

Hydrogen-Selective Sensors for Industrial Applications

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Real-time hydrogen detection is very important for various industrial applications, including in the headspace of distribution transformers. Solid-state metal-insulator-semiconductor (MIS) sensors are excellent candidates for this purpose [1]. These sensors are prepared by depositing a film of catalytic metal onto a thin layer of gate insulator material that has been grown on a semiconductor substrate. As such, either a capacitor or diode can be fabricated, depending on the process. The basic H₂ sensing mechanism for MIS devices has been described in the pioneering works by Lundström and coworkers [2, 3]. To provide a brief description, gas-phase H₂ dissociates on the surface of the catalytic metal to form H atoms. Then, these H atoms rapidly diffuse through the metal film to the metal-insulator interface, where they are preferentially trapped in stabilized adsorption sites. The layer of interfacial hydrogen created by this process exists in a dipole layer, creating an additional voltage drop across the MIS sensor that can be measured as either a shift in the capacitance-voltage curve of a capacitor, or in the current-voltage characteristic of a diode [1].

Several attempts have been made to apply solid-state sensor technology to monitor transformer fault gases over the last decade because of the unique sensitivity of the sensing surface to H atoms. These initial attempts were mostly unsuccessful because of inappropriate device fabrication methods and the complexity in fault gas sensing environment. While unsuitable preparation approaches caused contamination at the metal surface or the metal-insulator interface, the concurrence of multiple fault gases and their interaction with the metal surface make sensor responses hard to interpret.

To address these challenges, a reliable fault-gas sensor has been developed from a different direction. Early investigations have revealed why old generation MIS sensors should not be used to identify multiple fault-gas species and how various chemical species can affect the ability of MIS sensors to detect hydrogen. Also, it was found that oxygen and carbon monoxide bind more tightly than hydrogen on the Pd metal surface of MIS sensors and can block hydrogen from adsorbing [4,5]. While trying to understand more about how various fault gases interact with the sensor, we embarked on the study of adding a “H₂ filter layer” above the metal film of the sensor, which would screen out the effects of other gases and thus selectively detect hydrogen. This filter layer can be implemented via two primary modes – free-standing and attached membrane structure. Since the attached structure provides easier implementation, we primarily focus on this approach. Representative results of uncoated and coated sensor response to H₂ are presented in Figures 1 and 2, respectively. Figure 1 shows that the addition of fault gas resulted in a substantial increase in the uncoated sensor response signal. In contrast, Figure 2 demonstrates that the coated sensor response signal was not altered substantially by the addition of fault gases.

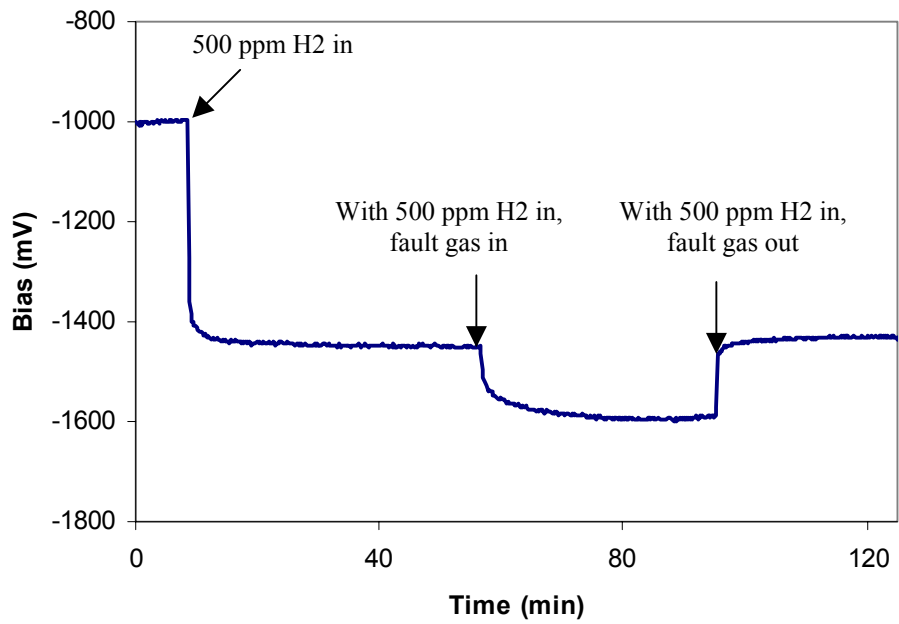


Figure 1. Fault gas effect on uncoated sensor response

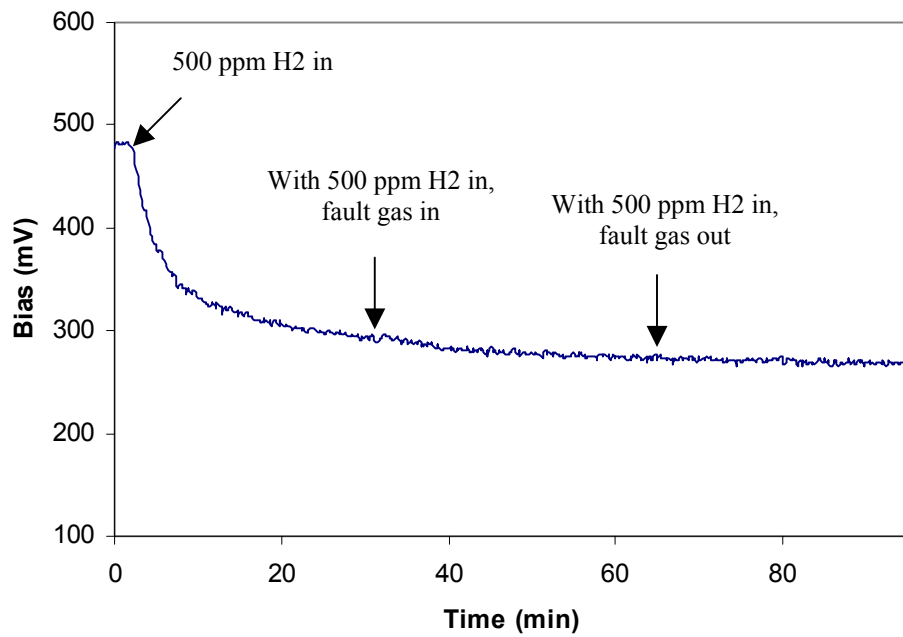


Figure 2. Fault gas effect on coated sensor response

References:

1. Lundstrom, I., *Why bother about gas-sensitive field-effect devices?* Sens. Actuators A, 1996. **56**: p. 75-82.
2. Lundstrom, I., *Hydrogen sensitive MOS-Structures: 1. Principles and applications.* Sens. Actuators, 1981. **1**: p. 403-426.
3. Lundstrom, I. and D. Soderberg, *Hydrogen sensitive MOS-Structures: 2. Characterization.* Sens. Actuators, 1981. **2**: p. 105-138.
4. Medlin, J.W., et al., *Effects of competitive CO adsorption on the hydrogen response of MIS sensors: the role of metal film morphology.* J. Appl. Phys., 2003. **93**(4): p. 2267-2274.
5. Medlin, J.W., R. Bastasz, and A.H. McDaniel, *Response of Palladium Metal-Insulator-Semiconductor Devices to Hydrogen-Oxygen Mixtures: Comparisons Between Kinetic Models and Experiment.* Sensors And Actuators B, 2003. **96**: p. 290-297.