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Palladium-based Electrical and Optical Hydrogen Gas Sensors

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Abstract

In this short review, we explore the recent progress in metal-based gas-sensing techniques. The strong interaction between the metal films and hydrogen gas can be considered to play a considerably important role in the gas-sensing technique. The physical and chemical reactions in Pd-Pd hydride systems were studied in terms of the phase transition and lattice expansion of the metals. Two types of represented detection, electrical and optical, were introduced and discussed along with their advantages.

Keywords: Hydrogen sensor, Electrical sensor, Optical sensor, Gas sensor

1. INTRODUCTION

Hydrogen has attracted increasing attention as a next-generation fuel energy source owing to its abundant and eco-friendly nature. Usually, hydrogen exists at a very low density and high diffusivity. However, it should be noted that it is highly flammable and easily ignitable, and has a high burning propagation velocity. Particularly in air, it is so reactive that it ignites explosively with a tiny spark in the concentration range (4–75%) [1]. Hydrogen gas is colorless, odorless, and tasteless; for its detection, highly sensitive, selective, and rapid techniques are crucial for expanding the application scope of hydrogen in many industries. Hydrogen sensors exploit the results induced by the interaction of hydrogen (catalytic and solubility reactions) with sensing elements. They cause changes in properties such as structure, size, refractive index, electrical properties, and atomic phase, depending on the hydrogen concentration. Palladium-based hydrogen sensors are widely used for this purpose because palladium interacts favorably with hydrogen [2–4].

The heat of formation enthalpy (ΔH) of metal hydrides during hydrogen absorption by metals shows a positive value. This indicates that hydrogen absorption is unfavorable for most metals. However, some transition metals, such as Pd, Ni, and Cr, show negative ΔH values [5]. Among the three transition metals, Pd forms a stable hydride via hydrogen absorption. Pd can dissociate H_2 into two H atoms on the Pd surface and then dissolve into the interstitial sites of the FCC Pd lattice to form a new phase (α). Therefore, the sensitive detection of hydrogen gas using chemical interactions between the gas and specific metals can be expected. Furthermore, Pd nanomaterials can enhance sensitivity detection and response time, due to its increased surface to volume ratio and sensitive response of hydrogen induced properties changes. For this reason, electrical and optical detection methods are explored with the benefit of the improved nanotechnology.

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2. Pd-Pd HYDRIDE SYSTEM

The Pd-Pd hydride system has the lowest activation energy that must be overcome for hydrogen molecules to dissociate and diffuse from the surface into the subsurface [6]. The hydrogen atoms diffused into the Pd lattice and were stored in the interstitial sites of the lattice. Under a certain partial pressure of hydrogen gas, hydrogen atoms dissolved in the Pd lattice structure to form a solid solution phase, which is the so-called Pd α-phase [7]. At higher partial pressures, Pd and hydrogen form different chemical bonds and lattice structures from those in the solid solution state. The hydrogen atoms are located at interstitial sites of the FCC Pd lattice, which is the so-called Pd β-phase [8]. The Pd β-phase shows different mechanical, electrical, and optical properties than the Pd α-phase. The hydrogen atoms in the Pd lattice are act as electron scattering centers which influence the change of electrical and optical properties. Therefore, understanding Pd phase transformation by the hydrogen concentrations is important. Fig. 1(a) shows the dissociation of hydrogen molecules into hydrogen atoms on the Pd surface and the diffusion of hydrogen atoms into the Pd subsurface along with the (100) surface of FCC Pd in each phase.

Fig. 1(b) shows the relationship between the partial pressure of hydrogen and the Pd α-phase (0–0.02) and β-phase (0.58~) in terms of the atomic ratio. One of the most distinctive phase transformations of the Pd-Pd hydride system is the coexistence of α and β, as

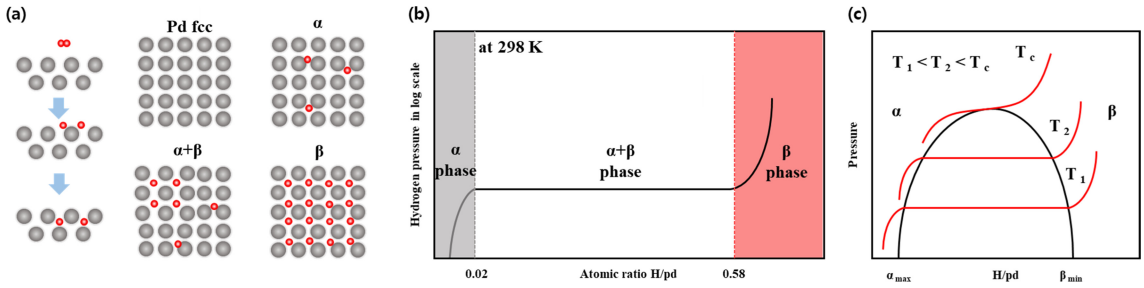

Fig. 1. (a) Hydrogen gas dissociation and absorption step on Pd surface and schematic illustrations of Pd and Pd hydride phase for the (100) surface. (b) Pressure-composition-temperature (PCT) curve for the Pd and Pd hydride system at the room temperature. (c) PCT curve with miscibility gap.

represented by the phase diagram in Fig. 1(c). While Pd and H in the Pd-Pd hydride system contain a miscibility gap below 570 K, phase transformation and propagation occur by the nucleation and diffusion of the β-phase in the α matrix [9]. In the Pd-Pd hydride phase transformation, a coherent or incoherent phase transformation occurs depending on certain factors, including the size of the Pd structures [10–14]. In these two transformations, the elastic stress induced inside the Pd structure is applied differently, resulting in a difference in the Pd-Pd hydride miscibility gap. Accordingly, the size of the Pd structure affects hydrogen solubility in the Pd lattice, as well as the phase transformation and phase equilibrium state [15]. This means that thermodynamic values, such as enthalpy and entropy of hydride formation, depend on the size of the Pd structures. As a result, Pd nano-particles (NPs) are widely used for hydrogen gas sensors because the change in the properties of Pd NPs between Pd and Pd hydride is relatively large, even under very low hydrogen concentrations [16, 17].

3. Pd-BASED HYDROGEN GAS DETECTION

3.1 Electrical Detection

Various types of hydrogen gas sensors use Pd structures and electrical detection methods. Electrical detection methods can be classified into two types. One such method works by measuring the difference in electrical signals from the number of physical contacts between the electrodes and the Pd structures. This type of sensor utilizes the change in the lattice expansion properties. The other method is by measuring the difference in electrical signals by the change in band structure and electrical properties of Pd structures due to the change in the density of state (DOS) of Pd and Pd hydride [18].

Electrical detection methods based on the number of electrical pathways can affect the volume expansion of Pd hydride because hydrogen atoms are located within the Pd lattice. These sensors are composed of deposited Pd nano-film or NPs between two electrodes. Under hydrogen exposure, hydrogen atoms are dissociated and diffused in the Pd lattice, the Pd structure expands, grains interconnect, and physical contacts of Pd nano-film or nano-particles are made [19]. As shown in Fig. 2(a), more electronic pathways are created when the Pd islands between the two gold electrodes are transformed by the hydride form relative to when pure Pd islands are used. The lattice constant of the β-phase is 3.5% larger than that of the α-phase, and the volume expansion induces the junction or break junction formed by the nano-scale gap between the Pd particles [20]. More pathways were created so that more electrical current is flowed between the two electrodes. Fig. 2(b) shows a switch signal in conductivity with the on and off conditions of the hydrogen gas. However, if the Pd films and Pd nano-clusters are deposited too thick, it is not possible to measure the sensitive Pd to Pd hydride change because it does not make a difference in the pathway described above. Therefore, appropriate amounts of Pd nano-films and Pd nano-clusters should be carefully deposited [21]. In addition, aggregation of Pd nano-films and nano-clusters occurs after Pd nano-clusters contact, which is called the percolation effect [22]. The percolation effect causes the conductivity values to be measured differently depending on the number of iterations, which is called aging. To solve this problem, inhibiting β-phase transformation through the specific geometrical design has been studied [23] and depositing titanium (Ti) or magnesium fluoride (MgF_2) under the Pd structure is used as a buffer layer or spacing layer [24].

The conductivities of the bulk Pd and Pd films decreased with hydride formation. The hydrogen atoms in the Pd lattice acted as electron scattering points that attracted electrons. Consequently, the mobility of electrons in the Pd crystals decreased when hydrogen atoms were absorbed. Fig. 2(c) shows the deposition procedure for Pd particles on the graphene layer between the two Au/Ti electrodes [25]. As shown in Fig. 2(d), hydrogen sensing was performed by depositing Pd particles on the graphene layer, and the conductivity of graphene was measured, which was changed by the difference in the DOS of graphene [26]. The difference in the DOS of graphene is indicated by the difference in the work functions of Pd and Pd hydrides. Pd hydride, which has a lower work function value than that of graphene, generates electron migrations and compensations of positive charged carriers in graphene on Pd hydride nano-particles [27].

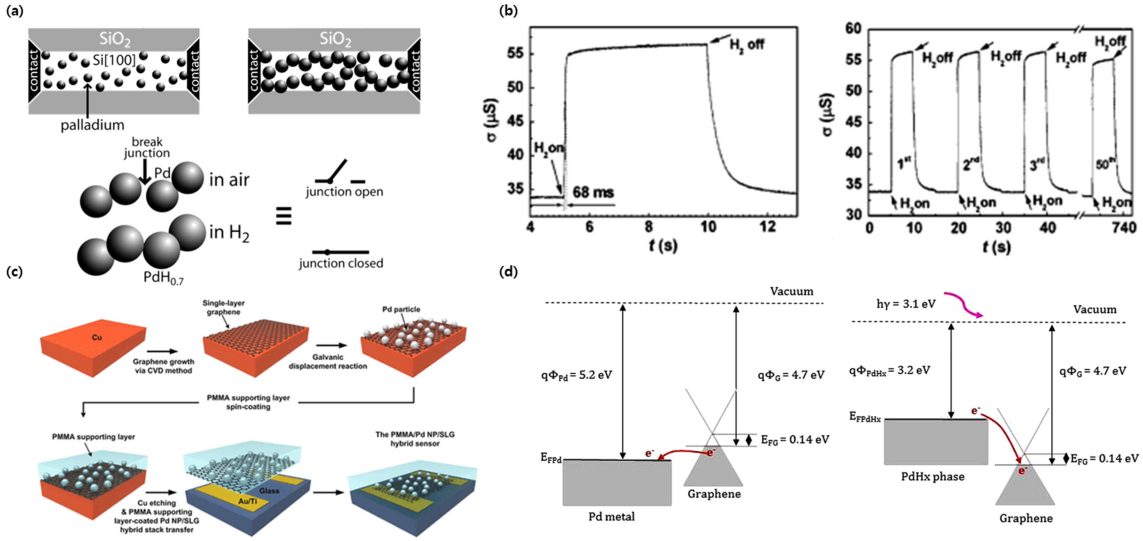

Fig. 2. (a) Schematic illustration of deposited Pd and Pd hydride clusters between the two electrodes, and open or closed junctions state as Pd α- or β-phase, respectively. Reprinted with permission from Ref [20]. Copyright (2003) American Chemical Society. (b) Measured conductance response of Pd film according to hydrogen absorption and repeated loading and unloading with a certain switching time. Reprinted with permission from Ref [22]. Copyright (2005) Applied Physics Letters. (c) Schematic illustration of the sequence for fabricating Pd particles on graphene between two electrodes. Reprinted with permission from Ref [25]. Copyright (2015) American Chemical Society. (d) Energy band diagram of Pd, Pd hydride and graphene. Reprinted with permission from Ref [26]. Copyright (2019) Springer Nature.

3.2 Optical Detection

Compared to the electrical measurements of hydrogen sensors, optical detection sensors are free from the risk of explosions. Optical measurements provide inherent safety as they do not generate sparks during detection. Owing to the merits of safety, many hydrogen sensors using optical measurements have recently been studied [28]. Optical detection methods mostly exploit the hydrogen-induced change in the optical properties between Pd and Pd hydride. For example, the complex refractive index can be a useful parameter to determine the amount of hydrogen in the optical pathway. The real part of the refractive index increases slightly, but its imaginary part decreases according to the hydrogen concentrations in the visible and infrared ranges [29]. These measurements are usually achieved by fabricating multi-layer structures containing Pd films or specific structures and measuring their transmittance or reflectance. Also, without any external electrical sources, optical gas detection methods using color changing materials called colorimetric or gasochromic have been proposed [30].

One type of optical sensor directly measures the difference in the transmittance signal, which is the photodetection of the difference in the dielectric constant of Pd according to the hydrogen concentration. The sample structure is composed of a MgF_2 buffer layer on the substrate to prevent the deformation of the Pd film and a gold film layer to suppress the catalytic activity of Pd hydride with oxygen [31]. One side of the Pd film was deposited on an optically transparent substrate, such as SiO_2 or Al_2O_3, which physically blocked the penetration of hydrogen gas. The other side of the Pd film was physically in contact with hydrogen gas. Therefore, the two photodiodes measured the difference in transmittance according to the hydrogen concentration. This method is sensitive to hydrogen gas but has a disadvantage in that it is difficult to distinguish other factors such as temperature, dust, and the aging effect.

Another type of optical sensor exploits the Localized Surface Plasmon Resonance (LSPR) or surface plasmon polariton (SPP) effects. Here, the important thing is the condition under which the Pd nano structures generate plasmon effects. Studies using this effect employ the lateral expansion of Pd with a nano-hole array structure acting as a nano-antenna, and the resonance peak shift and transmittance reduction due to the increase in the aspect ratio of the shaped Pd particles [32]. The resonance behavior of LSPR or SPP depends on the size, periodicity, shape, and dielectric properties of Pd nano structures, which guarantees a high sensing speed owing to the fast reaction kinetics, a characteristic property of nano-scale Pd [33]. Moreover, this method has the advantage of being able to measure the gas more sensitively because it uses not only the dielectric constant but also the resonance peak shift due to the deformation of Pd nano structures caused by volume expansion according to the hydrogen concentration. Fig. 3(a) shows the schematic diagram of so-called perfect absorber Pd nano-antenna structure which is composed of a MgF_2 buffer layer on a gold mirror layer. The change from Pd to Pd hydride causes a shift in the resonance peak and a difference in the far-field reflectance spectrum [34]. Fig. 3(b) shows how the localized plasmon oscillations in a Pd nano-metal wire can be measured using the difference in the

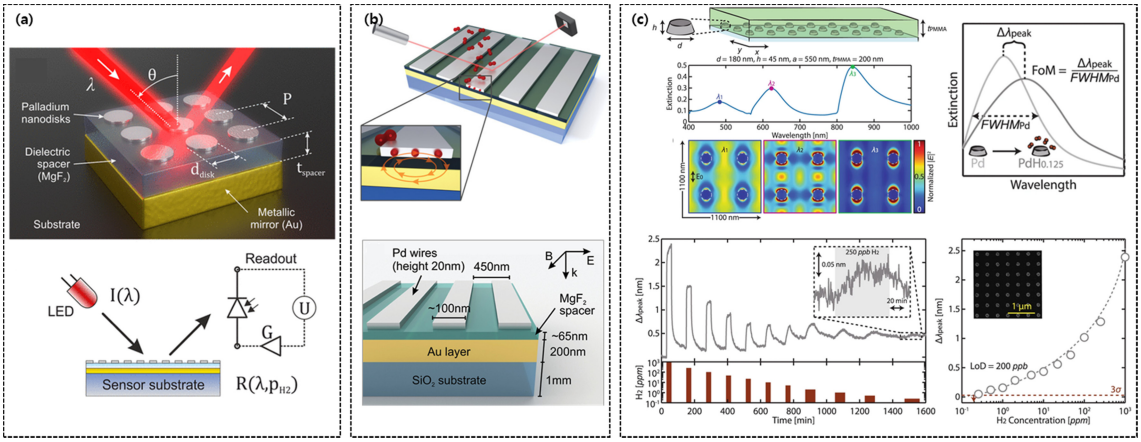

Fig. 3. (a) Schematic of the Pd nano-disks on the buffer MgF_2 layer and gold substrate layer, inducing reflectance spectrum. Reprinted with permission from Ref [34]. Copyright (2020) American Chemical Society. (b) Illustrated plasmonic effects in the Pd nano-wires structure and side view of it on layers. Reprinted with permission from Ref [35]. Copyright (2011) American Chemical Society. (c) Schematic illustration of Pd nano-particles in periodic array, 2D maps of normalized electric field distributions and measured spectral data. Reprinted with permission from Ref [36]. Copyright (2022) Springer Nature.

response depending on the width and optical properties of the medium under polarized light incidence [35]. Fig. 3(c) shows the highly sensitive hydrogen detection with signals having a high-quality factor by controlling the specific length of the Pd island array [36].

4. CONCLUSION

Various types of hydrogen-sensing methods that exploit Pd metal were reviewed. Electrical methods are mostly based on changing the properties of the lattice expansion of Pd. In these cases, the electrical contact and pathway are considered essential to define the exact amount of the injected hydrogen gas. Several physical parameters, such as the atomic phase transition of lattice change by exposure to hydrogen gas, are extremely sensitive to the structural condition of the metals, especially in nano-clusters, particles, or film states. Optical methods have also been introduced as promising candidates for sensitive hydrogen detection. Most of the decent optical techniques operate with the help of optical resonance characteristics such as LSPR or SPPs. The decreased signals in the measured transmittance or reflectance can be treated in terms of the optical properties of the metals changed by hydrogen gas. The results are explained by the complex refractive index, which provides quantitative and qualitative information simultaneously in a non-contact manner. More importantly, Pd volume expansion changes the structures that induce specific resonance behavior owing to the plasmon effect. Based on these effects, the sensitive detection of hydrogen is facilitated. More progress is expected with the development of high-quality factors of such resonant structures by the assistance of recent excellence in nano fabrication.

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