# Continuous Hot Electron Generation in Pt/TiO₂, Pd/TiO₂, and Pt/GaN Catalytic Nanodiodes from Oxidation of Carbon Monoxide

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Thin films (<10 nm) of platinum or palladium were deposited on TiO₂ or GaN to form Schottky diodes. We detected and monitored the continuous electron flow across the metal−oxide interfaces of Pt/TiO₂, Pd/TiO₂, and Pt/GaN during the catalytic oxidation of carbon monoxide. The electron excitation and flow in the metals were due to conversion of energy released by the oxidation of carbon monoxide into the kinetic energy of free electrons in platinum and palladium. The best conversion of three electrons per four CO₂ molecules was observed from 5 nm Pt/TiO₂.

## Introduction

The production of "hot" electrons in metals, with 1−3 eV kinetic energy upon excitation by short (femtoseconds) pulses of photons, has been well established by a great number of experiments. These are also frequently called "ballistic" or "exo" electrons as well, and they have a lifetime in a range of 10−20 fs and a mean free path of about 10 nm in metals. One reason for their production is the low electronic heat capacity of metals, about 2 orders of magnitude smaller than the lattice heat capacities at 300 K, which permits the faster excitation of the electron gas than the phonons (nonadiabatic transfer of energy). It was also reported[1] that highly vibrationally excited NO molecules underwent rapid deexcitation upon incidence on a gold surface by losing over 1.5 eV of the extra energy in 100 fs while no vibrational deexcitation was detectable when the excited NO molecules impinged on a LiF surface. This difference indicates that the molecular deexcitation process depends on the free electron concentration in a solid surface and the nonadiabatic channel dominates this process as well.

Exothermic surface reactions can also transfer energy into electrons at the metal surface, yielding electron emission into a vacuum. Bottcher et al.[2] observed this upon oxygen adsorption and reaction with a thin cesium metal film and Hellberg et al.[3] when chlorine reacted with potassium at 130 K.

Nienhaus et al.[4] detected hot electrons of kinetic energy greater than 0.5 eV injected into their Ag/Si diode when hydrogen or oxygen atoms adsorbed on the silver surface. 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 typical hot electron current induced by chemisorption, however, was at a maximum of a few nanoamperes when the gas molecules or atoms adsorbed on a clean metal surface, and decayed quickly to a negligible level when the saturation coverage of adsorbates was reached.

The Schottky diode model of electron flow at oxide−metal interfaces for catalyzed reactions has been considered periodically since the early work of Schwab,[5,6] Szabo,[7] and Solymosi.[8] Their experimental strategies were through the use of "inverse catalyst" systems, i.e., by depositing chemically inactive oxides on catalytically active transition metals. The catalyzed reactions ranged from carbon monoxide oxidation to sulfur dioxide oxidation, formic acid decomposition, ethylene hydrogenation, cyclohexene hydrogenation/dehydrogenation, and ammonia synthesis.[8,9] Depending on the nature of the oxide and its thickness, large changes in activation energies and turnover rates in the reactions were observed. The electronic structure at the oxide−metal interfaces was suggested to be the reason for the unique performance of the metal catalysts. There have been debates[10−12] of the importance of the Schottky effect to oxide-supported metal catalysts ever since the idea was suggested, mostly because of the absence of any direct experimental proof of the existence of electron excitation during the catalytic reaction. Nevertheless, experiments in our laboratory[13] where various oxides (niobium oxide, titanium oxide, tantalum oxide, and others) were deposited on rhodium metal clearly indicated a large increase in catalytic turnover rates for CO hydrogenation that reached a maximum at 0.5 monolayer of oxide coverage that corresponded to the maximum oxide−metal interface area, indicating the unique catalytic behaviors and high activity of oxide−metal interfaces. The resistance of reactivity of the oxide−metal interface to CO poisoning of ethylene hydrogenation has also been confirmed by experiments.[14]

Studies described in this paper confirm that chemical energy from an exothermic reaction can efficiently induce electronic excitations, leading to electron flow in supported catalysts. Catalytic diodes used to collect hot electrons consist of a thin layer (5 nm) of platinum on titania[15] or gallium nitride[16] and have a typical Schottky barrier of 1.2 eV. The catalytic diodes including a thin layer (5 nm) of palladium on titania has a typical barrier height of about 0.7 eV. Catalytic oxidation of carbon monoxide has been used to successfully generate a continuous flow of electron current in these catalytic nanodiodes.

By using catalytic nanodiodes, the role of electron flow in the performance (reactivity, selectivity) of the supported metal catalytic systems for various reactions can be directly investigated. Studies of catalyzed reactions by catalytic nanodiodes, therefore, provide valuable insight into the chemical effect of electron excitation and flow on oxide-supported metal catalytic systems.[17]

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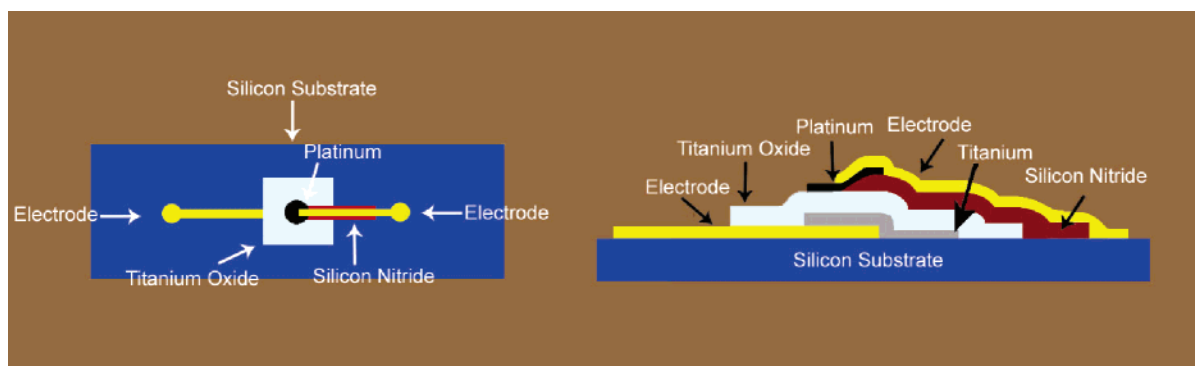*J. Phys. Chem. B, Vol. 109, No. 47, 2005* **22531**



**Figure 1.** Top view and cross section of the platinum/*n*-titanium oxide Schottky diode. The palladium/*n*-titanium oxide Schottky diode has the same configuration. The platinum or palladium has a diameter of 1 or 2 cm.

## Experimental Details

**Preparation of Catalytic Nanodiodes.** A scheme of the Pt/ $TiO_2$ Schottky nanodiode configuration utilized in our laboratory is shown in Figure 1. Pd/$TiO_2$ diodes have the same configuration. The procedure of sample preparation is as follows: A p-type Si(100) wafer covered by 100 nm $SiO_2$ was used as an insulating substrate. An electrode was first deposited on the $SiO_2$ consisting of a 200 nm gold and chromium or titanium underlayer that helps the adhesion of the noble metal to the oxide. A titanium oxide thin film with a thickness between 30 and 150 nm was then e-beam evaporated from a titania source at room temperature or 393 K under a base pressure of no more than $1 \times 10^{-6}$ Torr, or sputter deposited from a titanium target in a mixture of Ar and $O_2$ at room temperature. A plasma-enhanced chemical vapor deposited silicon nitride of 150 nm was then used to form an insulating layer between the front electrode and the titanium oxide. Platinum or palladium of 1 or 2 mm diameter with a thickness between 1 and 15 nm was then e-beam evaporated through a mask on the $TiO_2$. Finally, the front gold electrode was e-beam deposited onto the silicon nitride and the platinum to complete the diode circuit.

General Electric Global Research has fabricated the commercially available Pt/GaN through a standard microfabrication method. The configuration of the Pt/GaN nanodiode is shown in Figure 2. Platinum has a thickness of 8 or 24 nm and an area of 1 mm². An Al/Ti or Ti/Pt/Au electrode has been used to form an ohmic contact with the single-crystal n-type GaN semiconductor.

**Characterization.** A quartz crystal was used to monitor the film thickness in situ during the e-beam evaporations of the palladium or platinum films. The thickness has also been calibrated ex situ using a profilometer. To determine the real thickness of a thin platinum or palladium film, a thick film of platinum or palladium was first evaporated under the same conditions as the thin metal films. The thickness of these films was then measured by the profilometer. A tooling factor was determined to be the ratio of the real thickness of the films to the readings on the quartz monitor. When the thin films were deposited under the same conditions, the tooling factor was employed to estimate the real thickness of the thin films. Platinum or palladium of a thickness between 1 and 15 nm has been deposited to investigate the effects of the film thickness on the electron collection efficiency of the catalytic diode.

The roughness of thin films has been measured using an atomic force microscope with a silicon nitride tip. $TiO_2$ films are very smooth, due to a good wetting of the $TiO_2$ over the bottom gold electrode. The platinum or palladium thin films, however, were found to be very rough in terms of their small thickness. The typical roughness of 5 nm platinum on 150 nm
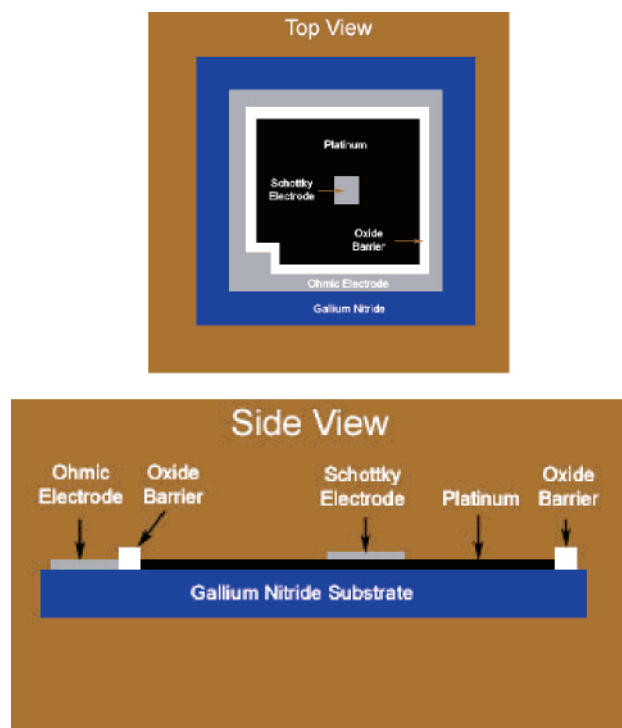


**Figure 2.** Schematic of the platinum/gallium nitride Schottky nanodiode. Gallium nitride is an n-type single crystal grown on a sapphire substrate. The platinum is 8 or 24 nm in thickness and 1 mm × 1 mm in area. The ohmic electrode is made of Al/Ti or Ti/Pt/Au. An oxide passivation barrier has been utilized to separate the platinum from the ohmic electrode.

$TiO_2$ was about 2 nm (Figure 3). Since an AFM tip has a typical radius of 15 nm, it was not possible for the tip to accurately measure the depth of a trench less than 15 nm wide in the films. The continuity of the films, therefore, could not be solely determined by the film roughness. It was found, however, that the film roughness was approximately a constant for less than 15 nm thick films. From the roughness measurements, it was possible to determine qualitatively that the thicker the film, the more continuous it was. Comparing the sheet resistance of different films deposited on a glass slide also proved the better continuity for the thicker platinum or palladium films.

The $TiO_2$ film that was e-beam evaporated has been determined to change from an amorphous microstructure to a mixture of brookite and rutile during annealing processes. The $TiO_2$ films that were e-beam evaporated on the silicon oxide substrate maintained at room temperature were found to have a porous structure. The density of the films could be improved by using a substrate temperature of 393 K or by using sputter deposition.
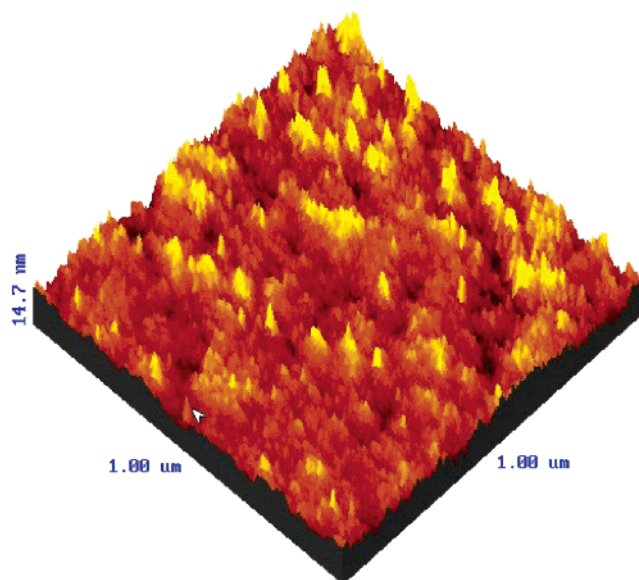
**Figure 3.** A three-dimensional atomic force image of a 5 nm platinum thin film e-beam evaporated on 150 nm $TiO_2$. The scanning area is 1 $\mu$m $\times$ 1 $\mu$m. The 5 nm platinum film has an rms roughness of 2.45 nm on 150 nm $TiO_2$, indicating a discontinuous coverage of platinum on the $TiO_2$. A 20 nm platinum film has an rms roughness of 5.3 nm, and thus has a better coverage.

$TiO_2$ films e-beam evaporated under vacuum exhibit semiconductor properties owing to oxygen vacancies in the $TiO_2$ lattice. The free carrier concentration in $TiO_2$ films produced by e-beam evaporation was determined to fall between $1 \times 10^{17}$ and $1 \times 10^{19}$ cm$^{-3}$ using Hall effect measurement.

The Schottky barrier height has been determined to be 1.2 eV for $Pt/TiO_2$ and Pt/GaN and no more than 0.7 eV for $Pd/TiO_2$ by using current−voltage curves. Platinum and palladium have work functions of about 5.8 and 5.2 eV, respectively. The energy band gaps of $TiO_2$ and GaN are about 3.0 and 3.2 eV, respectively. The height of a Schottky barrier formed between a metal and a semiconductor is influenced by many factors such as surface states, impurities in the metal, and interfacial uniformity. Impurities in the platinum or palladium thin film have been investigated by X-ray photoelectron spectroscopy and Auger electron spectroscopy with the capacity of depth profiling. It was found that a small quantity of magnesium from the fabrication process contributed to a lower barrier height of some of the platinum $TiO_2$ diodes.

**Catalytic Reactor.** A batch reaction system of about 1 L volume was built to carry out the gas-phase reaction (Figure 4). The reaction cell can be evacuated down to $1 \times 10^{-6}$ Torr by a turbo molecular pump backed by a roughing pump. A ceramic heater controls the sample temperature. A sampling loop including a gas chromatograph and a circulation pump measures reaction rates from reactant and product concentrations continuously. A picoammeter or a source meter measures the electron current from the sample during the reaction. The source meter is also used to measure the barrier height of the sample in situ.

### Results and Discussion

**Electron Current during the Catalytic Oxidation of Carbon Monoxide over Pt/TiO$_2$, Pd/TiO$_2$, and Pt/GaN.** Oxidation of carbon monoxide over platinum has been extensively studied.[18] The reaction follows a Langmuir−Hinshelwood mechanism. That is, carbon monoxide and oxygen first chemisorb on the platinum surface where the oxygen molecule dissociates. A reaction occurs in the adsorbed states between
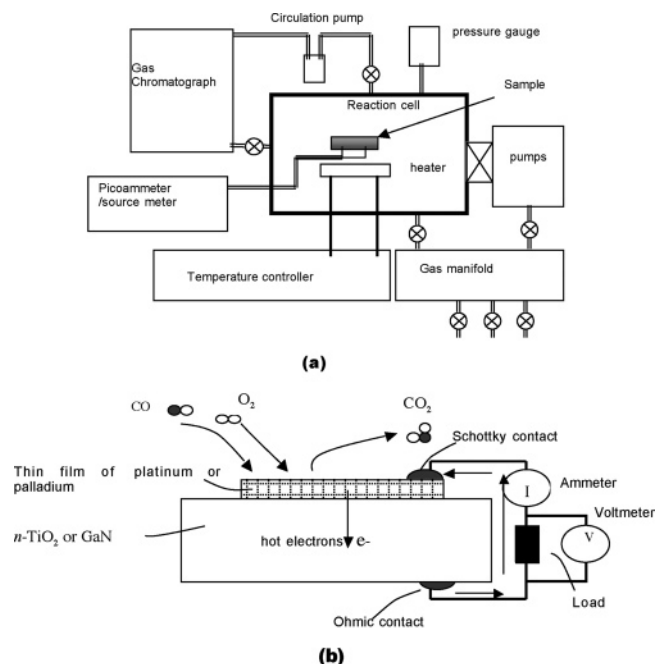


**Figure 4.** (a) Scheme of the batch reaction cell. (b) Schematic representation of measurement of a hot electron in a nanodiode. The arrows give the direction of hot electron flow. A short-circuit current ($I_{sc}$; see the text for the typical value) can be measured with a load of zero resistance, and an open-circuit voltage ($V_{oc} \leq 0.7$ V) with a load of infinite resistance.



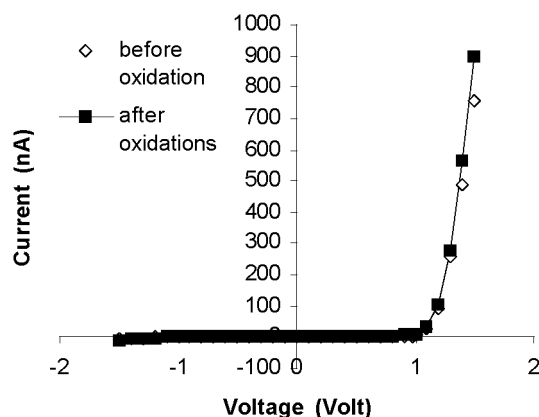**Figure 5.** Current−voltage ($I-V$) characteristics, taken at room temperature, of a 5 nm platinum/150 nm $n$-titanium oxide Schottky diode that had been annealed at 398 K for 15 min in Ar before and after the oxidation of carbon monoxide.

the carbon monoxide molecule and the oxygen atom, and the carbon dioxide that forms desorbs from the surface due to its low heat adsorption on the platinum. It is estimated that a total of 2.9 eV is released during the formation of a carbon dioxide molecule.[19] The reaction is thus highly exothermic. The reaction accelerates at the ignition temperature, above which it becomes self-sustaining, and is limited only by mass transport of reactants to the platinum surface. Below the ignition temperature, the reaction has a positive order in carbon monoxide under oxygen-rich conditions, but a negative order in carbon monoxide under carbon monoxide-rich conditions. All of the experiments have been carried out at below the ignition temperature of the oxidation of carbon monoxide and in an excess of oxygen.

The catalytic oxidation of carbon monoxide was carried out on the $Pt/TiO_2$, $Pd/TiO_2$, and Pt/GaN nanodiodes under 100 Torr of oxygen and 40 Torr of carbon monoxide at a temperature between 353 and 473 K. At higher temperature, the $Pt/TiO_2$
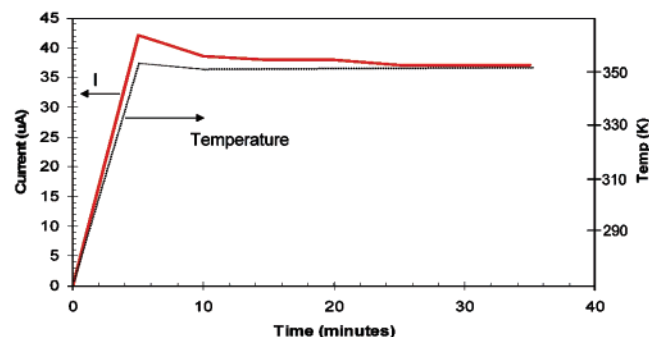
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**Figure 6.** Gas-phase catalytic oxidation of carbon monoxide on a 5 nm platinum/150 nm *n*-titanium oxide Schottky diode generates a steady-state electron flow of 37 $\mu$A (red curve) for over 1/2 h. The initial pressures of $O_2$ and CO are 100 and 40 Torr, respectively. The temperature (dotted line) was first ramped to 353 K in a few minutes and then kept constant.

diode was less stable. It was found that a moderate annealing of the Pt/TiO$_2$ sample at 398 K in Ar for 15 min improved the diode stability while high-temperature annealing usually destroyed the diode and increased the device conductivity. A comparison between current−voltage characteristics of the 5 nm Pt/TiO$_2$ annealed at 398 K before and after the CO oxidation reaction showed little change in the electrical property of the sample (Figure 5). The reason for the difference in annealing temperature is that low-temperature annealing improved adhesion of Pt to TiO$_2$ but high-temperature annealing destroyed the sharp interface in Pt/TiO$_2$ due to diffusion of metallic impurities (Cr, Au, and Pt) into the TiO$_2$. Reduction of the reactivity of the thin platinum sample after high-temperature annealing was also due to the covering of the platinum surface by TiO$_2$ or diffusion of platinum atoms into TiO$_2$ along the grain boundaries and pores.

Below 373 K, a constant reaction condition was maintained due to the low reaction rate that assured little change in the partial pressures of $O_2$ and CO during the experiment. The

catalytic reaction had a constant turnover rate of $3 \times 10^{14}$ carbon dioxide molecules per second at 353 K from one Pt/TiO$_2$ diode. The best conversion to electron flow per reaction event was achieved using a 5 nm thick platinum film on TiO$_2$ (Figure 6). With a current flow of 40 $\mu$A, the conversion rate to electron flow is about three electrons for every four carbon monoxide oxidation events.

Pt/GaN had the best thermal stability among the three diodes. Figure 7 shows hot electron generation and the CO$_2$ accumulation rate cycle between 423 and 323 K. The reaction conditions are 100 Torr of $O_2$ and 40 Torr of CO. The small platinum surface area and low temperature limited the total CO conversion to less than 12% in these experiments. The figure clearly shows that hot electron generation was controlled by the rate of CO oxidation on the platinum surface.

Pd/TiO$_2$ had the lowest thermal stability among the three diodes. Five nanometer palladium lost reactivity for the oxidation of carbon monoxide in a few minutes under 100 Torr of oxygen and 40 Torr of carbon monoxide at 353 K. This was due to the fast oxidation of palladium under oxygen-rich conditions and diffusion of palladium atoms into TiO$_2$ along grain boundaries.

We found that the detected current has two components, i.e., the thermoelectric current and the hot electron current, due to the catalytic reaction. By heating the nanodiodes in He or N$_2$, we could measure the thermoelectric current alone. The thermoelectric current was always in the direction opposite that of the flow of the hot electron current, and was a few nanoamperes when the conductivity of the semiconductor was low. Since reactions only occur on the platinum or palladium, hot electron transport was always from platinum or palladium into TiO$_2$ or GaN. When a current−voltage curve was measured during the catalytic reaction, the curve moved downward if the net current was hot electron flow. The thermoelectric current, on the contrary, moved the current−voltage curve upward. Figure 8 shows current−voltage curves measured in situ from
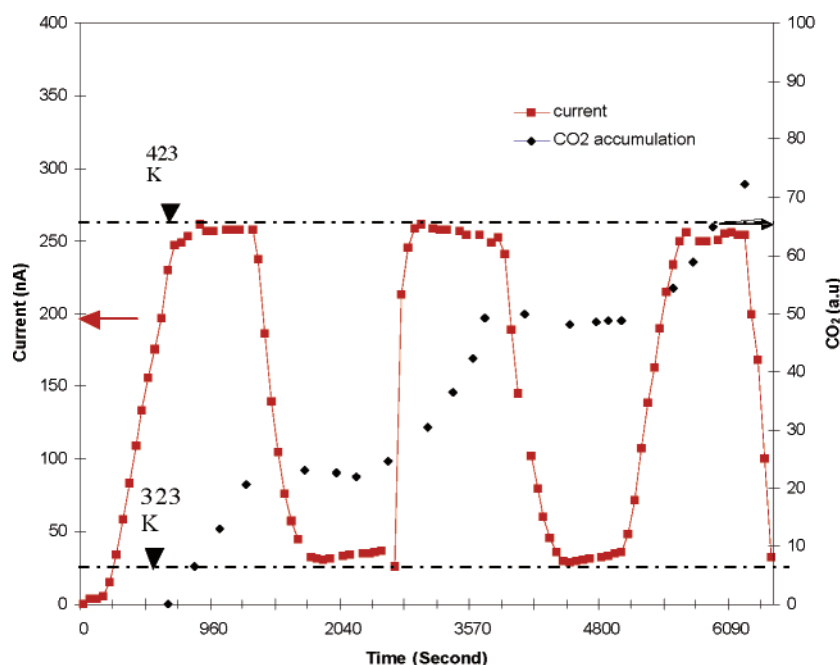


**Figure 7.** Hot electron generation and CO$_2$ accumulation cycling between 423 and 323 K using the Pt/GaN nanodiode. The initial reactants are 100 Torr of $O_2$ and 40 Torr of CO. The small platinum surface area and low temperature limited the total CO conversion to less than 12% in this experiment. The reaction temperature is ramped to 423 K and cooled to 323 K three times. At 423 K, CO accumulates and significant current flow is detected. At 323 K, CO oxidation stops and no current is detected. The figure shows clearly that hot electron generation is controlled by the reaction rate of CO oxidation on the platinum surface.
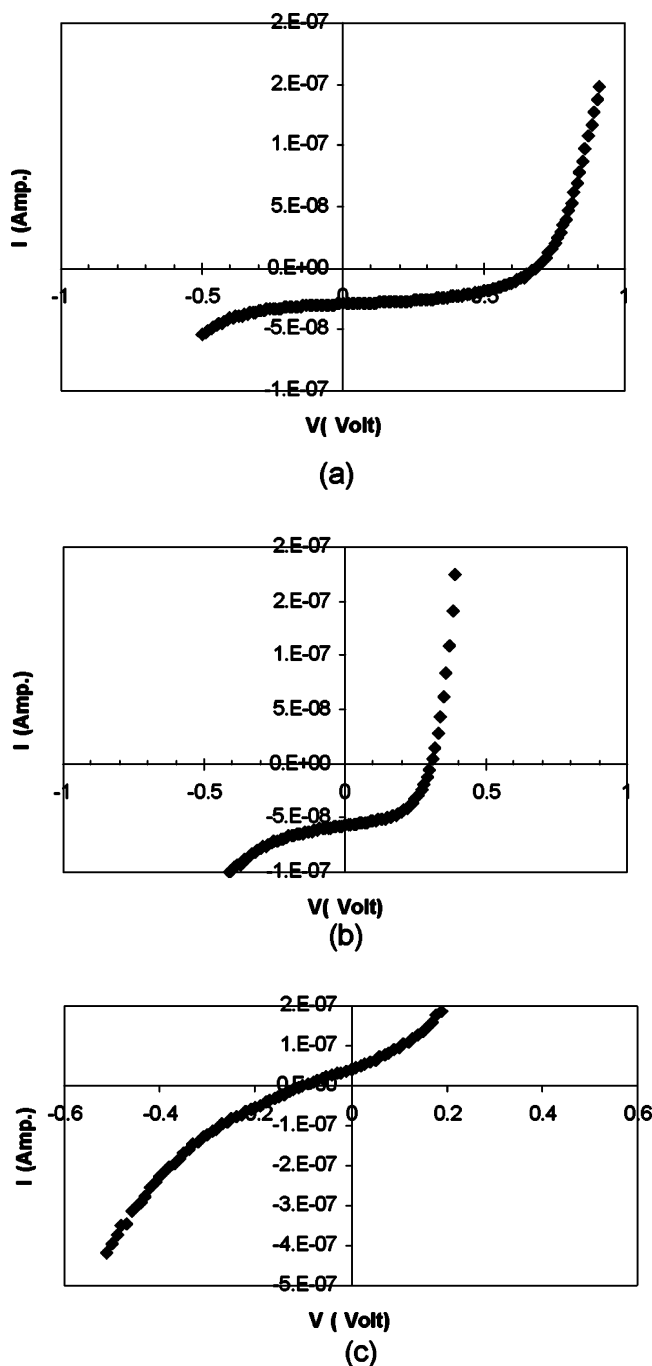
(a)



(b)



(c)

**Figure 8.** (a) $I-V$ characteristics of $Pd/TiO_2$ under 40 Torr of CO and 100 Torr of $O_2$ at 293 K. $I_{sc} = 29.1$ nA, and $V_{oc} = 0.68$ V. (b) $I-V$ characteristics measured in situ when the temperature was just ramped to 357 K. $I_{sc} = 57$ nA, and $V_{oc} = 0.30$ V. (c) $I-V$ characteristics of $Pd/TiO_2$ after 15 min of CO oxidation at 357 K.

$Pd/TiO_2$ under 100 Torr of $O_2$ and 40 Torr of CO from room temperature to 357 K. Due to a low reactivity at room temperature, we saw a small downshift of the current–voltage curve of the $Pd/TiO_2$. When the temperature reached 357 K, the current became bigger due to the higher reactivity. The lower open-circuit voltage, however, indicates that the electrical property of the sample had changed during the temperature ramping. The current–voltage curve moved above the origin after 15 min, indicating that the hot electron generation had dropped to such a level that the thermoelectric current dominated the current from the sample.

**Metal Thickness Dependence of the Conversion Efficiency.** Due to the high surface energies of palladium and platinum,
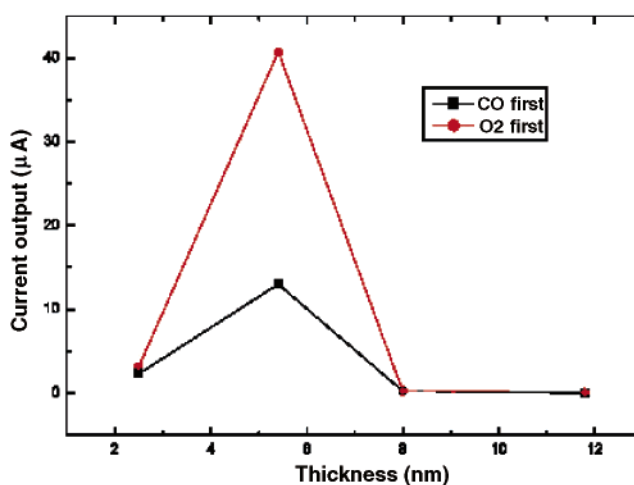


**Figure 9.** Maximum current output from platinum/$TiO_2$ diodes vs the thickness of the platinum film. Reactions were carried out under 100 Torr of $O_2$ and 40 Torr of CO at 353 K. The effect of the sequence of introducing reactants was more pronounced when the platinum film was 5 nm thick.

they grew islands on $TiO_2$ and GaN. Therefore, only a small portion of the available metals was in contact with the front electrode and could contribute to the electron flow to produce a constant current. When more metal was deposited, the islands coalesced and the continuity of the film improved. More and more of the film was now contributing to the constant hot electron current. When even more metal was deposited, however, some part of the film became so thick compared to the electron mean free path that hot electrons generated at that part of the metal surface had more chance of being scattered inelastically. These electrons then did not have sufficient kinetic energy to overcome the Schottky barrier, and could not be collected. As a result, the hot electron current first increased with the metal film thickness until the thickness reached the mean free path of electrons in the metals (Figure 9). It should be noted that 5 nm is the elastic mean free path and 9 nm is the inelastic mean free path of 1.2 eV electrons in platinum. Increasing the platinum film thickness to 10 nm reduced the current from 40 $\mu$A to the nanoampere region.

**Schottky Barrier Height Dependence of the Collection Efficiency.** Since hot electrons must possess enough kinetic energy to overcome the Schottky barrier to escape from platinum or palladium, the Schottky barrier height played a crucial role in the conversion efficiency of the $Pt/TiO_2$, Pt/GaN, and $Pd/TiO_2$ catalytic diodes. Even though oxidation of carbon monoxide released a total of about 2.9 eV per formation of a carbon dioxide molecule, the energy was released via several elementary reaction steps that included the chemisorption of carbon monoxide and oxygen molecules, dissociation to two oxygen atoms, and finally the reaction of a carbon monoxide and an oxygen atom to produce carbon dioxide. It is still unclear how the chemical energy was distributed among the different reaction channels or what the transition state was that led to hot electron generation in the metal. The optimal Schottky barrier height should perhaps be no greater than the minimum energy released by any step.

Hot electrons in the metal took several paths into the semiconductor. Electron transport over the Schottky barrier was valid for those hot electrons that possessed kinetic energies higher than the barrier. Using palladium instead of platinum, we reduced the Schottky barrier from about 1.2 to about 0.7 eV. This reduction in the Schottky barrier height, however, did not improve the collection efficiency of $Pd/TiO_2$, due to the

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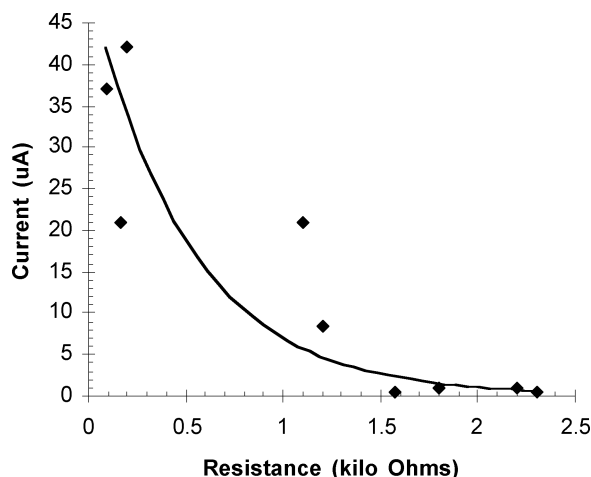*J. Phys. Chem. B, Vol. 109, No. 47, 2005* **22535**



**Figure 10.** Gas-phase catalytic oxidation of the carbon monoxide generated current as a function of the resistance of 150 nm *n*-titanium oxide. All diodes consist of 5 nm platinum and 150 nm *n*-titanium oxide.

great loss of reactivity of the palladium. Hot electrons with less energy had to tunnel through the barrier. The barrier width decreased when the free carrier concentration in the semiconductor increased. The conductivity of the titanium oxide film increased with the oxygen vacancy concentration. Figure 10 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, 353 K). It clearly shows that a higher concentration of oxygen vacancies improved the collection efficiency of electrons produced by the catalytic reactions by allowing more hot electrons to tunnel through the barrier.

## Conclusions

We observed continuous flow of electrons from a metal catalytic film of several nanometers thickness into a semiconductor substrate during the catalytic oxidation of carbon monoxide. The hot electron flow through the catalytic diodes of $Pt/TiO_2$, $Pd/TiO_2$, and Pt/GaN depends on (1) the reaction turnover rate, (2) the thickness of the platinum or palladium film, and (3) the Schottky barrier height and width of the semiconductor−metal interfaces. The mechanism for the catalytic reaction induced current flow is as follows: Hot electrons were produced at the platinum or palladium surface where the exothermic catalytic oxidation of carbon monoxide occurred. If the thickness of the platinum or palladium was less than the elastic mean free path of the electrons (∼5 nm), the electrons migrated to the edge of the Schottky barrier without losing much of their kinetic energy. Some of the electrons, which have

sufficient kinetic energy, moved across the potential barrier into the semiconductor. These electrons then must move through an external circuit to recombine with the holes in the metal, and were therefore measured as a short-circuit current. The transition state leading to hot electron generation during CO oxidation is yet to be determined.

The most efficient heterogeneous catalysts are usually nanoparticles of catalysts supported by oxides. It is still unclear whether the differences in semiconductor supports caused the different efficiencies of electronic excitation in $Pt/TiO_2$ and Pt/GaN. Several other properties of the systems such as the atomic structures and electronic structures of the supports and of the semiconductor−metal interfaces may contribute to the difference. These experiments provide new insights into the mechanism of heterogeneous metal catalysis. The electron flux that is produced could influence the turnover rates and selectivity of catalyzed reactions.

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