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ABSTRACT
Energy harvesting rectennas require ultrafast rectifying diodes that are efficiently matched to the optical nanoantenna. These diodes should possess low on-resistance and high responsivity. Here, we introduce a metal-insulator-metal diode composed of a new material, Ti-TiO$_2$-Al. This diode has a 1.0 nm ultrathin insulator layer fabricated using atomic layer deposition (ALD). It has a zero-bias resistance of 275 Ω and a maximum responsivity of 3.1 A/W. To further improve its performance, another ultrathin layer of ZnO was added. The proposed Ti-TiO$_2$/ZnO-Al metal-insulator-insulator-metal diode has a zero-bias resistance of 312 Ω and a maximum responsivity of 5.1 A/W. The two types of diodes are fabricated on a SiO$_2$ substrate using conventional photolithography and ALD. Between 20°C and 55°C, the I–V characteristics did not show much temperature dependence. The effective barrier height, dielectric constant, and electron effective mass in each insulator are extracted using a constrained and derivative-based optimization algorithm.

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I. INTRODUCTION
The continuing rise in energy demand worldwide has been a strong motivation to investigate untapped renewable energy sources. A popular option is to convert mainly visible and near infrared solar radiation into useful DC currents using photovoltaics (PV) based on inorganic, e.g., silicon and group III-V, semiconductor materials or organic/polymer semiconductor materials. Infrared radiation, which represents more than half of the whole solar radiation spectrum, is not captured by most photovoltaic devices. Therefore, there is a strong need to harvest this source of longer wavelength energy using alternative harvesting techniques.

One alternative energy harvesting technique is based on rectennas. A rectenna is an antenna coupled to a rectifying diode. In principle, rectennas are high-efficiency devices that transform infrared radiation into DC output currents. Since it was first proposed for harvesting of solar irradiation, several groups have examined its feasibility and have developed technologies to achieve reproducible and efficient energy harvesting devices.

A key component of a rectenna is the rectifying diode in the form of ultrastable (tunneling times ∼~ few femtoseconds) metal-insulator-metal (MIM) tunnel diodes. For high-efficiency rectennas, good impedance matching between the diode’s resistance and that of the nanoantenna and high diode responsivity are required. The responsivity is characterized by the nonlinearity characteristics of the diode.

The other component, the nanoantenna, has an input resistance that ranges from a few tens to a few hundreds of Ohms, which defines an upper bound to the resistance of the MIM diode. For operation in the infrared regime, the diode’s tunneling time should be at most a few femtoseconds. The diode’s responsivity is defined as the ratio of the DC output current to the AC power arriving at the diode’s terminals. Typically, a tunnel diode with a single insulator layer does not give a high zero-bias responsivity. However, multiple insulator layers with different bandgaps and electron affinities...
can improve the diode’s nonlinear behavior and accordingly attain higher responsivity.

In this work, we report on a fabricated MIM diode and an improved version, the metal-insulator-insulator-metal (MIIM) diode, with the goal to achieve both low zero-bias resistance and high responsivity. An optimization algorithm is used to select the materials that meet our design specifications. Insulator layers with a small difference in their electron affinities, in addition to low metal-insulator barrier heights, are preferable. These requirements lead to selecting the MIM material combination for our proposed Ti-TiO$_2$-Al diode. The fabricated MIM diode has an ultrathin 1-nm thick TiO$_2$ layer. To further improve the responsivity of this diode, an MIIM diode, with TiO$_2$ and ZnO insulating layers, is proposed to achieve higher responsivity while keeping the resistance low. The insulator layers TiO$_2$ and ZnO have electron affinities of 3.9 eV and 4.1 eV, respectively. The metals Ti and Al, with work functions of 4.33 eV and 4.28 eV, respectively, are excellent candidates for metal electrodes because of their low barrier heights. The energy band diagram shown in Fig. 1 is for the Ti-TiO$_2$/ZnO-Al MIIM diode.

II. EXPERIMENTS

MIM and MIIM diodes are fabricated on 3-in. diameter silicon wafers. The wafer has a 3000 Å-thick SiO$_2$ layer as a thermal oxide. The SiO$_2$ surface was cleaned using acetone and isopropanol alcohol (IPA) and dried using a dry N$_2$ flow before device fabrication. A layer of negative photoresist, maN-1410, of thickness ~1.27 μm-thick was spin-coated onto the SiO$_2$ surface. To remove the solvent in the photoresist, the sample was soft-baked at 100 °C for 90 s. The photoresist was then patterned using a contact mask aligner (Karl Sauss MA6). After that, the wafer was exposed for 35 s, and then, the sample was developed to remove the unexposed areas of the photoresist.

Next, a 1000 Å-thick titanium film was deposited on the patterned substrate using electron-beam evaporation with a base deposition pressure set to 4 × 10$^{-6}$ Torr. The photoresist was lifted-off, forming the bottom Ti electrode of the MIM diode. The thin insulator layers were deposited using atomic layer deposition (ALD) at a chamber temperature of 150 °C. Tetrakis (dimethylamido) titanium, TDMAT, and diethylzinc (DEZ) were used as precursors for TiO$_2$ and ZnO, respectively. The precursors were pulsed for 0.1 s followed by a purge time of 20 s. Next, de-ionized water (H$_2$O) as an oxidant was pulsed for 0.015 s followed by 20 s purge time. A purge time of 33 s was chosen after each completed layer. 21 cycles are used to form 1 nm layer of TiO$_2$, while it took 10 cycles for the 0.5 nm ZnO layer.

In the second photolithography step, the sample was aligned with the mask patterns for the deposition of the top electrode. Here, a 1000 Å-thick aluminum layer was deposited by electron-beam evaporation. The second lift-off step was then carried out to form the top Al electrode of the diode. The oxide layers on top of each electrode contact were removed using reactive ion etching (RIE) with Ar. Two diode structures are fabricated: Ti-TiO$_2$ (1 nm)-Al and Ti-TiO$_2$ (1 nm)/ZnO (0.5 nm)-Al. Figure 2 shows an SEM micrograph of the fabricated MIM diode. The diode area varies from 1 × 10 μm$^2$ to 10 × 10 μm$^2$ for all diodes. The insulator layers' thicknesses were measured using variable angle spectrometer ellipsometry (VASE) for an ultrathin layer from each dielectric over a clean silicon 3-in. wafer. After repeating the aforementioned ALD cycles, the thickness is found to be 1.05 nm and 0.52 nm for TiO$_2$ and ZnO, respectively. Furthermore, both ultrathin layers were characterized
using X-ray photoelectron spectroscopy (XPS), confirming their successful deposition. The Ti 2p core-level of TiO$_2$ and similarly Zn 2p core-level of ZnO have fitting peaks as in Ref. 18 and are shown in Fig. 3.

### III. MIM DIODE CHARACTERISTICS

The $I$-$V$ characteristics of the Ti-TiO$_2$-Al MIM diode were measured using an Agilent B1500A semiconductor device analyzer connected to a Signatone S-1160 probe station with a variable temperature chuck. Figure 4 shows the measured $I$-$V$ characteristic of the Ti-TiO$_2$-Al diode with a 1-nm thick TiO$_2$ layer. The current-voltage characteristics show an almost symmetric behavior within the dc-bias range from $-0.5$ V to 0.5 V. The thin insulator layer with low energy barriers on both sides is chosen to achieve a small MIM diode resistance. Typically, the diode’s small-signal resistance is estimated as the reciprocal of the first derivative of the dc current with respect to the voltage ($I'$) calculated at each biasing voltage, i.e., $R = 1/I'$. The responsivity $S$ of the diode is determined from its non-linearity characteristics, which is also a measure of the diode’s rectified dc output current per Watt of ac input power. $S$ is obtained from the ratio between the second and the first derivatives and is given by $S = I''/(2I')$. The trade-off between the MIM diode’s resistance and responsivity is expected to show that one of these two figures-of-merit improves at the expense of the other. The resistance and responsivity of the proposed Ti-TiO$_2$-Al were calculated as shown in Fig. 3. It is observed that the diode has a small zero-bias resistance of 275 $\Omega$. This low value is suitable for the integration of the diode with nanoantennas with low matching losses. On the other hand, the responsivity shown in Fig. 3 has an absolute maximum of 3.1 A/W at 120 mV and a zero-bias $S$ value of 0.15 A/W.

Tunneling is considered the dominant conduction mechanism of charge transport through the low barrier, thin insulator layers. The possible influence of thermal emission of the electrons is also studied. The temperature is varied from 20 $^\circ$C to 55 $^\circ$C in temperature steps of 5 $^\circ$C, and the corresponding variations in $I$-$V$ characteristics are measured. As shown in Fig. 6, the $I$-$V$ characteristics change very little with temperature for the Ti-TiO$_2$-Al MIM diode with a 1-nm thick TiO$_2$. This shows that our device does not behave as a Schottky junction, in which there is a strong temperature dependence of the $I$-$V$ characteristics due to thermionic emission.
IV. MIM DIODE PARAMETER EXTRACTION

The measured $I$-$V$ characteristics of the fabricated Ti-TiO$_2$-Al MIM diode are used to perform a parameter extraction step to estimate the effective barrier heights and material properties of the fabricated devices. For films of few nanometer thickness, several values of materials’ parameters were reported in the literature.\cite{16,18,24,27,28} In the simulations, $I(V_b)$ is the tunneling current at a bias voltage $V_b$, calculated using

$$ I(V_b) = \frac{4\pi e m_e}{h^3} \int_0^\infty T(E) \int_0^{E_b} (f_h(E) - f_l(E + eV_b)) dE dE_c, \quad (1) $$

where $e$ is the electron charge, $m_e$ is the effective mass of the electron, $h$ is Planck’s constant, and $f_h$ and $f_l$ are the Fermi-Dirac distribution functions for both left and right metal electrodes of the MIM. $T(E)$ is the transmission probability of an electron with an energy $E$ to tunnel through the barrier. It is estimated using the transfer-matrix-method (TMM) based on Airy functions described in Ref. 25. The current $I$ is calculated by multiplying the density $J$ by the contact area $A$ between the metals and the insulator where tunneling takes place. The effective electron mass in the TiO$_2$ layer is considered as another parameter. The work function of one metal electrode is kept fixed during the optimization as the simulations mainly depend on the barrier heights relative to one of the electrodes’ work function. Additionally, the insulator layer thickness is one of the optimization parameters to obtain best fit between simulated and measured curves with a minimum value of 1 nm. Therefore, the barrier lowering due to image force in this thin layer could be seen as insignificant. The contact area is fixed at 12.5 $\mu$m$^2$ as measured from SEM pictures. Therefore, the calculation of tunneling current requires the following parameters: the work function of the metals, the insulators’ electron affinities, the electron effective masses in each insulator, their dielectric constants, and thicknesses. These parameters used in the parameter extraction study form a vector $\mathbf{u}$ which is defined by (3) for the case of a single insulator MIM diode,

$$ \mathbf{u} = [u_1, u_2, u_3]^T, \quad (3) $$

where $u_1 = \phi_{\text{Al}}$, $u_2 = \chi_{\text{Ti}}$, and $u_3 = m_{\text{TiO}_2}/m_e$.

The work function of Ti used in the simulation is 4.33 eV.\cite{17} The parameter $\phi_{\text{Al}}$ defines the work function of Al, while ($\chi_{\text{Ti}}, m_{\text{TiO}_2}$) represent the electron affinity and electron effective mass for TiO$_2$. The range of parameters’ values, reported in the literature, is listed in Table I, and these values are used as upper and lower limits in the optimization algorithm.

The objective function of the parameter extraction step is defined as the vector of differences between the experimentally measured current and the simulated ones at $N$ bias voltages. Our target is to find the optimal set of parameters that would minimize the maximum difference between the measured and simulated current values. The corresponding optimization problem is given by

$$ \min_{\mathbf{u}} \max_j w_j(\mathbf{u}) = \min_{\mathbf{u}} \left| I_m(v_{b_j}) - I(\mathbf{u}, v_{b_j}) \right|, \quad \forall j, \quad (4) $$

where $I_m(v_{b_j}), j = 1, 2, \ldots, N$, is the $j$th experimental $I$-$V$ characteristics at a dc bias value of $v_{b_j}, I$ is the simulation current at the same bias value $v_{b_j}$, and $\alpha$ is a predefined scaling factor to yield reasonable values of the objective function. The Jacobian of the error functions $w_j$ is supplied to the optimizer to ensure fast convergence toward the optimal objective value.\cite{25} The Jacobian matrix $J$ is estimated using central finite differences (CFDs) and is given by

$$ J = \frac{\partial \mathbf{f}}{\partial \mathbf{u}} = \begin{bmatrix} \mathbf{g}_1^T \\ \mathbf{g}_2^T \\ \vdots \\ \mathbf{g}_N^T \end{bmatrix}, \quad (5) $$

where $\mathbf{g}_j = [\partial w_j/\partial u_i], j = 1, 2, \ldots, N,$

The optimal values of the design parameters are extracted to depict a schematic plot of the energy band diagram of our Ti-TiO$_2$-Al MIM diode, as shown in Fig. 7. The Al work function is extracted as 4.28 eV. The electron affinity for TiO$_2$ is extracted as 3.8 eV, and its electron effective mass is extracted as 1.4$m_e$. These values are consistent with those determined experimentally.\cite{16,17,24,27,28} The thickness of the TiO$_2$ layer obtained from the optimization is 1.25 nm which results in better fit with the experiment. The simulated $I$-$V$ characteristics using the transfer-matrix-method based on Airy functions
are then plotted against the experimentally measured ones, as shown in Fig. 8. A good agreement between the simulated values and the measured one is obtained. Mismatches between theoretical simulations and experimental measurements may be attributed to imperfect insulators and surface roughness in addition to the rounding errors accompanying the quantum simulator at very low bias voltages. The asymmetry noticed in diode’s response is not significant and can be illustrated through Fig. 9, where the MIM energy band is depicted at positive and negative biases. The small difference in work functions between Ti and Al ∼50 meV resulted in a relatively symmetric I-V characteristic and low total rectification efficiency. Therefore, it may not be practical to use this diode in self-biased energy harvesting applications.

V. PROPOSED MIIM DIODE CHARACTERISTICS

For our proposed Ti-TiO₂/ZnO-Al MIIM diode with 1 nm TiO₂ and 0.5 nm ZnO insulator layers, the current-voltage characteristics are measured following the same steps in Sec. III. Lower values of current are expected for the fixed diode contact area because of the larger insulator thickness. The measured I-V characteristics of the MIIM diode are presented in Fig. 10. However, the I-V asymmetry and consequently the current rectification ratio are improved as compared to the MIM diode and shown in Fig. 11. Moreover, the range of the diode’s responsivity is enhanced. The current values are fitted to a 7th order polynomial and used to calculate the derivatives to determine the resistance and responsivity. Figure 12 shows the resistance and responsivity of the MIIM diode. The zero-bias resistance is calculated as 312 Ω accompanied with a zero-bias responsivity of 1.6 A/W. The MIIM diode exhibits a maximum responsivity of 5.1 A/W at a bias of −200 mV.

For comparison, we show in Table II the resistance and responsivity values of different MIM or MIIM diodes previously reported in the literature. In the table, a comparison of the zero-bias resistance, the zero-bias responsivity, the maximum responsivity, and the thickness of insulators’ layers and diode’s contact area is given. The diodes included in this comparison are the ones whose zero-bias resistance and responsivity were reported together. The sensitivity values reported previously, calculated as $S = I''/I'$, are scaled down by a factor of 2 to have a fair comparison with our responsivity values. Thus, the comparison is made consistent by normalizing all the published results in the table to the contact area. Additionally, the cut-off frequency, as defined in Ref. 31, is calculated for all diodes and tabulated in the last two columns in Table II. The cut-off frequency is calculated for all diodes by considering the area of

![Figure 8](image1.png)

**FIG. 8.** The current-voltage characteristics of the MIM diode; the measured results (−) vs the simulation results using the extracted parameters (red filled diamonds).

![Figure 9](image2.png)

**FIG. 9.** The energy band diagram for the MIM diode with extracted materials’ parameters at (a) positive bias ($V_b = 0.5$ V) and (b) negative bias ($V_b = −0.5$ V).

![Figure 10](image3.png)

**FIG. 10.** The measured current-voltage characteristics for the Ti-TiO₂/ZnO-Al MIIM diode, with a ZnO layer thickness of 0.5 nm.

![Figure 11](image4.png)

**FIG. 11.** The measured current-voltage characteristics for the Ti-TiO₂/ZnO-Al MIIM diode (black solid curve) compared with Ti-TiO₂-Al MIM diode (blue dashed curve); TiO₂ layer of 1 nm thickness.

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0.01 μm² and an antenna resistance of 55 Ω. The dielectric constants used in the calculations are the given ones in the corresponding publications, as in Table II, otherwise from the literature.²⁷ By considering the zero-bias responsivity and cut-off frequency, our proposed MIIM diode shows a comparable performance with the higher cut-off frequency compared with the other diodes listed in Table II.

VI. MIIM DIODE PARAMETER EXTRACTION

The measured I-V characteristics of the fabricated Ti-TiO₂/ZnO-Al MIIM diode are used to perform a parameter extraction step similar to that in Sec. IV to estimate the effective material properties using Eqs. (1)–(5). The insulator layer thicknesses are fixed at 1 nm and 0.5 nm for TiO₂ and ZnO, respectively. In the transfer-matrix-method (TMM), the ratio between the dielectric constants of each insulator layer is important, rather than the absolute value of each one as the image force effect on lowering the barrier is still considered insignificant in these ultrathin insulator layers.²⁷ The voltage difference (drop), dv, across each insulator layer is calculated through the following formulas:

\[
\begin{align*}
\Delta v_1 &= \frac{d_1}{\varepsilon_{r1}} (\Delta \phi + \varepsilon_{b1}) = \frac{\varepsilon_{r1}}{\varepsilon_{r2}} (\Delta \phi + \varepsilon_{b2}) = \frac{d_1}{\varepsilon_{r1}} (\Delta \phi + \varepsilon_{b2}), \\
\Delta v_2 &= \frac{d_2}{\varepsilon_{r2}} (\Delta \phi + \varepsilon_{b2}) = \frac{d_2}{\varepsilon_{r2}} (\Delta \phi + \varepsilon_{b2}), \\
\Delta v_j &= \frac{d_j}{\varepsilon_{rj}} (\Delta \phi + \varepsilon_{bj}) = \frac{d_j}{\varepsilon_{rj}} (\Delta \phi + \varepsilon_{bj}), \\
\Delta v &= \frac{d}{\varepsilon_1} (\Delta \phi + \varepsilon_{b1}) = \frac{d}{\varepsilon_1} (\Delta \phi + \varepsilon_{b2}),
\end{align*}
\]

where εᵣ and dⱼ are the dielectric constant and thickness of the jth insulator layer, respectively. Δϕ is the work function difference between the two metals used as electrodes, and vₒ is the bias voltage. It is noticed that the voltage drop across each insulator depends on the ratio εᵣ/ε₂. Therefore, this ratio is added to the parameter set. The parameters used in the parameter extraction study form a vector u which is defined as

\[
u = \left[ u_1, u_2, u_3, u_4, u_5, u_6 \right]^T,
\]

where u₁ = ϕ₁, u₂ = χ₁, u₃ = χ₂, u₄ = εᵣ1/ε₂2, u₅ = m₁/m₂, and u₆ = m₂/ε₁. (χ₁, m₁) and (χ₂, m₂) represent the electron affinity and electron effective mass for TiO₂ and ZnO, respectively.

The optimal values extracted from the MIM diode case are used to obtain the remaining material properties of the MIIM diode. The electron affinity for ZnO is extracted as 4.16 eV combined with electron effective mass of 0.23m₀. The ratio between dielectric constants of TiO₂ and ZnO is estimated as 2.5. The diode area of 50 μm² from SEM images is used. By combining design parameters of the materials used in our proposed Ti-TiO₂/ZnO-Al MIIM diode, a schematic energy band diagram is presented in Fig. 13. These material properties are consistent with those determined experimentally in the literature²⁰,²⁷,²².²² The material properties extracted from optimization as compared to the theoretical values are shown in Table I. Simulated I-V characteristics are then plotted against the

### TABLE II. Comparison of different MIM/MIIM diode structures and corresponding zero-bias resistance, zero-bias, maximum responsivity, and cut-off frequency.

| References | Diode type | Contact area (μm²) | Oxide thickness (nm) | Zero-bias resistance (Ω) | Zero-bias resistance normalized to 12.5 μm² (Ω) | Zero-bias responsivity (A/W) | Maximum responsivity (A/W) | Cut-off frequency normalized to 0.01 μm² (THz) |
|------------|------------|-------------------|----------------------|--------------------------|-----------------------------------------------|-------------------------------|-----------------------------|-------------------------------|
| 6          | Ni-NiO/ZnO-Cr | 400               | ~7                   | 234 M                    | 7.48 G                                        | 1.3                          | 8.0                         | 36.4                          |
| 19         | Pt-HfO₂/TiO₂-Ti | 400               | 3                    | 100 k                    | 3.20 M                                        | ...                         | ~0.1                        | 2.6                           |
| 20         | Al-Al₂O₃-Pt   | 5.6 × 10⁻³        | ~2                   | 220 k                    | 99                                            | 0.25                         | ~1.15                       | 9.1                           |
| 8          | Ni-NiO-Cr/Pt  | 1.45              | 3                    | 0.5 M                    | 58 k                                          | 0.5                          | 2.5                         | 11.7                          |
| 9          | Ti-OTS-Pt     | 100               | ~2                   | 80 k                     | 0.64 M                                        | 2.75                         | ~6.5                        | 40.1                          |
| 21         | Pt-ZnO-Ti     | 9 × 10⁴           | ~4                   | 1210                     | 8.71 M                                        | 0.125                        | 0.55                        | 5.2                           |
| 22         | Ni-NiO-Ni     | 0.018             | ~2.3                 | 42.4 M                   | 61.03 k                                       | 0.41                         | 2.65                        | 8.9                           |
| 31         | Au-Al₂O₃-Ti   | 0.04              | ~1.5                 | 98 k                     | 314                                           | 0.44                         | ~2                          | 10.5                          |
| This work  | Ti-TiO₂-ZnO   | 12.5              | 1                    | 275                      | 275                                           | 0.15                         | 3.1                         | 7.8                           |
| This work  | Ti-TiO₂/ZnO-Al| 50                | 1.5                  | 312                      | 1248                                          | 1.6                          | 5.1                         | 17.4                          |
FIG. 13. The extracted energy band diagram of the proposed Ti-TiO$_2$/ZnO-Al MIIM diode at equilibrium: the thickness of TiO$_2$ and ZnO layers is 1 nm and 0.5 nm, respectively.

The capacitance of the MIM diode is measured as 36.9 fF/μm$^2$. This corresponds to a dielectric constant of the TiO$_2$ 1-nm layer of 4.2 which agrees with that reported for a 2-nm ultrathin layer. Additionally, the dielectric constant ratio obtained from the parameter extraction step is 2.42. The dielectric constant of the ultrathin ZnO layer is thus estimated as 1.7. These dielectric constants for the proposed ultrathin oxides result in a capacitance of 16.6 fF/μm$^2$. Therefore, the materials proposed in our work represent a promising material combination for MIIM diodes working at terahertz (THz) frequencies, but in this case, the diode’s area should be less than 0.01 μm$^2$. These small areas should allow an RC time constant in the range of 9.1 fs with a cut-off frequency of 17.4 THz by considering a 55 Ω antenna resistance.

In the case of rectenna devices, the RC coupling efficiency multiplied by the diode-nanoantenna impedance matching efficiency is used to estimate the total efficiency of the diode.

Figure 15 shows the change in the energy band profile according to bias voltages with different polarities. During the positive bias in Fig. 15, the electrons undergo a direct tunneling through TiO$_2$ and ZnO. By increasing this bias, the ZnO barrier tilts more, allowing Fowler-Nordheim tunneling through the triangular barrier. This consequently results in a significant current flow.

In the case of negative bias voltages, as shown in Fig. 15, the electrons undergo direct tunneling through a 1.5-nm thick barrier even with increasing bias voltages. Therefore, an asymmetric behavior in I-V characteristics is achieved at these low bias conditions.

The diode efficiency vs frequency: the efficiency plotted as the product of matching efficiency between the diode and the nanoantenna assuming an antenna resistance of 55 Ω and the RC coupling efficiency.

VII. CONCLUSION

A Ti-TiO$_2$-Al MIM diode with a 1-nm thin insulator layer was fabricated and characterized. The proposed MIM diode has a zero-bias resistance of 275 Ω. The maximum responsivity is calculated as 3.1 A/W at 120 mV, where the corresponding resistance is 200 Ω. An improved diode, the Ti-TiO$_2$/ZnO-Al MIIM diode with 1 nm TiO$_2$ and 0.5 nm ZnO, ALD deposited, layers, was also fabricated
and studied. This MIIM diode has a zero-bias resistance of 312 Ω and a zero-bias responsivity of 1.6 A/W. A maximum responsivity of 5.1 A/W is achieved at a bias of 0.2 V. A gradient-based constrained optimization algorithm was utilized to extract the effective physical parameters of the fabricated devices based on the tunneling mechanism. Good agreement between the measured responses and the simulation results was achieved using the extracted parameters. The proposed MIIM diode has a capacitance of 16.6 fF/μm², allowing a time constant of approximately 9.1 fs for 0.01 μm² diode area. Therefore, the material combinations presented in this work offer promising candidates for energy harvesting applications in the terahertz frequency range by considering 0.01 μm² area or smaller.

REFERENCES

1. A. McEvoy and T. Markvart, Solar Cells: Materials, Manufacture and Operation (Academic Press, 2012).
2. C. Deibel, V. Dyakonov, and C. J. Brabec, IEEE J. Sel. Top. Quantum Electron. 16, 1517 (2010).
3. G. Moddel, Rectenna Solar Cells (Springer, 2013), pp. 3–24.
4. R. L. Bailey, J. Eng. Power 94, 73 (1972).
5. S. Grover and G. Moddel, Solid-State Electron. 67, 94 (2012).
6. I. Azad, M. K. Ram, D. Y. Goswami, and E. Stefanakos, Langmuir 32, 8307 (2016).
7. P. Maraghechi, A. Foroughi-Abari, K. Cadien, and A. Y. Elezzabi, Appl. Phys. Lett. 99, 253503 (2011).
8. S. Krishnan, H. La Rosa, E. Stefanakos, S. Bhansali, and K. Buckle, Sens. Actuators, A 142, 40 (2008).
9. D. Etor, L. E. Dodd, D. Wood, and C. Balocco, in 2016 41st International Conference on Infrared, Millimeter, and Terahertz Waves (IEEE, 2016), pp. 1–2.
10. N. Alimardani and J. F. Conley, Jr., Appl. Phys. Lett. 105, 82902 (2014).
11. I. Z. Mitrovic, A. D. Weerakkody, N. Sedghi, S. Hall, J. F. Ralph, J. S. Wrench, P. R. Chalker, Z. Luo, and S. Beeby, ECS Trans. 72, 287 (2016).
12. M. Bareiß, P. M. Krenz, G. P. Szakmany, B. N. Tiswari, D. Kälblein, A. O. Orlov, G. H. Bernstein, G. Scarpas, B. Fabel, U. Zschieschang et al., IEEE Trans. Nanotechnol. 12, 1144 (2013).
13. J. G. Simmons, J. Appl. Phys. 34, 1793 (1963).
14. J. C. Ramírez, M. J. Deen, and C.-H. Chen, Microelectron. Reliab. 46, 1939 (2006).
15. F. J. González and G. D. Boreman, Infrared Phys. Technol. 46, 418 (2005).
16. X. Liu, S. Wang, J. Zhang, J. Zhang, and Y. Gu, J. Appl. Phys. 116, 245101 (2014).
17. S. Kar, High Permittivity Gate Dielectric Materials (Springer, 2013).
18. R. I. Z. Hoyer, B. Ehrler, M. L. Bohm, D. Muñoz-Rojas, R. M. Altamimi, A. Y. Alyamani, Y. Vaynzof, A. Sadhanala, G. Ercolano, N. C. Greenham et al., Adv. Energy Mater. 4, 1301544 (2014).
19. O. A. Ajayi, Ph.D. thesis, University of South Florida, 2014.
20. A. A. Khan, G. Jayaswal, F. A. Gahaffar, and A. Shamim, Microelectron. Eng. 181, 1 (2017).
21. K. Choi, F. Yesilkoy, G. Ryu, S. H. Cho, N. Goldsman, M. Dagenais, and M. Peckerar, IEEE Trans. Electron Devices 58, 3519 (2011).
22. F.-C. Chiu, Adv. Mater. Sci. Eng. 2014, 1.
23. S. B. Herner, A. D. Weerakkody, A. Belkadi, and G. Moddel, Appl. Phys. Lett. 110, 223901 (2017).
24. I. E. Hashem, N. H. Rafat, and E. A. Soliman, IEEE J. Quantum Electron. 49, 72 (2012).
25. M. Bakr, *Nonlinear Optimization in Electrical Engineering With Applications in MATLAB* (Institution of Engineering and Technology, 2013).
26. K. Jacobi, G. Zwicker, and A. Gutmann, Surf. Sci. 141, 109 (1984).
27. B. Enright and D. Fitzmaurice, J. Phys. Chem. 100, 1027 (1996).
28. J. Zhang, P. Zhou, J. Liu, and J. Yu, Phys. Chem. Chem. Phys. 16, 20382 (2014).
29. T. Zhang, P. Zhou, J. Liu, and J. Yu, Phys. Chem. Chem. Phys. 16, 20382 (2014).
30. M. Bareiß, D. Kälblein, C. Jirasek, E. Ankevich, P. Vlatchkova, B. Lotsch, U. Zschieschang, H. Klauck, G. Scarpas, B. Fabel et al., Appl. Phys. Lett. 101, 83113 (2012).
31. G. Jayaswal, A. Belkadi, A. Merev, B. Pelz, G. Moddel, and A. Shamim, Mater. Today Energy 7, 1 (2018).
32. X. L. Zhang, G. J. Wu, C. L. Zhang, T. L. Xu, and Q. Q. Zhou, Atmos. Chem. Phys. 15, 12139 (2015).
33. J. Kischkat, S. Peters, B. Gruska, M. Semtsiv, M. Chashnikova, M. Klinkmüller, O. Fedosenko, S. Machulik, A. Aleksandrova, G. Monastyrskyi et al., Appl. Opt. 51, 6789 (2012).