1. General introduction

Current status of the H_2 gas sensor

Fuel cells based on H_2 have recently attracted attention as a clean energy source for the future.[1] However, hydrogen is the smallest atom and thus the H_2 gas can leak easily. In addition, it can catch fire, for example, from a spark. For this reason, there is a big demand for reliable, inexpensive H_2 gas sensors. At present, there are several types of H_2 gas sensors which are partly on the market.[2] Among these, oxide semiconductors (SnO_2/Pd, ZnO/Pt, Pd-TiO_2 Pd/MoO_3, Pd/WO_3 etc.) have been most extensively investigated that utilize a change in surface conductivity under various gases, for examples, O_2, H_2, NH_3, city gas, LPG etc. The electrical conductivity of semiconductors can change with reactions of either conduction or valence band with electro-donating (for example, H_2) or electro-accepting (for example, O_2) gases. That is, if the charge transfer level of H_2/H^+ is located near the conduction band, H_2 can impart electrons into the conduction band, resulting in an increase in conductivity. Similarly, if the O_2/O_2^- level exists near the valence band, then the electron in the valence band can be transferred to the adsorbed O_2 at the surface to form O_2^-, leaving behind a hole in the valence band. Therefore, it is quite difficult to differentiate a given gas under consideration from others. To obviate this problem, some membranes made of SiO_2, for example, are sometimes attached before the sensor for the sake of gas-selectivity. Another issue is associated with the surface conditions of oxide semiconductors. Since the surface plays the most important role for the conductivity change, it is crucial to keep the surface clean or active in order to catch gases and cause subsequent reactions to occur. For this reason, the sensors are normally heated, up to around 400 °C. Aside from these drawbacks, the present sensor is highly sensitive and the response is about several ms.

There is another type of H_2 gas sensors which make use of the heat of combustion of H_2.[2] The sensor is composed of Pt wires together with (Pt or Pd) /(Al_2O_3 or SnO_2) which constitutes a Wheatstonebridge. Because of the conductivity change due to combustion heat of H_2, the electrical balance in Wheatstonebridge is lost, giving a signal for the H_2 detection. The present sensor is again sensitive and the response time is several ms.

A new type of H_2 gas sensors has recently appeared which is based on the thermoelectric power.[3] In this sensor, one part of the thermoelectric element is covered with Pd and the other is not. The sensor detects the difference in thermoelectric power between two areas. At the moment, there are issues associated with sensitivity and response time.

The most recent topics concern the H_2 gas sensor of the SAW type developed by Ball Semiconductors Co. Ltd.[4] “SAW” stands for “surface acoustic wave” which travels on the surface of piezo-electric materials. On the surface of a sphere made of piezo-electric material, there are a number of interdigital electrodes covered partly with Pd. SAW travels effectively in the absence of H_2. However, SAW is blocked as soon as H_2 is adsorbed on the sphere to disturb the matching between interdigital electrodes. In this way, the signal is detected. There is no detailed information about this sensor. The most difficult issue seems to be the fabrication of an extremely small element and its cost.

Under the above circumstances, we have newly developed a high-performance H_2 gas sensor that utilizes a proton affinity of pyrrolopyrrole derivatives.[5]

Background and scope of the thesis

The purpose of the present investigation is to develop a high performance H_2 gas sensor utilizing a high proton affinity of 1,4-diketo-3,6-bis-(4'-pyridyl)-pyrrolo-[3,4-c]-pyrrole (DPPP) on the basis of the crystal and electronic structure of DPPP and its geometrical isomers. This application is based on the accidental finding of a high proton affinity of the N atom of the pyridyl ring in DPPP. To our surprise, protonation at the N atom is found to bring about a drastic color change from vivid red to violet, accompanied by a remarkable reduction of the electrical resistivity by five orders of magnitude, as well as the appearance of high photoconductivity. This prompted us to believe that we can develop a high-sensitive H_2 gas sensor, provided that we succeed in effectively dissociating H_2 into protons. We have solved this obstacle by directly incorporating Pd or Pt into interdigital electrodes in the form of island. In this way, we have achieved a high performance H_2 gas sensor.

The present thesis is composed of five chapters. Chapter 1 describes the current status of H_2 gas sensors as well as the background of the present study.

Chapter 2 deals with the design of the H_2 gas sensor based on DPPP, its fabrication as well as the device performance. Also discussed are the sensor characteristics of other DPPP derivatives (*ortho*- and *meta*-DPPP) from the standpoint of electron transfer within a molecule as studied by ^{13}C-NMR.

In Chapter 3, we present the result on carrier determination as well as frequency response of the H_2 gas sensors. Charge carriers are determined to be electrons on the basis of the Seebeck effect. This result directly bears out the operation principle of our sensor. Device operation of DC (direct current) or AC (alternating current) has also been discussed to draw a conclusion that the device should be driven with AC in the

frequency range between 10 and 500 Hz.

Chapter 4 presents the two crystal structures of DPPP (phases I and II: polymorph) and their electronic characterization on the basis of single crystals. Phase I is found to be appropriate for H_2 gas sensors because the N atom of the pyridyl ring remains unbonded and is available for protonation. On the other hand, in phase II, one of the N atom is blocked due to the formation of NH···N intermolecular hydrogen bonds.

Chapter 5 describes the conclusions of the present study.

Details on the crystal structure are given in Appendices I, II and III.

References

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