



Optical hydrogen sensing with nanoparticulate Pd–Au films produced by spark ablation



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ABSTRACT

We have produced nanoparticulate Pd–Au (88–12 at.%) thin films using, for the first time, spark ablation and inertial deposition on glass substrates. Films having thicknesses that range from ca. 150 to 200 nm exhibit high enough contrast (i.e., range of optical transmittance) and negligible hysteresis during H₂ adsorption/desorption cycles, thereby providing an almost one-to-one relation between applied H₂ pressure and transmittance. Films having thicknesses larger than 200 nm exhibit hysteresis, which can be attributed to the cracks formed by the higher mechanical stresses associated with phase transition of the film during H₂ absorption and/or desorption. All samples exhibit a reasonably stable response upon cycling at room temperature. Their response times are less than 30 s, which are considerably shorter compared to those of their counterparts produced by sputtering. Considering that the method used to produce the nanoparticulate films is simple and inexpensive, the findings reported in this paper open new opportunities for the design, optimization and production of optical H₂ gas sensors.

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1. Introduction

The development of reliable and inexpensive sensors for hydrogen detection is an increasing demand for numerous applications including energy conversion and storage [1–3], industrial manufacturing [4], and medical diagnostics [5]. A number of H₂ sensors employing catalytic, thermal conductivity, electrochemical, resistance based, work function based, mechanical, optical and acoustic methods have been proposed over the years [6]. Among those, optical techniques are advantageous due to their simplicity, fast response, low power consumption and ability to operate at ambient conditions. Furthermore, optical sensors are safe to use in a variety of environments due to the absence of electrical connections of the sensing material with the electronics of the sensors.

Pd is an ideal material for H₂ sensing. Upon exposure to H₂ it progressively converts to Pd–H causing an increase in the Fermi level and a subsequent decrease of the dielectric function, which

in turn changes the optical properties of the material. Despite its widespread use for H₂ detection, pure Pd films exhibit a number of limitations. Absorption and desorption of H₂ by/from Pd causes respectively expansion and contraction of the lattice, leading to surface discontinuities and eventual buckling of the films. This severely limits their practical use as reliable hydrogen sensors, especially when continuous/cyclic H₂ sensing is required [7–9]. In addition, the presence of a plateau pressure due to the phase transition of the films, makes pure Pd more suitable for H₂ detectors rather than for sensors. The hysteresis effect observed with pure Pd films during the H₂ absorption/desorption cycles yields bi-valued transmittance for specific H₂ pressures, thereby limiting further their potential use for H₂ sensing. Apart from their use in optical sensors, the above-mentioned limitations of pure Pd films also restrict their potential application in chemiresistive sensors.

Alloying Pd with metals [10–14] can overcome the above-mentioned limitations to a certain extent. This is because the lattice parameter change upon hydrogenation is smaller in Pd-alloy than in pure Pd films [15], which prevents them from being damaged upon cycling. Compared to pure Pd, the α – β phase transition of Pd-based alloys is suppressed (i.e., the critical temperature is

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lowered) [16–18] or sometimes even disappears depending on the H₂ concentration [15]. This prevents large structural changes [19] and fracturing of the films associated with phase transitions. The extent to which the α – β transition and the associated hysteresis is reduced, depends on the type and amount of the alloying element in the Pd. For example, 20 at.% Au or 10 at.% Ta in pure Pd (i.e., 80–20 at.% Pd–Au and 90–10 at.% Pd–Ta alloys, respectively) have been shown to suppress the phase transition and hysteresis to a large extent [20]. Interestingly, the suppression of the phase transition is also associated with a significant reduction of the optical contrast of the films, which makes them more attractive for use in sensors. To further increase the contrast of the films one can also increase their porosity by nanostructuring without changing their composition.

Here we investigated the optical H₂ sensing properties of nanoparticulate Pd–Au alloy (88–12 at.%) films. This choice is based on preliminary tests showing that while structural deformations are suppressed by the presence of Au, we can still observe the effect of nanostructuring on hysteresis in our samples as compared to their flat thin-film counterparts. To prepare the films we use, for the first time, nanoparticle building blocks generated by spark ablation followed by inertial deposition [21]. The optical sensing capabilities of the films are determined by measuring their transmittance as a function of H₂ pressure, optimal thickness.

2. Experimental

2.1. Nanoparticle synthesis and film preparation

Nanoparticulate thin films were prepared using nanoparticle building blocks synthesized by spark ablation: a high-purity evaporation–condensation method introduced by Schwyn et al. in 1988 [21–23], that is capable of producing nanoparticles of mixed materials [24]. In brief, material from two conductive electrode rods that are placed very close to each other is evaporated by repeated spark discharges induced by a high potential difference applied between them. The resulting vapour cloud is rapidly cooled down to room temperature by a high quenching gas flow passing through the gap between the two electrodes. Upon cooling, the vapours form atomic clusters by nucleation that grow to nanoparticles and agglomerates by condensation and coagulation, respectively. Two alloyed electrodes of the same composition (88 at.% Pd and 12 at.% Au) were used to synthesize the Pd–Au nanoparticles used in this work. The resulting particles were deposited onto glass substrates by focused inertial impactation [25], thereby forming the nanoparticulate thin films.

The nanoparticle deposition rate on the substrate was determined by measuring the thickness of the deposited films over specific time intervals using a Dektak profilometer. The profile measurements were made before the start of the experiments. Because the deposited films are not flat but have a slightly concave profile, as an indication of their thickness we used the maximum value (excluding any individual spikes) at the central part of the film.

2.2. Sensor testing setup

A hydrogenography system, as described in detail by Westerwaal et al. [26], was used to test the optical sensing performance of our thin films [27,28]. To do so, the films were placed in a temperature-controlled cell where they were exposed to a range of H₂ pressures. The hydrogen pressure inside the cell was step-wise increased (loading or hydrogenation stage) or decreased (unloading or dehydrogenation stage) between 1 and 1000 mbar. White light from a 150-W diffusive lamp was passed through the thin films,

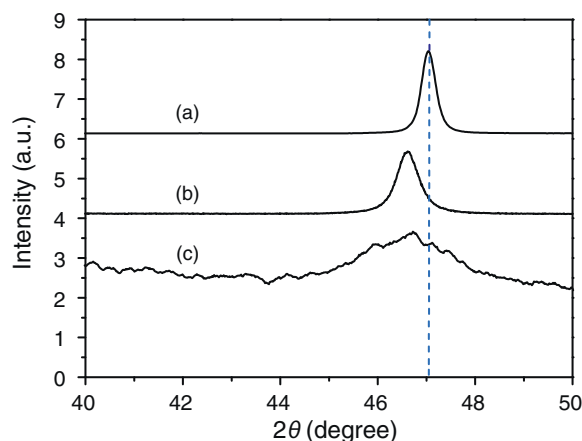


Fig. 1. XRD spectra of a pure Pd film prepared by magnetron sputtering (a), a Pd–Au (88–12 at.%) alloy film prepared by magnetron sputtering (b) and a nanoparticulate Pd–Au (88–12 at.%) film prepared by spark ablation (c). The 2θ position indicated by the vertical dashed line corresponds to the peak of pure Pd.

while a charged-coupled device (CCD) camera (Sony Model XC-003) was used to continuously measure the intensity of the transmitted light.

2.3. Film and nanoparticle characterization

The crystalline structure of the deposited film was studied by X-ray diffraction (XRD; Bruker AXS D8 Advance) with a Co K α radiation source ($\lambda = 1.78897 \text{ \AA}$). X-ray diffraction patterns were measured in 2θ angles ranging from 40° to 50° . Structural characterization of the sample was performed using a scanning electron microscope (SEM; JEOL JSM-6010LA) operated at 5 kV. To further observe the distribution of Au and Pd in the film, we used energy-dispersive X-ray (EDX) spectroscopy with the SEM operated at 20 kV. All samples for SEM analysis were prepared by focused inertial impactation of the Pd–Au nanoparticles, produced by spark ablation, onto glass substrates.

Individual nanoparticles produced by the spark discharge generator (SDG) were also observed under a transmission electron microscope (TEM; JEOL JEM 1400). The samples were prepared by depositing the particles downstream the SDG on a copper grid (Quantifoil® microgrid).

A scanning mobility particle sizer (SMPS; [29]) was used to measure the size distribution of the particles produced by spark ablation. For these measurements the particles were initially size-selected by electrical mobility classification using a custom-made differential mobility analyzer (DMA; [30]) before they were counted using a condensation particle counter (CPC; [31]).

3. Results and discussion

3.1. Material properties

Fig. 1 shows the XRD spectrum of a film produced by depositing Pd–Au particles produced by the SDG onto a glass substrate. For comparison, the XRD pattern of pure Pd and Pd–Au (88–12 at.%) alloy thin films produced by magnetron sputtering are also included in Fig. 1. The Pd–Au alloy films exhibit a shift in the peak positions of the spectrum, with respect to that of pure Pd, due to the alloying with Au [15,32–34]. The peak broadening observed in the Pd–Au sample prepared by spark ablation indicates that the film is nanocrystalline with a crystal (particle) size being ca. 5 nm as deduced from the XRD patterns alone. Elemental composition analysis of the samples using EDX spectroscopy indicated that the film

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