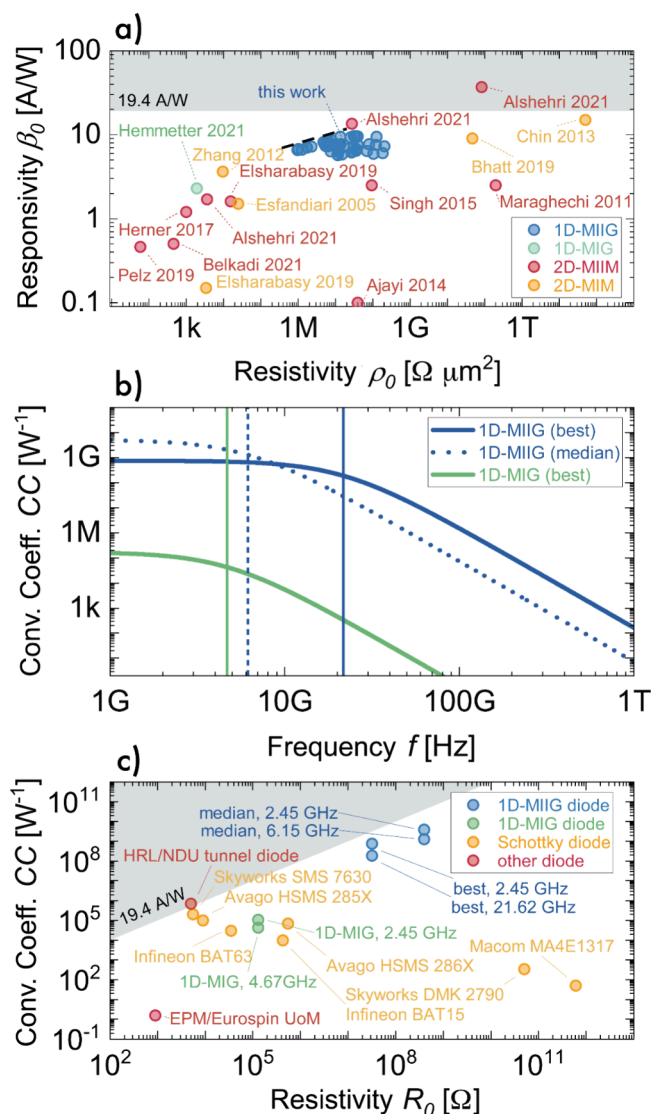


Figure 4. Benchmarking of the fabricated 1D-MIIG technology. (a) Zero-bias responsivities and zero-bias resistivities of different insulator-based diodes reported in the literature (MIM, MIIM, and MIG) are compared with those of the diodes measured in this work (1D-MIIG). The responsivity limit for thermal processes (19.4 A/W) is shown in gray. The trade-off between responsivity and resistivity in the 1D-MIIG diodes is shown by the black dashed line as a guide for the eye. (b) Logarithmic plot of the estimated conversion efficiency with respect to frequency. The 1D-MIIG devices are shown in blue, with the best device as a solid line and the median performance as a dotted line. For comparison, the estimated conversion efficiency for a previously fabricated 1D-MIG diode²⁷ is shown in green. The estimated cutoff frequencies are shown as vertical lines. (c) Comparison of the conversion coefficient with respect to the zero-bias resistance of different commercial diodes, assuming perfect impedance matching. This plot is adapted from Hemour et al.³ and has been extended with the estimated conversion coefficients for the 1D-MIIG diodes (best and median, shown in blue) at 2.45 GHz and the respective cutoff frequencies. The gray area marks the conversion coefficient that can be reached when the thermal responsivity limit is above 19.4 A/W.

with those of other rectifying technologies using the same PCE estimation method.

Based on the estimated intrinsic oxide capacitance and access resistance, we predict bandwidths of 21.62 GHz (best)

and 6.15 GHz (median) for these devices (see SI S10 for details on the calculation). This compares well with the estimated cutoff frequency of 4.67 GHz for previously fabricated 1D-MIG diodes. The frequency response in lateral diodes can be improved by further shortening the graphene channel to reduce the series resistance.

The overall RF-DC power conversion efficiency is given by³

$$\text{PCE} = \frac{P_{\text{in}} \mathcal{R}_I^2 \eta_M^2 R_j}{(2 + 2\omega^2 C_j^2 R_j R_s)^2} \quad (3)$$

where P_{in} is the available power from the receiver antenna; $\mathcal{R}_I$ is the rectifier current responsivity (i.e., the ratio of the rectified DC current and RF input power), which equals β under square-law operation at low input powers;³ and η_M is the matching efficiency between the antenna and the RF-DC converter. $R_j = \rho_0 \times A$ represents the junction resistance; R_s represents the Ni-graphene contact resistance and graphene sheet resistance; and C_j represents the $\text{TiO}_2/\text{TaO}_5$ geometrical capacitance. This expression is obtained assuming $R_s \ll R_j$ and perfect load matching, which is achieved when the load resistance, R_L , satisfies $R_L = R_j$.

We define the conversion coefficient, a figure of merit for harvesting purposes, as $\text{CC} \equiv \text{PCE}/P_{\text{in}}|_{\eta_M=1}$. Figure 4b shows the frequency dependence of CC for the best-performing device (blue solid line) and the median performance across the 1D-MIIG technology (blue dotted line). Additionally, the CC of a previously fabricated 1D-MIG diode²⁷ has been reported for comparison (green solid line).

Conversion coefficients of approximately $\text{CC} \approx 1.9 \times 10^8 \text{ W}^{-1}$ for frequencies up to 21.62 GHz and $\text{CC} \approx 1.3 \times 10^9 \text{ W}^{-1}$ for frequencies up to 6.15 GHz are projected for the best-performing device and the median of the 1D-MIIG technology, respectively. Notably, owing to the inherently high impedance of these devices, in a practical scenario, a portion of the RF energy received by the antenna may be reflected. The matching efficiency can be increased only at the expense of lower conversion efficiency.

Figure 4c presents a comparison between the projected conversion coefficient of 1D-MIIG diodes from their previously characterized metrics (under ideal, lossless matching conditions) and those of conventional rectifying technologies. Although additional factors—such as parasitic effects arising from fringe capacitances, the inductive and resistive contributions of metal interconnects and contact pads, among others—may reduce the impressive projected performance, 1D-MIIG technology demonstrates strong intrinsic potential for enabling efficient ambient RF energy harvesting in future ubiquitous IoT systems.

CONCLUSION

We have experimentally demonstrated high-performance one-dimensional metal–double-insulator–graphene diodes. Our devices were designed based on comprehensive numerical simulations, and fabricated in viable, scalable semiconductor technology. Our results suggest that the rectification of conventional MIM diodes can be improved by using double-dielectric barriers, one graphene electrode for work function modulation, and 1D junctions. Our 1D-MIIG diodes showed large zero-bias responsivities, making them suitable candidates for rectennas in RF energy harvesting applications in the mmWave range. Further optimization routes include shorter

graphene channels and higher qualities of the deposited oxides. Simulations of optimized devices suggest that cutoff frequencies in the THz range may be achievable. This would enable the harvesting of ambient parasitic RF energy to power distributed sensor networks and IoT devices.

METHODS

Design of the MIIG Heterostructure

We limited the design of the MIIG heterostructure to dielectrics available in our facilities. Among the dielectrics, Al_2O_3 and TiO_2 can be deposited via atomic layer deposition (ALD), enabling film thicknesses from 3 to 6 nm in 1 nm increments. In contrast, SiO_2 and Ta_2O_5 can be deposited via electron-beam evaporation (physical vapor deposition, PVD), resulting in minimum practical thicknesses of 10 nm to achieve pinhole-free films. Anode (Ti) and cathode (Ni) metallizations were chosen based on previous experience on MIG diodes^{11,20,28} and graphene contacts.³⁰

The material properties considered for the fabricated diode are listed in Table S1. The work function of Ni is assumed to correspond to the literature value of 5.15 eV.⁴² The work function of the Ti/Au layer is considered to lie within the range of the work functions of the respective bulk materials (Ti: 4.33 eV,¹⁸ 5.1 eV⁴²), as numerically modeled by Yadava and Chauhan.⁴³ Based on this, we estimate the work function of the Ti/Au contact as 5.0 ± 0.1 eV. The work function of pristine graphene at the Dirac point (4.3 eV²²) is modified by electrostatic doping. Transferred CVD-grown graphene on insulators is typically *p*-doped,⁴⁴ thus increasing its effective work function.²²

We developed a numerical approach to predict the electrical performance of MIIG diodes based on the experimental design space. First, the electrostatics were solved over a voltage bias range of $V_{\text{bias}} = -1$ to 1 V. Second, the transfer matrix method (TMM) was employed, using the previously obtained position-dependent potential across the MIIG stack to compute the energy-dependent electron transmission probability and, eventually, the current density for each V_{bias} . The details of the modeling framework are given in the section below.

The simulations were performed for 66 different MIIG structures with different dielectric materials (Al_2O_3 , SiO_2 , TiO_2 , and Ta_2O_5) and thicknesses, considering room temperature (RT) operation. We plotted the resulting current density J vs V_{bias} characteristics (SI, subsection S1) and extracted several key FOMs: current density at positive and negative bias, J_{IV} and $J_{-1\text{V}}$, and current asymmetry $\alpha = |J_{\text{f}}/J_{\text{r}}|$, where J_{f} and J_{r} denote the forward and reverse currents within the ± 1 V bias window. Since the current–voltage characteristics of the different MIIG configurations are not known a priori, the forward direction in the expression of α is defined as the one exhibiting the higher current magnitude, regardless of polarity.

Figure S1a,b show colormaps of the simulated values of the forward current at ± 1 V ($J_{\text{f},\pm 1\text{V}}$) and α for all the configurations considered. The white boxes correspond to combinations of equal insulators, which were not explored. The boxes with hatched lines indicate structures where $J_{\text{f}} < 10^{-10}$ $\mu\text{A}/\mu\text{m}$. This is too low for practical MIIG implementations, and these combinations have also been discarded. Finally, each box is framed in blue or red to distinguish between diodes with different maximum current directions, i.e., $J_{\text{f}} = J_{-1\text{V}}$ and $J_{\text{f}} = J_{1\text{V}}$, respectively.

Electrostatic Simulation

The one-dimensional (1D) electrostatics of an MIIG heterostructure can be derived following a similar framework as that previously developed by some authors for the metal–insulator–graphene junction.⁴⁵ The double-insulator stack sets the electrostatic coupling between the graphene layer and the anode metal via a series of combinations of their geometrical capacitances per unit area, given by $C_{\text{ox}} = C_{\text{ox1}}C_{\text{ox2}}/(C_{\text{ox1}} + C_{\text{ox2}})$, where $C_{\text{ox1}} = \epsilon_{\text{ox1}}/t_{\text{ox1}}$ and $C_{\text{ox2}} = \epsilon_{\text{ox2}}/t_{\text{ox2}}$ correspond to the insulator closer to the anode electrode and to the graphene, respectively. Here, ϵ_{ox1} (ϵ_{ox2}) and t_{ox1} (t_{ox2}) are the permittivity and thickness of each insulator. By applying the principles

of charge conservation and analyzing the potential loops, the electrostatic behavior of the MIIG structure leads to⁴⁶

$$\begin{aligned}\phi_{\text{m,a}} - (\phi_{\text{g}} + V_{\text{ch}}) &= V_{\text{bias}} - \Delta_{\text{ox}} \\ \phi_{\text{m,c}} - (\phi_{\text{g}} + V_{\text{ch}}) &= \Delta_{\text{d}} \\ Q_{\text{a}} + Q_{\text{c}} + Q_{\text{g}} &= 0\end{aligned}\quad (4)$$

In eq 4, $\phi_{\text{m,a}}$, $\phi_{\text{m,c}}$, and ϕ_{g} denote the work functions of the anode metal, cathode metal, and graphene, respectively. The applied bias is defined as $V_{\text{bias}} = V_{\text{a}} - V_{\text{c}}$, where V_{a} and V_{c} are the voltages applied to the anode and cathode, respectively. The graphene chemical potential is expressed as $V_{\text{ch}} = (E_{\text{D}} - E_{\text{F,g}})/q$, where q is the elementary charge, $E_{\text{F,g}}$ is the graphene Fermi level, and E_{D} is the Dirac energy (the energy at which the valence and conduction bands in graphene touch each other). Note that the term $(\phi_{\text{g}} + V_{\text{ch}})$ corresponds to the effective, tunable work function of graphene. The term Δ_{d} represents the potential drop across the dipole layer formed at the graphene–cathode interface due to charge redistribution. The surface charge density induced on the anode is given by $Q_{\text{a}} = C_{\text{ox}}\Delta_{\text{ox}} + Q_{\text{f}}$, where Q_{f} accounts for fixed charges present within the dielectric layer adjacent to the graphene interface.⁴⁷ Similarly, the cathode-induced charge per unit area is $Q_{\text{c}} = -C_{\text{d}}\Delta_{\text{d}}$, where $C_{\text{d}} = \epsilon_0/t_{\text{eq}}$ represents the effective capacitance per unit area associated with the cathode–graphene dipole and $t_{\text{eq}} \sim 2.05$ Å denotes the equilibrium dipole separation.⁴⁸ The total charge density associated with the graphene layer can be expressed as $Q_{\text{g}} = Q_{\text{net}}[V_{\text{ch}}] + Q_{\text{it}}[V_{\text{ch}}] + Q^*$, where Q^* accounts for any residual or unintentional doping⁴⁹ (here $Q^* = 0.5$ pC/ μm^2), and $Q_{\text{it}}[V_{\text{ch}}] = C_{\text{it}}V_{\text{ch}} + Q'$ represents the contribution from possible interface traps, with $Q' = C_{\text{it}}(\phi_{\text{g}} - \chi_{\text{ox2}} - \phi_0)$, where C_{it} is the interface-trap capacitance per unit area (0.8 pF/ μm^2), χ_{ox2} is the electron affinity of the second oxide layer, and ϕ_0 is the charge neutrality level. The net mobile charge density in graphene (Q_{net}) is determined from the density of states of graphene resulting from the linear energy dispersion relationship as follows:

$$Q_{\text{net}}[V_{\text{ch}}] = q(p - n) = \frac{2q(k_{\text{B}}T)^2}{\pi(\hbar v_{\text{F}})^2} \left(\mathcal{F}_1 \left[\frac{qV_{\text{ch}}}{k_{\text{B}}T} \right] - \mathcal{F}_1 \left[-\frac{qV_{\text{ch}}}{k_{\text{B}}T} \right] \right) \quad (5)$$

In eq 5, p and n are the hole and electron carrier densities, respectively; $\mathcal{F}_1$ is the first-order Fermi–Dirac integral; k_{B} is the Boltzmann constant; T is the temperature; $\hbar$ is the reduced Planck's constant; and $v_{\text{F}} \sim 10^6$ m/s is the Fermi velocity in graphene.

By consolidating the above expressions into eq 4, the full electrostatic profile of the MIIG heterostructure can be described:

$$C_{\text{ox}}V_{\text{bias}} + (C_{\text{ox}} + C_{\text{it}} + C_{\text{d}})V_{\text{ch}} + Q_{\text{net}}[V_{\text{ch}}] = Q_0 \quad (6)$$

The final residual charge density, denoted as Q_0 , is obtained as

$$Q_0 = -(Q^* + Q' + Q_{\text{f}} + C_{\text{ox}}(\phi_{\text{g}} - \phi_{\text{m,a}}) + C_{\text{d}}(\phi_{\text{g}} - \phi_{\text{m,c}})) \quad (7)$$

In our proposed MIIG technology (Figure 1a), carrier transport occurs laterally between the edge of the graphene sheet (1D) and the 3D metal anode, which contrasts with the widely studied vertical MIG configuration.⁴⁵

To fully capture the potential advantages arising from tunneling transport phenomena and potential resonant and step tunneling inherent in the double-insulator configuration, we used the transmission matrix method (TMM) to obtain the transmission coefficient across the electrostatic barrier.

The current density was later obtained from the integral in *k*-space of the current spectrum as

$$J = qg_{\text{s}}g_{\text{v}} \int [f_{\text{L}}(E(k)) - f_{\text{R}}(E(k))] v_z(k_y) T(k_y) d^3k \quad (8)$$

With this approach, we are able to predict the current–voltage characteristics of the 1D-MIIG structure in the forward and backward regimes.

Various charge transport mechanisms are expected to contribute to double-insulator rectifier operation, such as tunneling through thin oxide layers and temperature-dominated transport like thermionic emission over the double barrier. A simplified expression of the thermionic current can be derived and used for experimental fitting from the work of L. K. Ang et al.⁵⁰ In particular, the lateral Dirac-Schottky current per unit length, which scales with the graphene width and accounts for the density-of-states mismatch between materials of different dimensionalities, is given by⁵⁰

$$J_{\text{th}} = \frac{4q\sqrt{\phi_b}}{\hbar^2 v_F} \left(\frac{k_B T}{2\pi} \right)^{3/2} e^{-q\phi_b - \frac{\delta_p^2}{2k_B T} / k_B T} (e^{qV_{\text{bias}}/\eta k_B T} - 1) \quad (9)$$

where ϕ_b is the Schottky barrier height (SBH), δ_p accounts for the broadening of the Fermi level (here assumed to be 47 meV), and η denotes the ideality factor ($\eta = 2$). Notably, this configuration predicts a universal scaling of $T^{3/2}$, in contrast to the T^3 dependence reported for vertical 2D MIG configurations or the Richardson-Dushman scaling of T^2 for bulk materials.⁵⁰

The Schottky barrier lowering (SBL) due to the image force (IF) effect is also accounted for in the ϕ_b . A good approximation for the SBH that includes the image potential along the insulator thickness (y -coordinate) is given by Simmons:^{51,52}

$$\phi[y] = \phi_{b0} - \Delta_{\text{ox}} \frac{y}{t_{\text{ox}}} - 1.15 \frac{\ln[2]}{8\pi} \frac{q}{C_{\text{ox}}} \frac{1}{y(y - t_{\text{ox}})} \quad (10)$$

where $t_{\text{ox}} = t_{\text{ox1}} + t_{\text{ox2}}$ is the total thickness of the double barrier.

The maximum barrier height ϕ is determined by solving $d\phi[y^*]/dy = 0$, where $\phi[y^*] = \phi_b = \phi_{b0} - \text{SBL}$. The intrinsic SBH, ϕ_{b0} , is evaluated at the graphene-oxide interface ($\phi_{b0}^{\text{g} \rightarrow \text{o}} = \phi_g + V_{\text{ch}} - \chi_{1,2}^{\text{min}}$) and the metal-oxide interface ($\phi_{b0}^{\text{m} \rightarrow \text{o}} = \phi_{\text{m,a}} + V_{\text{ch}} - \chi_{1,2}^{\text{min}}$), where $\chi_{1,2}^{\text{min}} = \min\{\chi_{\text{ox1}}, \chi_{\text{ox2}}\}$.

Device Fabrication

We fabricated 1D-MIIG diodes with the selected dielectric stack of 3 nm TiO_2 and 10 nm Ta_2O_5 . The design included 50 devices, with graphene channel lengths between 2 and 10 μm . The micrograph in Figure 1g shows one of the fabricated devices with a channel length of 5 μm . A p -doped Si substrate with 90 nm SiO_2 is covered with 40 nm Al_2O_3 by plasma-enhanced atomic layer deposition (PE-ALD) at 300 °C with trimethylaluminum (TMA) and oxygen plasma as precursors. Commercial monolayer graphene grown by chemical vapor deposition (CVD) from the company General Graphene (Knoxville, USA) with a size of $1 \times 1 \text{ cm}^2$ was transferred to the Al_2O_3 surface via a frame-based wet transfer technique.⁵³ After thorough drying and removal of the protective transfer polymer layer on top of graphene, we encapsulated the graphene layer with 20 nm Al_2O_3 via a thermal ALD process at 150 °C with trimethylaluminum (TMA) and water vapor as precursors.

First, optical contact lithography defines the ohmic contact (M1) to graphene with image reversal resist AZ5214E. We then etched through the top encapsulation and graphene and into the bottom encapsulation using an inductively coupled plasma reactive ion etching (ICP-RIE) process with SF_6/Ar chemistry in an Oxford Plasmalab 100 ICP RIE tool. This step exposes the one-dimensional graphene edge. The edge was then covered with 40 nm of Ni metal via a rotating electron-beam evaporation process, followed by liftoff in acetone. This process formed an ohmic edge contact between Ni and graphene.

The rectifying contact (M2) was created in a similar way. However, after lithography and etching, we first deposited 3 nm TiO_2 by PE-ALD at 150 °C with the precursors TiCl_4 and oxygen plasma and then evaporated 10 nm Ta_2O_5 and 15/35 nm Ti/Au metal onto the edge via a rotating process. The excess material is removed in acetone. A final positive lithography step masked the graphene channel area, and the excess graphene was etched via the same SF_6/Ar RIE process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaelm.5c02741>.

(S1) Material selection for MIIG diodes; (S2) MIIG heterojunction design; (S3) I - V characteristics of 1D-MIIG configurations with forward current higher than $10^{-10} \mu\text{A}/\mu\text{m}$; (S4) Simulation of the Ni-graphene-3 nm TiO_2 -10 nm Ta_2O_5 -Ti heterostructure; (S5) Additional temperature-dependent measurements; (S6) Water-induced negative differential resistance in unencapsulated 2D-MIIG diodes; (S7) Fowler-Nordheim plots; (S8) Material properties, including measurements of the dielectric constants for TiO_2 and Ta_2O_5 ; (S9) Distribution of figures of merit; (S10) Estimation of the cutoff frequency (PDF)

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Author Contributions

A.H., Z.W., and M.C.L. conceived the experiments. A.H., E.M., and F.P. designed the devices. A.H. fabricated the devices and performed electrical and temperature-dependent characterization. E.M., F.P. and A.G. performed the numerical modeling. All the authors contributed to discussions and the analysis and interpretation of the results. All authors cowrote and approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

A.H., Z.W., and M.C.L. acknowledge the European Union's Horizon 2020 research and innovation programme. This work was financially supported by the European Union's Horizon 2020 research and innovation programme under grant agreement Nos. 101006963 (GreEnergy), 101189797 (2D-PL), and 101135571 (AttoSwitch). This work is part of the research project CNS2023-143727 RECAMBIO funded by MCIU/AEI/10.13039/501100011033 and the European Union NextGenerationEU/PRTR. F.P. and E.G.M. acknowledge the research project P21_00149 ENERGHENE funded by Consejería de Universidad, Investigación e Innovación de la Junta de Andalucía. E.G.M. and A.G. acknowledge the support of the Spanish Government through the research project PID2023-150162OB-I00 ADAGE funded by MCIU/AEI/10.13039/501100011033 and by FEDER, UE. F.P. also acknowledges the R+D+i project A-ING-253-UGR23 AMBI-TIONS, cofinanced by Consejería de Universidad, Investigación e Innovación and the European Union under the FEDER Andalucía 2021-2027. The authors acknowledge Dr. Christine Hendriks for detailed structural and language feedback on the manuscript.

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