FTIR study of CO adsorption and electrical characterization of novel Pt/TiO_2 Nanowire Catalysts fabricated using Electron Beam Lithography.

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Introduction

Model supported catalysts on flat surfaces form an important link between single crystal surfaces and real world supported catalysts. The use of nanofabrication techniques to prepare such model catalysts has received a lot of attention in recent years [1]. In the present study Pt/TiO_2 catalysts have been fabricated using e-beam lithography (EBL) and used to characterize the electrical properties of metal-support junction.

Materials and Methods

TiO_2 films were prepared by electron beam evaporation of titanium metal on a silicon wafer followed by thermal oxidation in air. Platinum nanowires were prepared by electron beam lithography. Zep-520A e-beam resist was spun on the substrate, followed by e-beam exposure using JEOL 9300 tool, development, platinum metal deposition and liftoff (at Center for Nanoscale Materals, Argonne National Laboratories). The e-beam exposed pattern was developed using a novel cold development process [2] which helped improve the resolution. This allowed e-beam writing at a high beam current of 1nA. 25nm nanowires with 200nm spacing covering a 4mmx4mm area were fabricated using an exposure time of less than two hours. For electrical characterization of the fabricated samples, bottom and top gold pads connected to TiO_2 support and Pt nanowires respectively were also fabricated. These nanofabricated samples were characterized using SEM and AFM imaging. Current-voltage (I-V) measurements were performed on the samples after oxidation-reduction treatments at several temperatures. CO chemisorption on the fabricated Pt nanowires was studied using specular reflection FTIR spectroscopy. Novel $Pt(nanowires)/TiO_2/Au$ structures with optimized TiO_2 thickness were fabricated which allowed significant enhancement of FTIR signal and thus improved the detection limits.

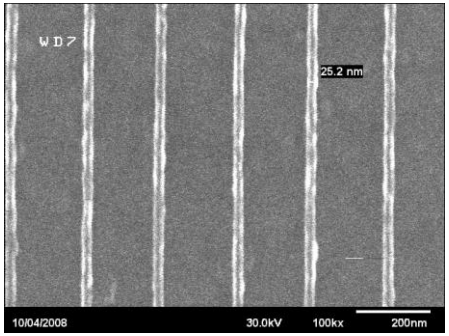

Figure 1. SEM image of the Pt nanowires supported on TiO2 substrate fabricated using electron beam lithography.

Results and Discussion

SEM and AFM studies show that the fabricated nanowires were about 25nm wide and 8nm high. The continuity and uniformity of nanowires over a large area was good. The fabrication method described above was faster than other EBL based catalysts fabrication reported in the literature and thus improves the throughput to some extent. Figure 1 shows the SEM image of one sample. The rectifying behavior seen in the I-V curve for a Pt nanowire – TiO_2 junction was found to be different from a Pt film – TiO_2 junction (figure 2) due to effect of increased interfaces and boundary sites. Additionally a difference of about 50 wavenumbers was found in the FTIR peak position of the adsorbed CO on a continuous film and that adsorbed on the nanowires.

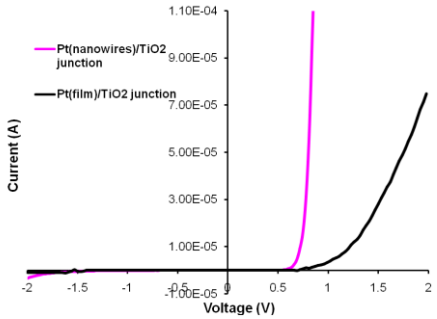

Figure 2. Comparison between the current-voltage (I-V) behaviors of Pt nanowire/TiO_2 junction and a Pt film/TiO_2 junction.

The I-V behavior of nanowires samples after different oxidation and reduction treatments at temperatures up to 500°C is being studied to understand the changes in junction properties and metal – support charge transfer due to increased donor electron density in TiO_2 after reduction [3]. We expect to see shifts in CO adsorption peaks in the FTIR measurements with these changes in the electrical properties of the junction. Further, the effect of in-situ biasing of the nanowire-support junction, using an external potential, on CO adsorption peaks and catalytic activity of the nanofabricated catalysts will also be investigated. Ab-initio studies have been performed to investigate CO adsorption on Pt(111) surface and indicate a significant effect of electric fields resulting from an external potential on C-O normal mode vibrational frequencies.

Significance

This work demonstrates the ability to use nanofabrication techniques to directly characterize the properties of metal-support nano-junctions using electrical measurements. This will help understand the electronic effects attributed to metal-support boundary and extent to which it plays a role in catalysis. It is an additional advantage of lithographic techniques along with the ability to fabricate structures with well defined shape, size and composition.

Acknowledgement

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References

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3. Jochum W., Eder D., Kaltenhauser G. and Kramer R., *Top. Catal.* 46(1-2), 49-55 (2007).