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CO adsorption and oxidation studies on nanofabricated model catalysts using multilayer enhanced IRAS technique

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ABSTRACT

CO adsorption and oxidation studies have been performed on model Pt catalysts using multilayer enhanced infrared reflection absorption spectroscopy (MEIRAS) technique demonstrated in our laboratory. The multilayer model catalysts prepared for this study consist of semitransparent thin Pt films or Pt nanowires over SiO_2 or TiO_2 dielectric films of varying thicknesses with reflecting gold films underneath. CO adsorption results show that different types of oxidation and reduction pretreatments on $Pt/SiO_2/Au$ thin film catalysts lead to changes in the CO stretch region of the spectra and in morphology of Pt films. Ignition behavior of CO oxidation reaction was studied on these catalysts and a change in the baseline of the spectra was observed as an indication of change in surface oxygen coverage with change in reaction conditions. CO adsorption studies on $Pt/TiO_2/Au$ nanowires catalysts show a shift in the peak position towards lower wavenumbers with a decrease nanowire width. The results indicate that these spectral changes might be related to the boundary adsorption sites near the edges of Pt particles and nanowires. Further, experiments involving modification of boundary sites at Pt/TiO_2 junctions by applying external voltage to a catalytic nanodiode with Pt nanowires on TiO_2 are in progress.

1. Introduction

Progress in surface science has led to the development of a number of analytical techniques that can provide useful information about model catalyst surfaces such as single crystals [1,2]. However, extrapolation of these results to heterogeneous catalysis has seen only a limited success, even though some examples exist where such limitations have been overcome under special conditions [3,4]. The progress in this front has been hindered by two main obstacles known as the "material-gap" and the "pressure-gap". Heterogeneous supported catalysts are complex materials and their catalytic properties are determined by a number of parameters such as atomic structure, composition, shape and size of particles, and support's nature [5]. Moreover, these surfaces undergo changes in structure and composition in response to temperature, pressure and concentration of reactant gases [6,7]. Thus, the information collected from clean surfaces under UHV conditions might not always be applicable to catalysts under real working conditions. In attempts to "bridge" these "gaps", many techniques have been recently developed to perform surface science experiments at elevated pressures that are closer to real working conditions. PM-IRAS [7,8], SFG [9–11], high pressure XPS [12,13], high pressure STM [14,15], etc. are a few examples of such developments. Although these developments are relatively recent, they seem promising. In addition to these, several methods of preparing model catalysts have been developed which can yield well-defined surfaces and introduce the complexity of real catalytic materials in a controlled way [16].

Nanofabrication is routinely used in the microelectronics industry to make electrical circuits. These techniques in principle can be used to prepare model catalyst surfaces with a precise control over structure and composition, thus they are potentially useful in catalysis research. One of the early attempts in this direction was made in our group about 15 years ago. A regular array of Pt particles on a flat silica support was prepared using optical lithography and used to study butadiene hydrogenation reactions [17–19]. Unfortunately, the techniques available at the time were not suitable for creating nanostructures and no special size effects were observed. In the recent years Somorjai and coworkers have explored a range of modern nanoscale lithographic techniques to prepare model catalysts [20–24]. In addition to preparing model catalysts with nanoscale features, lithographic patterning and thin film deposition methods can provide additional tools for studying catalyst surfaces and reactions. One example is the fabrication of a catalytic diode to measure hot electrons generated as a result of a chemical reaction [25,26]. The hot electron generation, being proportional to the turnover frequency of the reaction can be used as a sensitive measurement of the reaction rate [27].

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Table 1
Different types of metal/dielectric/metal multilayer model catalyst samples prepared using nanofabrication techniques.

Sample number	Top metal layer	Dielectric layer	Bottom metal layer
Thin film samples			
1	5 nm Pt film	1125 nm SiO_2	50 nm Au/10 nm Pt
2	5 nm Pt film	450 nm TiO_2	50 nm Au/10 nm Pt
Nanowire samples			
3	Pt nanowires (width ~25 nm)	250 nm TiO_2	50 nm Au
4	Pt nanowires (width ~60 nm)	250 nm TiO_2	50 nm Au
5	Pt nanowires (width ~90 nm)	250 nm TiO_2	50 nm Au
Catalytic diode samples			
6	5 nm Pt film connected to top Au electrode	450 nm TiO_2	50 nm Au/10 nm Pt connected to bottom Au electrode

We recently continued research along these lines, which involves using electron beam lithography to prepare catalytic nanodiodes consisting of Pt nanowires on a TiO_2 thin film deposited on a gold electrode. The aim of this ongoing work is to use such nanofabricated model catalysts for studying electronic effects associated with metal–support junctions. Theoretical DFT based simulations of CO adsorption on a Pt single crystal surface subjected to an electric field, indicated that CO adsorption is affected by electric field as reflected in the shifts of the CO vibrational frequency [28]. To demonstrate these theoretical simulations, a technique capable of sensing infrared signals from CO adsorbed on small area Pt nanowires was needed. This was achieved using a novel multilayer enhanced infrared reflection absorption spectroscopy (MEIRAS) technique recently developed in our laboratory. We found that metal/dielectric/metal multilayer structures create optical interference effects which can significantly enhance the FTIR sensitivity to CO adsorbed on Pt films [29]. We have and performed a detailed theoretical analysis of such interference effects [30] to fully understand the enhancement mechanism and interpret the spectra obtained from this technique. The MEIRAS technique can be used to study CO adsorption on thin films, and oxide-supported nanoparticles and nanowires under elevated pressures and reaction conditions without any special optical instrumentation such as the PM-IRAS [7] and the SFG [9].

In the present work, Pt/SiO_2/Au and Pt/TiO_2/Au multilayer structures, with Pt thin films or Pt nanowires as the top layer, are prepared and used for CO adsorption oxidation studies using MEIRAS. The results show changes in spectra with a change in the catalyst nanostructure and the pretreatment process which can be related to properties of the adsorption sites near metal support interfaces. CO oxidation reaction was studied and a change in the shape of baseline of the spectra was observed as an indication of increase in surface oxygen coverage during the reaction. Further work involving thin film and nanowire catalysts with increased complexity including a catalytic nanodiodes is underway.

2. Catalyst preparation

Model catalysts consisting of metal/dielectric/metal multilayer structures were fabricated using the methods described below. The bottom metal layer was a reflecting Au film while the dielectric layer consisted of either SiO_2 or TiO_2. The top layer of the multilayer structure was either a Pt film or Pt nanowires. Some Pt/TiO_2/Au samples had a more complex design with additional gold electrodes connected to the bottom and top metal layers, similar to the catalytic diodes described by Somorjai and coworkers [27]. Table 1 summarizes the structure and layer thickness in different samples prepared.

2.1. Multilayer structures

Fig. 1a shows a schematic of the cross-section of a typical multilayer structure. The Pt/SiO_2/Au multilayer samples were prepared using physical vapor deposition of metal films and plasma enhanced chemical vapor deposition (PECVD) of SiO_2 films on (1 0 0) silicon wafers. We have previously described the detailed preparation methods and shown that depending on the thickness of SiO_2 layer the reflectance of the multilayer structure goes through a minimum at a particular infrared wavelength [29]. In the present study the SiO_2 layer has a thickness of 1.1 μm which is close to a quarter of the CO adsorption infrared wavelength (2100 cm^{-1}) in SiO_2. Optical interference occurring in this geometry resulted in reflectance minimum of the sample near this wavelength and maximum enhancement in infrared sensitivity for CO adsorption. However, this thickness limits the range of wavenumbers for which the spectral enhancement can be observed as the reflectance becomes high in the 3000 cm^{-1} range. Alternatively, a smaller SiO_2 thickness could have been chosen which would lead to a smaller enhancement in the 2100 cm^{-1} region but at the same time increase the total range of wavenumbers that can be used [29,30]. Some samples used TiO_2 as the dielectric in place of the SiO_2 layer in the above description. The TiO_2 films were prepared by electron beam evaporation of Ti metal followed by thermal oxidation for several hours at temperatures between 450 and 500 °C. For the bottom metal layer in some of the multilayer structures a bi-layer deposition with a thin Pt under Au was used in place of Au deposition only to improve its thermal stability during oxidation process.

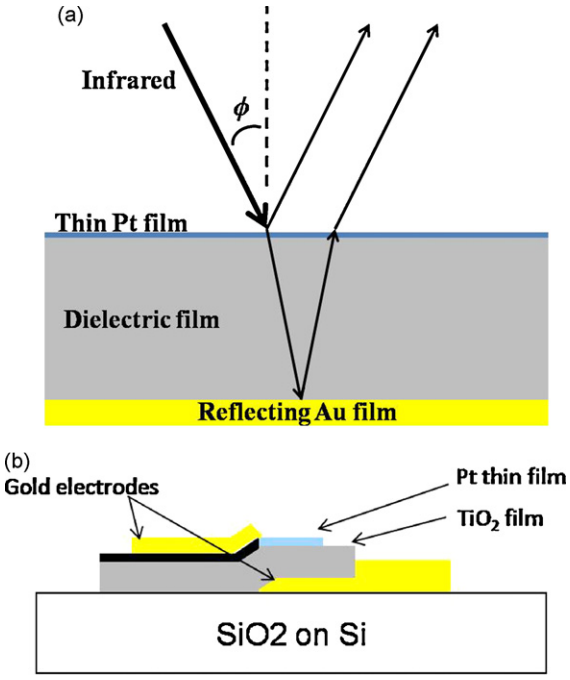

Fig. 1. Schematic of (a) a metal/dielectric/metal layered structure and (b) a catalytic diode sample.