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# **Catalytic Diodes for Micropower Applications: Verification of High Energy Conversion Efficiency**

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# **Catalytic Diodes for Micropower Applications: Verification of High Energy Conversion Efficiency**

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## **Abstract**

Our ability to field useful, nano-enabled microsystems that capitalize on recent advances in sensor technology is severely limited by the energy density of available power sources. The catalytic nanodiode (pioneered at Berkeley by Somorjai, 2005) is an alternative revolutionary source of micropower (see <http://pubs.acs.org/cen/news/83/i15/8315notw1.html>). A sizable fraction of the chemical energy is harvested via hot electrons (or ballistic electrons) that are created by the catalytic chemical reaction. The reported efficiency of the chemical to electrical conversion can be remarkably high, with 3 electrons collected for every 4 CO<sub>2</sub> molecules produced. This project is a feasibility study to verify the reported high energy conversion efficiency. If verified, we hope to follow this research with a new project that would: 1) Investigate the underlying physics and chemistry of these devices, and 2) Explore alternative chemical reactions and catalysts that could serve as more convenient sources of chemical energy.

## **Acknowledgements**

The authors thank Robert K. Grubbs (Org. 2452) for depositing TiO<sub>2</sub> films by ALD, and Alex Yun-Ju Lee (Org. 1816) for depositing TiO<sub>2</sub> films by reactive sputtering and sol-gel technique.

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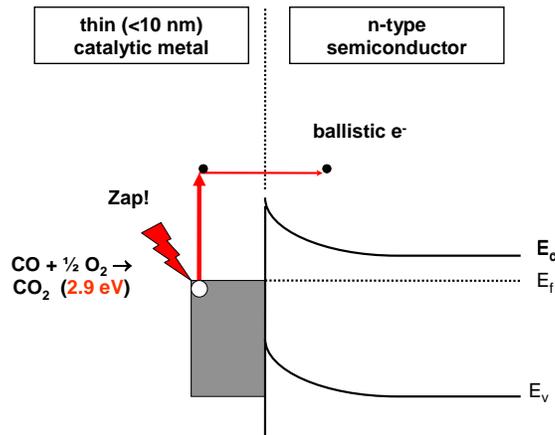
## NOMENCLATURE

ALD	atomic-layer deposition
DOE	Department of Energy
MESA	Microsystems and Engineering Sciences Applications
MOCVD	metal organic chemical vapor deposition

## 1. Introduction

The development of micropower sources will enable remote microsensors and actuators that are necessary for the development of microsystems that have the ability to sense their surroundings and communicate the gathered data. Microsensor systems are of interest for a variety of applications such as remote sensing of chemicals, radioactivity, or biological agents to address issues related to the detection, location, and composition of weapons of mass destruction and to assist in various nonproliferation efforts of DOE. Our ability to field useful, nano-enabled microsystems that capitalize on recent advances in sensor technology is severely limited by available power sources. Many such applications require power system volumes on the order of  $\frac{1}{2}$  cm<sup>3</sup> to 1 mm<sup>3</sup> in various form factors. Power density levels on the order of 1-10 microwatts/mm<sup>2</sup> are of greatest interest. Batteries and fuel cells are two conventional methods of providing micropower, each with its own set of advantages and disadvantages.

In 2005-2006 a revolutionary type of micropower source was announced by Gabor Somorjai's research group (Berkeley); see <http://pubs.acs.org/cen/news/83/i15/8315notw1.html>, and refs. 1-4. They coined the term "catalytic nanodiode", and the device is simply a Schottky diode where the metal contact is made of an ultrathin (1-10 nm) catalytic metal, such as platinum or palladium. Two wide bandgap n-type semiconductors were investigated; TiO<sub>2</sub>, and GaN. The source of energy is a catalytic reaction, in this case the CO oxidation reaction,  $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$ , which liberates about 2.9 eV of energy. A sizeable fraction of this chemical energy is dissipated by creation of hot (or ballistic electrons) in the catalytic metal. If the metal is thin enough, many of these ballistic electrons will live long enough to migrate to the semiconductor side of the Schottky diode. This mechanism is shown schematically in Fig. 1. Before the recent breakthrough there had been reports of small levels of transient ballistic electron generation by surface chemical reactions, but Somorjai's group are the first to successfully demonstrate a steady-state device.



**Figure 1. Energy level diagram of the catalytic nanodiode, in this example with the CO oxidation reaction providing the energy source (lightning bolt)**

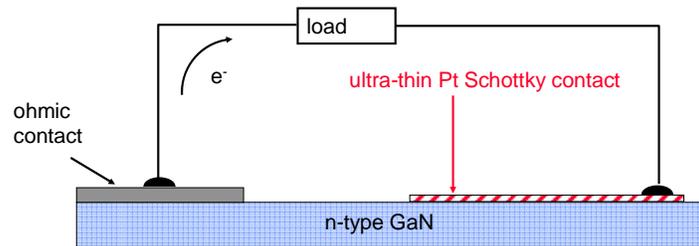
In an ambient of CO and O<sub>2</sub>, the best device (5 nm Pt/TiO<sub>2</sub>) produced a short-circuit current ( $I_{sc}$ ) of 40 microamps (area  $\sim 1\text{mm}^2$ ) at 80°C, and operated for 30 min with no sign of failure. The complete I-V characteristics of this particular device (while operating) were not reported, but given the open-circuit voltage ( $V_{oc}$ ) of  $\sim 1$  volt, power levels in the 10 microwatts/mm<sup>2</sup> range are expected. By simultaneously measuring the CO<sub>2</sub> production rate Somorjai found that up to 3 electrons were created and harvested per 4 CO<sub>2</sub> produced, which corresponds to rather remarkable quantum efficiency of  $\sim 75\%$ . After accounting for some chemical energy losses, the overall efficiency of the best device is approximately 25%.

To summarize, this new device converts chemical energy to electrical energy by oxidizing a fuel, similar to a fuel cell. But it is quite different from a fuel cell in design and operation. Unlike a fuel cell, there is not a second electrode, and the transport of other charged species (e.g H<sup>+</sup>) across an aqueous or solid media is not required. The fuel and oxidizer may be in the gaseous or liquid state. In this respect the catalytic nanodiode is a simple, compact, and possibly robust technology. It is also potentially disruptive in that it could replace microbatteries and microfuel cells in many micropower applications. This technology maps extremely well onto Sandia's expertise in semiconductor device fabrication (MESA), micropower applications, solid-state physics, and surface chemistry and catalysis. The ability to use a vapor based fuel source opens up many new environments from which we may harvest energy.

The goal of the Late Start LDRD is to: (1) Use MESA facilities to fabricate prototype Pt/GaN and/or Pt/TiO<sub>2</sub> nanodiodes, and (2) Test nanodiodes for micropower generation and verify the claims of high chemical to electrical energy conversion efficiency.

## 2. Nanodiode fabrication

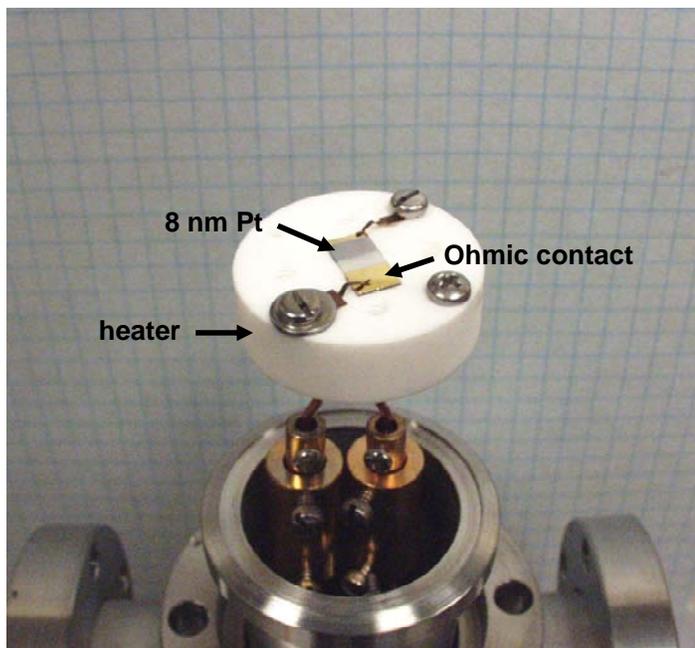
Given the compressed timeframe for the Late Start LDRD we decided to first focus on the Pt/GaN device, since we have more experience with this material combination. For simplicity, we also chose to fabricate the diodes using a shadow mask technique. A planar diode structure was designed (see Fig. 2) using GaN on sapphire as the substrate. The GaN films (run #DNZ01330) were grown by MOCVD on c-plane sapphire wafers to a thickness of 3.6 microns. The films were moderately doped with silicon (using silane) to yield n-type carrier concentrations of  $2 \times 10^{17} \text{ cm}^{-3}$ . The GaN/sapphire wafers were diced into rectangles of  $\sim 6 \times 12$  mm dimensions.



**Figure 2. Schematic of a catalytic nanodiode (Schottky diode) device structure.**

Before the metal evaporation steps, the samples were briefly cleaned for 3 minutes in dilute HCl and rinsed in DI water. Samples were then loaded onto the shadow mask jig and the ohmic contact was deposited. For these contacts we used a rather standard Ti/Al/Ni/Au structure. The shadow mask jig was removed from the evaporator and the samples repositioned for the Schottky contact. The jig was reloaded and 8 nm of Pt was deposited on the opposing

side of each sample. The jig was removed and an additional mask was placed over most of the sample(s), exposing only a ~ 1mm strip of the Schottky contact. The jig was reloaded and a final 20 nm Pt/200 nm Au film was deposited. This thicker metal strip at the edge of the diode structure facilitates making electrical contact to the very thin (8 nm) Pt layer. One complete device (1<sup>st</sup> generation) mounted on a heat stage is shown in Figure 3.



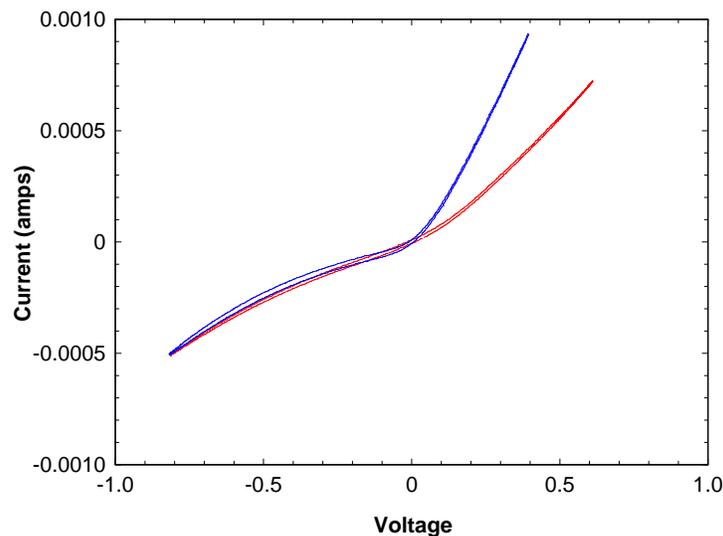
**Figure 3. First generation Pt/GaN nanodiode mounted on heat stage.**

The best catalytic nanodiode performance from the Berkeley group [1-4] came from the Pt/TiO<sub>2</sub> material combination. However, deposition of well-characterized semiconducting TiO<sub>2</sub> is not a standard MESA process (as compared to GaN deposition). In late FY07 we identified three possible sources of TiO<sub>2</sub> thin films. One method is a low temperature CVD variation known as atomic layer deposition (ALD). A second method uses a variation of titanium sputtering in a low background of O<sub>2</sub> gas. A final method uses a sol-gel technique. Sandia personnel grew TiO<sub>2</sub> films on sapphire using all three approaches, but we were not able to characterize the electrical properties before the end of FY07. It is likely that annealing in vacuum or reducing atmospheres will be necessary to convert some of this material into useful

semiconducting  $\text{TiO}_2$  thin films. This is a complex issue because recrystallization and phase-transformation are likely to occur during annealing.

### 3. Electrical testing

Before proceeding with plans for chemical-to-electrical conversion testing, we first measured the baseline I-V characteristics of the Pt/GaN nanodiodes. Two representative examples from the first set of samples are shown in Fig. 4. Unfortunately, the rectifying characteristics of the 1<sup>st</sup> generation Schottky nanodiodes were far from ideal. The diodes did not exhibit a well-defined turn-on voltage under forward bias, and exhibited considerable leakage under reverse bias. Two possible sources of the poor behavior are; 1) a GaN surface conduction layer between the ohmic and Schottky contact, and 2) a poor Pt/GaN interface due to impurities or incomplete removal of native oxide (e.g.  $\text{GaO}_x\text{N}_y$ ). We grew several more test structures, but were not able to make any significant progress on this issue during the remainder of FY07. Improving the I-V characteristics of the Pt/GaN nanodiodes will be the first topic of the new FY08 LDRD.



**Figure 4. I-V measurements from two 1<sup>st</sup> generation Pt/GaN nanodiodes.**

For the chemical-to-electrical tests the goal was to build a small vacuum system with a gas-handling system capable of handling CO and O<sub>2</sub>. Unfortunately we were not able to complete the construction of this new apparatus in FY07, in part because of the ES&H issues of handling carbon monoxide. We did finish one critical component, the heat stage (see Fig. 3), which is necessary to heat the diode to drive the CO oxidation reaction (50-300°C). The stage also has the necessary contacts for chemical-to-electrical conversion measurements and two thermocouple junctions for temperature measurements.

#### **4. Summary**

As an FY07 late-start LDRD we made considerable progress on this new research topic. Hardware and procedures were developed for fabrication and testing of Pt/GaN nanodiodes. The first generation Pt/GaN nanodiodes were rectifying, but exhibited non-ideal behavior. Some probable cause(s) of the poor behavior were identified, but we were not able to solve this problem in the short time available. Possible sources of semiconducting TiO<sub>2</sub> thin films were identified and will be pursued in FY08. Some critical components of the chemical-to-electrical experimental apparatus were built, but the gas-handling system was not finished by years end. Although progress on the late-start LDRD fell short of our best-case scenario, it nonetheless provided a valuable jumpstart for our FY08 Project.

#### **5. References**

- [1] Z.J. Xiao and G.A. Somorjai, *J. Phys. Chem. B* 109 (2005) 22530.
- [2] J. Xiaozhong, A. Zuppero, J.M. Gidwani, and G.A. Somorjai, *J. Amer. Chem. Soc.* 127 (2005) 5792.
- [3] J. Xiaozhong, A. Zuppero, J.M. Gidwani, and G.A. Somorjai, *Nano Letters* 5 (2005) 753.
- [4] J.Y. Park and G.A. Somorjai, *J. Vac. Sci. Technol. B* 24 (2006) 1967.

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