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Nanostructured Platinum and Platinum Alloy Based Resistive Hydrogen Sensors: A Review

Necmettin Kilinc[1*] and Mustafa Erkovan[2,3]

[1] Department of Physics, Faculty of Science & Arts, Inonu University, Malatya, Türkiye; necmettinkilinc@gmail.com
[2] Instituto de Engenharia de Sistemas E Computadores—Microsistemas e Nanotecnologias (INESC MN), 1000-029 Lisbon, Portugal;
[3] Department of Fundamental Sciences and Engineering, Faculty of Engineering and Natural Sciences, Sivas University of Science and Technology, Sivas, Türkiye; mustafa.erkovan@sivas.edu.tr
* Correspondence: necmettinkilinc@gmail.com
† Presented at the title, place, and date.

Abstract: As a future energy source hydrogen is used in many industrial applications such as chemical, semiconductor, transportation, etc. Hydrogen gas, which has many unusual properties compared to other gases, has the risk of being flammable and explosive when it is present in the atmosphere at concentrations of 4% and higher. We need hydrogen sensors both to determine the risks in advance and because we do not want the hydrogen gas, which is the source of energy, to be lost due to leakage. Hydrogen sensors are used in hydrogen production plants to determine hydrogen purity, for leakage and safety in all areas where hydrogen gas is used, and also in the medical application as hydrogen gas is a marker in disease diagnosis. Considering the classification of hydrogen sensors according to the physico-chemical sensing mechanism, the performance of resistive metallic hydrogen sensors is one of the two best [1]. In metallic resistive hydrogen sensors, Pd, Pt and their alloys are generally used as sensing materials [2,3]. In this study, the nanostructured platinum (Pt) and Pt alloy based resistive hydrogen sensor are reviewed and discussed in detail. Hydrogen sensing properties of Pt, Pt alloys, Pt layered structures in many nanostructures such as nanowires, nanoporous, thin films have been investigated [4-10]. The sensing mechanism of Pt-based resistive hydrogen sensors has been explained with scattering of charge carriers at surface, from defects, from grain boundary and formation of hydride (PtH_x) phenomenas depending on the increase or decrease of resistance in hydrogen environment.

Keywords: Platinum; Alloy; Thin film; Nanowire; Nanoporous; Hydrogen sensor; Resistive sensor

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1. Introduction

Hydrogen, a naturally abundant renewable energy source, holds remarkable potential as an efficient and environmentally clean option. It finds diverse industrial applications across sectors such as chemistry, where it serves as a crucial reducing agent in crude oil refining, plastics production, and the flat glass industry. Additionally, its utility extends to food product processing through oil and fat hydrogenation, semiconductor fabrication as a process gas for thin-film deposition and annealing atmospheres, and even transportation applications involving fuel cells and spacecraft [11].

However, it is a gas with a low ignition energy of hydrogen and a lower explosion limit of 4% in air. Therefore, a slight gas leak can cause serious concern and the use of hydrogen poses a serious safety concern. Since hydrogen gas is colorless, odorless, tasteless and cannot be detected by the human senses, safety is an important parameter when working with hydrogen-containing gases [11]. Given these imperatives, the development of hydrogen sensors assumes a pivotal role. Rapid responsiveness, an extensive sensing

range, and the capacity for integration into large-scale urban networks stand as prerequisites. Furthermore, ongoing research endeavors aim to refine sensitivity, selectivity, response time, and overall reliability of these sensors. Simultaneously, concerted efforts are directed towards minimizing sensor dimensions, reducing costs, and optimizing power consumption, aligning with the prospective surge in hydrogen's technological applications [1].

Hydrogen gas sensors are purposefully designed devices intended to monitor, detect, and measure the presence and concentration of a hydrogen gas within a designated area using various methods. In light of the discernible physicochemical principles governing their detection mechanisms, hydrogen sensors have undergone comprehensive studies and can be systematically categorized into nine well-defined groups. These classifications encompass resistive sensors (semiconducting metal–oxide and metallic resistor), work function-based, catalytic, electrochemical, optical, thermal conductivity, mechanical, acoustic, and magnetic [1,12]. Notably, within this diverse range, resistive metallic hydrogen sensors have consistently showcased exceptional performance, securing a coveted position among the forefront of these categories [1]. In the realm of metallic resistive hydrogen sensors, it is commonplace to utilize Pd, Pt, and their corresponding alloys as primary sensing materials [2,3]. This study aims to comprehensively analyze various Pt nanostructures and Pt-based alloy resistive hydrogen sensors, delving into their performance and sensing mechanisms. By conducting an in-depth exploration through extensive literature review, the goal is to enhance our understanding of hydrogen sensing technologies, potentially influencing their future applications and development.

2. Sensing mechanism of Pt based resistive hydrogen sensor

Fundamantally, the sensing mechanism of Pt based resistive hydrogen sensor could be examined with two mechanism depending on the increase or the decrease in the resistance of the sensor during exposure to hydrogen. The decrease in the resistance of Pt nanostructures in hydrogen exposure generally explained with surface scattering phenomenon [4,6,7,13,14]. At normal atmosferic condition the surface of Pt nanostructures covered with absorbed oxygen atoms. During exposure to hydrogen, the hydrogen atoms replaced with oxygen atoms at Pt surface and the number of charge charier scattering at the surface decreases and as a consequence the resistance of Pt nanostructures decreases.

The phenomenon of enhanced resistance observed in Pt nanostructures in hydrogen-rich environments can be explained by three distinct mechanisms. Firstly, the increase in Pt resistance resulting from hydrogen exposure can be traced back to the formation of PtHx hydride [5]. Notably, it has been confirmed that the presence of oxygen in the surrounding environment does not exert any noticeable influence on the hydrogen sensing capabilities of the resistive Pt sensor [5]. Secondly, the observed elevation in Pt resistance within the hydrogen environment can be attributed to electron scattering phenomena arising from inherent defects within the Pt nanostructure [8]. Lastly, the escalation in Pt resistance experienced in the hydrogen environment can also be associated with electron scattering occurring at the grain boundaries of the Pt nanoparticles [15].

3. Discussions

A comprehensive literature review of hydrogen gas sensor performences using Pt and Pt-based alloys is presented in Table 1. This review focuses on variations in thicknesses, chemical compositions, and structural configurations, presenting a comprehensive exploration of the intricate interplay between these elements and the resulting sensing capabilities.These materials encompass an assortment of formats, ranging from standalone Pt nanowires to intricately designed Pt nanowire arrays. The sensitivities exhibited by these materials span an intriguing range, extending from approximately 3.5% to an impressive 18.4%, a variance inherently tied to the intricate dynamics of concentra-

tion and temperature modulation. Additionally, the influence of alloying and hybridization emerges as a significant factor in the observed sensitivities, particularly evident in the cases of Pt modified Pd nanowires and core-shell nanocrystal layers, where sensitivities converge around the 4% range, potentially enhanced by temperature effects. A closer look at the Pt-based thin films reveals a wide variety of thicknesses, ranging from 2 nm to 150 nm. These films, embodying differing thicknesses, have been meticulously tailored to respond optimally to distinct hydrogen concentration ranges and temperature conditions. As the table elucidates, the range of sensitivities for these films encompasses values as varied as 0.4% to an astonishing 261%. This span underscores the criticality of film thickness and operating parameters in determining the efficiency of these sensors. Noteworthy variations in performance are showcased through nanoporous Pt films and bimetallic Pt/Pd films, revealing elevated sensitivities of approximately 13.5% and 13.0%, respectively. Further enriching the diversity of Pt-based materials are Pt alloys, such as Pt75Co25 and Pt79Ni21, which contribute valuable insights into the influence of alloy composition on sensitivity performance. Displaying sensitivities ranging from 1.25% to 2.6%, these alloys highlight the intricate relationship between material composition and the consequent sensor response. Ultimately, the table shows the complexities of Pt-based hydrogen sensing materials' behavior with respect to concentration ranges and temperatures. This compilation underscores the crucial role played by material design, composition, and environmental factors in shaping the efficacy and potential applications of these sensors, providing a nuanced perspective that contributes to the continual evolution of advanced hydrogen sensing technologies.

Table 1. Conducting a literature review to compare hydrogen gas sensitivities across different Pt-based material types, their corresponding structural forms and different operating temperatures.

Materials	H_2 Concentration range (ppm)	Temperature (°C)	Sensitivity (S%)	Ref
Pt nanowire	1000–50 000	RT - 277	~3.5 (275°C for 10 000ppm)	[6]
Pt nanowire array	1–1 000 000	200	~18.4 (for 10 000ppm)	[8]
Pt nanowire array	1–1000	RT	~5 (RT for 1000ppm)	[14]
Pt modified Pd nanowires	500–50 000	RT to 100	~4 (RT for 10 000ppm)	[16]
Pd@Pt core-shell nanocrystal layer	10–40 000	RT to 250	~3.6 (150 °C for 10 000ppm)	[17]
Pt@Au core–shell nanoparticle layer	1000–100 000	RT to 80	~15 (RT for 100 000ppm)	[15]
PtOx/Pt nanowire	0.5–1000	RT	~65 (for 500 ppm)	[18]
Ultrafine Pt nanowire network	1–5000	RT	~261 (for 5000 ppm)	[19]
3.5nm Pt thin film	10 - 1000	RT	1 (for all conc.)	[4]
		100	~4 (for 500 ppm)	
		200	~8 (for 500 ppm)	
10nm Pt thin film	10 – 10 000	RT to 60	~1.5 (RT for 10 000ppm)	[20]
20nm Pt thin film			~0.5 (RT for 10 000ppm)	
40nm Pt thin film			~0.4 (RT for 10 000ppm)	
5nm Pt thin film	100–10 000	RT	~4 (for 10 000ppm)	[21]
2nm Pt thin film	1000–10 000	RT to 200	~2.8 (RT for 1000ppm)	[7]
5nm Pt thin film	0.5 – 200	150	~4.5 (for 200ppm)	[13]
2nm Pt thin film	30 – 1000	RT to 100	~2.4 (RT for 1000ppm)	[22]
150 nm Pt nanoporous film	100 – 1000	RT to 100	3.5 (RT for 1000ppm)	[5]
3nm Nanoporous Pt Film	10–50 000	RT to 150	13.0 (RT for 10 000ppm)	[10]
Pt/Pd bimetallic film	10–40 000	RT to 150	13.5 (150 °C for 10 000ppm)	[23]
2nm Pt75Co25 alloy thin film	10–50 000	RT to 150	1.25 (150 °C for 10 000ppm)	[24]
2 nm Pt79Ni21 alloy thin film	25 – 1000	RT to 200	~2.6 (RT for 1000ppm)	[9]

4.Conslusions

As a conculusion, this review paper delves into the intricate realm of Pt-based hydrogen gas sensors, shedding light on their intrinsic potential and highlighting the pivotal role of various structural attributes. The profound importance of these attributes, including ultrathin films, nanopores, nanowires, and core-shell configurations, in shaping hydrogen gas sensitivity has been thoroughly expounded. Throughout this exposition, it becomes resoundingly clear that the Pt structure's surface stands as a fundamental and non-negotiable determinant of sensing performance, unveiling a key dimension for future explorations.

In a review that synthesizes existing knowledge, it is evident that purposeful modifications to the Pt surface serve as a beacon of promise, offering a pathway for substantial enhancement in sensor efficacy. Beyond surface modifications, the intricate manipulation of nanostructure dimensions has exhibited the dual capability of heightening sensitivity while significantly refining response and recovery times. Moreover, the strategic introduction of surface defects within Pt nanostructures emerges as a judicious strategy, augmenting sensitivity levels and subsequently elevating the overall sensing performance.

As this review journeys through the expansive landscape of Pt-based hydrogen gas sensors, it also foresees a panorama of possibilities for future advancement. The envisioned innovative avenues encompass the discerning formulation of Pt alloys, incorporating diverse metallic constituents, as well as the intricate realization of layered structural motifs. Furthermore, the orchestrated engineering of intricate core-shell architectures and hybridized structures hold promise for advancing hydrogen gas sensors to new horizons. Collectively, these nuanced strategies unearthed within the breadth of this review underscore the rich potential for propelling Pt-based hydrogen gas sensors into a realm of heightened sensitivity and extended utility, thereby shaping the future landscape of sensing technologies.

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