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The Catalytic Nanodiode: Gas Phase Catalytic Reaction Generated Electron Flow Using Nanoscale Platinum Titanium Oxide Schottky Diodes

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ABSTRACT

Forty microampere current was generated on a platinum–titanium dioxide Schottky diode during the platinum catalyzed steady-state oxidation of carbon monoxide at 80 °C. For reaction events that produced four CO_2 molecules, three injected electrons were collected in a diode comprising a 5 nm thick platinum and a 150 nm titanium dioxide film. The electron injection flux depends on the thickness of the platinum and the titanium dioxide diode properties as well as the conditions of the catalytic reactions.

Chemisorption of the atoms on surfaces has been able to produce electrons with high kinetic energy, often referred to as hot or ballistic electrons. Bottcher et al.[1] observed these upon oxygen adsorption on a thin cesium metal film, and Hellberg et al.[2] when chlorine adsorbed on potassium at 130 K. Huang et al.[3] found efficient (> ∼50%) excitation of electrons in gold on the subpicosecond time scale by NO molecules prepared in high vibrational excited states (v =15) impinging on the metal surface. They showed that, compared to the short time scale of molecular vibration metal electron energy transfer, other forms of molecular energy transfer processes (vibration, rotation and vibration, translation) have very low probability.

Nienhauss et al.[4] detected electrons of kinetic energy greater than 0.5 eV injected into their diode when hydrogen or oxygen atoms adsorbed on silver thin films. The hot electrons could travel in excess of the ∼20 nm electron mean free path in silver and surmount the ∼0.5 eV Schottky barrier, formed at the junction of silver and the underlying semiconductor. The hot electrons thermalize within picoseconds in the semiconductor. In all these observations the electron current maintained in the picoampere per square centimeter range until high monolayer coverages were reached.

Independently, a method of conversion of chemical energy directly into an electron current was published in a patent by Zuppero and Gidwani[5] and is used in this study. One innovation enabling chemical energy generated at surfaces of nanometer dimensions to be directly converted into other useful energy forms, including electricity, was the use of catalysts as the conducting surfaces. The reaction products would rapidly leave the surface, making way for more reactions through turnover. The resulting currents would be orders or magnitude greater than picoAmps.

We report here the steady-state production of electron flow during the platinum catalyzed reaction of 100 Torr of oxygen and 40 Torr of carbon monoxide using a nanodiode fabricated from platinum and titanium oxide. A 5 nm thick platinum film acts both as the catalyst[6−9] and the source of electrons that are injected into the wide band gap titanium oxide semiconductor and measured as a current between the gold contact electrode and the platinum electrode. The catalytic reaction has a turnover rate of 3×10^{14} CO_2 molecules per second (∼10 CO_2 produced per platinum site per second) at 80 °C, which produces 40 μAmp in our configuration. Thus, the electron conversion rate is about three electrons for every four CO_2 molecules produced. The diode device produces current in steady state for over 30 min tested, which corresponds to the production of more than 5×10^{17} CO_2 molecules.

A scheme of the diode device is shown in Figure 1. A p-type Si(100) wafer covered by 100 nm SiO_2 was used as an insulating substrate with a predictable smooth surface. A back gold electrode was deposited using a chromium underlayer that helps the adhesion of the noble metal to the

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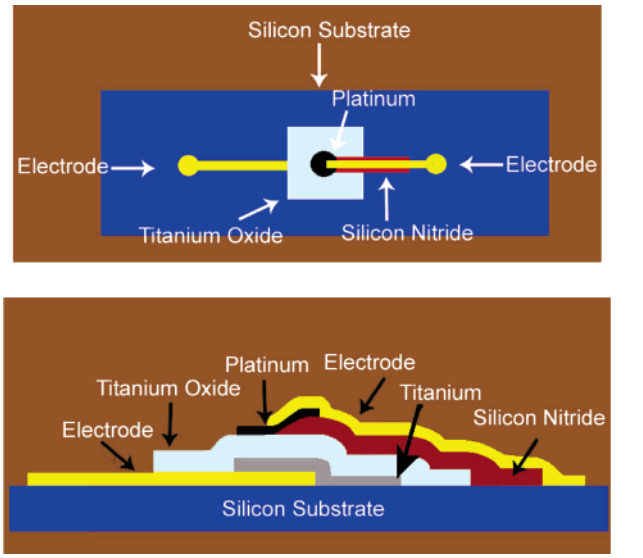

Figure 1. The top view and the cross-section of the platinum/*n*-titanium oxide Schottky diode.

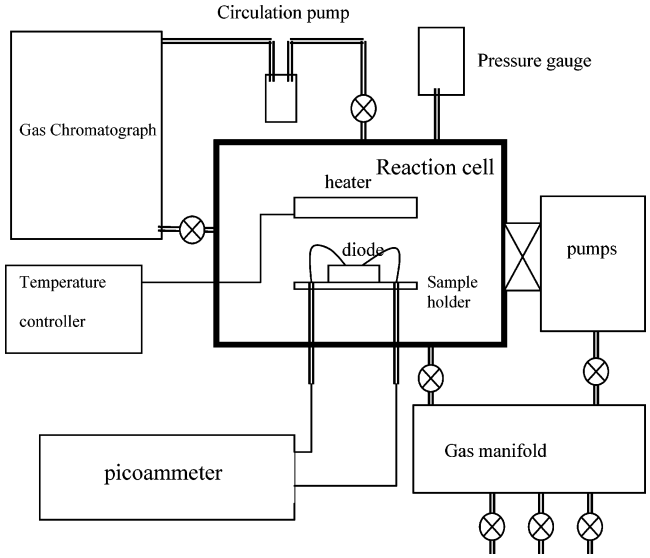

Figure 2. Scheme of the setup for *in situ* measurements of hot electron flux generated by catalytic oxidation of carbon monoxide on platinum/*n*-titanium dioxide Schottky diode.

oxide. A titanium oxide thin film was then deposited by e-beam evaporation at 120 °C, or sputter deposition at room temperature with a variable thickness of between 30 and 150 nm. Plasma-enhanced chemical vapor deposited silicon nitride of 150 nm was then used to form an insulation layer between the front electrode and the titanium oxide. Platinum with thickness between 1 and 15 nm was then e-beam evaporated through a mask to produce a 1 mm diameter dot. Finally, a front gold electrode was e-beam deposited onto the silicon nitride and the platinum to complete the diode circuit. The typical device has a barrier height of 1.2 eV.

The oxidation of carbon monoxide was carried out using 100 Torr of oxygen and 40 Torr of oxygen at a temperature between 80 °C and 200 °C in a batch reaction system of about one liter in volume (Figure 2). A steady-state production of electron flux was achieved at low temperature, and a constant reaction condition was maintained due to the low

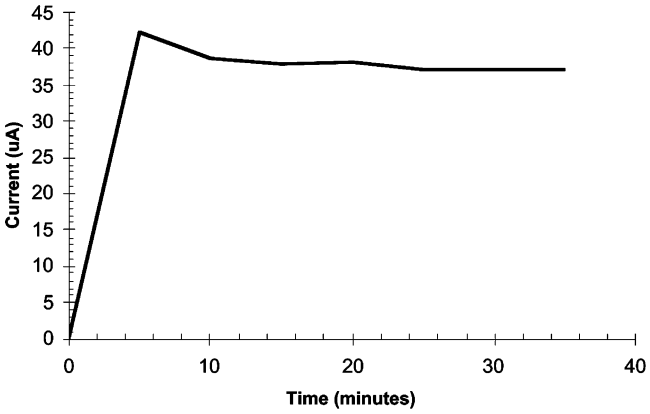

Figure 3. Gas-phase catalytic oxidation of carbon monoxide on 5 nm platinum/150 nm *n*-titanium oxide Schottky diode generates a steady-state electron flow of 37 microampere for over half an hour.

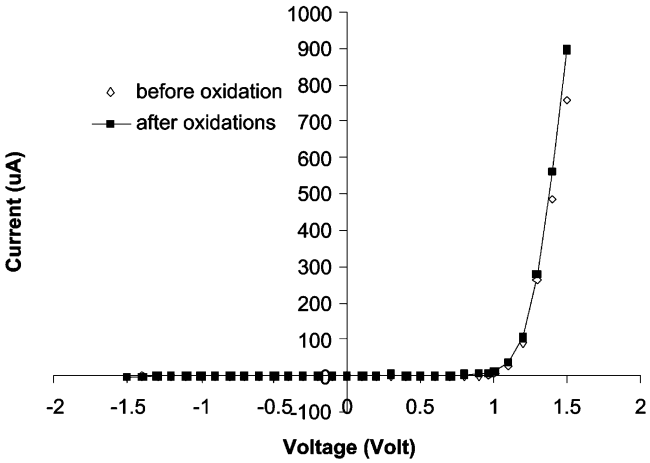

Figure 4. Plots of current voltage characteristics of 5 nm/150 nm *n*-titanium oxide Schottky diode before and after the oxidation of carbon monoxide.

reaction rate that assured little change in the partial pressures of O_2 and CO during the experiment. The catalytic reaction had a typical turnover rate of 3×10^{14} carbon dioxide production per second at 80 °C from one diode.

The best conversion per reaction event was achieved using a 5 nm thick platinum film (Figure 3). It should be noted that 4 nm is the elastic mean free path of 1.2 eV electrons in platinum. With a current flow of 40 μAmp, the electron conversion rate is about three electrons for every four carbon monoxide oxidation events. Increasing the platinum film thickness to 10 nm reduced the current from 40 μAmp to the nanoAmpere region. It should be noted that 9 nm is the inelastic mean free path for 1.2 eV electrons in platinum. The platinum film also has to be annealed in argon at 125 °C for 15 min. It was found that the annealing process improved the adhesion between the platinum layer and the n-type titanium dioxide layer in a reactive atmosphere at elevated temperature, thus stabilizing the electrical properties of the devices. Figure 4 shows a comparison between current−voltage characteristics of the annealed device before and after the CO oxidation reaction. Note that the current at a forward bias of ~0.8 V is practically zero compared to the 40 μAmp of measured current from injected electrons.

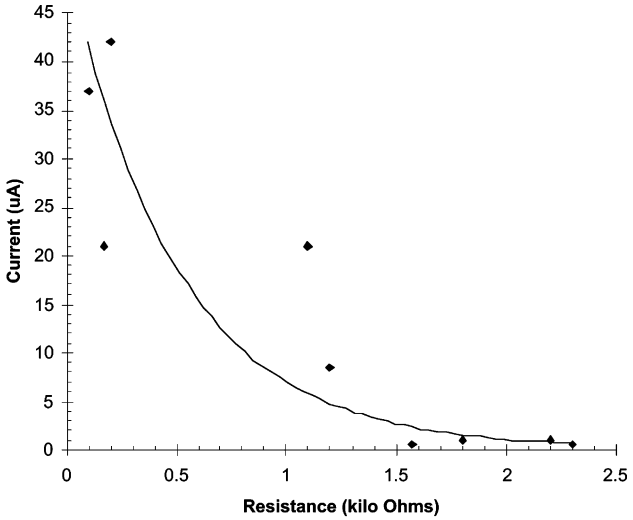

Figure 5. Plot of gas-phase catalytic oxidation of carbon monoxide generated current as a function of the resistance of *n*-titanium oxide.

This indicates that loss mechanisms for electron transport are at least not dominant.

The resistance of titanium oxide film changes with oxygen vacancy concentration, which, in turn, depends on the oxygen partial pressure and oxygen-sticking coefficient during the e-beam evaporation. Figure 5 shows the dependence of the diode current on the resistance of the oxide film at a constant film thickness of 150 nm and under constant reaction conditions (e.g., 100 Torr of O_2, 40 Torr of CO, 80 °C). It appears that higher concentration of oxygen vacancy improved the collection efficiency of electrons produced by the catalytic reactions.

Since the current flow is Ohmic past the Schottky barrier width, this behavior indicates that the semiconductor thickness is of the order of the barrier width. As the resistance decreases, the Schottky barrier width becomes narrower to the point where it is less than the dimensions of the semiconductor. In this circumstance the diode can then more efficiently capture the injected electrons. When the resistance is high, the Schottky barrier width is greater than the thickness of the titanium oxide semiconductor and the diode performs poorly. Measuring the resistance is a relatively simple way to assess the state of the diode.

The electron flux through the diode depends on (1) the reaction turnover rate, (2) the thickness of the platinum film, (3) the Schottky barrier height and width, and (4) the nonstoichiometry (oxygen vacancies) and thickness of the oxide. A likely mechanism for the catalytic reaction induced current flow is as follows: hot electrons are produced at the platinum surface where the exothermic catalytic reaction occurs. If the thickness of the platinum is less than the inelastic mean free path of the electrons (~9 nm), the electrons can migrate to the edge of the Schottky barrier without losing much of their kinetic energy. Some of the electrons, which have a kinetic energy higher than the barrier height, can move across the potential barrier into the n-type nonstoichiometric titanium oxide. This injects electrons into the diode and can be measured as a short-circuit current. These electrons would necessarily have to have energy greater than the Schottky barrier. The near-zero current at forward voltages below approximately 0.8 V shown in the $I-V$ curve of Figure 4 would be consistent with this as the likely mechanism.

A high concentration of oxygen vacancies and imperfections in the titanium dioxide make it strongly n-type and introduce traps and narrow the barrier width. This could be the other likely mechanism where the oxygen-vacancy-enhanced[10] conduction, indicated by a low resistance titanium dioxide, would permit short-circuit current from electrons with kinetic energy significantly less than the Schottky barrier. Note that the narrowing of the barrier width may cause the diode performance to degrade.

The potential energy diagram for the oxidation of carbon monoxide has been reported.[11] The reaction is exothermic and produces over 3 eV energy for each CO_2 molecule produced. We find that for four chemical reaction events, approximately three electrons had enough energy to move through the metal and be collected as a short-circuit current in a diode.

The isothermal environment during the catalytic reaction excludes thermoelectric and thermionic sources of ions, and the gas-phase surface reaction geometry excluded inadvertent electrochemical sources (such as battery or fuel cell). The steep decrease of current when the conducting platinum catalyst thickness was increased beyond the electron mean free path also argues against electrochemical current production.

Using direct conversion of chemical energy from a gas-phase catalytic reaction has potential of achieving higher fuel efficiency than most of the existing electricity generation technologies. The turnover rate of suitable gas-phase reactions can be altered by orders of magnitude by increasing flow rates and temperature of operation. The diode materials can be tailored to catalytic reaction conditions of the type of gas (hydrogen, methane, ethanol, or methanol, for example) and the nature of the oxidizers or other wide bandgap semiconductors such as SiC or GaN.[12] We are pursuing research to explore the mechanisms responsible for the steady state electron flow during catalytic reaction turnover by measuring the electron kinetic energy distribution and its response to the type of chemical reaction that controls hot electron generation. It is clear that the chemical and thermal stability of the diode assembly as well as the choice of semiconductor and metal catalyst used are important issues that must be addressed in fabricating systems for steady-state chemical energy conversion to electron flow.

To the best of our knowledge, our work is the first report of steady-state current flow produced from steady-state catalytic reaction. The results suggest that using exothermic catalytic reactions with fast kinetics, chemical-to-electric power conversion is possible at high speed and high power density.

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(12) We have also tested several platinum−gallium nitride (Pt/GaN) nanodiodes used as hydrogen sensors by General Electric Global Research for CO oxidation under identical conditions used for our Pt/TiO_2 nanodiodes. We could generate steady-state electron flow in the 100−250 °C range for hours with conversion ratios of reaction events to hot electrons similar to the Pt/TiO_2 nanodiode of the same thickness (8 nm). The barrier height of the Pt/GaN nanodiode was also around 1.2 eV. Since the GaN semiconductor in the Pt/GaN nanodiode is single crystal, we could rule out oxygen vacancy mediated current flow in this circumstance that we suggested for the Pt/TiO_2 nanodiode system. We can also rule out incidental electrochemical effects. This test also seems to suggest the simple over-the-barrier hot electron injection into the semiconductor as the current generating mechanism. It appears that catalytic nanodiodes with a wide range of materials chemistry can be used to convert exothermic reaction energy into hot electrons subject to chemical and thermal stability of the systems.

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