Dynamic and Static Manifestation of Molecular Absorption in Thin Films Probed by a Microcantilever

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Mechanical resonators shaped like microcantilevers have been demonstrated as a platform for very sensitive detection of chemical and biological analytes. However, their use as an analytical tool requires fundamental understanding of the molecular absorption-induced effects in the static and dynamic sensor response. The effect of absorption-induced surface stress on the microcantilever response is here investigated using palladium hydride formation. It is shown that the dynamic and static responses of the cantilever monitored simultaneously exhibit excellent correlation with the crystalline phases of hydride formation. However, the resonance frequency shifts and quasistatic bending are observed to be independent during the solid solution phase. Importantly, absorption-induced changes in the elastic parameters of the palladium film are found to play a dominant role in the static and dynamic response. The presented results help in discerning between changes in swelling and elastic modulus that control the cantilever response as well as the relationships between these parameters.

It is now well established that adsorption or absorption of atoms and molecules on a microfabricated cantilever oscillator results in a down-shift of its resonance frequency spectrum (ω_n, $n = 1, 2, \ldots$) and when the process is asymmetrically constrained, it deforms following quasi-static approximations. To optimize the deformation, a layer of a chemical or biological receptor is immobilized only on one of the surfaces of the cantilevers. The selective interface can be thin metal films, self-assembled monolayers, thin polymer films, or biomolecules. The resonance frequency shift $\delta\omega_n$ and cantilever bending δr originate from multiple effects that depend on the adsorbate-cantilever system [1,2]. For example, δr can originate from absorption-induced swelling of the interfacial film, free energy change [3], surface charge accumulation, alloy formation, changes in elastic parameters [4], and chemical bond formation [5]. On the other hand, $\delta\omega_n$ can originate from adsorbate mass loading, changes in dimensions, viscous effects, and changes in the elastic characteristics of the surface layer. Therefore, the exact reason for the cantilever response can be elaborate and case specific.

One outstanding question regarding the fundamental mechanism behind cantilever sensor signal generation is the controversial effect of surface stress. There exist many experimental results supporting as well as negating the role of surface stress variations in $\delta\omega_n$. Based on their simultaneous measurements of mercury vapor adsorption-induced static and dynamic sensor response, Chen *et al.* proposed variations in surface stress are manifested by $\delta\omega_n$ [6,7]. Recent investigation by Karabalin *et al.* [8] concluded a negligible effect of δr on $\delta\omega_n$, using cantilevers that were a few microns in length coated with piezoelectric material and their electrical potential-induced bending as the model system. Karabalin *et al.* report that unlike doubly clamped beams [9], cantilevers show negligible changes in resonance frequency, corresponding to part per million levels, as a function of stress.

In this paper, we investigate the relation between surface stress and $\delta\omega_n$. We select hydrogen (H) interaction with palladium (Pd) thin film deposited on a microcantilever [10–12] as a model system since the Pd-H hydride formation is a well-studied system with a well-established phase diagram [13]. Molecular H dissociates on the surface of Pd and diffuses into the system and it is well known that Pd films undergo large swelling due to H absorption

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resulting in very large δr. Another contributing factor is asymmetric swelling of the cantilever beam with respect to its neutral axis. A systematic study of simultaneous measurement of δr and $\delta\omega_n$ in vacuum conditions shows that unlike absorption on Pd in air, H absorption in vacuum conditions results in a large δr. This bending, which is 2 orders of magnitude larger than that observed in the ambient, introduces surface stresses that have not been previously reported. δr shows an excellent correlation with film swelling due to hydride formation, while $\delta\omega_n$ is governed by the changes in the Young's modulus E of Pd [14,15]. As pointed by Sader *et al.* [9,16], the current opinion appears to be divided over the question of the coupling between δr and $\delta\omega_n$. However, most experiments that deal with simultaneous measurements of δr and $\delta\omega_n$ are carried out in gases as the frequency measurements in liquids have poor resolution due to a much reduced Q factor.

In the case of adsorption of small molecules that do not form strong bonds with the monolayer-level chemical interfaces, δr and $\delta\omega_n$ follow each other. In such cases, $\delta\omega_n$ is attributed to mass loading while δr is assumed to be due to a differential surface stress when molecules interact preferentially only on one side of the cantilever. In these analyses, the bending stress and surface free energy changes are equated as in the case of the surface tension of liquids. In the case of chemisorption, relatively large δr is observed as compared to the case of physisorption, which could result in $\delta\omega_n$ [17,18]. For example, stretched strings vary their frequency depending on the stress in the string. It is also observed that microcantilevers coated with gold show dramatic differences in $\delta\omega_n$ when exposed to mercury vapor [19]. The frequency of such a system tends to increase, which is attributed to changes in elastic properties of the system. Since these experiments are carried out on surfaces exposed to the ambient airflow (or atmosphere), the surface condition cannot be ascertained. Early on, it has been speculated from mercury vapor adsorption studies that the force constant of the cantilever may vary due to stress generated from δr. To ascertain the effect of molecular adsorption and the relationship between δr and $\delta\omega_n$, we investigate the adsorption of H on Pd thin films coated on a microcantilever. From the linear formulation of the elastic deformation of a solid, $\delta\omega_n$ is a function of material density, geometric dimensions, and elastic parameters of the cantilever, all of which can be perturbed by atomic and molecular adsorption or absorption, resulting in a cantilever response. While the eigenfrequencies ω of the composite and multilayer cantilever with a stress tensor σ and displacement field $\bar{u}$ can be obtained computationally from Fourier transform of Cauchy equation

$$-\mu\omega^2\bar{u} - \bar{\nabla}\sigma = \bar{F}_\nu, \qquad (1)$$

as shown in Supplemental Material [20] for the behavior of the leading frequencies of the employed cantilever as

functions of the elastic properties, they can also be approximated (Euler-Bernoulli theory) as

$$\omega_n = \left[\frac{k}{\mu} + \frac{bh^3E}{12\mu}\left(\frac{\lambda_n}{l}\right)^4 - \left(\frac{\gamma}{2\mu}\right)^2\right]^{1/2}, \qquad n = 1, 2, ...,$$

$$(2)$$

where λ_n satisfy $1 + \cos\lambda\cosh\lambda = 0$ for a rectangular cantilever. Here μ is mass per unit length, l, b, and h denote cantilever length, width, and thickness, and γ and k model a viscoelastic (Kelvin-Voigt) dissipation. Formally, an equation for adsorption or absorption-induced spectral shifts is obtained by differentiating this equation. In the above equation, we do not consider the influence of large bending on ω_n, which can entail nonlinear or threshold effects. Unlike a string where tension is uniform across its cross section, a cantilever undergoing bending has both compressive and tensile stresses [6]. Therefore, it is possible that the effect of stress on ω_n may be negligible or even nonexistent.

Experimentally, we employ tipless rectangular silicon (Si) microcantilevers with dimensions $(l, b, h) = (250, 35, 1)$ μm vacuum evaporated with thin films of Pd of thickness $h_{Pd} = 10$, 30, 60 nm. Absorption measurements are carried out in high vacuum of 10^{-7} bar (see Supplemental Material [20]).

As implied by Eq. (2), while the mass dependence can implicitly involve the dissipative and elastic properties, the H has very low mass and therefore the effect of mass loading on $\delta\omega_n$ can be neglected within the experimental errors, that is, $m(t) = m(0) + m_H(t) \approx m(0)$, where $m(t)$ is the total sensor mass as a function of time t and m_H is the adsorbed H mass (for a fixed density, the frequency variation as a function of Young modulus and Poisson ratio is given in the Supplemental Material [20]). Assuming that both mass loading and transient thermal stress due to H adsorption are negligible, stress perturbations due to film swelling and changes in Young modulus due to chemical interactions yield a signal we intend to decipher. We begin by fitting a Lorentzian to the first resonance peak of the used cantilever and obtain a Q factor of 600, when measured in vacuum. Figure 1 shows the variation of the Q factor as a function of H partial pressure P_{H_2} as the Pd enters into the $\alpha + \beta$ phase. The inset shows the amplitude versus excitation frequency for four different P_{H_2}. A Q factor of 50 or lower observed at $P_{H_2} > 10^{-3}$ bar makes the frequency shift measurement less accurate at higher P_{H_2}. The three phases of the Pd-H system can be recognized by changes in the slope of δr as a function of P_{H_2}, as shown in Fig. 2. In the log-log plot, a linear behavior is observed in the α phase while response observed in the $\alpha + \beta$ phase is more complex. As can be seen, in the β phase, δr reaches a plateau. When δr and $\delta f_1 = \delta\omega_1/2\pi$ are measured simultaneously as a function of time under H exposure, α and initial stages of $\alpha + \beta$ phase formation can be discerned, as
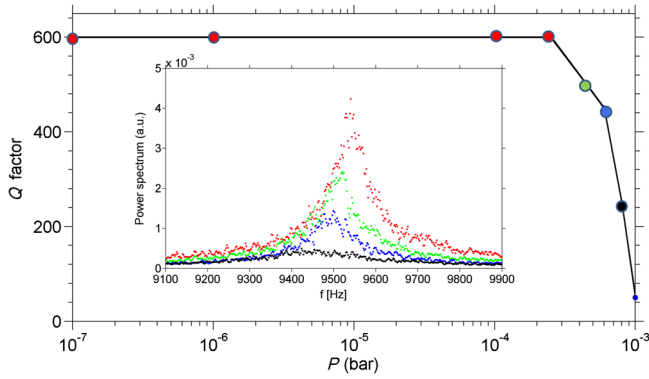
FIG. 1.   The quality factor Q of a Si cantilever with 30 nm Pd film on one side, as a function of P_{H_2}. The inset shows resonance amplitudes of the Pd-Si cantilever for three $P_{H_2} = 2$, 4, and 8×10^{-4} bar. Above pressures 10^{-3} bar, the Q factor is too low for accurate measurements.
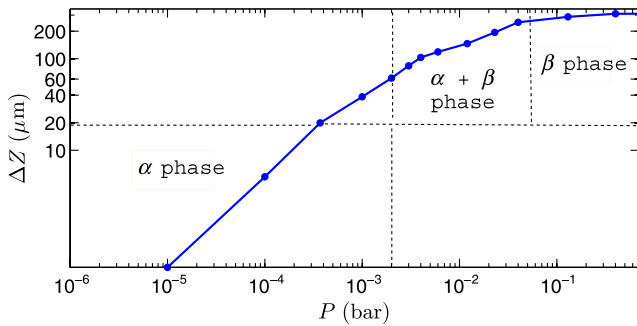

FIG. 2.   The bending response δr of the Si-Pd cantilever as a function of P_{H_2}. In the log-log plot, the bending is linear for α until the beginning of the $\alpha + \beta$ phase. In the β phase the bending does not change appreciably.

shown in Fig. 3. While the cantilever deforms as the α phase of the Pd-H starts to form, $\delta\omega_1$ does not exhibit any changes. The slope of δr is unaffected as the Pd-H system enters the $\alpha + \beta$ phase. However, $\delta\omega_1$ shows a dramatic
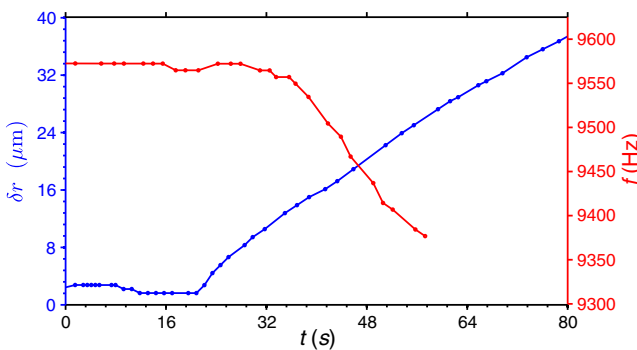

FIG. 3.   Simultaneous measurement of cantilever bending and resonance frequency shift during H absorption as a function of time. The resonance frequency variation f lags behind the bending response. The resonance frequency of the cantilever does not show a response until a P_{H_2} of 10^{-3} bar.
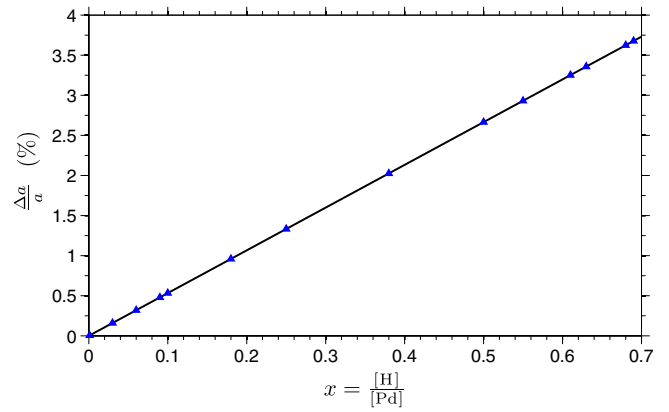

FIG. 4.   Film swelling as a function of the [H]/[Pd] ratio. In the α phase there is only a small swelling, less than 0.1% up to $P_{H_2} < 10^{-3}$ bar. In the β phase the Pd swelling is around 10%.

decrease as the system enters the $\alpha + \beta$ phase. From these results, it is clear that δr and $\delta\omega_1$ are not in phase. Furthermore, Fig. 4 shows a linear variation in swelling as a function of the stoichiometry $x = [\text{H}]/[\text{Pd}]$. Figure 5(a) shows the changes in E_{Pd}, as a function of P_{H_2}, which as seen from Fig. 5(b), is in accordance with $\delta\omega_1$. However, below certain P_{H_2}, the loss of Q factor prevents accurate measurements of $\delta\omega_1$.

The Pd-H system undergoes two crystalline phases depending on P_{H_2} at the ambient temperature. For low concentrations of H when the system remains in the α phase, no crystallographic changes are expected. In this phase H atoms are in a solid solution and diffuse from site to site without affecting the electronic structure of neighboring Pd atoms. This process results in swelling of the Pd films where the Pd lattice constant a increases from $a_0 = 0.3889$ to 0.3895 nm. At higher stoichiometry x (> 0.015), the Pd hydride constitutes of coexisting α and β phases. The α phase progressively disappears in favor of the β phase as
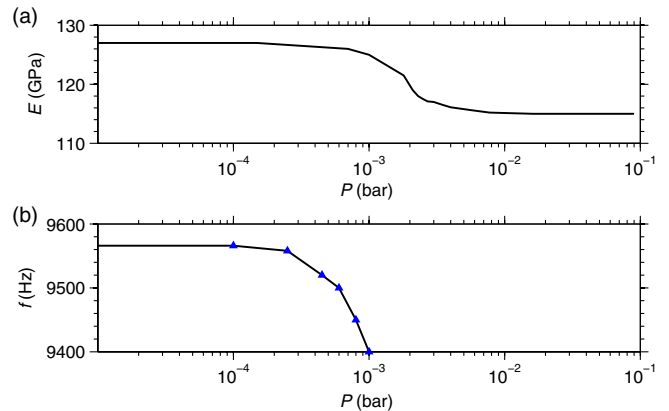

FIG. 5.   (a) Young's modulus of the Si-Pd cantilever as a function of P_{H_2}. (b) The frequency response as a function of P_{H_2}. The frequency changes follow changes in Young's modulus. The Young's modulus variation occurs in the $\alpha + \beta$ phase.

a function of P_{H_2}. In the β phase, the lattice constant remains fixed at 0.4029 nm. The H atoms form metallic bond with the Pd atoms in the β phase. The Young modulus of the β phase is very different from the α phase (127 GPa). The drop of the Q factor as the Pd-H system enters the $\alpha + \beta$ phase is due to the decrease in E_{Pd} by 10 GPa. The resonance response also shows a drastic change during this transition. Since the Q factor is related to internal energy losses, formation of nucleation centers of the β phase may increase the internal friction. Such nucleation centers increase in size and finally the entire Pd is converted into the β phase.

The linear δr observed at low P_{H_2} is consistent with linear swelling. In the $\alpha + \beta$ phase δr increases by a factor of 100 or more due to the β phase formation, while it is not very significant in the β phase. As seen from Fig. 4, the swelling is linear up to $x = 0.7$ (start of β branch). E_{Pd} begins to decrease in the $\alpha + \beta$ phase. Since the stress in the film is the product of E_{Pd} and strain, δr follows the stoichiometry response with P_{H_2} (see Supplemental Material S1 [20]).

In the α phase δr and $\delta \omega_1$ do not show any correlation. Since the mass of adsorbed H is negligible, $\delta \omega_1$ can be attributed to variation in E_{Pd}. The behavior of $\delta \omega_1$ with P_{H_2} shown in Fig. 3 strongly suggests that δr and $\delta \omega_1$ originate from two different processes. $\delta \omega_1$ is not correlated directly to the film stress. Figure 3 shows that δr reaches a value of 10 μm when $\delta \omega_1$ starts to show a change. However, $\delta \omega_1$ correlates well with changes in E_{Pd}. The frequency variation calculated from Young modulus variation agrees very well with the measured frequency shift calculated using changes in the Young modulus. This basically shows that δr does not influence $\delta \omega_1$. It is noteworthy that the corresponding change in resonance frequency due to swelling can be written as

$$\frac{\delta \omega}{\omega_0} \approx \frac{\delta h_{Pd}}{h_{Pd}} + 2 \frac{\delta l}{l}. \tag{3}$$

However, in the α phase, $\delta l/l$ and $\delta h_{Pd}/h_{Pd}$ are around 0.1% and therefore do not affect $\delta \omega_1$. On the other hand, $\delta \omega_1$ is significantly influenced by changes in elasticity. For a bimaterial cantilever, $\omega = \omega_0 + \delta \omega$ is given by

$$\frac{\delta \omega}{\omega_0} = \frac{k_1}{k_2 k_3}, \tag{4}$$

where ω_0 is the fundamental uncoated cantilever resonance measured under vacuum, and

$$k_1 = 3 \frac{E_{Pd}}{E_{Si}}, \tag{5}$$

$$k_2 = \frac{\rho_{Pd}}{\rho_{Si}} + 2 \frac{t_{Pd}}{t_{Si}}, \tag{6}$$

with $\rho_{Pd} = 12.020 \text{ g cm}^{-3}$ and $\rho_{Si} = 2.3310 \text{ g cm}^{-3}$ being the mass density of Pd and Si, and

$$k_3 = \frac{1 - \nu_{Pd}^2}{1 + \nu_{Si}^2 - 2\nu_{Si}\nu_{Pd}}, \tag{7}$$

with $\nu_{Pd} = 0.39$ and $\nu_{Si} = 0.42$ being the Poisson ratios of Pd and Si, respectively. Typically, when the stoichiometry $x < 0.2$, no change in E_{Pd} occurs and with just the swelling (term k_2) considered, the changes $\delta \omega$ are negligible. When $P_{H_2} > 10^{-4}$ bar, E_{Pd} begins to decrease from 127 to 122 GPa at $P_{H_2} = 10^{-3}$ bar. At this point, $\delta \omega/\omega_0 = -4\%$ as observed in the experiments. Therefore, for the Pd-H system, the bending varies almost linearly with P_{H_2} in the α phase due to swelling. We can attribute the linear response as being due to film swelling. The change in film stress is given mostly by the product of E_{Pd} and the swelling $\delta a/a_0$. At the end of the α phase, $E_{Pd} = 127$ GPa is almost unchanged and the swelling $\delta a/a_0 = 0.1\%$.

The swelling-induced δr does not influence ω_1, which is drastically influenced by the formation of the β phase in the Pd-H system leading to changes in E_{Pd}. In the α phase, δr exhibits a linear behavior due to swelling of the film, but does not show any shift in ω_1. In the β phase, where E_{Pd} experiences a large change, no appreciable δr is observed. In the $\alpha + \beta$ phase both δr and ω_1 undergo drastic changes. This trend basically demonstrates that changes in E_{Pd} play a major role in absorption-induced δ_r and ω_1. Swelling of the Pd film has no effect on ω_1, while δ_r exhibits a linear dependence. These results illustrate the variation in E_{Pd} to have a dominant effect on δ_r and ω_1. These findings provide the fundamental mechanism in the adsorption-induced cantilever response. Much of the previously reported results can now be explained. For example, large δr and ω_1 (an increase) are reported for Hg adsorption on gold-coated cantilevers. The observed increase in ω_1 can be explained as being due to an increase in the Young's modulus due to Hg-Au alloy formation. Another example of ω_1 variation observed with ionic concentration can be explained as being due to changes in the double layer thickness due to the increased ionic concentration. In the liquid, many layers adjacent to the cantilever act as a part of the cantilever.

In conclusion, our H-Pd adsorption experiments reveal that the cantilever bending response can be deciphered into three different regimes depending upon whether the hydrogen diffuses in the α phase or it forms metallic bound with the Pd matrix in the β phase. Whereas a linear behavior with very small slope is observed in the α phase, the bending showed an exponential change in the $\alpha + \beta$ phase with no significant change in the β phase. However, simultaneous spectral measurements show that the resonance frequency is unaffected by the bending (and swelling) in the α phase. On the contrary, the resonance

frequency variation is found to undergo a dramatic decrease in the mixed $\alpha + \beta$ phase following the changes in the Young's modulus of palladium. These conclusions clearly suggest that other mechanisms than the adsorption on self-assembled monolayers immobilized on cantilevers must be sought when no dependence between the cantilever resonance frequency and bending is observed. Similar frequency shifts have been observed for explosive detection, but also in the case of adsorption in ionic solutions or in electrochemical conditions, where induced surface charges may stiffen the cantilever. These findings are of relevance in areas such as gas detection, where gas absorption leads to polymer swelling, but also—and possibly even more relevant—in biological systems, where molecular adsorption-induced swelling is expected.

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