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RPPR Final Report
as of 14-Dec-2018

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Proposal Number: 70069EGRIP **Agreement Number: W911NF-17-1-0179**
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Begin Performance Period: 17-Apr-2017 **End Performance Period:** 16-Jul-2018
Report Term: 0-Other

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1 **STEM Participants:**

Major Goals: PI Maria received ARO support for a high throughput dedicated physical vapor deposition tool for the production of polaritonic conducting metal oxides and reactive nanolaminates with in situ thickness control, stable sputter cathode sources, the ability to control acceptor and donor doping in the range between high 1017 cm-3 and mid 1020 cm-3, and an integrated variable pressure annealing station. The configuration proposed is designed specifically to propel the new NCSU- led MURI program “Multi-modal Energy Flow at Atomically Engineered Interfaces” but will also benefit a broad set of existing ONR, DoD, and NSF research programs. Our instrument goals that were achieved inlcude:

1) High throughput deposition of metallic and oxide thin films using radio frequency (RF) and modulated pulsed power (MPP) plasmas – MPP are particularly interesting given their ability to promote high ionization fraction, and thus high deposition rates, full oxidation of metal cations in the reactive mode, and smooth terminal surfaces. Furthermore, they offer very stable depositions when sputtering metal oxides from metallic targets in a reactive atmosphere;
2) To facilitate fast reproducible growths of complex structures, and broad distribution of samples to collaborators;
3) In situ thickness monitoring for films between 15 and 10,000 nm thickness – this is particularly important for achieving target thicknesses in a chamber where multiple magnetrons operate simultaneously, and whose individual power densities can alter deposition rates;
4) A magnetron configuration allowing a parent metal oxide, a candidate dielectric, a candidate acceptor, and a candidate donor to be accessible simultaneously.

The instrumentation will enable the synthesis of inorganic thin films and multilayers with extreme-tight control of thickness, surface roughness, interface smoothness, adhesion, carrier concentration, electrical and optical properties. This instrument will introduce new capabilities to the Maria group and their collaborators, the collection of which are central to numerous current DoD programs at NCSU and its partner universities.

Ultimately, with instutional support and spare parts owned by the Maria Group, we were able to construct two chambers instead of only one and to expand upon the original capabilities that we planned.

Accomplishments: Accomplishments are discussed in the attachment.

Training Opportunities: Through the duration of this grant, Evan Runnerstrom (postdoc) and Evyn Lee (grad) assisted in system design and construction. As such they received valuable training in vacuum instrumentation assembly and operation.

RPPR Final Report
as of 14-Dec-2018

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Jon-Paul Maria
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Evan Lars Runnerstrom
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Evyn Lee
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

DESCRIPTION OF INSTRUMENTATION

Our team constructed two advanced PVD systems accommodating a heated manipulator, multiple cathode sources, i*n situ* thickness monitoring, a microwave plasma source, and a combination of RF and pulsed DC plasmas. **Figure 1** shows a schematic of chamber #1 which is dedicated to preparing conductors to support IR plasmon polaritons while Figure 2 shows chamber #2 which is dedicated to supporting materials for optical absorbers and plasmonic devices. The section following the figure articulates the role of each component and its connection to program needs

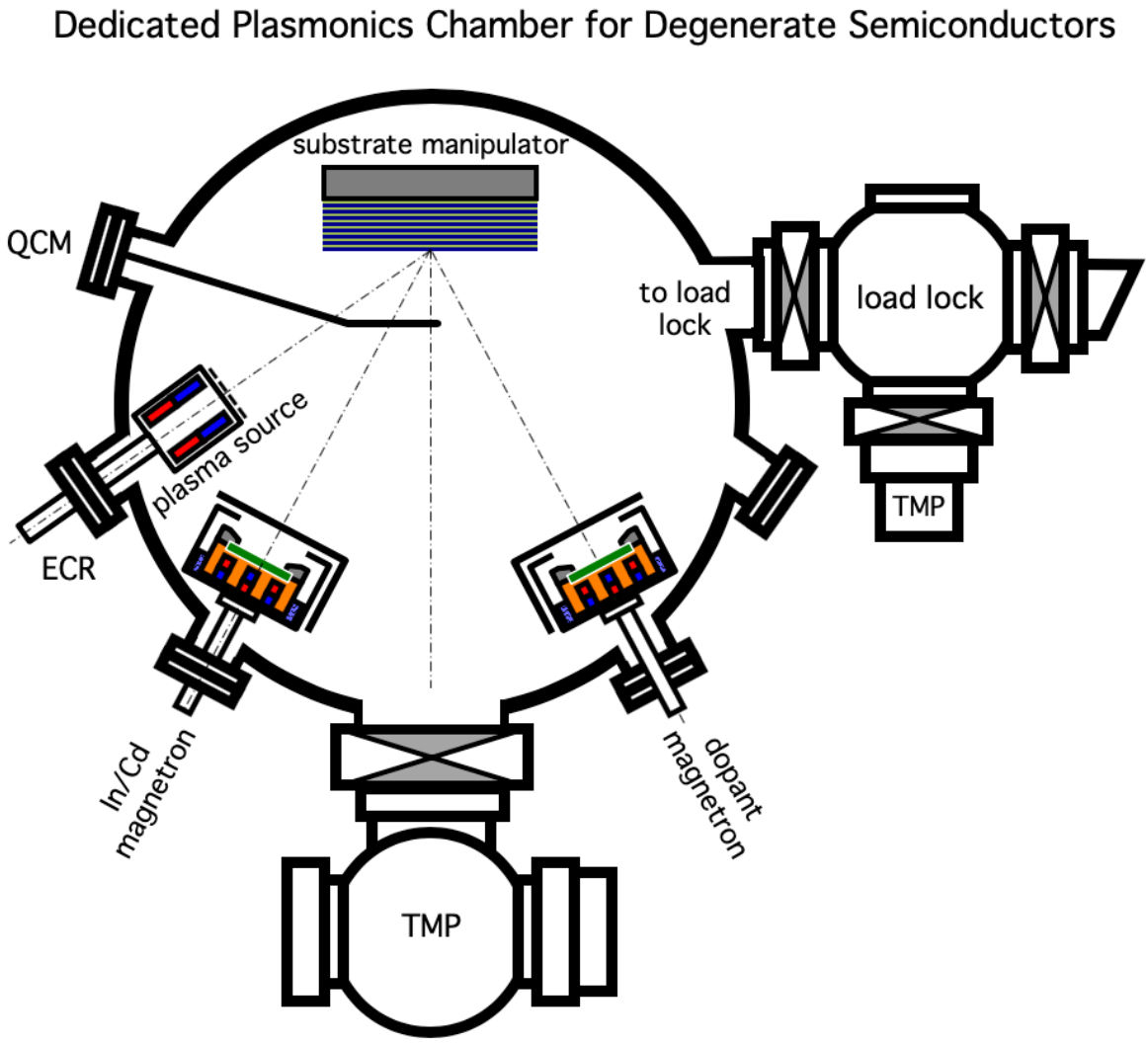


Figure 1: *Schematic representation of Chamber #1, a dedicated tool for preparing degenerate semiconductors that support IR plasmon polaritons. The instrument is a true UHV chamber with a microwave plasma for achieving high levels of cation oxidation in oxide and nitride systems.*

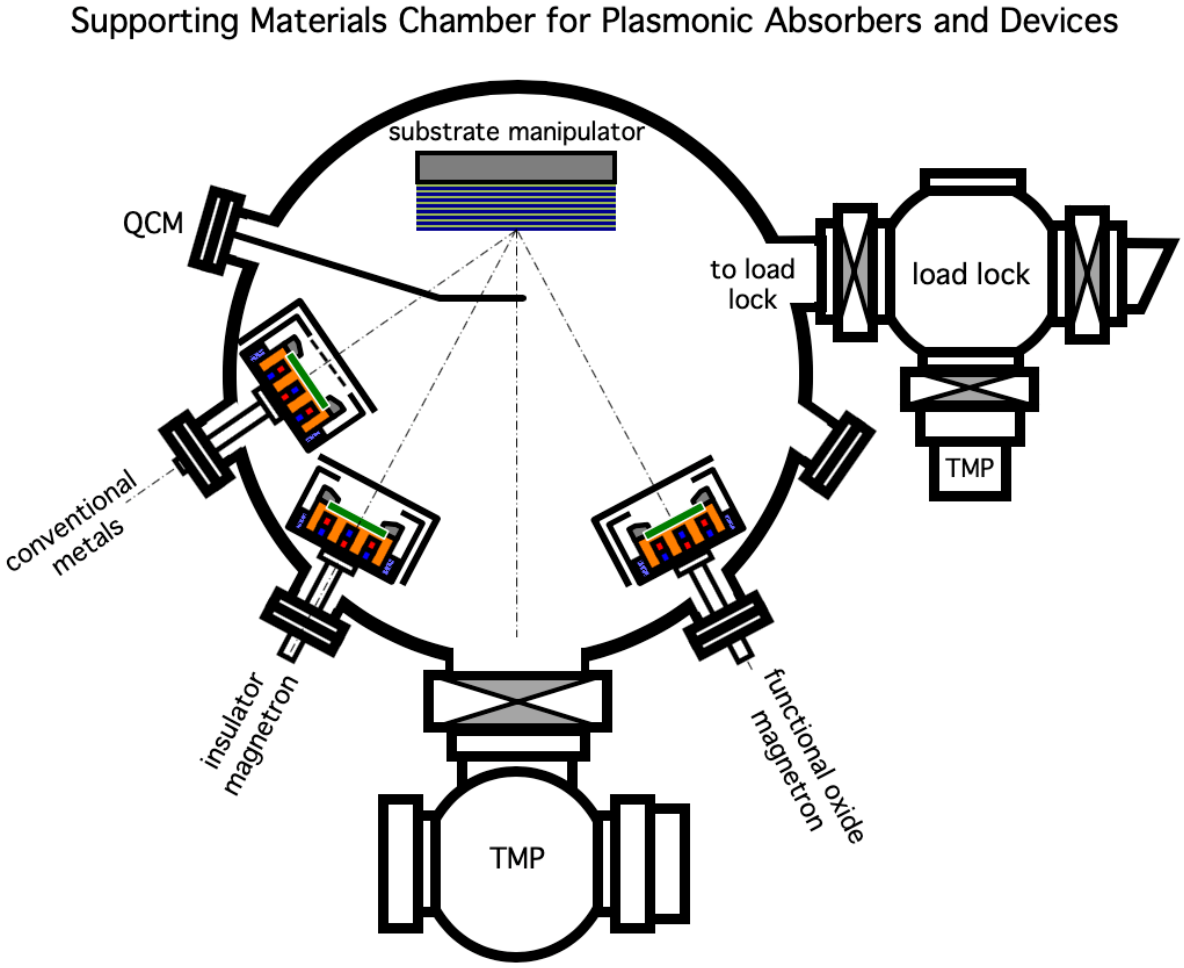


Figure 2: Schematic representation of Chamber #2, a dedicated tool for preparing "supporting" materials for plasmonic devices such as metal mirrors, grating dielectrics, tunneling dielectrics, and non-linear electro-optic layers.

DESCRIPTION AND JUSTIFICATION OF CONFIGURATION

Both chambers were configured for specific synthesis capabilities that target program needs of the Maria group and the Maria group collaborators. The most important include:

1. Load Lock: Engineering film properties, particularly for electronic materials and reactive materials, requires a tightly controlled atmosphere in the deposition and anneal environments. To achieve the necessary control while maintaining an expeditious process, it is best to isolate both from room ambient. To do so, we include a load chamber and sample transfer capability for both systems. With this configuration, one can maintain background levels of water and hydrocarbon contaminations are very low.

2. High temperature sample manipulator: To control the kinetics of growth, to ensure a favorable morphology, to activate dopants, and to promote crystallinity, a heated substrate is essential. To prepare compositionally homogeneous layers from a multisource environment, the substrate must be rotated during growth. Both aspects will be supported by a high-temperature manipulator based on a quartz lamp heaters. Both chambers support 5" diameter pucks that guarantee uniform temperatures over the center 4".

2. Sputter Chamber: We propose a multisource deposition chamber with RF and pulsed DC power supplies, a high temperature sample manipulator, in-line automatic pressure control, and *in situ* thickness measurement. The justification for each feature is given below, and a subsequent figure provides a schematic for the deposition module showing the configuration of pertinent components:

3. Pulsed-DC sputtering: For preparing complex oxide transparent conductors controlling defect chemistry is critical for understanding and engineering the electrical and optical properties because oxygen stoichiometry creates the backdrop for the net defect equilibrium. Pulsed DC sputtering includes the modulated pulsed power (MPP) and high power impulse magnetron (HIPIMS) sputtering regimes. In both cases, one achieves a very high degree of cation ionization (several thousand times higher than in RF or DC) due to the intense plasma pulsing. In both regimes one benefits from cation bombardment of the growing film (at a level that improves morphology), there is very little anion bombard (which allows high oxygen partial pressure to be used), and deposition rates can be very high[1-3]. Collectively, this enables one to fully oxidize metal cations when prepared from an elemental source and to minimize concentrations of vacant oxygen sites. It is important to note that elemental metallic sources are typically less expensive, more available, and higher purity than the oxide counterparts. High starting purity and full oxidation are central elements for the precise and accurate control of carrier density.

MPP sputtering is also important because it enables one to create extremely smooth surfaces, even with film thicknesses are large. Because of the cation bombardment, one can achieve a situation where surface roughness and film thickness are decoupled. Consequent to these benefits, both chambers include High Power Impulse Magnetron Sputtering (HiPIMS) power supplies such that the benefits can be realized in both material sets.

3. **RF sputtering:** For the polaritonic and reactive laminate films we wish to prepare, access to "Molecular beam epitaxy (MBE) grade" doping is a critical need. By MBE grade, we refer to dopant control in the range spanning ppt to ppb, a range typically controlled by effusion cells. RF magnetrons provide very stable plasmas under low power densities an thus flux values consistent with this dopant range. As such, we include two RF sources for donor and acceptor dopants respectively. In addition, RF plasmas can be used to sputter almost any material, while there are limitations to dc and pulsed dc power supplies. Consequently, an RF supply was also added to chamber #2.

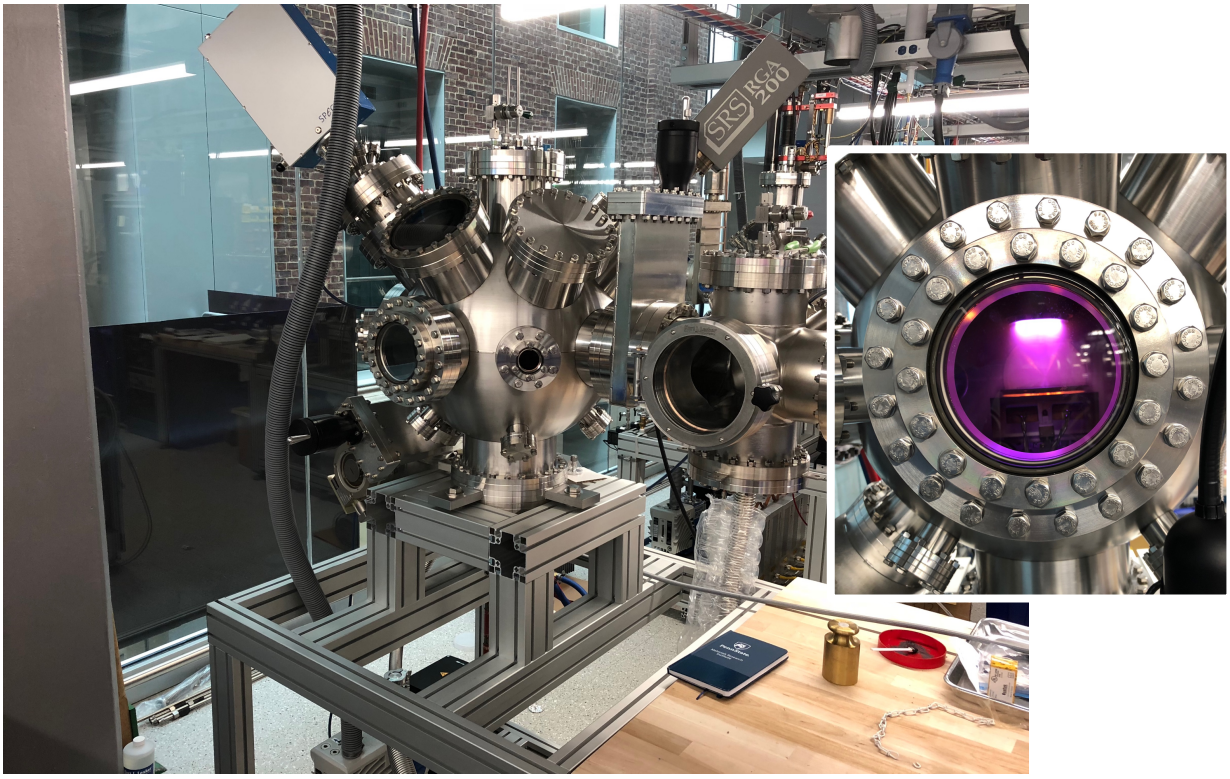
4. *In situ* film thickness monitor: Controlling thickness is an essential, and non-trivial, aspect of film growth. The challenge is expressed strongly in a multi-cathode deposition environment due to "communication" between plasmas. Consider the example experiment of a dopant series where one prepares a parent composition (*e.g.*, CdO from a Cd target using MPP) with a ladder of dopant

concentrations controlled by the RF power applied to an adjacent acceptor gun. We know from experience that RF power will influence the MPP plasma and change the deposition rate. An *in situ* thickness monitor will greatly assist our ability to characterize these unavoidable effects, to better control film properties, and to ensure quality and reproducibility of materials provided to our collaborators. Both chambers are configured with quartz crystal oscillators that can be rotated into and out of the deposition plume to monitor flux continuously.

5. Microwave plasma source: The plasmonic hosts central to our ARO programs are degenerate semiconductors whose carrier density is controlled by engineering the intrinsic and extrinsic defect chemistry that originates from naturally occurring deviations from stoichiometry (usually anion deficiencies), and from intentionally added donor cations. The control level that we desire is facilitated by an ability to engineer the anion chemical potential. To do so we incorporated a plasma source that can produce a beam of reactive N or O containing species that are far more reactive than their diatomic source gases. In so doing, we can better nitridize or oxidize a metal flux from a sputter gun and minimize unwanted native donors that originate from incomplete oxidation.

CHAMBER #1: CONSTRUCTION AND CAPABILITIES

Image of Chamber #1 at PSU labs

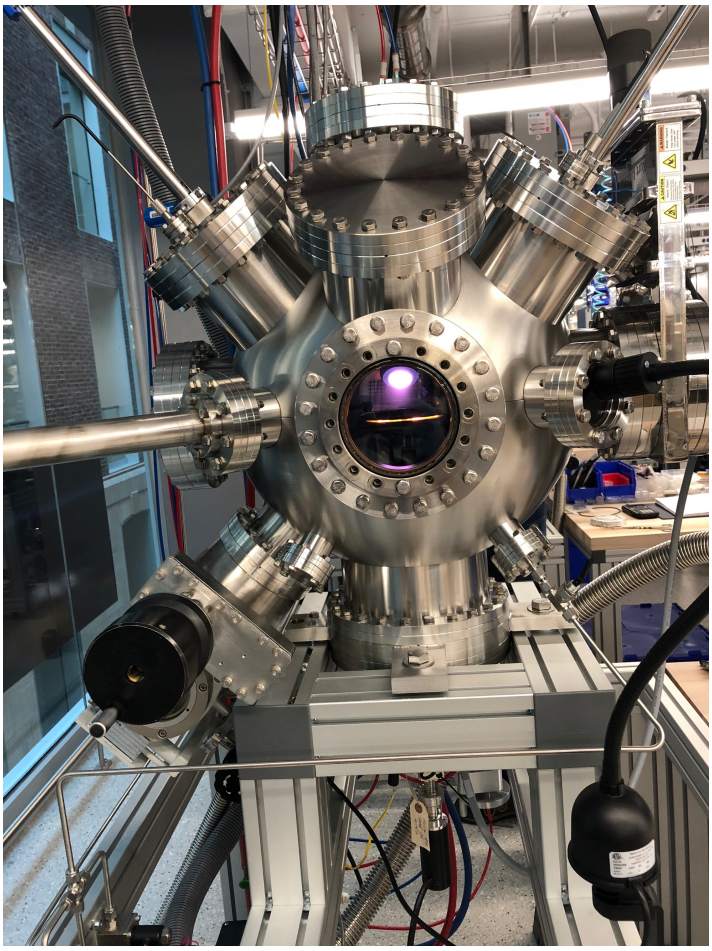


Chamber #1 was designed to prepare plasmonic oxides and nitrides. Specifically, it was conceived to grow InN, which is the nitride analog to CdO, the material with which our current MURI has been experiencing substantial successes. According to literature reports, InN can be prepared with

even higher mobilities than CdO, but at a slightly lower carrier density range that CdO probably cannot access. This will allow our MURI to extend its explorations of interfacial polaritonic excitations into the longwave portion of the IR spectrum. For this task the nitrogen plasma source was an important addition as it enables one to oxidize a high purity In metal sputter source. The chamber is currently equipped with a UHV magnetron with a 3" 7N In metal target for nitride sputtering. Initial depositions are just underway. If InN does not prove successful, the chamber will be converted to oxide deposition of CdO. This only requires a new Cd target and plumbing the plasma source with oxygen instead of nitrogen. The oxygen plasma promises to boost oxygen activities, to more fully oxidize Cd, and to lower intrinsic carrier densities to even lower values with even higher mobilities.

CHAMBER #2: CONSTRUCTION AND CAPABILITIES

Image of Chamber #2 at PSU labs



Chamber #2 was designed to prepare support materials for both the plasmonic and energetic tasks of the Maria ARO MURI. The chamber is currently configured with a oxygen compatible hot stage, is HV constructed, and has 3 2" magnetrons. The design allows for an additional two magnetrons if experimental needs dictate. The chamber includes 2 pulsed DC power supplies and

one RF power supply. Currently it is configured to make clean smooth refractory metals, linear dielectrics, and clean transition metals. The clean smooth refractory metals are intended as IR mirrors that enable IR coupling into our plasmonic absorbers, the linear dielectrics are intended as tunnel barriers for MIM diodes, and the transition metals are intended as work-function tuned electrodes for MIM diodes. The following schematic provides an example of the plasmonic device that is pursued in the Maria MURI.

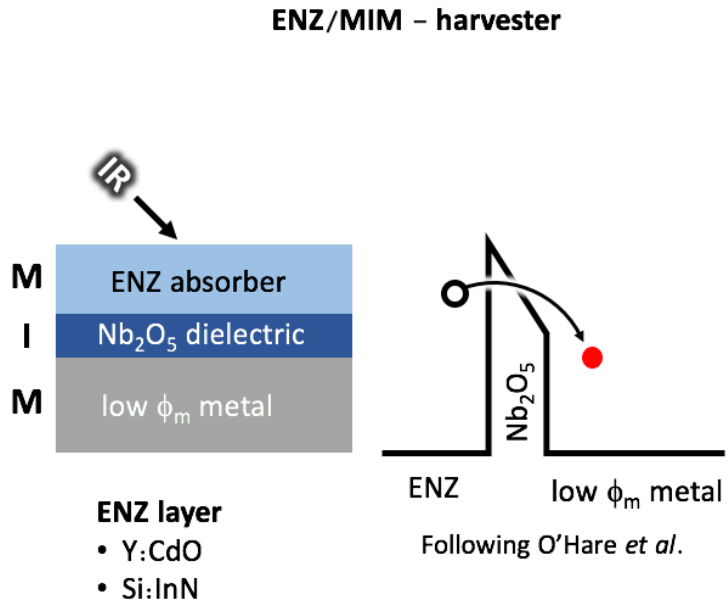


Figure 3: *Proposed rectenna structure designed for plasmonic excitation of hot interfacial carriers that can be collected across a tunneling diode stack*

Figure 3 shows a rectenna structure, where one couples to electromagnetic radiation with an antenna in a circuit with extremely low-voltage rectification, is an excellent candidate for collecting the low energy electron-hole pairs that can be generated from IR light absorption. This **Plasmonic Rectenna** replaces the conventionally patterned antenna with a polaritonic perfect absorber. In our case it is a simple CdO or InN layer with carrier density and thickness tuned for a desired ENZ polaritonic mode. The ENZ plasmonic layer is integrated directly into an asymmetric MIM diode to achieve rectification, as illustrated in **Figure 3**. Utilizing a work function engineering approach it is possible to create MIM diodes with turn-on voltages below 100 mV. This is one example of a plasmonic device for which these new tools are designed to create, that will enable our group and our collaborators to conduct more sophisticated investigations of light matter interactions that probe non-equilibrium interfacial excitations.

These tools are operational currently and serving ARO and DoD research needs.