

Hydrogen Sensors for Oxygen-Free Ambient

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Summary:

Hydrogen sensors for oxygen-free atmosphere are special branch of sensors characterized by another sensing mechanism different from usual devices operating in air. These sensors are specially interesting because it is necessary to monitor the state of the lithium ion batteries, transformers, technological gases. We consider the application of hydrogen adsorbing films, field effect transistors, metal oxide sensors, and percolation effect sensors for such applications. It was demonstrated that Ag and Cu doped Pd film can detect low concentrations of hydrogen in inert gas on ppm level.

Keywords: hydrogen sensor, inert and oxygen-free atmosphere, oil

Introduction

The main part of usual gas sensors is designed for the application in normal O₂ containing atmosphere. For example, the sensitivity mechanism of metal oxide gas sensors involves the chemisorption of oxygen on the surface of *n*-type semiconductor nanoparticles in ionic form. At working temperature of the sensor, oxygen ions interact with reducing gases, this leads to the oxidation of H₂, CH₄, VOC, etc. and to the injection of electrons to the conductance band of semiconductor. A similar but opposite mechanism is valid as in the case of the application of p-type semiconductors and at the detection of oxidizing gases.

However, the gas sensors of different types can be used also in oxygen-free ambient: in vacuum, inert atmosphere, even in liquids like transformer oil. It is notable that the very first metal oxide sensors were investigated since 1955 in vacuum. The detection of gases and, in particular, hydrogen in inert ambient is important in many applications: in the monitoring of Li-ion batteries, H₂ fuel cells, nuclear power stations, oil filled power transformers, etc.

The sensors, which can be used in inert atmosphere, are metal oxide semiconductor sensors, Pd-film resistive sensors, MIS structures with Pd film gate and the sensors based on percolation effect based on Pd nanoparticles dispersed in polymer matrices.

The sensors based on Pd-Ni thin film is used as a detector of H₂ dissolved in transformer oil in a

Vaisala MHT410 instrument. The saturation of thin Pd-Ni film with H₂ dissolved in oil leads to an increase in film resistance. Typical sensitivity of such film is of about 1 % of resistance change per 1 % of hydrogen in gas atmosphere. Of course such sensor operating at near room temperature is slow, characteristic time of the sensor response is of about 1 hour.

Field effect devices with Pd gate can be used not only for the detection of H₂ in gas, but also in oil [1]. The sensor immersed to the oil is characterized by a detection limit of about 10 ppm and rather long response time of several hours. This is not a big disadvantage for the oil monitoring, because the degradation processes in a transformer are relatively slow.

Metal oxide sensors based, first, on ZnO can be used for the detection of active gases in inert atmosphere and in vacuum [2]. The mechanism of the detection of H₂ in this case is very simple, this is just dissociative adsorption of hydrogen in ionized form, and this gives a square root dependence of sensor conductivity as a function of H₂ concentration.

Experiment

In the experiment we applied gas sensors based on pure SnO₂ fabricated using thick film technology. The working temperature of the sensor was fixed at 350°C, the specific surface area of the sensing material was of about 50 m²/g. The experimental installation made of stainless steel was equipped with oxygen measuring instrument "Zirkon" based on solid elec-

trolyte gas sensor. It enabled the measurement of O_2 concentration with detection limit of 0.1 ppm. The tubes of the installation were purged by pure Ar with residual concentration of O_2 of <1 ppm for 5 hours to get the concentration of O_2 in gas of about 1 ppm. After this, we introduced H_2 using mass flow controller.

Thin films of Pd-Ag and Pd-Ag/Cu were deposited on Al_2O_3 substrates via magnetron sputtering using Pd, Ag, and Cu targets. The choice of the sensing material was motivated to avoid the phase transition in pure palladium at the saturation with hydrogen. For example, it is shown in [3] that the saturation of one side of Pd plate with hydrogen leads to the bending of the plate. Evidently, periodic saturation of the film leads finally to the peeling of the Pd film from the substrate. The application of dopant (Ag, Ru, Cu) blocks this process. The Pd-Ag film was prepared by sputtering Pd at 75 W and Ag at 10 W for 45 s. In contrast, the Pd-Ag/Cu film was deposited under identical conditions for Pd and Ag, with a concurrent Cu deposition at 25 W for 15 s. The hydrogen response of these films was evaluated at room temperature using H_2 concentrations ranging from 50 ppm to 20000 ppm in an N_2 background. The sensor response was defined as $R = (R_{H_2} - R_{N_2}) / R_{N_2}$, where R_{H_2} and R_{N_2} denote the resistance in the H_2/N_2 mixture and pure N_2 , respectively.

The application of Pd/polymer composite also permits the minimization of the peeling effects of H_2 in the film. When Pd concentration in amorphous polymer is near percolation threshold, the conductivity of sensor drops with hydrogen pressure, detection limit reaches 10 ppt. The gas-sensitivity properties of polymer composite coatings were found to be directly related to their morphology.

Results and Discussion

It was shown that the tin dioxide based gas sensor is characterized by a strong response to hydrogen in oxygen-free atmosphere. The threshold level of oxygen changing completely the sensor response is a concentration compatible with the concentration of H_2 . at this concentration the mechanism involving the catalytic oxidation of hydrogen is substituted by direct dissociative ionosorption of H_2 . Thus, if O_2 concentration exceeds H_2 concentration (we deal with ppm level concentrations), the response time of the sensor has usual order of magnitude of few seconds. In opposite case, the H_2 response increases by approximately one order of magnitude, and the response and recovery time increases up to ~ 1000 s.

As shown in Fig. 1, the response of the Pd-Ag film saturates and even decreases at H_2 con-

centrations above 5 000 ppm, likely due to the α -PdHx to β -PdHx phase transition. In contrast, the response of the Pd-Ag/Cu film increases steadily as the H_2 concentration rises from 50 ppm to 20 000 ppm, reaching 5.5% at 20 000 ppm. Moreover, the Pd-Ag/Cu film exhibits excellent response and recovery behaviors, with both response and recovery times decreasing with increasing H_2 concentration, achieving 69 s and 492 s at 20 000 ppm H_2 , respectively.

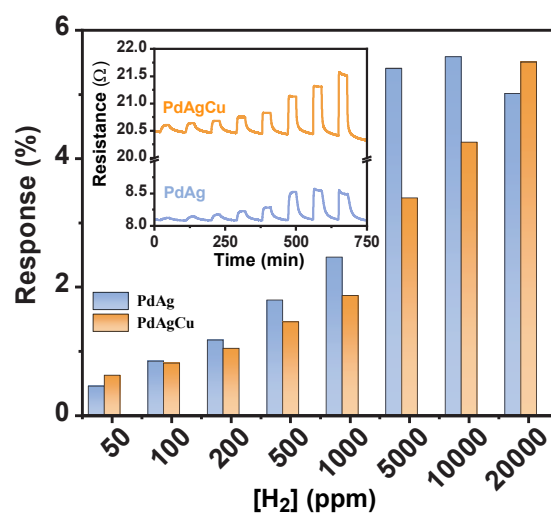


Fig.1 Response of Pd-Ag and Pd-Ag/Cu to H_2 concentrations from 50 ppm to 20000 ppm.

Therefore, the sensor based on the Pd-Ag/Cu film demonstrates outstanding H_2 sensing performance in an oxygen-free environment.

Conclusion

We analyzed the application of different gas sensors for the discovery of hydrogen in oxygen-free ambient: in inert atmosphere and in liquids. It was demonstrated that the thin resistive Pd-Ag/Cu film can be used for the detection of hydrogen with high sensitivity of about 5.5 % (change of resistance) per 2 % of H_2 in gas. The sensor based on SnO_2 demonstrates response time of about 20 min and detection limit of about 1 ppm.

References

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