

University of South Florida Beyond Photovoltaics - Nanoscale Rectenna for Conversion of Solar and Thermal Energy to Electricity

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Description: The main objective of the proposal is to commercialize and scale up a new technology, the rectenna, to convert waste heat energy to electricity. Although the prediction of highly efficient (~85%) solar rectennas was published almost 30 years ago, serious technological challenges have prevented such devices from becoming a reality. Since the ultimate goal of a direct optical frequency rectenna photovoltaic power converter is still likely a decade away, our plan is to convert optical solar radiation to thermal radiation (~30 THz regime) using an innovative blackbody source. Leveraging the research efforts of the world-class team members, we plan to further develop the rectenna technology that is within reach of efficient radiation conversion at 30 THz. A fully integrated, blackbody converter and a ~30 THz rectenna system will be capable of converting at least 50% of the solar and thermal energy into usable electrical power, clearly demonstrating a truly transformational new technology in the renewable energy technology sector. For the reporting period, emphasis has been placed on the development of the plasmonic emitter that converts solar radiation to infrared radiation, and the diode that acts as the rectifier in the rectenna concept.

Budget: \$598,500 **Universities:** USF **External Collaborators:** Bhabha Atomic Research Center, India, Florida International University

Progress Summary

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TASK 1. Development of a diode for the rectification of the antenna output.

<u>**Task 1A:**</u> Fabrication, characterization and testing of Metal-Insulator-Metal tunnel junctions The main research objective of this sub-task is to develop a high efficiency MIM tunnel diode using inorganic materials. Towards this, the follow sub-tasks were pursued,

- Determine the AC and DC behavior of a Nickel Oxide-Zinc Oxide MIM tunnel diode.
- Investigate the effect of metal oxides as insulator layers in MIM junctions.

To simulate an asymmetric (P-N junction type) of diode Nickel Oxide-Zinc Oxide combinations wereused. Nickel Oxide (NiO) is known to behave as a p-type semiconductor and Zinc Oxide (ZnO) as an n-type. By combining the two, an effective P-N junction can be created. This P-N junction is in effect a Schottky Barrier Diode (SBD) and behaves similar to it. The carrier concentration is much lower in the NiO and tunneling of electrons from the ZnO layer to the NiO layer takes place across the very thin interface.

A top view of the MIM tunnel diode is shown in Fig. 1.







Current Vs Applied Voltage

Figure 2 shows the DC voltage current and power vs voltage characteristics of this diode.



Figure 3 Comparison of Sensing Capabilities between NiO/ZnO junctions and commercial Zerner diodes.

The results were compared with a standard zener diode which is a pure semiconducting p-n junction diode. As can be observed in Fig. 3, the NiO device outputs a higher signal when excited with radiation compared to the commercial Zener diode. The sensitivity of the device was also measured by biasing it at the turn on voltage and exciting the device with a 2V pulse. The device sensitivity was low since the area was not optimized, but it will be in future measurements.

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The device also responded well to UV light when it was pulsed in 1 second intervals. The sharp rise and fall of the peak shows that the device switch speed is very fast. NiO/ZnO tunnel junctions show great promise as very fast switching diodes that can be used for sensing and detection and ultimately for energy harvesting.

TASK 1B. Self-assembled organic monolayer based MIM junctions

This study aims to produce near atomically-flat metallic films for the purpose of self-assembled monolayer growth. Self-assembled monolayers (SAMs) are formed from organic molecules which spontaneously chemisorb onto (in the case of thiol chemistry) noble metal surfaces. Films are exactly one monolayer and thus very thin—typically on the order of 1 - 2 nm. Because nearest neighbor interactions contribute greatly to the uniformity and tightness of packing, substrate roughness should be well below these thickness values.

Conventional microfabrication toolsets typically employ e-beam or thermal evaporation for the deposition of metal thin films. While these techniques are fast and relatively low cost, the roughness of the metal is unacceptable for the desired application (Fig. 4, shown below)). We have designed and fabricated a low cost thermal annealing solution which is open-air and reel-to-reel process compatible.



Above – (Left) Atomic Force Microscope image of thermally evaporated gold showing roughness. (Center) In-progress annealing shows "lakes" of annealed metal. (Right) Large near atomically flat planes following annealing.





Thermal evaporation of 15 nm of Chromium as an adhesion layer and 250 nm of Gold were applied to offer a baseline rough metal surface (above at left). Subsequently, the wafer was diced into 10mm x 10mm dies for small scale experiments. Initially, annealing was performed by using a high

Roughness analysis of stripped Au surfaces		
	10x Mag	50x Mag
Hexane 500hrs	13.66 nm	20.45 nm
Water 500hrs	20.99 nm	31.25 nm
Acetone 500hrs	51.99 nm	40.30 nm
Ethanol 500hrs	16.3 nm	11.36 nm
Air (Control)	3.13 nm	*0.69 nm
Evaporated Film	(AFM)	2.61 nm
Annealed Film	(AFM)	0.76 nm

temperature flame (right) with the sample held in an inert gas purged glass envelope. Following this an electric heat annealing setup was devised utilizing a PID controller for more accurate ramp and hold temperature profiles. Annealing temperatures and times varied from $550 - 650^{\circ}$ C and 60 - 240 s, respectively.

Long term aging of above described films and template stripped films are summarized in the table at

left reporting roughness in nanometers. We see that after immersion in various environments for 500 hours at 20°C, the roughness is reported and better understanding of process damage is gained.

Exploration into a soft top contact for the delicate self-assembled monolayer has lead to innovations in printing of conductive nanoparticles and conductive polymers. Conductivity of these AuNP (Gold Nanoparticles), AgNP (Silver Nanoparticles), and polyaniline was tested using interdigitated



Figure 5 – Optical profiler z-height study of unpopulated interdigitated electrodes upon which conductivity studies were carried out.

electrodes (Figure 5). The quantity of material deposited was then studied via an optical profiler and electrical measurements. A formulation of AuNP and AgNP was created for printing with off the shelf, low-cost inkjet printers. The top contacts were deposited at room temperature and ambient conditions. Furthermore. workup using electroless plating solution can permit a "hard shell" to be formed following the loose deposition of nanoparticles resulting in a more durable and stable contact.

Here we also report experimentation using the previously described setup consisting of a liquid metal contact. Using porphyrin molecules as the tunnel barrier, we were able to realize a hybrid organic-

inorganic tunnel junction which had improved rectification ratio and very consistent performance (Figure 6). The hybrid junction results in a sharper turn-on inflection at around 1.2V when negatively biased.







Figure 6 – Liquid metal contact resulting in hybrid organic-inorganic tunnel barrier and the resultant current-voltage response

TASK 2. Plasmonic infrared emitter

The main objectives of Task 2 are: (a) Fabrication of a plasmonic emitter and measurements of its infrared radiation spectrum; and (b) Characterization of dimensions, choice of substrate, and surface metal layer for the emitter to achieve optimum concentrated infrared radiation over a narrow frequency range

Description

The infrared spectrum of the patterned emitter is shown in Fig. 7. We expect to observe a narrow band, high intensity response when using plasmon excitation. This concentrated radiation subsequently can be fed into the antenna and later the coupled electromagnetic radiation at the antenna site can be rectified.

Figure 7. Black body and plasmonic emitter radiation spectra.

Results:

Fabrication of the plasmonic emitter involved nanoscale processing techniques such as lithography and deep reactive ion etching (DRIE). A variety of dimensions for the pattern was





used in the design of the photomask in order to be able to analyze the effect of pitch and etch depth of the microstructure on the resulting IR spectrum.



Figure 8. A micrograph of the fabricated plasmonic emitter with a depth of 2.7 microns and grating pitch of 9.3 microns.

An experimental setup as shown in Fig. 9 was used in order to gather the spectral results for our fabricated emitter as a source of infrared radiation.





Figure 9: Experimental setup for the detection and measurement of the Infrared Spectrum.

A Graseby HgCdTe detector was used for the detection of incoming radiation. The setup (as shown above) was mounted on an optical bench to ensure linearity and focus of the beam radiated from the heated emitter. Weaker radiation from the edges of the sample emitter (weaker radiation because of differential heating across its surface) had to be masked off using a cold Aluminum sheet while recording the spectral response.



Figure 10: IR spectrum with patterned Ni Surface at 108°C



A narrow peak IR spectrum was observed for the patterned silicon sample with Nickel deposition on the surface but the desired concentration is yet to be achieved with further experimentation.

In a number of experiments the expected behavior of the emitter (with a high intensity emission at certain wavelengths) was not observed. The cause of this discrepancy was found to be imperfect duty cycle, an example of which is shown below:



Figure 11. High Resolution image using Focused Ion Beam technique to show microstructures on emitter surface with inappropriately high duty cycle.

Funds leveraged/new partnerships created

We are currently collaborating with Bhabha Atomic Research Center, India in developing an organic based tunnel junction. Proposals are also under development for additional funding from federal agencies.

Journal and Conference publications:

- 1. M. Celestin, S. Krishnan, E. Stefanakos, Y. Goswami, S. Bhansali, "A review of Alkanethiol Self-Assembled Monolayers for Low Cost Nano Rectenna Energy Harvesting," Progress in Energy and Combustion Science, 2012. (Under Review)
- 2. M. Celestin, S. Koiry, S, Krishnan, Y. Goswami, "Metal Thin-film Roughness Mitigation Through Thermal Annealing for Self-Assembled Monolyaer Growth" USF Research Day, 2011.

