

# Monday Morning, October 19, 2015

**Electronic Materials and Processing**  
**Room: 211A - Session EM+AS+SS-MoM**

## **Rectenna Solar Cells, MIM Diodes, and Oxide Interfaces**

**Moderator:** John Conley, Oregon State University, Dale Kotter, RedWave Energy, Inc.

8:20am **EM+AS+SS-MoM1 Harvesting Energy with Optical Rectennas: Challenges and Innovations, Garret Moddel**, University of Colorado and RedWave Energy, Inc., *S. Joshi, B. Pelz, A. Belkadi, S. Yuan*, University of Colorado at Boulder, *P. Brady, D. Kotter*, RedWave Energy, Inc.

**INVITED**

Optical rectennas are of interest for radiant heat and light energy harvesting, and ultra-fast detectors that work for terahertz waves up through visible-light wavelengths. The devices work under constraints that are different from those of either microwave rectennas or conventional solar cells. These antenna-coupled diodes incorporate micron-scale antennas and diodes that must operate at frequencies in the tens to hundreds of terahertz, but the antenna size and diode speed are not the most daunting challenges. The current produced by the antenna – particularly for rectennas operating at close to visible-light frequencies – samples the diode at discrete voltages described by a quantum approach instead of at continuously varying voltages described by classical electromagnetic theory – which makes for a fascinating theory of operation. The consequence is a quantum limit to the power conversion efficiency, similar to the Shockley-Queisser limit for conventional solar cells. The optical frequency and intensity determine whether the rectenna operation can be described classically or must involve a quantum analysis. Because rectennas gather current from the entire antenna, if the light is not spatially coherent cancellation occurs, resulting in reduced efficiency. This limits the amount of power received by each diode, which further limits the diode rectification efficiency. Over the last decade the number of groups investigating various parts of rectenna technology has grown from almost none to at least 50. This growing community of researchers, with innovative solutions, is needed to meet optical rectenna challenges and enable a practical technology. Some emerging solutions will be presented.

9:00am **EM+AS+SS-MoM3 Demonstration of Traveling-Wave Metal-Insulator-Metal Diodes for 28 THz (10.6  $\mu$  m) Rectennas, Bradley Pelz**, University of Colorado at Boulder, *G. Moddel*, University of Colorado at Boulder and Redwave Energy

Lumped element rectennas encounter an efficiency limitation above several terahertz due to the RC time constant of an MIM diode. A traveling-wave diode (TWD) takes advantage of nanoscale geometries to achieve a lower capacitance than that of a lumped element diode. The TWD behaves as a MIM transmission line for surface plasmons in which the rectification occurs as the wave travels down its length. Due to the distributed nature of the rectifier, the impedance seen by the antenna is the characteristic impedance of the transmission line. COMSOL simulations have shown this gives a reactive component of diode impedance that is substantially smaller than either the real component of the characteristic impedance for the TWD or the reactance from the parallel plate capacitance of an equivalently sized lumped element MIM diode. This allows for a much higher coupling efficiency from the antenna than in the case of a lumped element diode, and a substantially reduced RC time constant.

To obtain a resistance that matches that of the antenna simulations show that the TWD requires a width of 100 nm or less, which is too small for conventional lithography techniques. This small critical dimension was achieved using a germanium shadow mask technique. After fabrication, the DC junction characteristics were measured using a four-point technique. The open circuit voltage of these unbiased devices was measured under 28 THz illumination using a CO<sub>2</sub> laser and a lock-in amplifier. The TWD coupled to a bow tie antenna showed both polarization and power dependence. Since these measurements were completed at zero bias, the response could not have been bolometric, and the device must have been operating in energy harvesting mode.

9:20am **EM+AS+SS-MoM4 Basic Efficiency Limits for Rectenna Solar Power Conversion, Heylal Mashaal, J.M. Gordon**, Ben-Gurion University of the Negev, Israel

The prospect of employing aperture rectennas for solar power conversion will be explored in this presentation. Sunlight is commonly viewed as incoherent – hence seemingly unsuitable for antenna harvesting – but all electromagnetic radiation exhibits spatial coherence on a sufficiently small scale. The first direct measurement of the spatial coherence of sunlight will

be presented, and the ramifications for using optical concentrators that can effectively replace orders of magnitude of antenna and rectifier elements will be discussed.

Rooted in the partial spatial coherence of sunlight, a derivation of the thermodynamic limit for coherence-limited solar power conversion will be presented – an expansion of Landsberg's elegant basic bound, originally limited to incoherent converters at maximum flux concentration. The results do not depend on a particular conversion strategy. As such, they pertain to systems that span geometric to physical optics.

Last, a basic upper bound will be presented for the ability to rectify the broadband signals using a full wave rectification scheme.

Our findings indicate promising potential for rectenna power conversion.

9:40am **EM+AS+SS-MoM5 Coherence Effects in Periodic Arrays of Nano-Antennas used for Energy Harvesting and Self-Imaging, Peter Lerner**, SciTech Associates, LLC, *P.H. Culter, N.M. Miskovsky*, Penn State University

## **Coherence effects in periodic arrays of nano-antennas used for energy harvesting and self-imaging**

P. B. Lerner [1], N. M. Miskovsky<sup>1,2</sup>, P. H. Cutler<sup>1,2</sup>

Modern technology allows the fabrication of antennas with a characteristic size comparable to the electromagnetic wavelength in the optical region. [1] This has led to the development of new technologies using nanoscale rectifying antennas (rectennas) for solar energy conversion and sensing of terahertz, IR and visible radiation. For example, a rectenna array can collect incident radiation from an emitting source and the resulting conversion efficiency and operating characteristics of the device will depend on the spatial and temporal coherence properties of the absorbed radiation. For solar radiation, the intercepted radiation by a micro- or nano-scale array of devices has a relatively narrow spatial and angular distribution. Using the Van Cittert-Zernicke Theorem, we show that the coherence length (or radius) of solar radiation on an antenna array is, or can be, tens of times larger than the characteristic wavelength of the solar spectrum, i.e., the thermal wavelength,  $\lambda_T = 2\pi\hbar c / (k_B T)$ , which for T=5000K is about 2 microns. Such an effect is advantageous, making possible the rectification of solar radiation with nanoscale rectenna arrays, whose size is commensurate with the coherence length. Furthermore, using the van Cittert-Zernicke Theorem, we also examine the blackbody radiation emitted from an array of antennas at temperature T, which can be quasi-coherent and lead to a modified self-image, analogous to the Talbot-Lau self-imaging process [2] but with thermal rather than monochromatic radiation. This coherence of the antennas' blackbody radiation can also introduce an angular spectrum, which may be concentrated (enhanced) along certain spatial directions, giving rise to additional features not present in the original array. The self-emitted thermal radiation may be important as a non-destructive means for quality control of the array.

[1] Miskovsky, N. M., P. H. Cutler, A. Mayer, B. L. Weiss, B. Willis, T. E. Sullivan, and P. B. Lerner (2012) Nanoscale Devices for Rectification of High Frequency Radiation from the Infrared through the Visible: A New Approach, *Journal of Nanotechnology*, Article ID 512379, 19 pages, <http://dx.doi.org/10.1155/2012/512379>.

[2] Gori, F. (1979) Lau Effect and Coherence Theory, *Optics Communications*, 31(1), 4.

1 SciTech Associates, Woodland Drive, State College, 16803.

2 Physics Department (emeritus), Penn State University, University Park, 16802.

10:00am **EM+AS+SS-MoM6 Metamaterial Enhanced Rectenna for Efficient Energy Harvesting, D. Lu, Won Park**, University of Colorado Boulder, *P. Brady*, Redwave Energy Inc.

Rectenna solar cell offers an important alternative to the conventional semiconductor solar cell technology. Direct rectification of electromagnetic radiation faces many challenges one of which is the high frequency of operation. Thermal emission from hot bodies peaks at 10 ~ 100 THz while solar radiation has its maximum at around 600 THz. One may circumvent this difficulty if sufficiently strong thermal radiation is available at lower frequencies. In general, thermal emission is described well by the theory of blackbody radiation while the property of the non-black surface is characterized by its emissivity. When the surface supports surface waves, however, the properties of thermal emission can deviate substantially from the blackbody radiation, offering a new avenue for engineering thermal emission. For example, spatially coherent and spectrally selective thermal emission may be achieved. The presence of surface waves also means

enhanced local density of states near the surface, which consequently leads to strongly modified thermal emission intensity and spectrum in the near field. In this paper, we report a metamaterial design to achieve enhanced thermal emission at 1 THz.

Two types of metamaterial designs were investigated: a 1D array of parallel trenches and a 2D array of holes etched on copper. The metamaterial surface was designed to support surface waves resembling the surface plasmon on metal surface. Numerical simulations by the finite element method confirmed the presence of surface waves and strong electric field near the surface at 1 THz. The strongly enhanced electric field is the direct consequence of enhanced local density of states. To further confirm the surface modes can be excited by thermal emission, we also conducted finite-difference time-domain simulations in which thermal emission was calculated by using the fluctuation dissipation theorem. Once the enhanced thermal emission is confirmed, a bowtie antenna was placed close to the metamaterial surface to capture the enhanced thermal emission in the near field. The antenna was optimized to maximize the electromagnetic energy delivered to the antenna gap. Since the antenna should couple efficiently with the surface modes, the optimal antenna design became quite different from the free space bowtie antenna operating at the same frequency. The optimized metamaterial and antenna design resulted in an antenna voltage of 10 mV at 1 THz, three orders of magnitude larger than the free space antenna. Such a large enhancement makes the metamaterial approach a highly promising route to efficient energy harvesting with rectenna.

11:00am **EM+AS+SS-MoM9 Modeling of and Power from Nb-NbOx-based Nanorectenna Arrays**, *Richard M. Osgood*, US Army NSRDEC, J. Xu, G.E. Fernandes, Brown University, M. Rothschild, K. Diest, MIT Lincoln Laboratory, M. Kang, K.B. Kim, Seoul National University, Republic of Korea, L. Parameswaran, MIT Lincoln Laboratory, P. Periasamy, IBM, M. Chin, Army Research Laboratory, S. Kooi, MIT Institute for Soldier Nanotechnologies, S. Giardini, US Army NSRDEC, R. O'Hayre, P. Joghee, Colorado School of Mines

We investigate arrays of "microrectennas" (with sub-micron features tuned for the near- and short-wave infrared) consisting of "stripe-teeth" metamaterial antennas conducting vertically through the coupled, underlying metal-insulator-metal (MIM) diode into a metallic substrate. Stripes, with cross-stripe resonances, conduct current out of the array, while antenna-like teeth break left-right symmetry and concentrate a high vertical electric field ( $E_z$ ) at the end of the teeth at their antenna resonance. If plasmonic field enhancement and concentration reduce the capacitance and/or increase the effective voltage across the MIM diode, new research and development of large-area ultrafast optical rectennas will be enabled, requiring patterning and alignment of only the top metal layer.

Stripe-teeth arrays were designed, fabricated, and analyzed both experimentally and theoretically. Substrates were layers ("ground planes") of Nb and Al, and a Au nanowire array patterned using novel high-throughput e-beam technology.<sup>1</sup> Substrates were oxidized/anodized, or had oxides deposited, to form microantenna-coupled MIM diodes consisting of Al-Al<sub>2</sub>O<sub>3</sub>-Al, Au/Ti-NbO<sub>x</sub>-Nb, Al-Al<sub>2</sub>O<sub>3</sub>-Au, Ag/Ti-NbO<sub>x</sub>-Nb, Ag/Ti-NiO-Ni, Pt-NbO<sub>x</sub>-Nb, after deposition of top metal layers of Ag/Ti, Au/Ti, Pt, and Al (only a few nm of Ti). Conduction through 10-25 nm thick oxide layers in the MIM diodes occurred via quantum mechanical tunneling and thermionic emission, with asymmetric barrier heights all less than 1 V except for the Al-Al<sub>2</sub>O<sub>3</sub>-Al diodes. The Au-Al<sub>2</sub>O<sub>3</sub>-Al system required modeling the "hot spot" from top metal protrusions into the Al<sub>2</sub>O<sub>3</sub> barrier layers and in close (tunneling) proximity to the ground plane, probably because of the surface roughness and variation in Al<sub>2</sub>O<sub>3</sub> thickness; the planar-planar MIM diode model was inapplicable in this case.

The top metal was patterned into the stripe-teeth arrays. Reflective Al substrates provided sharp optical antenna resonances while Nb layers produced broader, weaker antenna resonances due to Nb absorption, similar to stripe-only arrays reported in Ref. 2. We also report the result of visible light (514 nm – 630 nm) laser illumination of Nb/NbO<sub>x</sub>/Ag(Ti) stripe-teeth arrays, including the observation of a short-circuit current and open-circuit voltage, in response to power densities in the range 80 W/cm<sup>2</sup>.

1. H. S. Lee, *et. al.*, "Electron beam projection nanopatterning using crystal lattice images obtained from high resolution transmission electron microscopy", *Adv. Mats.* **19** 4189 (2007).

2. Wu, C., *et.al.* "Large-area wide-angle spectrally selective plasmonic absorber," *Phys. Rev. B*, Vol. 84, 075102-7, 2011.

11:20am **EM+AS+SS-MoM10 Metal-Insulator-Insulator-Metal Diodes for Rectenna Applications**, *Shijia Lin*, N. Murari, J.F. Conley, Jr., Oregon State University

A metal-insulator-metal (MIM) tunnel diode has a capacitor-like structure with a thin insulating layer sandwiched by two metals. Because of their potential for femtosecond-fast transport when dominated by tunnel transport, MIMs are of interest for rectenna based solar cells, hot electron

transistors, and IR detectors. The common strategy to achieving rectification in MIM devices relies on the use of dissimilar work function metal electrodes to produce an asymmetric electron tunneling barrier with polarity dependent tunneling probability. The performance of single layer MIM devices is limited by the workfunction difference that can be achieved between the electrodes and the metal-insulator band offsets. Small electron affinity oxides are limited by high  $V_{ON}$ . Large electron affinity dielectrics have small  $V_{ON}$ , but tend to have limited asymmetry due to thermal emission dominated conduction. An alternative approach to controlling asymmetry is to use nanolaminate pairs of insulators with different bandgaps and band offsets to produce asymmetric tunnel barrier metal-insulator-insulator-metal (MIIM) diodes. Asymmetry in MIIM devices may be enhanced by step tunneling<sup>1</sup> or defect enhanced direct tunneling.<sup>2</sup>

In this work, we investigate asymmetry in HfO<sub>2</sub>/ Nb<sub>2</sub>O<sub>5</sub> bilayer insulator MIIM diodes. HfO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> were deposited via atomic layer deposition (ALD) using tetrakis (ethylmethylamino) hafnium (TDMAHf) and niobium ethoxide metal precursors, respectively with H<sub>2</sub>O as the oxidant. Nanolaminate films were deposited at a chamber temperature of 250°C in one continuous run without breaking vacuum. Sputtered TaN or amorphous metals were used as the bottom electrode and evaporated Al dots were used as a top electrode. MIIM I-V asymmetry and non-linearity are shown to be a function of stack thickness, relative layer thickness, and insulator layer position with respect to the electrodes. Overall, bilayer insulators are shown to be an effective method of enhancing the performance of MIIM tunnel diodes.

1. N. Alimardani and J.F. Conley Jr, *Appl. Phys. Lett.* 102, 143501 (2013).

2. N. Alimardani and J.F. Conley, Jr., *Appl. Phys. Lett.* 105, 082902 (2014).

11:40am **EM+AS+SS-MoM11 Built-in Potential in Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> Superlattices for Improved Photoexcited Carrier Separation**, *Tiffany Kaspar*, D.K. Schreiber, S.R. Spurgeon, S.A. Chambers, Pacific Northwest National Laboratory

Hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, is an ideal photocatalyst to split water as a source of H<sub>2</sub> fuel because it is non-toxic, Earth-abundant, stable in aqueous environments, and possesses a bandgap in the visible wavelength range (~2.1 eV). However, fast photogenerated electron-hole recombination, facilitated in part by slow carrier transport kinetics, has long been identified as a major obstacle in the utilization of hematite photocatalysts. A direct method to reduce photogenerated carrier recombination is to employ heterojunctions to spatially separate excited electrons and holes. Our approach is to engineer built-in electric fields by exploiting the band alignment characteristics of epitaxial Fe<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub> heterojunctions. The Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> system exhibits non-commutative band offsets which differ by approximately 0.4 eV depending on the order of deposition. The non-commutative band offset properties of Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> interfaces can be utilized in a superlattice structure, deposited by oxide molecular beam epitaxy, to build up an intrinsic electric field; this potential may be sufficient to spatially separate photogenerated electrons and holes. We demonstrate precise control over the Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> interface structure with atomic-resolution atom probe tomography and scanning transmission electron microscopy. Direct evidence that Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> superlattice layers generate an intrinsic built-in potential is observed with x-ray photoelectron spectroscopy. The individual interfacial band offset values, and thus the overall potential, can be tailored by altering the cation stoichiometry at the interfaces. Doping the component layers to improve transport characteristics requires a deep understanding of the dopant-induced electronic structure changes. To illustrate how the built-in potential in optimized Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> superlattice structures can be harnessed to drive holes to the surface and electrons into the bulk, photoconductivity and photochemical degradation results will be presented.

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