Improvement and stabilization of optical hydrogen sensing ability of Au-Pd alloys

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Abstract: Formation of metal hydrides is a signature chemical property of hydrogen and it can be leveraged to enact both storage and detection of this technologically important yet extremely volatile gas. Palladium shows particular promise as a hydrogen storage medium as well as a platform for creating rapid and reliable H₂ optical sensor devices. Furthermore, alloying Pd with other noble metals provides a technologically simple yet powerful way of enacting control over the structural and catalytic properties of the resultant material. Similarly, in addition to alloying, different top-down and bottom-up Pd nanostructuring methods have been proposed and investigated specifically for creating optical H₂ sensors. In this work it was determined that the hydrogen sensing ability of a series of Pd-Au alloy films could be improved by way of a hydrogen over exposure (HOE) treatment. Structural investigation showed that the HOE treatment, in addition to irreversibly altering the film morphology, results in a 1 to 2% expansion in the lattice constant of the metal. By combining a cyclic HOE treatment and alloy aging through annealing, the hydrogen detection sensitivity and response rates of Pd-Au films could be stabilized so that their performance would no longer be appreciably affected by repeated hydrogen uptake and release cycles. This work takes a further step towards routine all-optical detection of part-per-million level hydrogen gas concentrations in Pd-Au alloy films and discussion of ways to enhance response rates is provided.

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1. Introduction

Hydrogen is a promising energy resource and its usage is expected to accelerate to serve wider fields beyond the chemical industry, especially in development of future transportation. To handle explosive hydrogen safely, it is important to have a capability to detect it at the very initial stages of small leaks, preferably at sub-ppm levels, and to have a fast rate of detection for monitoring the occurring changes in real time [1–9]. Au-Pd alloys and composites will be used to support the needs of future society due to their unique properties well suited for hydrogen storage, hydrogen generation/reaction catalysis, and hydrogen sensing [10–12].

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When Au-Pd alloys react with hydrogen and incorporate its positively charged ions into their lattice, due to the reduction in density and mean free path of free electrons, substantial changes in their optical permittivity are induced, as was demonstrated in preceding work [13]. This phenomenon is now quite well understood and can be leveraged in a variety of ways to enable the creation of optical hydrogen sensors. For instance, hydrogen uptake is associated with increasing optical transparency of sufficiently thin metal layers, and this behavior can be used to realize exceedingly simple yet robust light intensity measurement-based $H_2$ detection schemes [13]. Conversely, nanostructured Pd-Au alloy films can be employed to create plasmonic devices and metamaterials, in which permittivity changes translate into resonance wavelength shifts [14]. However, optical constants are not the only relevant metal properties undergoing change as a result of hydrogen gas exposure. $H_2$ dissociation and incorporation into Pd and its alloys is associated with considerable metal lattice expansion needed to accommodate the ionic interstitials. There are numerous implications of this expansion, and exploring its effects on Pd-Au alloy film hydrogen interaction performance as well as longevity has recently drawn considerable research interest. The stresses induced by substrate-metal film interaction have been shown to be particularly pertinent to hydrogen absorption capacity of Pd-Au thin films [15], and utilizing nanostructuring has been show as a viable way of alleviating the thermodynamic barrier required to undergo deformations during uptake and release [16].

In addition to the magnitude of $H_2$ induced changes in Pd-Au alloys (underpinning detection sensitivity) the rate of response is likewise important to ensure rapid sensing. Previous contributions have demonstrated that alloying Au and Pd can realize an improvement of optical hydrogen sensing due to reduction of detection time for both hydrogen intake and release. This was attributed to the altered electrostatic properties and electron affinity of the alloy [13]. During many cycles of hydrogen and nitrogen (air) exposure experiments it was observed that certain samples developed fine micro-cracks in the film coating following extended exposures to either

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**Fig. 1.** (a) Photograph of HOE treated sample on a silica glass substrate from front and back-side views. (b) Micro photograph of the Pd-Au alloy film with 56% Pd as deposited and (c) after HOE treatment. FFT analysis (not shown) revealed a random pattern of grain sizes centered around 7-12 $\mu$m. (d) SEM image of a HOE treated sample (top). (e) Hydrogen response of Pd-Au alloy film with 56% Pd content before and after HOE treatment. In both cases pure $H_2$ exposure was used.
4% diluted hydrogen or pure 100% hydrogen. Especially under the 100% hydrogen condition, a non-reflective appearance of the initially mirror-like surface developed within only a few seconds. Such a condition is referred to as hydrogen over exposure (HOE). The cracking was permanent and was not changed after returning the sample to an air or pure nitrogen atmosphere.

Figure 1(a) shows photographs of a HOE treated thin film Pd-Au alloy acquired from both sides of the transparent silica substrate. It illustrates the extensive changes that the 50 nm films are subjected to, most prominent of which being the formation of dense network of cracks which propagate throughout the entire layer thickness. More detailed information can be deduced from optical microscopy images in Fig. 1(b,c), where Au-Pd film before and after HOE is clearly contrasted, and these observations are further verified by a scanning electron micrograph in Fig. 1(d). In this work it was also found that after HOE the response time of hydrogen intake/release and the optical extinction change is improved relative to as deposited films, as shown in Fig. 1(e). It is important to better understand the mechanism of this phenomenon, as it could be of considerable utility in construction and improvement of Pd-alloy based optical hydrogen sensors. In this study, we investigate and report on the mechanism of sensor performance enhancement as a result of HOE and demonstrate its stabilizing effect applicable towards predictable hydrogen sensing performance.

2. Experimental: samples and methods

Various compositions of Au-Pd alloy films were prepared by co-sputtering followed with an annealing at 250°C to obtain a thoroughly intermixed alloy, as demonstrated previously [13]. No adhesion layer materials were used. The atomic ratio of Au and Pd was controlled by adjusting the bias power used during magnetronic sputtering. Alloy hydrogen exposure response has investigated using an optical transmission measurement system, comprised of a hydrogen chamber with an optical fiber coupled into it. The sample was illuminated using a halogen light source and an optical power meter was used as detector for the optical-fiber collected transmitted light. The flow rate of hydrogen was maintained at 1.5 litres per hour.

The lattice constant of alloys was measured using X-ray diffraction (XRD; SmartLab, Rigaku) by way of the $2\theta - \theta$ method using the Cu-K$\alpha$ line irradiation ($\lambda = 1.5418$ Å). The scan range was set to span from 35° to 45° with a 0.01° increment and a 4.0°/min scan speed. X-ray measurements under a 4% hydrogen gas exposure condition were conducted using custom cell holders for XRD measurements.

3. Results and discussion

3.1. Mechanism of crack formation during HOE

Figure 2 details the experimental results of optical transmittance response to hydrogen uptake and release for the various Pd atomic ratio films. Pure Pd and Au substrates were also prepared for reference. In the case of optical extinction losses, films with 56%, 65% and 100% Pd showed a drastic improvement following the HOE procedure. However, Au-Pd alloy with only 41 % of Pd in its composition exhibited less change even after HOE treatment. Conversely, the response time of hydrogen uptake and release improved in all samples after HOE (Fig. 2). In general, alloys exhibited a hydrogen uptake and release rates that were more than double that of as-deposited films. The response to hydrogenation is strongly affected by the affinity between hydrogen and metals. Pd is quite prolific in this regard, as it can incorporate up to 600 times its volume in gaseous hydrogen. As mentioned previously, crack formation signifies that the crystal volume was altered in some way during the HOE treatments. Au and Pd are very similar in terms of their lattice constants and ion sizes – respectively 407.82 pm (Au), 389.07 pm (Pd) and 166 pm (Au), 163 pm (Pd) – hence form alloys readily.
The lattice constant of Au-Pd alloys as well as its changes as a result of H$_2$ absorption were measured by XRD under hydrogen exposure condition, with experimental results summarized in Fig. 3(a). Both, as deposited and HOE treated samples showed angular shift of the XRD peak to lower 2$\theta$ angles over the course of 4% hydrogen exposure. This can be attributed to an increase of the lattice constant as it expands to accommodate dissociated hydrogen ions. Notably, HOE treated samples exhibited a somewhat smaller lattice constant than as-deposited samples and, furthermore, allowed for a slightly larger lattice expansion during hydrogen exposure, as summarized in Fig. 2(b).

Taken together SEM imaging and XRD analysis support a combined structural and morphological explanation as the possible mechanism, illustrated in Fig. 3(c). Initially, when films absorbed hydrogen, their lattice constant and therefore volume expanded. The extent of such an expansion in terms of lattice constants is evident in Fig. 3(a) and (b), and ranged between 1 and 2% in the case of >4% hydrogen gas mixture exposure. This expansion is expected to be much more sizeable during the 100% hydrogen HOE treatment, however, due to safety reasons it was not possible to conduct in-situ XRD acquisition in our setup under these conditions. During hydrogenation a strong pressure was exerted onto the poly-crystalline alloyed film grain boundary interfaces, which have a lower strength for mechanical failure and crack initiation compared to a defect-less crystal. Therefore, grain boundaries were readily damaged during the HOE treatment. After hydrogen release from the film, the volume of crystals returned to its original size exposing larger cracks between grains, leaving behind permanent nano-/micro-cracks. This is consistent with the known hydrogen embrittlement of metals.

The largest contributors to the film volume change are the hydrogen species stored inside Pd phase in proton H$^+$ and molecular ion H$_2^+$ states. Their dissociation from and recombination into a larger H$_2$ molecule occurs at the interfaces, along with the electron exchange reactions with the metal. Furthermore, a steric hindrance related to the H$_2$ molecule being larger compared to dissociated ions [17] is suggested to be responsible for the release time being larger than the
uptake. Similarly, small interface-permeable \( H_2^+ \) can enter metal phase faster than be released during the reversible water splitting reaction mediated by electron transfer between electrode and water. Hydrogen embrittlement and the observed crack formation are leveraged in this work for sensor applications. Cracks provide a larger surface area for hydrogen uptake and release. More notably, metal film and substrate interactions have recently been identified as significant contributors to the thermodynamic barrier required to undergo the atomic rearrangements required to accommodate hydrogen [15,16]. The cracks that develop during HOE can be considered to be a spontaneous self-organized nanotexturing of the Pd-Au film into irregular islands separated by trenches, which serves to decrease mechanical stress due to hydrogenation. Not only the alloy film, but also pure Pd film shows a similar tendency, however, the amount of change was smaller than that for the alloys. Therefore, this behavior represents a further advantage of alloying Pd with Au, in addition to the a hysteresis free behaviour compared to pure Pd.

3.2. Aging of Pd-Au alloy by thermal treatment

Despite their noble metal status, Pd and Au film surfaces can get contaminated in ambient atmosphere due to presence of sulfides. This is illustrated by the black curve in Fig. 4, where after two to three years after its deposition a 63% Pd-Au thin-film sample exhibited no optical response to hydrogen exposure. However, after annealing this film for 4 hours at a 400°C in an ambient atmosphere it became considerably more transparent and became responsive to hydrogen. However, its full sensitivity and responsiveness returned only after a 10 min stabilization under a hydrogen stream, as shown by the red curve in Fig. 4.
Structural changes induced by the aging recovery process, detected as changes in the lattice constant, were probed using XRD. Initial anneal and HOE treatment produced a notable increase in alloy lattice constant, hence, the result was indicative of Pd and Au atom mobility. More importantly, this anneal and HOE induced a full recovery of hydrogen sensing capability. The behavior was explored further by repeatedly cycling annealing and HOE processes with XRD measurements conducted in between, and the results are summarized in Fig. 5. After hydrogen sensitivity was restored during the first cycle parameters related to H\(_2\) interaction, such as extinction loss change as well as uptake and release times, remained almost unchanged. It was also observed that the lattice constant remained mostly constant with a tendency to expand somewhat after being subjected to an increased number of annealing cycles (Fig. 5(a)). Conversely, the interspersed HOE treatments had a slight opposite effect on the lattice constant. This implies that the stable atomic coordination is marginally different after annealing and HOE treatment. It could be explained by an onset of Au and Pd segregation at a 400\(^\circ\)C temperature. Since the aging treatment induced considerable lattice constant changes in thin films of Au-Pd alloys, as revealed by XRD, it should be observable as a change in electrical conductivity as well. Therefore, such an aging process could become essential to stabilizing various applied chemical sensors. Furthermore, annealing along with overexposure treatments has the potential to recover the sensing ability from deterioration due to extended use or storage.

Hydrogen detection performance of the thermally aged Au\(_{0.35}\)-Pd\(_{0.65}\) films is outlined in Fig. 6 where optical response to 1-4\% H\(_2\) gas mixture exposure is plotted. Low noise performance with high fidelity judgement on saturation of extinction was observed. Responsiveness can be quantified by measuring slope of changes (Fig. 6(a)) as \(S = \Delta Ext/\Delta t_{up, re}\) for the uptake and release \(\Delta t_{up, re}\), respectively. For 4\% hydrogen concentration \(S = 1.2 \text{ [dB]} / 40 \text{ [s]} = 3 \times 10^{-2} \text{ dB/s}\) is obtained. The experimental limit of detection (LOD) of 10 ppm level was reached; LOD is defined as 3\(\sigma\) of the noise level, where \(\sigma\) is the standard deviation. It is informative to evaluate the theoretical saturation limit of hydrogen detection in a 40-nm-thick film illuminated by a 100 \(\mu\)m optical focal spot at the 4\% vol explosive threshold hydrogen concentration. The Au\(_{0.5}\):Pd\(_{0.5}\) alloy is considered for simplicity. By counting the number density of Pd in the illuminated volume and applying the 0.69 saturation constant [13] for H(proton)-to-Pd atomic ratio, one would arrive to 0.95 ppm (by mass as usually defined). Since the atomic mass ratio H/Pd = 1.007/106.42, this sensitivity limit is 100.3 ppm by the number of atoms, at which all Pd in the focal volume have accommodated a 0.69 fraction of protons (hydrogen form in the
Fig. 5. (a) Lattice constants of Au-Pd alloy film with 63% of Pd with aging treatment. (b) Extinction vs. aging cycles and hydrogen sensing ability - response time - change with aging treatment. The annealing cycles were at 400°C.

 alloy. Here we used number density $N_a \rho V/M$ calculated by the Avogadro number $N_a$, volume of the illuminated sensor film $V$, mass density $\rho$ and molar mass $M$. Responsiveness - how fast this saturation number is reached - can be improved by increasing the sensor surface affinity to hydrogen. This can be achieved by augmented electronegativity of the alloy’s surface due to presence of Au in the alloy [13], an electrochemical potential of sensor surface, a fast lateral in-film diffusion of protons out of illuminated area, and a physical increase of surface area as well as decrease in tension discussed in this study. Also, a surface-to-volume ratio of illuminated sensor affects sensitivity via signal-to-noise ratio.

Fig. 6. Hydrogen sensing ability of different concentration of hydrogen after aging treatment. Amount of Pd in the Pd-Au alloy was 65%. (a) Optical transmittance response under hydrogen exposure. (b) The $\Delta$ extinction loss $\Delta Ext = -10 \log T$. (c) Response times for hydrogen uptake and release.

4. Conclusion and outlook

In this study, the improvement of the hydrogen sensing ability of Au-Pd alloy films following a hydrogen over exposure treatment was demonstrated. Further sensitivity increase is possible by implementing a lock-in detection approach, which is particularly straightforward to realize.
for optical transmission measurements. By applying a bias potential onto the Au-Pd electrode it should become possible to enable a more rapid hydrogen uptake reaction $H_2$ (from gas) $\rightarrow H^+_2 + e$ for positive potentials, and facilitate a more thermodynamically favorable release $H^+_2 + e \rightarrow H_2$ (to gas) at the negative potentials; here interface reactions are considered, where the gas phase $H_2$ is outside of the electrode/interface while $e$ is the electron supplied from/to the electrode. Furthermore, this reaction is reversible which is favorable for the long term stability of the sensor surface [18], and alloy function diminished due to aging can be reconstituted through annealing. The outlined methods are expected to be instrumental for improvement of all-optical detection of hydrogen aiming to enable the most sensitive and responsive monitoring of hydrogen concentration in real time. Current sensors geared towards such applications are based on observing changes in electrical resistivity, and operate with a 10 s refresh cycle. The demonstrated optical transmission sensors operate at the optical telecommunication spectral range without risk of electrical discharge, and can become competitive with the established resistivity sensors. In addition, optical sensors at 1.3-1.5 $\mu$m wavelengths are compatible for integration with CMOS chips.

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**Disclosures**

The authors declare no conflicts of interest.

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