Solar Spectrum Rectification Using Nano-Antennas and Tunneling Diodes
(Invited Paper)

Mario Dagenais, Kwangsik Choi, Filiz Yesilkoy, Athanasios N. Chryssis, Martin C. Peckerar
Department of Electrical and Computer Engineering, University of Maryland,
College Park, MD 20742, USA

ABSTRACT

Our goal is to develop a rectifying antenna (rectenna) applicable to solar spectrum energy harvesting. In particular, we aim to demonstrate viable techniques for converting part of the solar spectrum not efficiently converted to electric power by current photovoltaic approaches. Novel design guidelines are suggested for rectifying antenna coupled tunneling diodes. We propose a new geometric field enhancement scheme in antenna coupled tunneling diodes that uses surface plasmon resonances. For this purpose, we have successfully implemented a planar tunneling diode with polysilicon/SiO$_2$/polysilicon structure. An antenna coupled asymmetric tunneling diode is developed with a pointed triangle electrode for geometric field enhancement. The geometrically asymmetric tunneling diode shows a unique asymmetric tunneling current versus voltage characteristic. Through comparison with crossover tunneling diodes, we verified that the current asymmetry is not from the work function difference between the two electrodes. Results of RF rectification tests using the asymmetric diode demonstrate that our approach is practical for energy harvesting application. Furthermore, we describe how surface plasmons can enhance the electric field across the tunnel junction, lowering the effective “turn-on” voltage of the diode, further improving rectification efficiency.

Keywords: MIM diode, tunneling diode, asymmetric tunneling diode, surface plasmon, surface plasmon resonance

1. INTRODUCTION

MIM tunneling diode research started in the 1960s [1]. The early MIM tunneling diodes consisted of a sharp metal tip on a different metal plane with a thin insulation layer or air gap in between. This was similar to the whisker or point-contact diode in use since the nineteenth century for RF detection. These new whisker diodes showed good performances for detecting and mixing high frequency waves up to infrared and visible range [2-4]. However, the whisker device characteristics had some important drawbacks: it was not easy to get reproducible devices, and the devices were mechanically fragile. A new type of MIM diode was developed to overcome those weaknesses that used thin film technologies. These thin film MIM diodes were developed by Gustafson and Bachner in 1974 [5, 6]. Their thin film techniques provided process reproducibility, integration ability with other popular electronics, and device robustness for MIM diodes. Thanks to modern high resolution e-beam patterning technology, thin film tunneling diodes are now implemented with small geometries that are proper for high frequency operation [7-9].

Based on the rectification properties of MIM diodes, most research has focused on detecting and mixing high frequency waves. The rectification characteristic of high frequency waves leads to the potential application of MIM diodes to energy harvesting including direct solar energy conversion [10, 11]. However, the low rectification efficiency of tunneling diodes is a main barrier to efficient harvesting. Kale described the conversion efficiency of tunneling devices [12], and Hobbs restated the efficiency factors using recent developed MIM tunneling diodes [13]. In these references, the total conversion power efficiency ($\eta$) for an antenna coupled MIM diodes is expressed as follows:

$$\eta = \eta_a \eta_s \eta_c \eta_j$$

where $\eta_a$ is the antenna efficiency defined by the ratio of collected power to intercepted power, $\eta_s$ is the efficiency related to the antenna material, $\eta_c$ is the matching efficiency between the antenna and the tunneling diode impedance,
and $\eta_j$ is the quantum efficiency of a tunneling diode. Therefore, the integrated antenna needs to be designed to resonate at a particular wavelength in order to obtain high antenna efficiency. Furthermore, the antenna material needs to be selected carefully by considering the loss at the wavelength of interest in order to obtain high $\eta_j$. Also, reducing the tunneling junction resistance is critical for the impedance matching between an antenna and a tunneling diode because the antenna resistance is usually small (typically below several hundred ohms).

Furthermore, describing the tunneling diode as a simple one pole system, the parallel configuration of a tunneling junction resistor and capacitor should have a small enough RC time constant for high frequency operation. The quantum efficiency is defined by the ratio of the generated electrical power to the incident optical power. So, it is directly related to the diode sensitivity and is expressed by

$$\eta_q = -\frac{h\nu}{q} \cdot \frac{S}{2},$$

where $h$ is the Plank’s constant, $\nu$ is angular frequency, $q$ is the electron charge, and $S$ is the diode sensitivity, which is explained more explicitly in the next section. As shown in Eq. (2), increasing the diode sensitivity is directly related to increasing the quantum efficiency, and the sensitivity can be increased by improving the nonlinearity of tunneling current in tunneling diodes. For solar energy conversion application, we have to maximize each efficiency factors. Until now, we have focused our efforts mostly on improving the quantum efficiency.

In this paper, rectenna design guidelines for solar energy conversion are introduced by combining two core concepts of optical antennas and antenna coupled tunneling diodes. Also, we introduce our unique tunneling devices, a perfect planar tunneling diode and an asymmetric tunneling diode, which were developed according to our guidelines. The detailed fabrication and measurement of developed diodes are given, and RF rectification results using an asymmetric tunneling diode are presented.

## 2. OPTICAL RECTENNA: COMBINING OPTICAL ANTENNA & TUNNELING DIODE

### 2.1 Tunneling Diode

The main current transport mechanism of MIM diodes is tunneling through a potential barrier, which is described by quantum mechanics. Figure 1 shows the energy band diagram of a MIM diode that has the same metal for the two electrodes. The Fermi levels are located at the same level at equilibrium state as shown in Figure 1 (a), so that there is no net current flow between the two electrodes. A net current flow can be achieved by applying an external bias to the MIM diode as shown in Figure 1 (b). For the tunneling current, the barrier thickness is required to be thinner than 4 nm typically. Over 4 nm barrier thickness, thermal current may dominate [14].

![Energy band diagram of a MIM tunneling diode with same metal electrodes: (a) equilibrium state and (b) biased state. Here, $E_F$ is the Fermi level of the metal, $\varphi$ is the barrier height, which is work function of the metals also, and $d$ is the barrier thickness.](image)
The basic mechanism for detecting waves in MIM tunneling diodes is the rectification of an incident wave to a DC output through the nonlinearity of tunneling current. The rectified DC voltage can be expressed as

\[
V_{\text{rect}} = -\frac{1}{4} \frac{I''(V_{\text{bias}})}{I'(V_{\text{bias}})} V_{\text{ac}}^2 = -\frac{1}{4} S V_{\text{ac}}^2, \tag{3}
\]

where \(V_{\text{bias}}\) is the injected AC signal into a tunneling junction, \(V_{\text{ac}}\) is the applied DC bias voltage, \(I'\) is the first derivative of tunneling current, \(I''\) is the second derivative of tunneling current, and \(S\) is the device’s sensitivity, a figure of merit for tunneling diodes, defined by the ratio of the second derivative to the first derivative of the tunneling current \[15\]. Also, the rectified DC current is proportional to the second derivative of the tunneling current, the curvature of the tunneling current. Therefore, increasing the nonlinearity is the key to improving the rectification performances of MIM diodes.

2.2 Optical Antenna

An optical antenna is a device that efficiently couples incident waves into a confined region of sub-wavelength size through the lightning rod effect, so it can generate higher field intensity than the intensity of the incident wave. In a coupled structure like a bowtie shape with a gap between the two flares, the gap is working as a resonant cavity. The field intensity inside the gap is further enhanced through antenna-like resonances or surface plasmon resonances. The surface plasmon resonances can be excited through direct light illumination on nanometer size patterns without a specific coupling technique. Through experiments and simulations, many researchers have observed the field enhancement effect by illuminating nano-size metal patterns and optical antennas \[16-19\]. This near field enhancement effect, due to both the lightning rod effect and the cavity resonances in the gap, is the first core operating principle of an optical antenna and can be exploited in antenna coupled tunneling diodes for performance improvement.

2.3 Rectenna Design Guidelines for Solar Spectrum Rectification: Combining a Tunneling Diode with an Optical Antenna

To convert solar energy efficiently, we want to combine a tunneling diode with an optical antenna that strongly enhances the electric field. The tunneling diode is located at the mid-point of the dipole antenna. Previous works have also used tunneling diodes with antennas. Typically, the antennas that were made did not take full advantage of the lightning rod effect (the first core principle of operation) to enhance the electric field at the tip of the metal electrodes near the center of the antenna or of the enhanced electric field in the center gap of the antenna. Also, very often, the tunneling diode was not coplanar with the antenna. This is our second core operating principle. Therefore, these tunneling diodes could not take advantage of the enhanced electric field with in-plane polarization. In our approach, we remedy this situation by taking advantage of the enhanced electric field due to a very sharp metal tip electrode and by controlling the size of the gap between the sharply pointed electrode and the other metal electrode forming the optical antenna. We also advocate using the enhanced in-plane electric field to enhance the tunneling current in the in-plane tunneling diode.

These two differences provide two basic design guidelines for tunneling diode development: planar and pointed tunneling junction structure. Therefore, an antenna coupled tunneling diode underlying such structures can use the near field enhancement effect of an optical antenna in the tunneling barrier. This can have the same effect as increasing the incident power, so the magnitude of the injected AC signal can be effectively increased in the tunneling barrier. Furthermore, a sharp tip helps carrier tunneling due to the lightning rod effect. Therefore, the nonlinearity of the tunneling current can be improved, and the quantum efficiency can be increased.

3. PLANAR TUNNELING DIODE DEVELOPMENT

3.1 Perfect Planar Tunneling Diode for Rectenna

Initially we focused our efforts on developing a planar tunneling diode with a bowtie antenna shape using polysilicon instead of metals. Polysilicon is easier to pattern than metals, allowing us to achieve structures with sharp points (low radius of curvature). Also for device fabrication, we focused on achieving extremely small tunneling junction area to
reduce junction capacitance for high speed operation. The details of the process and measurement made on the resulting structures are presented below.

3.2 Fabrication Process of Perfect Planar Tunneling Diode

First, for device isolation, we start with SiN deposition on a Si wafer using PECVD, and then a polysilicon layer is deposited on the SiN using LPCVD to create the active device material. Each layer is of 800 Å and 600 Å thickness, respectively. Polysilicon doping is performed using a spin-on-dopant (SOD) for phosphorus diffusion, followed by RTA to diffuse the dopants. After SOD coating, the sample is baked at 200 °C for 20 minute on a hot plate. A simple RTA process at 1000 °C during 30 second transfers the dopants into the deposited polysilicon layer. Finally, the SOD is removed using a buffered oxide etchant (BOE).

For device patterning, we use e-beam writing instead of optical lithography because of its higher resolution. A bowtie is chosen for the basic device shape with 60° flare angle. HSQ and CD-26 are used as e-beam resist and developer, respectively. A 10 kV acceleration voltage and 10 um aperture size result in 12 pA current for a Raith e-LiNE writer. The 160 uC/cm² writing dose gives almost perfect dose clearance for the bowtie patterns. After development, RIE etching is applied using SF₆ and O₂ to etch out the polysilicon layer. Electron exposed HSQ patterns work as an etch stop layer during RIE etching and is removed using BOE after dry etching. Figure 2 shows a bowtie pattern after RIE etching. Right after the RIE etching, the two flares of the bowtie are connected by a thin polysilicon knot (the inset SEM image in Figure 2). Note that the antenna was not designed for a specific wavelength.

![Figure 2](image.png)

Figure 2. A SEM image of a perfect planar antenna coupled diode after RIE etching. The inset image shows a really thin polysilicon knot.

To implement a tunneling barrier, we use a boiling water oxidation process. This accelerates growth of the native oxide [20]. Before oxidation, a native oxide layer is etched out using BOE. Then, the sample is oxidized in boiling water for 1 minute. This etching and oxidation process is repeated until a polysilicon knot is transformed to a SiO₂ layer. The transformation is monitored by DC current-voltage measurements.

To check the polysilicon etch rate by the boiling water oxidation and the BOE etching process, an experimental cycle was set: 20 second etch in BOE and 1 minute oxidation in boiling water. The etch rate is monitored by SEM for the different number of cycles on different samples. From the experiments, the average etch rate is approximately 7 Å per cycle. This is a highly controlled process! The same etch and boiling process was applied to a real device, which had really tiny knot size as shown in Figure 3 (a). Figure 3(b) shows a SEM image of the same bowtie pattern after one cycle of the etching/oxidation process using boiling water. The SEM images show that the polysilicon knot is etched out after one cycle etching and oxidation process.
3.3 Measurement Result of Perfect Planar Tunneling Diode

DC current-voltage measurements were performed to observe the tunneling currents using a probe station and a parameter analyzer at room temperature. Figure 4(a) shows the IV result of the device in Figure 3 (a), before the etching and oxidation process. A linear IV relation was recorded. However, the IV characteristic becomes nonlinear after the etching and oxidation process, as shown in Figure 4(b). The filled circle line is a theoretical fit using Simmons tunneling current model [14]. For the fit, the junction area and insulator type are assumed to be 60 nm² and SiO₂, respectively. The theoretical fit yields a 1.38 nm oxide thickness.

For further analysis, the fifth order polynomial fit is applied to the measured data, shown in Figure 4. Using the polynomial fit, I’ and I” are obtained. The sensitivity is calculated as I”/ I’. Figure 5 shows each processed data. The highest sensitivity was around 6 at 0.35V.

Figure 3. Before and after applying boiling water oxidation process to a polysilion knot.

Figure 4. DC current-voltage measurement data: (a) before boiling water etching & oxidation process, and (b) after one cycle of boiling water etching & oxidation process.
4. ASYMMETRIC TUNNELING DIODE FOR OPTICAL RECTENNA

4.1 Asymmetric Tunneling Diode for Rectenna

We successfully implemented a perfect planar tunneling diode using polysilicon. However, the process yielded less than 50% good diodes. The surviving diodes were prone to electrical overstress. Also, although the tunneling junction was extremely small, the tunneling resistance was relatively large due to the small tunneling junction area. This can be a serious problem for impedance matching between an integrated antenna and the tunneling junction. So, three things were considered in the second stage of our tunneling diode development for solar energy conversion: developing a simple but high yield process, increasing the tunneling current level, and achieving an asymmetric tunneling current characteristic.

Sufficient asymmetry makes it possible to operate the tunneling diode at zero-bias condition for detecting incident waves, so this is a very critical point for energy harvesting applications of tunneling diodes [9]. A common approach for achieving asymmetric currents in tunneling diodes is using dissimilar metal electrodes [9, 21]. The combination of different density of states and different work functions leads to current voltage asymmetric relation in a MIM structure [22]. However, this scheme is limited by material properties.

Based on the two design guidelines and the three considerations, we have developed a unique asymmetric tunneling diode using a geometric field enhancement scheme. A sharply pointed tip of a triangle electrode, of which the end part is covered by another electrode, implements the geometric field enhancement scheme. Details of the diode fabrication and test results are summarized below.
4.2 Fabrication Process of Asymmetric Tunneling Diode

The fabrication procedure and used materials are similar to the previously described “perfect” planar tunneling diode except for the electrode shape. Figure 6 shows the process flow of an asymmetric diode using a cross view through a line L1 on the top view shown in Figure 6(i). Instead of a bowtie shape, a single triangle with a pointed tip is prepared by RIE etching doped polysilicon layer. The entire triangle polysilicon electrode is passivated by a boiling oxidation process to make a tunneling barrier. For the other electrode and pads, a common metal lift-off process is used with Ti/Au metal evaporation process. More details of the fabrication process can be found in [23].

![Diagram of fabrication process](image)

Figure 6. Process flow of asymmetric tunneling diode fabrication. Each schematic is a cross view through the line L1 in the schematic (i). In the schematic (i), surface oxide is not shown.

Figure 7(a) shows a sharp polysilicon tip of a triangle electrode after polysilicon etch using RIE. A completed tunneling diode with a polysilicon-SiO$_2$-metal structure is shown in Figure 7(b).
Figure 7. SEM images of an asymmetric tunneling diode: (a) a pointed polysilicon triangle pattern after RIE etching, and (b) a completed asymmetric tunneling diode. The inset photo in (b) shows entire diode shape.

4.3 DC Measurement Result of Asymmetric Tunneling Diode

The same DC measurement set-up is used. For all tests, the metal electrode is grounded, and a bias is applied to the polysilicon electrode. The measured DC current-voltage result is shown in Figure 8 for an asymmetric tunneling diode with a polysilicon electrode of 0.35 um² tunneling junction area. The nonlinear I-V relation demonstrates that the boiling water process makes a continuous surface tunnel oxide layer on polysilicon electrode. The result in Figure 8 shows a clear asymmetric tunneling current characteristic. The asymmetry factor is defined as the absolute value of the ratio of the reverse to forward currents, shown with empty triangles in Figure 8. As the applied bias goes up, the asymmetry factor continuously increases and reaches a value of 5 at 0.4 V.

![Graph showing current-voltage relationship](image)

Figure 8. DC current-voltage measurement data for an asymmetric tunneling diode.

As mentioned before, this kind of asymmetric tunneling characteristic can be the result of the work function difference between doped polysilicon and titanium, the first metal layer of the other metal electrode. To verify the geometric effect on tunneling current, another type of tunneling devices using a crossover pattern of the same doped polysilicon and the Ti/Au metal line is prepared together with asymmetric triangle diodes. The DC current-voltage result of the crossover diodes show almost symmetric tunneling current characteristic, and the asymmetry factor is below 1.2 at the same bias range. From this result, it can be concluded that the asymmetric I-V characteristic of a sharp triangle diode is mainly due to the geometric field enhancement through a pointed tip, not from the work function difference between the doped polysilicon and the metal electrode.
Using the same procedure, further data analysis is performed and shown in Figure 9. The differential resistance is calculated using the first derivative of tunneling current and plotted in Figure 9 (b). The zero-bias resistance is around 120 MΩ. The maximum sensitivity is -14.5 V⁻¹ at -0.14 V, as shown in Figure 9 (d).

Figure 9. (a) DC current-voltage measured data and 5th order polynomial fit. (b) Differential resistance using 1st derivative of the tunneling current. (c) The 2nd derivative of the tunneling current. (d) Calculated diode sensitivity.

Another possible current transport mechanism in tunneling diodes is thermionic emission. If thermionic emission dominates, the diode cannot detect high frequency incident waves [4]. Thermionic emission can be removed from tunneling current through low temperature measurements. In Figure 10, DC current-voltage measurement data at room temperature and 77 K are plotted together, and the diode sensitivity is extracted using a polynomial fitting method for another asymmetric diode of 0.54 um² junction area. At 77 K, the current level is decreased, but it still shows an asymmetric behavior. The reduction of tunneling current may be mainly due to a small decrease of the conductance of the doped polysilicon electrode, not to the thermionic emission reduction. The plot also shows sensitivity improvement at 77 K compared to the room temperature results.
4.4 RF Rectification Test using Asymmetric Tunneling Diode

An RF rectification test was performed using an asymmetric tunneling diode. The overlap tunneling junction capacitance is estimated to be around 2 fF, and the zero-bias tunneling resistance is about 100 KΩ. This gives a RC time constant of 0.2 x 10^9 second (cutoff frequency ~ 5 GHz). Note that this diode was not designed for high frequency operation.

For testing the rectification characteristic of the diode, a commercial log periodic antenna with ultra-wideband (part# HG2458-08LP) is used as a transmitter, and HP 8350B sweep oscillator is used for a RF source in the continuous wave mode with 12.5dBm input power. The antenna is aligned such that the polarization of the radiated RF waves from the antenna is parallel with the axis of symmetry of an I-V asymmetric tunneling diode. The distance between the diode and the antenna is about 9 cm. Without applied bias, the diode current is sampled continuously during 240 seconds by a parameter analyzer. The RF source is turned on and off at around every 10 seconds by increasing the frequency with a 200MHz step.

Figure 11 shows the rectified DC current from an asymmetric tunneling diode under zero-bias. To confirm that this result is not from a “parasitic” antennas (bond wires, bond pads, probing pin, etc.), which can pick up the incident waves, we conducted the same test on two different Ni/NiO/Ni tunneling diodes fabricated on the same wafer. One diode structure uses a triangular shape electrode; the other uses a rectangular junction. Note that the nickel triangle electrode was not as sharp as the polysilicon triangle because it was fabricated through a common metal lift-off process. The fabrication process, the diode gap distance, and all pads and bias feeding lines are the same as for the previous asymmetric tunneling diode. After tests, only the diode with a triangle electrode responded to the incident waves. The rectangular diode did not exhibit any response to the RF waves, even though it had a similar calculated RC time constant to the triangle diode. It appears that the bond wires assisted the triangle antenna together with the lightning rod effect in generating the RF signal rectified by the tunneling diode.

The polarization dependence for the polysilicon asymmetric tunneling diode was tested by rotating the diode. The maximum rectified current was obtained when the diode was aligned to be parallel to the incident wave’s polarization. As the rotation angle was increased, the rectified current was reduced. When the diode was rotated at 90° from the maximum output position, the response disappeared. Through the tests, we verified that the rectified DC current is the output of the asymmetric diode itself.

The DC rectification result of the asymmetric tunneling diode, shown in Figure 11, proves that our approach is practical and useful for RF energy harvesting applications at least. The different DC current levels measured at different frequencies may be due to the antenna own frequency response. On the other hand, we checked the S11 response of the emitting antenna using a network analyzer, and its response did not agree with the observed frequency dependence for the detected signal over the 2.3GHz ~ 6.5GHz range.

Figure 10. DC current-voltage measurement data and calculated diode sensitivity at room temperature and 77K for another asymmetric tunneling diode.
Based on our suggested guidelines for optical rectenna development that favor a planar and a very sharply pointed structure, we have first implemented a perfect planar antenna coupled tunneling diodes using e-beam writing and a boiling water oxidation process. The boiling water process transforms the polysilicon bowtie knot into an oxide layer for a perfect planar tunneling diode. Using SEM and DC current-voltage measurements, the perfect planar tunneling diode was characterized.

For further improvement, an asymmetric tunneling diode is successfully implemented using a geometric field enhancement scheme. This, to our knowledge, is the first thin film tunneling diode in which the asymmetric tunneling characteristic is achieved by exploiting the geometric field enhancement rather than using the work function difference. The completed diode showed a very high device sensitivity of -14.5 V⁻¹. Furthermore, we verified the validity of our approach through RF rectification tests.

The geometric field enhancement scheme can easily be merged with a dissimilar electrodes scheme, so further improvement of the nonlinear and asymmetric tunneling current characteristics will be possible. Combining these two schemes will lead to a high quantum efficiency. Therefore, our unique approach can play a critical role in improving the tunneling diode characteristics for solar spectrum rectification.

With asymmetric antenna coupled tunneling diodes, we will shortly conduct rectification tests in optical ranges such as the infrared and visible wavelength range to demonstrate solar spectrum rectification. Before doing the experiments, antenna geometry scaling and optimization will be performed according to the wavelength of interest. Also, asymmetric tunneling diodes using a pointed metal electrode will be implemented. The metal electrode reduces the tunneling resistance, and so will increase the matching efficiency and move the pole to much higher frequency. Therefore, it is envisioned that much higher conversion efficiency will be achieved at mid IR frequencies where optical rectification of the blackbody radiation from the earth is of interest.

6. ACKNOWLEDGEMENT

This work was supported in part by NAVAIR, Grant No. N00042-1081003, with Charles D. Caposell as program manager.
REFERENCES