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High-Sensitivity Hydrogen Detection: Hydrogen-Induced Swelling of Multiple Cracked Palladium Films on Compliant Substrates**

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Development of efficient and selective sensors for hydrogen detection is an important step towards the hydrogen economy.[1] The existing sensor technologies, such as thermal conductivity, catalytic and electrochemical sensors, and metal-oxide chemiresistors have significant drawbacks, with cross-sensitivity often being the most serious one.[1b,c] Palladium-based sensors for hydrogen detection are highly selective but are not yet sensitive enough to detect low hydrogen concentrations. An important contribution to the development of more sensitive palladium-based hydrogen sensors has been the recent works by Lee et al.[2] and others.[3] The improved sensitivity is due to several innovations: 1) reversible swelling of multiple cracked Pd films in which the cracks act as nanogaps,[3a] 2) use of elastomeric substrates as a compliant support for palladium films to accommodate the swelling, 3) use of Pd–Ni alloys having large hydrogen solubility as hydrogen-sensitive receptors,[3c] and 4) wafer-scale fabrication of Pd films and nanoswitches.[3a,b]

As is well-known, palladium as well as almost all other transition and rare-earth metals easily dissolves hydrogen, forming nonstoichiometric hydrides of general composition MH_x ($x_{max} = 3$ for LnX_3).[4] The palladium–hydrogen system is the most studied system[4a] in part because the high specific solubility of hydrogen in palladium is widely used in several industrial processes, for instance in membranes for hydrogen purification,[5] hydrogen storage materials,[6] and in gas sensors. In PdH_x the hydrogen atoms occupy octahedral sites in the cubic close-packed palladium lattice. As there are four Pd atoms and four octahedral interstitial sites per unit cell of Pd, the maximum theoretical composition corresponds to PdH ($x = 1$). The filling of the interstitial sites by hydrogen atoms causes a local expansion of the palladium lattice which is manifested as a “swelling” of palladium (Figure 1). The corresponding volume expansion is about 2.8 $Å^3$ per H atom at low hydrogen concentrations in palladium ($H/Pd < 0.7$) and about 0.3–0.7 $Å^3$ per H atom at high hydrogen concentrations ($H/Pd > 0.7$). As dissolved hydrogen atoms also cause an increased scattering of conducting electrons, there is a corresponding decrease in conductivity of α-PdH_x; this effect is the basis of palladium-based resistive gas sensors (chemiresistors). Because of the relatively low miscibility gap (below 570 K) hydrogen has a maximum solubility in a hydrogen-poor α-PdH_x (x_{max} of around 0.01 for bulk α-PdH_x, α_{max}). Above this concentration, a phase transformation occurs above a H/Pd ratio of 0.01 with the formation of the so-called β-phase where the lattice constant drastically increases from around 3.90 to around 4.04 Å (x_{min} of around 0.57 for bulk β-PdH_x, β_{min}). Accordingly, the α-PdH_x and β-PdH_x each having different properties, for instance hydrogen content, lattice parameters, conductivities, mechanical properties coexist in the H/Pd range between 0.01 and 0.7, which leads to a discontinuity of the property–concentration rela-

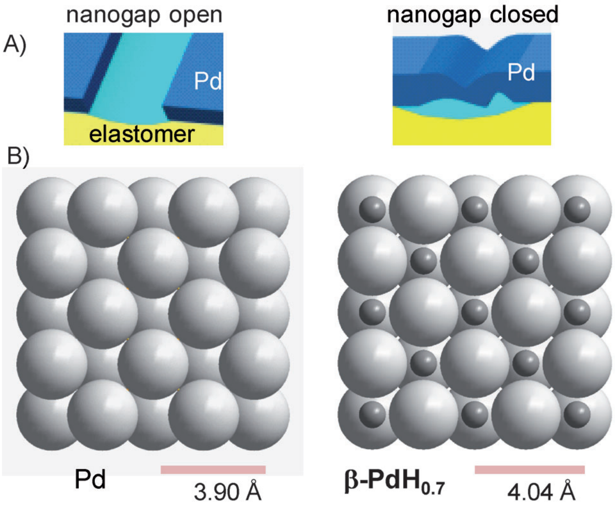

Figure 1. A) Closing of nanogaps caused by the palladium swelling because of the hydrogen dissolution shown in (B). Comparison between two extremes: {100} surfaces of fcc-Pd (left) and β-$PdH_{0.7}$ (right). The bars represent the shortest distances between two palladium atoms corresponding to the lattice parameters. Palladium atoms ($r_{at} = 120$ pm) are shown as large circles, hydrogen atoms ($r_{at} = 53$ pm) as small circles.

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tionship and limits the applicability of palladium for hydrogen detection.

The $\alpha \rightarrow \beta$ phase transition has to be avoided in sensors because the linear dependence of electrical resistance with hydrogen concentration breaks down. Three possible strategies exist to do this: 1) limiting the target concentration of hydrogen gas to that corresponding to α_{max}, 2) using smaller Pd particles since they have an increased hydrogen solubility, a narrowing of the miscibility gap and larger Sievert's constants,[7] that extends the H/Pd range of α-PdH_x stability and broadens the range of detectable hydrogen concentrations (Figure 2),[8] and 3) using palladium alloys (such as Pd–Ni) having a smaller miscibility gap and larger hydrogen solubility.[9]

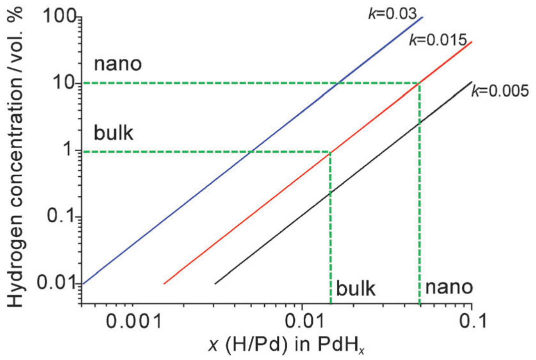

Figure 2. Using smaller Pd particles with an increasing hydrogen solubility (x_{max} of around 0.05) and showing larger Sievert's constants in adsorption isotherms $x = kp_{H_2}^{1/2}$ (k of around 0.013 $\mathrm{kP_a}^{-1/2}$) extends the H/Pd range of α-PdH_x stability and broadens the range of detectable hydrogen concentrations.[7,8]

The reversible Pd swelling upon hydrogen absorption was exploited for hydrogen detection as early as 2001.[10] However, previous applications of palladium for hydrogen detection were limited by the irreversible degradation of the Pd receptors (films, nanowires, nanocrystals) after long-term operation and cycling because of spalling and delamination of the Pd from rigid substrates (e.g. silicon) caused by repeatedly swelling/shrinkage of palladium upon hydrogen absorption/desorption.

This is where the approach taken by Lee et al. is so innovative because it overcomes many of these shortcomings. Cracking is usually avoided at all costs, whether a component is a structure, an electronic device or a circuit. Indeed, part of the motivation for the development of the enormous field of fracture mechanics over the last fifty years has been to understand and predict the conditions under which cracks nucleate and grow so that cracking can be avoided. Lee et al. turn this logic on its head by exploiting one of the intriguing findings in fracture mechanics to create a dense, parallel array of narrow cracks to form a vast number of electrical break junctions for gas sensing. The essential idea that Lee et al. utilize is that the reversal swelling of Pd when exposed to hydrogen causes the cracked Pd film to expand laterally, altering the width of the cracks and hence the electrical conductivity of the multiply cracked Pd film.

Multiple cracking is an example of a class of mechanics problems associated with the release of mechanical strain energy created in films on substrates, for instance by deposition stresses, matrices in fiber composites on loading, and drying of paint films or mud. So ubiquitous are these phenomena that they have household names, "mud-cracking", "crazing", and "crocodiling". In each, a differential strain is produced in the film or substrate until at a critical value of the strain energy density the least compliant component cracks. There are well-established equations that relate the average spacing between the cracks to the film and substrate thicknesses, the elastic moduli of the film and substrate, and the differential strain.[11] What makes the multiple-cracking phenomenon so intriguing is that arrays of cracks form in an apparently collective manner and that a hierarchy of ever smaller crack spacings can form with further straining. The underlying cause for the appearance of multiple cracking lies with the way in which stresses are shared and transferred from one component to the other as the strain energy builds up. The key parameter is the shear strength of the interface between the two components which is determined by the bonding between them. Once one crack forms, it unloads a volume of material in its immediate vicinity so no other crack can form locally but further away, the strain energy per unit volume is unchanged so another crack can subsequently form elsewhere. This process continues in a stochastic fashion until the average crack spacing corresponds to approximately twice the load transfer length.

A two-dimensional array of multiple cracks, for instance in mud-cracking, usually forms but if the mechanical loading is in one direction, as reported by Lee et al., or the fibers in a brittle matrix composite are all aligned, then only one parallel array of cracks forms. In the work of Lee et al. the film is made of Pd, which has a lower strain to failure than the elastomer, so it multiply cracks. When the preload is removed the elastomer elastically returns to its original state closing up the cracks in the Pd film, riding on top of the elastomer but not eliminating them leaving numerous potential break-junctions along each crack. This requires good adhesion between the Pd film and the elastomer otherwise the metal will simply rupture by necking.[12] The multiply cracked Pd film is then ready to be used as a hydrogen sensor. Exposure to hydrogen causes the Pd film to expand laterally compressing the contact points across the cracks and increasing the film conductivity; removing the hydrogen causes the film to return to its original dimensions and the cracks to open up. As the elastomer is unaffected by hydrogen it does not swell or shrink but nevertheless provides a compliant substrate thus avoiding the traditional problems of spalling and delamination of Pd films on rigid substrates.

This work by Lee and colleagues shows once again that the palladium–hydrogen system still holds surprises and continued combinations of fundamental and engineering studies remain essential. Despite progress achieved in recent work about hydrogen sensing with palladium nanowires and films[2–3] as well as about mechanism of hydrogen dissolution in ultrasmall palladium particles accompanied with phase transitions[7b,13] and strain/stress development,[14] the basic understanding of the relationship between the amount of absorbed hydrogen, conductivity, volume expansion, phase transitions, and size of Pd particles remains to be fully established. In addition, there are several other intriguing questions about the contribution of Joule heating,[15] the role of vacancies,[16] and metal–insulator transition[17] to the overall sensing response. This fundamental understanding is extremely important for technological advances in the fields of hydrogen storage, purification, and detection in which palladium-based materials have and will continue to have a variety of applications.

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