Communication

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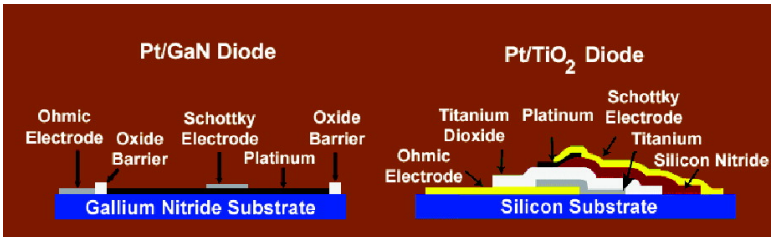

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Electron Flow Generated by Gas Phase Exothermic Catalytic Reactions Using a Platinum−Gallium Nitride Nanodiode

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Ji et al.[1] constructed a platinum−titanium dioxide Schottky nanodiode (Pt/TiO_2) and carried out carbon monoxide oxidation catalyzed by the platinum. Using a nanodiode consisting of a 5 nm platinum thin film with a diameter of 2 mm formed on a 150 nm titanium dioxide film, hot electron currents up to 40 μA were generated in steady state for over an hour. This experiment clearly verified that the proposed method converts exothermic chemical catalytic reaction energy directly into hot electrons.[1] This sharply contrasted prior work, which generated transient nanocurrent utilizing adsorption reactions in ultrahigh vacuum at 130 K. It was reported that three electrons could be collected for the production of four CO_2 molecules at 353 K using 100 Torr of O_2 and 40 Torr of CO. A scheme of the experimental nanodiode configuration that uses surface-catalyzed reactions to generate steady-state current is shown in Figure 1. A patent[2] describing the method for the same was published and is used in this study. Evidence of hot electron generation under a variety of experimental conditions is reported elsewhere.[1−3]

In this communication, we report steady-state generation of electrons through a platinum−gallium nitride (Pt/GaN) nanodiode during the platinum-catalyzed oxidation of CO. Such a nanodiode has been utilized by General Electric Global Research as a hydrogen sensor. Taking such a nanodiode off the shelf, we carried out CO oxidation in the 373−523 K temperature range using 40 Torr of CO and 100 Torr of O_2. We observed a hot electron flux stable for several hours and investigated hot electron generation on the Pt/GaN nanodiodes as a function of platinum film thickness and reaction temperature.

The planar configuration of the Pt/GaN nanodiode is shown in Figure 2 along with the Pt/TiO_2 nanodiode that was used successfully in our previous studies.[1] Platinum acts as both the catalyst and the Schottky electrode, while the Al/Ti or Ti/Pt/Au electrode forms an ohmic contact with the single-crystal n-type GaN semiconductor. The barrier height of the Pt/GaN nanodiode is about 1.2 eV. This means that only hot electrons of kinetic energy greater than 1.2 eV can surmount the barrier at the platinum n-type gallium nitride interface and charge the diode-junction capacitor. We used nanodiodes with average platinum film thicknesses of 8 and 24 nm.

The batch reactor is about 1 L in volume, and concentrations of reactants and products can be monitored during a reaction from a sampling loop, including a gas chromatograph and a circulation pump.[1] These data provide the reaction turnover rate, the number of CO_2 molecules produced per second. A steady-state production of hot electrons was achieved at low temperature (Figure 3), and 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.

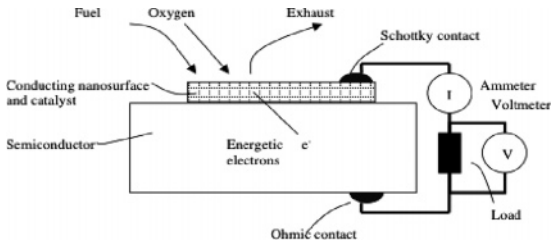

Figure 1. Schematic representation of hot electron generation by exothermic catalytic reactions using a nanodiode.

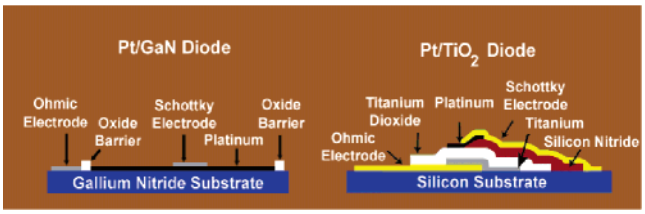

Figure 2. Scheme of platinum−gallium nitride Schottky nanodiode. Gallium nitride is an n-type single crystal grown on a sapphire substrate. The platinum is 8 or 24 nm in thickness and 1 mm × 1 mm in area. The ohmic electrode is made of Al/Ti or Ti/Pt/Au. An oxide passivation barrier has been utilized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

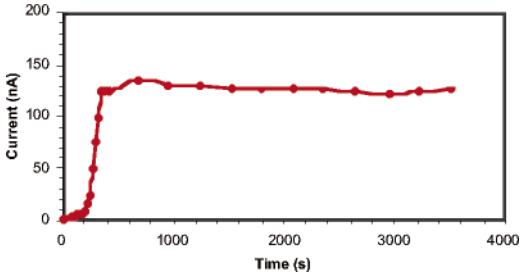

Figure 3. Gas-phase catalytic oxidation of carbon monoxide (100 Torr of O_2, 40 Torr of CO, 423 K) generates a steady-state hot electron flux of about 140 nA in an 8 nm platinum−gallium nitride Schottky nanodiode for about an hour.

The hot electron generation can be varied by cycling the temperature as shown in Figure 4. The temperature dependence of the catalytic turnover yields an activation energy of 14 kcal/mol for both Pt/GaN nanodiodes. This is the same as that obtained for CO oxidation over platinum single-crystal surfaces or over platinum nanoparticles above the ignition temperature of the reaction.[4,5]

Table 1 lists the currents detected during CO oxidation over the Pt/GaN nanodiodes with platinum films of different thicknesses. We found that the collection efficiency of the hot electrons depends on the thickness of the platinum film. Note that the 24 nm thick nanodiode produced less current than the 8 nm thick nanodiode, but not exponentially less as would be expected based on hot electron, elastic mean free path (mfp) considerations. The elastic

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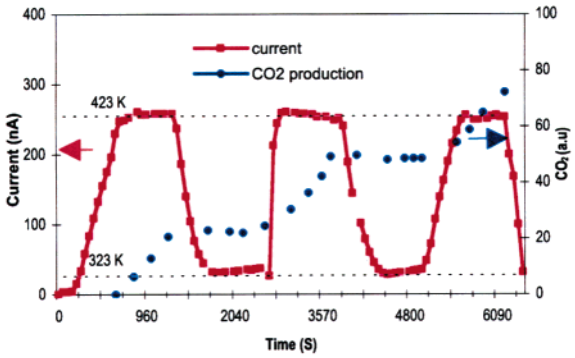

Figure 4. Hot electron generation and CO_2 accumulation rate cycle between 423 and 323 K. The reaction condition is 100 Torr of O_2 and 40 Torr of CO at 0 s. Small platinum surface area and low temperature limited the total CO conversion to less than 12% in this experiment. The figure clearly shows that hot electron generation was controlled by reaction rate of CO oxidation on the platinum surface.

Table 1. Hot Electron Fluxes Detected during Carbon Monoxide Oxidation over Pt/GaN Nanodiode with a Platinum Film of Different Thicknesses (chemical reaction conditions are 100 Torr of O_2 and 40 Torr of CO)

	Current (nA)	
temperature (K)	8 nm platinum	24 nm platinum
523.15		2500
498.15	2340	1160
473.15	885	389
448.15	244	105
423.15	136	24.2
398.15	11.5	4.54
373.15	3.99	0.975

mfp is on the order of 5 nm, and the inelastic mfp ~ 9 nm for 1.2 eV hot electrons in platinum.

We also found that the continuity of the platinum film affects the collection efficiency of hot electrons in the nanodiodes. The relatively small difference (factor of 2−3) in current between 8 and 24 nm thick platinum film catalysts may indicate that the hot electron collection, not production, was probably concentrated in the regions of the rough platinum film where the platinum was sufficiently thin and possibly less than the elastic or inelastic mfp. There is also evidence from atomic force microscopy studies that our platinum films were discontinuous. This indicates that the hot electrons were collected only from a small area of the platinum film connected to the Schottky contact. Nevertheless, the electron flow remains steady for hours in this circumstance.

The electron flux that can be generated by a catalytic Schottky nanodiode depends on the exothermicity of the chemical reaction that is utilized and on reaction intermediate paths leading to product formation. Presently, we are studying catalytic oxidation of hydrogen, methanol, and CO. In addition, the materials chemistry and design of the catalytic nanodiode are of key importance. Measurements of the kinetic energy distribution of hot electrons are in progress. The thermal and chemical stabilities of the thin metal film (thickness on the order of the electron mean free path) and the semiconductor that makes up the nanodiode are important for obtaining steady-state current flow. Ideally, a stable nanodiode system should allow turnover rates to be altered by orders of magnitudes by changing the reaction temperature to obtain the desired current flux.

Metal catalysts are usually metal nanoparticles in the 1−10 nm size range deposited on oxide supports. Although hot electron current cannot be measured for the individual particles in the absence of contact electrodes, there must be electron flow in these metal nanoparticles during exothermic catalytic reactions. The catalytic nanodiodes, Pt/GaN and Pt/TiO_2, may serve as models for studying the electron current-induced chemical behavior of supported metal catalyst nanoparticles. Furthermore, flow of electrons from the metal nanoparticles to the support would generate electric fields at the oxide−metal interfaces which should give rise to chemical effects. There is evidence that platinum−silica and platinum−alumina interfaces formed when platinum nanoparticles are deposited on these oxides remain catalytically active when the rest of the metal is deactivated. When ethylene hydrogenation or cyclohexene hydrogenation/dehydrogenation reactions are poisoned by carbon monoxide, the reaction rates become proportional to the oxide−metal interface area.[6,7] Gold nanoparticles deposited on titanium oxide supports show high activity for catalytic reactions in a certain range of metal particle size.[8] It would be important to correlate hot electron generation with the catalytic activity of systems that exhibit Schottky diode characteristics, as well.

The results of this study have potential practical applications in direct conversion of chemical energy to electricity. We also hope to learn more about the role of electron flow in metal surface-catalyzed chemical reactions.

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