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Supporting Information

Frequency shift caused by hydrogen

The resonant frequency of a clamped-clamped beam is given by:

$$f_{res} \approx \frac{1}{2\pi} \sqrt{500 \frac{\langle EI \rangle}{\langle \rho A \rangle} \frac{1}{L^4} + 12.3 \frac{\langle \sigma A \rangle}{\langle \rho A \rangle} \frac{1}{L^2}}$$
(S1)

Where $\langle EI \rangle$ is the beam bending stiffness, $\langle \rho A \rangle$ is the mass per unit length, *L* is the length, and $\langle \sigma A \rangle$ is the longitudinal tensional force. Eq. (S1) is only valid when the second term inside the square root is much smaller than the first term. For simplicity, we will consider now the case of a monomaterial beam made out of Pd, in which case Eq. (S1) can be expressed as:

$$f_{res} \approx \frac{1}{2\pi} \sqrt{42 \frac{E_{Pd}}{\rho_{Pd}} \frac{t^2}{L^4} + 12.3 \frac{\sigma}{\rho_{Pd}} \frac{1}{L^2}}$$
 (S2)

When hydrogen diffuses into Pd, two different effects are attained: mass loading and expansion. It is possible to write the relative change in resonant frequency as:

$$\frac{\Delta f}{f_{res}} \approx -\frac{1}{2}\frac{\Delta m}{m} + \frac{1}{2}\frac{\Delta V}{V} + \frac{\Delta t}{t} - 0.1475\frac{\sigma}{E}\left(\frac{L}{t}\right)^2$$
(S3)

Where *m* is the mass of the unit cell in the crystallographic structure of Pd or PdH_x, *V* is the volume of such unit cell, and *t* is the thickness of the beam. The first term, when Pd is saturated with hydrogen (atomic ratio close to 1:1) is about $1/210 \approx 0.5\%$. The other three terms depend on the expansion coefficient of Pd, $\varepsilon \approx \alpha [H]^{1/2}$, which is about 1-3% depending on the Pd phase.

$$\frac{1}{2}\frac{\Delta V}{V} + \frac{\Delta t}{t} - 0.1475\frac{\sigma}{E}\left(\frac{L}{t}\right)^2 \approx \varepsilon \left(2(1-\nu) - 0.1475\left(\frac{L}{t}\right)^2\right)$$
(S4)

Finally, considering that $L \gg t$, we can transform Eq. (S3) into Eq. (1) of the paper:

$$\frac{\Delta f}{f_{res}} \approx -\frac{1}{2}\frac{\Delta m}{m} + \varepsilon \left(2(1-\nu) - 0.1475\left(\frac{L}{t}\right)^2\right) \approx -0.1475\frac{\sigma}{E}\left(\frac{L}{t}\right)^2 \tag{S5}$$

Priming effect

Figure S1 shows some typical results of how the resonant frequency changes as the device is exposed to 4% H_2 in 15 s intervals. A priming effect can be observed, featuring a growing response during the first and second exposures and thereafter being very stable. In the particular case of the experiments illustrated in Figure S1, the H_2 diffuses out of the chamber without purging, making the gas exchange the dominant limiter of the recovery time, defined as the time from the end of the exposure until 90% resonant frequency recovery.



Figure S1. Repeatability test. The test chamber is flushed with 4 % H_2 in 15 s intervals. The response is highly repeatable. The anomaly seen in the first and second response is believed to be caused by oxide that is initially present on the Pd film.

Recovery time

As seen in Figure S2, showing the first exposure, the mechanical response, manifested as a drop in resonant frequency, commences simultaneously with the onset of H_2 . The recovery can be fitted to the following exponential decay:

$$f_{res} \propto -1.05 \ e^{-t/45}$$

giving a decay rate of $\tau \approx 45 \pm 5 s$.



Figure S2. Recovery time. When N_2 is flushed into the chamber, the frequency of the device follows an exponential decay.

Thermal simulations

To know the temperature of the beam during the heating experiment, an equivalent simulation model was built using COMSOL 4.2a. The model featured a freestanding structure of three layers: 750 nm of a-Si, 30 nm of Au and 30 nm of Pd. A steady state solver was used. All material properties were retrieved from the material library, and are specified in Table S1. Figure S3 shows the temperature distribution as a current of 3 mA runs through the beam. The maximum temperature elevation is ΔT =4.17 K in the center of the beam. The temperature is significantly lower in the non-free standing part due to the heat dissipation into the underlying silica and, more importantly, the proximity to the highly thermally conductive gold electrodes. The simulation was repeated for several different currents. For each of those, the maximum temperature elevation attained in the volume of the beam was extracted from each solution. The result is presented in Figure S4.



Figure S3. Temperature profile along the length of the beam. The scale bar marks the 30 μ m free-standing beam, with a 500 nm gap to the underlying silica substrate. The maximum temperature corresponds to an elevation of Δ T=4.17 K compared to the boundary surfaces.



Figure S4. The maximum temperature elevation attained at different currents. The simulation was repeated for different currents. Each time, the maximum was extracted from a steady-state solution.

Table S1. Material properties for Simulation
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Material	Thermal expansion coeff.	Young's modulus [GPa]	Poisson ratio	Stress change at ∆T=4.17 K [MPa]
a-Si	2.6E-6	80	0.22	1.11
Pd	11.8E-6	121	0.39	9.76
Au	14.2E-6	79	0.44	8.35

RH effect on resonant frequency

Figure S5 illustrates a measurement of the resonant frequency as the relative humidity (RH) changes from dry air to saturated air. Each increasing step represents a rise of 50 % in relative humidity. Indeed a decrease of resonant frequency is observed of, at most, 5 %. This is thus more or less comparable to the response obtained after a 60 s exposure to 0.5 % H₂. This effect is in general negligible compared to the effect of hydrogen and, in addition, could be considered as a background from where the hydrogen affects the beam.



Figure S5. The device resonant frequency at different relative humidities. The full range from dry air to saturated air is tested.

Estimation of frequency stability

As discussed in the main manuscript, the frequency stability of the resonator determines the final resolution of a resonant sensor. The way this measurement is usually performed is by calculating the Allan Deviation of the closed-loop system. However, in our experiments we did not build any closed loop. Therefore the measure we used for the frequency stability was the RMS of the measured frequency in the open loop system. Different results were obtained depending on the conditions at which this frequency was measured. For illustration purposes, we show here two representative cases in Figure S6. Figure S6.a corresponds to the first 2 minutes in Fig. S5. In that case, the system is undergoing measurements with respect to humidity and the RMS is $\approx 1.2 \cdot 10^{-3}$. Figure S6.b, however, shows a measurement where the system was exposed to different flows of nitrogen, and we can observe that for short time scales, the RMS is $\approx 0.4 \cdot 10^{-3}$, whereas for long time scales (accounting for the drift) is $\approx 0.7 \cdot 10^{-3}$. Considering this, we selected the higher RMS as the limitation for our frequency stability, and considered that deviations larger than 2σ could be taken as valid measurements. That is why the value 0.0025 is used in the main manuscript as the minimum detectable change in frequency.



Figure S6. Frequency stability. Frequency tracking versus time for (a) a case when the system is undergoing measurements versus RH and (b) when the system is studied versus different nitrogen flows.

T effect on response time

The response time follows an Arrhenius dependence with the temperature:

$$\tau(T) = \tau_0 e^{-\frac{E_a}{RT}}$$
(S6)

which means that by fitting $\ln(\tau)$ to $\frac{1}{T}$, it is possible to extract the activation energy of the adsorption process, which is about 28 kcal/mol. This value is higher than the values reported elsewhere and this difference will be further investigated in the future. No strong conclusions can be drawn of this fact because only three different values of T were sampled. The fitting is presented in Figure S7.



Figure S7. Response time versus temperature. Arrhenius plot of the response time versus the inverse of the beam temperature.