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Selective acetylene detection through surface modification of metal–insulator–semiconductor sensors with alkanethiolate monolayers

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ABSTRACT

Palladium-based metal–insulator–semiconductor sensors were functionalized with self-assembled monolayer coatings derived from alkanethiols with 6, 12, and 18 carbons. The functionalized sensor showed enhanced response to acetylene in a hydrogen background while showing negligible response to a similar gas, ethylene. The presence of sulfur alone on the surface resulted in a small acetylene response, suggesting that palladium–sulfur bond formation plays a role in the response. However, the response of alkanethiol SAM coated sensors was five times greater, indicating that the alkyl chain also affects acetylene detection.

1. Introduction

Functionalization of metal–insulator–semiconductor (MIS) sensors enables the selective detection of many analytes despite the sole ability of hydrogen atoms to directly produce a response in these devices. A common approach for enhancing the selectivity of these sensors, and other metal-oxide–semiconductor capacitor or transistor-like devices, is the application of surface coatings to improve the detection of analytes of interest. Monolayer and thin coatings that bind through analyte-specific interactions have been exploited in the detection of amines [1,2] and complex biomolecules such as penicillin and DNA [3]; however, their utility in modifying the performance of small gas sensors has not been widely studied, likely because of an expected lack of specific interactions. Instead, membrane coatings such as polymers [4] and metal oxides [5] have been applied for the specific detection of hydrogen and light gases.

MIS sensors consist of a layer of doped silicon and a layer of a catalytic gate metal separated by a thin (<100 nm) layer of a dielectric. The sensor gate is composed of a metal that can dissociate hydrogen, such as Pd, Pt, or Ir. Hydrogen atoms adsorbed on the surface can diffuse to the metal–insulator interface and cause a shift in the capacitance–voltage (*CV*) curve of the device which produces a measurable response [4]. Gas response is determined by measuring the change in voltage (bias) required to maintain a constant capacitance at the inflection point of the *CV* curve [4,6]. Previous work has shown that the response scales with the hydrogen partial pressure from the ultra high vacuum range ($<10^{-8}$ torr) to near atmospheric pressures [6]. Due to the high sensitivity of these devices, large surface areas are not required, which makes the use of MIS sensors applicable to gas detection within small spaces in machinery such as transformers and reactors.

The current work focuses on the selective detection of acetylene in a hydrogen background. The detection of acetylene in hydrogen containing environments is important in many applications including the detection of fault gases in transformers [4] and in ethylene streams for polyethylene production [7]. In this contribution, we report the unexpected enhancement of acetylene selectivity on MIS devices coated with a self-assembled monolayer (SAM) film derived from alkanethiols and discuss possible mechanisms for this enhanced response.

2. Experimental

2.1. Sensor fabrication

Devices used in this study were fabricated at the Compound Semiconductor Research Laboratory at Sandia National Laboratories in New Mexico. The devices consisted of an n-Si base (1–100 Ω cm), 50 nm of thermally grown SiO_2, and 50 nm of Pd deposited through electron beam evaporation. Chromium–gold ohmic contacts were adhered to both sides of the sensors to improve

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signal quality. This fabrication technique yielded a device structure similar to that used in previous work [4].

2.2. SAM deposition

The SAM deposition protocol was based on a method reported in a previous study of alkanethiol SAMs on Pd [8]. The sensors were first cleaned in alternating baths of water and detergent (Electron Microscope Sciences Micro 90, 2% in water) followed by rinsing in isopropanol (Fisher Scientific, 99.9%) and alternating baths of acetone (Fisher Scientific, 99.5%) and toluene (Fisher Scientific, 99.9%). Next, the sensors were placed in a UV-ozone cleaner (Boekel model 135500) for 20 min. The clean sensors were then placed in a 10 mM solution of hexanethiol (C_6SH), dodecanethiol ($C_{12}SH$), or octadecanethiol ($C_{18}SH$) (all thiols from Fluka, >95%) in ethanol (Sigma–Aldrich, 200 proof) and the solution was purged with nitrogen (Airgas, ultra-high purity). Polyethylene glycol (PEG)-containing SAMs were deposited by placing the sensor in a solution of 10 mM $HS(C_2H_4O)_{113}CH_3$ (synthesized in house) in 95% ethanol (5% water) (Sigma–Aldrich) and purging with nitrogen (Airgas, ultra-high purity). The sensors were allowed to remain in the thiol solutions for 24 h before being rinsed with ethanol (Sigma–Aldrich, 200 proof) and tested.

To verify the quality of the SAM coatings, advancing water contact angles were measured before testing with analyte gases. Although deposition procedures for alkanethiol SAMs are well-established, it is nevertheless well-known that subtle differences in conditions can result in significant variability of SAM formation kinetics or even final SAM quality [9]. For this reason, as described in more detail below, multiple samples were prepared and evaluated for each alkanethiol studied in this work, and advancing water contact angle was employed as a measure of relative coverage. Evaluation of absolute alkanethiolate coverage is in practice difficult, though previous studies of similar monolayers on Pd surfaces have estimated that formation of a full monolayer corresponds to a fractional coverage near 0.33 adsorbed SAM molecules per surface Pd atom [8]. The maximum contact angle observed in the present studies was 102°, which is ca. 10° below values measured in previous studies of model surfaces, but still indicates a highly hydrophobic surface [8,10]. The average receding water contact angle was ca. 14° smaller than the advancing angle, consistent with a significant degree of roughness in the monolayer surface, likely associated with grain boundaries and defects on the Pd surface [8].

Since SAM coatings on Pd are known to oxidize over a period of days at room temperature [8], care was taken to minimize exposure to air by acquiring water contact angles and placing the coated sensor in the testing apparatus immediately upon removal from the thiol solution. Typical exposure times for sensors to air did not exceed 20 min.

Surfaces coated with atomic sulfur were fabricated by exposing the sensor to 100 ppm H_2S in nitrogen (Airgas) until equilibration of the sensor response (~2 h). Since H_2S dissociates on the palladium surface, leaving surface hydrogen and sulfur [11], the change in sensor response is a measure of the extent of sulfur dosing.

2.3. Flow cell testing

Sensors were placed in to a system described elsewhere [4] and connected to a capacitance meter (Boonton). Changes in the CV curve of the sensor were measured by recording the voltage required to maintain the capacitance at the inflection point of the CV curve. The system was heated through a combination of a conductive button heater (Heatwave Labs Inc.) located underneath the sensor and heating tape (Omega Engineering) wrapped around the system. The temperature of the sensor was measured by a thermocouple attached to the sample holder. The sensor was first exposed to 500 ppm H_2 in N_2 at a flow rate of 400 sccm. After reaching equilibrium, the system was exposed to varying doses of dilute acetylene or ethylene in nitrogen. For testing of SAM coated sensors with varying tail lengths and functionalities, devices coated with each SAM tail functionality were exposed to 20, 100, and 400 ppm acetylene in the hydrogen/nitrogen background at 50 °C. Each experiment was repeated three times using separate devices. For acetylene/ethylene selectivity studies, devices were exposed to three repeated doses of 100 ppm acetylene followed by three repeated doses of 100 ppm ethylene in the hydrogen/nitrogen background at 25, 50, 75, and 100 °C. The response in every case was evaluated by taking the difference between the steady state bias after acetylene or ethylene exposure and before acetylene or ethylene exposure. The error was computed by taking a standard deviation of calculated values. In all cases, the acetylene or ethylene was removed after exposure to demonstrate a return to the original hydrogen response. This final step is important to distinguish real response from a well known drift problem where the CV curve can shift up to 10 mV/h [12]. The total flow rate was kept constant to prevent background hydrogen from having an effect on the response. All gases were ultra high purity and obtained from Airgas.

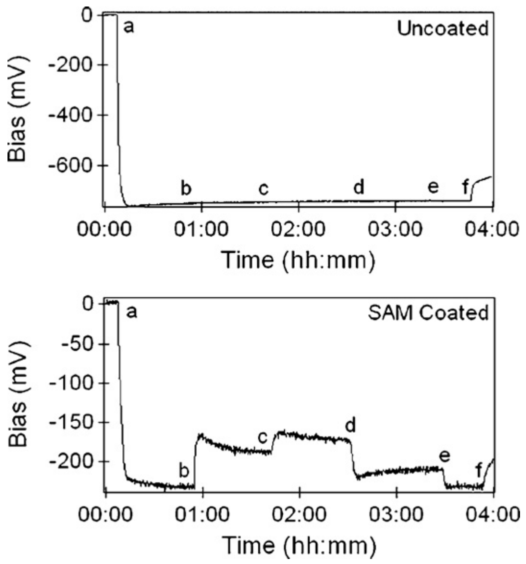

Fig. 1. Response of C_{18} alkanethiol SAM coated and uncoated sensors to acetylene. (a) Added H_2, (b) added 100 ppm acetylene, (c) increased acetylene to 400 ppm, (d) reduced acetylene to 20 ppm, (e) removed acetylene, and (f) removed H_2.

3. Results and discussion

3.1. Effect of acetylene on SAM coated and uncoated sensors

Fig. 1 shows representative responses of C_{18} SAM coated and uncoated sensors to doses of 100, 400, and 20 ppm acetylene in a background of 500 ppm hydrogen in nitrogen at 50 °C. This concentration range (including the hydrogen concentration) is important for detection of acetylene in fault gas analysis of electrical transformers, and the selected sequence shows the effect of both increasing and decreasing concentration. These results demonstrate an increase in acetylene response from no statistically significant response in the uncoated sensor to a significant response that varies with acetylene concentration in the C_{18} SAM coated sensor. The SAM coated sensor also shows a reduced apparent response to hydrogen, which we attribute to the well known poisoning effect of sulfur on surface reactions and the reduced number density of vacant adsorption sites due to the monolayer coating.