Control of Metal-Insulator-Semiconductor Sensor Performance through Surface Modification

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Introduction

The detection of hydrogen and hydrocarbons using inexpensive tools is a highly sought after venture. Numerous applications for a robust sensor technology include hydrogen leak detectors, transformer fault gas detection, and detection of volatile aromatics [1,2]. Metal-insulator-semiconductor (MIS) sensors are a viable tool for achieving this goal. These devices consist of a layer of a catalytic gate metal (e.g., Pd) and a semiconductor separated by a dielectric (e.g., SiO_2). Hydrogen can diffuse from the metal surface to the metal-insulator interface and cause a shift in the capacitance-voltage curve which can be measured for many decades of gas phase partial pressure (Fig. 1).

One drawback of MIS sensors is limited selectivity due to the variety of surface reactions that can be catalyzed by the gate metal. Modifying of the metal surface according to principles from heterogeneous catalysis and surface science may improve sensor design for selectivity to specific analytes of interest. The focus of this work is to evaluate the effect of surface composition and surface coatings on sensor performance. In addition, we propose that the high sensitivity of these systems demonstrates their utility for catalyst discovery.

Materials and Methods

MIS structures were fabricated using facilities at Sandia National Laboratories with commercially supplied n-type Si wafers coated with a thin thermal oxide on one side [1,2]. Metal films were deposited on the oxide using a dual electron beam evaporator. Using this technique, bimetallic films of controlled composition can be generated to explore compositional effects on sensor performance. For some of the studies, sensors were coated with polyimides and self-assembled monolayers (SAMs) of alkanethiolates using standard techniques described in previous work [3] to modify surface functionality. Once prepared, the capacitance-voltage response of sensors was tested using a flow cell device that enabled the dosing of 100-1000 ppm levels of analyte gases to the sensor surface.

Results and Discussion

Sensor response has been characterized for a variety of structures and analytes. For example, one objective of this work was to design a device that selectively responds to H_2 and not to other gases. The incorporation of H_2-selective membranes above the catalytic metal has been demonstrated to be an effective method for meeting this objective. More recently, sensor response to an analyte of interest, acetylene, has been characterized in the presence of H_2 using sensors with polyimide and SAM coatings in conjunction with bimetallic alloy gate metals. Polyimide coatings show a complete attenuation of acetylene response caused by slow diffusion of acetylene molecules across the polymer. On the other hand, certain SAM-coated and bimetallic sensors show a dramatic increase in acetylene response (Table 1).

The mechanisms for this enhanced response are still under investigation, but appear to be related to an improvement in the rate of acetylene hydrogenation relative to the rate of dissociative hydrogen adsorption on the catalytic metal film. In the case of the SAM films, this effect is unexpected. However, the use of SAMs as a coating offers many advantages in determining the mechanism for acetylene response enhancement, since SAM coatings are well-ordered layers, and the head and tail groups of the SAM-forming molecules may be altered to change the chemical environment. We will present our initial studies of variables such as SAM tail length, and discuss parallels between sensitivity for unsaturated molecules on MIS devices and hydrogenation activity trends for high-surface area supported metal catalysts.

Table 1. Pd-SiO_2-Si Sensor Response to 100 ppm acetylene by Coating Type

	No Coating	Polyimide Coating	15% Cu alloy	15% Ag alloy	SAM Coating
Acetylene Response (mV)	7	0	83	52	60

Significance

Development of a viable solid state gas sensor may lead to economical detection for hydrogen storage devices as well as a wide variety of environmental pollutants. As will be discussed in this presentation, MIS sensors provide an interesting platform on which to study surface reactions relevant to catalysis, including the influence of the SAM environment on surface activity for various reactions.

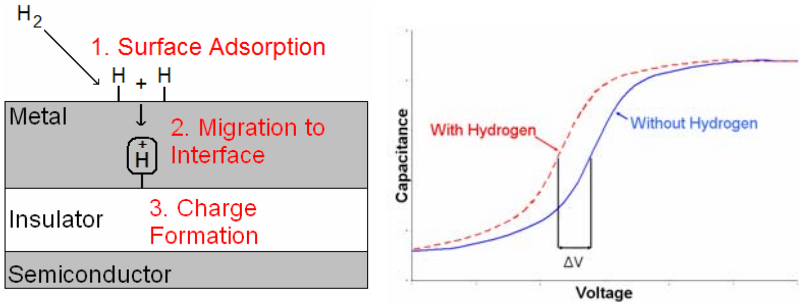

Figure 1. Metal-Insulator-Semiconductor sensing mechanism and resulting Capacitance-Voltage curve shift.

References

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