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Palladium Film Chemical Sensor

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Abstract **– Palladium-based sensors are gaining wide popularity in the industry due to their reliability and high specificity to hydrogen. Any hydrogen sensor technology needs to satisfy the basic requirements sensitivity, in this research Palladium thin films have been prepared on glass sub-strates and explored as a fast response sensor to hydrogen gas. Films are prepared by vaporization deposition technique with annealing temperature is around 600 C^0. The optical characteristics of prepared films show that they are highly sensitive, but their properties vary considerably when the measurements are conducted in vacuum or in air. The response-recovery time of Pd materials to hydrogen gas is characterized to be relatively extremely short.**

Keywords **– Palladium, Semiconductor, Spectrometer, Sensor, Thin-Film.**

I. General Introduction

Hydrogen, which occupies about more than 90% of the atmosphere "is a highly flammable gas and will burn at concentrations as low as 4% in air. The lower explosive limit and upper explosive limit are the two most common terminologies used to indicate the flammable levels for many fuels including hydrogen. But it has a larger window (4–75% v/v H_2) of flammability in comparison to natural gas, gasoline, propane, ethane, methane, propylene, etc. The flammability limit of hydrogen is seven times wider than methane. It is, therefore, critical for a hydrogen sensor to have a wider measurement range (1–99% v/v H_2) for safety applications than most common fuels. Hydrogen is the lightest of elements and the smallest molecule; it, therefore, has the greatest tendency to leak. Thus, for a process safety application, a hydrogen leak can be more dangerous and its detection becomes more challenging than other gases" [1].

II. Mechanisms for Hydrogen Sensing

Numbers of approaches were used to sense and detect hydrogen. "Numbers of which are used in industry include the typical gas chromatography (GC), mass spectrometry (MS), catalytic bead (CB), and thermal conductivity. Semiconducting metal oxide and CB sensors are popular solid-state technologies, which employ heated catalysts to sense hydrogen. These sensors require heating to about 300°C to enable surface reactions that promote hydrogen sensing. Electrochemical sensors are based on known electrolytic reactions of hydrogen. Sensors based on catalytic combustion are generally nonspecific, electrochemical hydrogen sensors with liquid or solid type electrolytes having leakage issues. The hydrogen sensors based on thermal conductivity, CB, metal oxide, and electrochemical technologies require the presence of oxygen for sensor operation. Oxygen plays a crucial role in promoting the grain boundary formation in metal oxide sensors and electron transfer reactions in electrochemical sensors. The most promising solid-state technology is based on a hydrogen-specific material, palladium, which does not require oxygen for operation. Palladium-based sensors are gaining wide popularity in the industry due to their reliability and high specificity to hydrogen. Any hydrogen sensor technology needs to satisfy the three basic requirements sensitivity, selectivity, and specificity" [1].

III. Traditional Approaches to Hydrogen Sensing

Number of traditional approaches can be used to detect Hydrogen, these may include:

A. Thermal Conductivity (TC): is the most widely applied measuring principle for the determination of hydrogen. "The measuring principle is based on the differences in thermal conductivity of the gases to be measured. A Thermal Conductivity Detector (TCD) measures the concentration of a gas in a binary gas mixture by measuring the thermal conductivity of the sample gas and comparing it to the thermal conductivity of a selected reference gas" [1].

B. Gas Chromatography (GC): is also another widely applied measuring principle for hydrogen detection. "The disadvantages of GC are long response times (minutes) due to the chromatography, time-intensive sample preparation, consumable (carrier and calibration gases), and labor-intensive handling procedures. An advantage, however, is the ability to measure other gases such as nitrogen, oxygen, and carbon dioxide in the presence of hydrogen. But, this adds time to the total analysis" [1].

IV. Solid-state Approaches to Hydrogen Sensing

A wide variety of solid-state sensors based on hydrogen-specific palladium, "Metal Oxide Semiconductor (MOS), CB, electrochemical, and Surface Acoustic Wave (SAW) technology are used in the industry for several years. Microelectromechanical systems (MEMS) and nanotechnology-based devices for the measurement of hydrogen are the recent developments. These developments are mainly driven by the demands of the fuel cell industry. Solid-state approaches are gaining rapid popularity within the industry due to their low cost, low maintenance, replacements, and flexibility of multiple installations with minimal labor" [1].

"Hydrogen-Specific Palladium-Based Sensors are of three major classes of palladium-based hydrogen sensors"

[2]. The most popular class of palladium-based sensors is based on palladium resistors. A thin film of palladium deposited between two metal contacts shows a change in conductivity on exposure to hydrogen due to the phase transition in palladium. The palladium Field- Effect Transistors (FETs) or capacitors constitute is the second class, wherein the sensor architecture is in a transistor mode or capacitor configuration. The third class of palladium sensors includes optical sensors consisting of a layer of palladium coated on an optically active material that transforms the hydrogen concentration to an optical signal.

V. Types of Palladium Hydrogen Sensors

Several types of palladium-based hydrogen sensors have been reported in the literature. The most notable ones are based on Pd thin-film resistors, FETs, Pd nanowires, Pd nanoparticle networks, Pd nanoclusters, and Pd nanotubes.

Palladium Field-Effect Sensors: "Hydrogen sensors based on the "field effect" of palladium have been investigated extensively in the literature" [3]. "The field effect results due to the rapid dissolution of hydrogen in the palladium surface arranged in a Pd–SiO_2–Si configuration. The sensor relies on an electric field resulting from the charge transfer between palladium and hydrogen on its surface. The FETs" [4] and "metal–insulator–semiconductor (MIS)" [5] are the two major types of device structures that have been studied for palladium-based hydrogen sensing. Palladium is catalytically active, permeable to hydrogen, and can be readily used in FET and MIS devices.

A. Palladium-Based Resistors: "Thick- and thin-film palladium-based resistors have been reported for hydrogen sensing" [6]. The thick-film device uses printed palladium paste on a ceramic substrate in a four- resistor network. Two opposed resistors are covered to isolate them from the ambient atmosphere. "The exposure of the uncovered resistors to hydrogen results in a change in resistivity of the thick-film material and a shift in the balance point of the bridge, which can be scaled to the hydrogen concentration. The thin-film device is equivalent in design to the thick film; here, much thinner films (typically vacuum deposited) are used as the resistors. Thin-film palladium detectors have been prepared by depositing palladium through electron beam evaporation" [7], "RF magnetron sputtering" [8], "micro con-tact printing" [9], and wet electrochemistry. Most palladium resistors have fouling issues on the palladium surface due to impurities and pollutants in, or reaction with the air. The fouling on the palladium surface can be reduced by the addition of a second metal (alloy) to palladium.

B. Palladium-Coated Fiber Optic Sensors: A fiber optic hydrogen sensor consists of a palladium coating at the end of an optical fiber that senses the presence of hydrogen in air. "When the coating reacts with the hydrogen, its optical properties are changed. Light from a central electro-optic control unit is projected down the optical fiber where it is either reflected from the sensor coating back to central optical detector or is transmitted to another fiber leading to the central optical detector. A change in the reflected or transmitted intensity indicates the presence of hydrogen. The fiber optic detector offers inherent safety by removing all electrical power from the test sites and reduces signal-processing problems by minimizing electromagnetic interference. The fiber optic hydrogen sensors can be fabricated using a palladium-coated single-mode tapered optical fiber" [10]. The attenuation change of the fiber-mode when the device was exposed to hydrogen is used to detect and measure hydrogen concentration in gaseous atmospheres.

VI. Sensor Components

This system consists basically on seven components including chamber, white photo diode, spectrometer, vacuum unit, gauge pressure, cylinder of hydrogen gas, and computer as shown in schematically in figure (1) and figure (2) below illustrate sensor component and sensor setup successively. A sample of Palladium coated glass slide sensor should be prepared first to detect hydrogen, and should be tested by X-ray to cheek its crystallization.

- The coated glass substrate (Palladium thin films): should be placed inside the developed polymer square test chamber of 50 mm square base and of 75 mm height with the top removable cover. The effective volume of the chamber is 187500 mm^3; it has an inlet to allow the test gas to flow in.
- White photo diode: is the light source used in the sensor.
- CCS Spectrometer: used to measure transmitted.
- Vacuum unit: to evacuate the test chamber.
- Gauge pressure: to measure the current pressure of the chamber.
- Cylinder of hydrogen gas of a known concentration: to flow through the test chamber during measurement.
- Computer: to process the recorded signal.

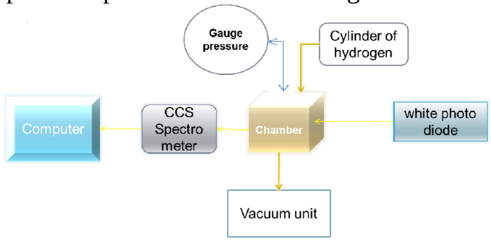

Fig.1. Sensor component

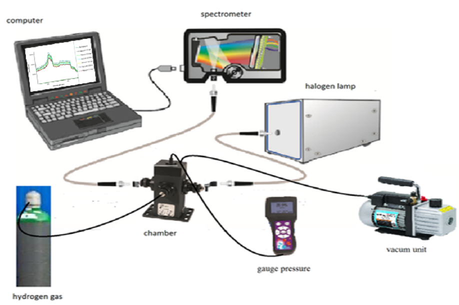

Fig.2. Sensor set up

VII. Measurements and Results

Tow testes were carried out to examine the developed palladium thin film sensor. In both tests, results were obtained through adopting the following steps:

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- Opening the test chamber to place the palladium thin film sensor on the sensor holder and close it.
- The necessary light source is then directed by optical fiber and allowed to pass through the sample to the spectrometer.
- The rotary pump is then switched on to evacuate the test chamber to about -0.7 bars.
- Next, the hydrogen gas of a known concentration allowed passing from the cylinder through the special inlet to the test chamber by opening the cylinder valve.
- Test chamber pressure should be measured by observing the gauge pressure.
- Spectrometer is then detects and analyzes transmitted signals and sends the data to the computer.
- Numbers of measurements were carried out in different pressures.

Six readings were observed for each sample test including pressures of -0.6, -0.5, -0.4, -0.3, -0.2 and -0.1bar. Frequency against transmitted light intensity graphs were produced for each reading. The six graphs were then combined together in one diagram with a background graph representing -0.7 pressure without Hydrogen.

Figure (3) and figure (4) below represent the resultant combined graphs for both sample tests.

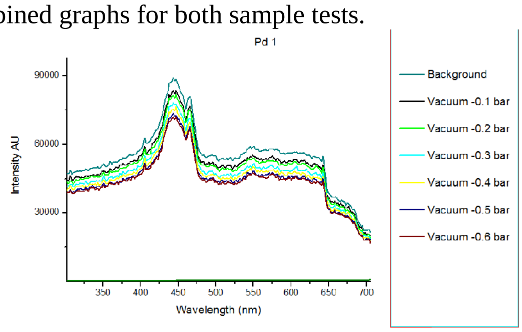

Fig.3. Combined graphs of the first sample

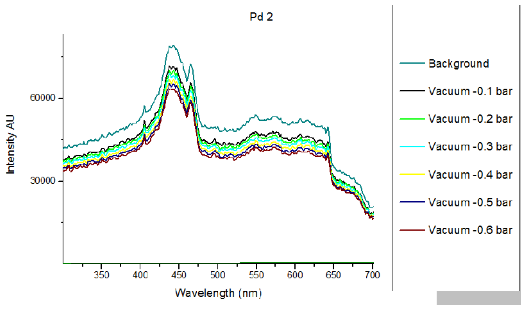

Fig.4. Combined graphs of the second sample

From the figures obtained above it can be noted that by increase of concentration of hydrogen gas in the test chamber a transmitted light is also increase which means that the palladium thin film sample successfully detect hydrogen gas.

From both figures it can obviously note that the suitable wavelength that can be used to detect hydrogen gas is a visible band that located in the region of 500-650 nm.

VIII. Conclusions

This work is directed to develop a new sensor design that depends on the Palladium coated glass thin film that able to detect hydrogen gas. From measurements carried out and results obtained it can be concluded with that the new proposed sensor detects hydrogen successfully. Moreover, the new design provides number of advantages that include:

- Rapid response to low hydrogen concentration,
- Wide dynamic range but more sensitive in 500-650 nm range.
- Electromagnetic Interference free,
- Safe,

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