Supporting Information

Pd-Functionalized ZnO:Eu Columnar Films for Room Temperature Hydrogen Gas Sensing: A Combined Experimental and Computational Approach

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Supporting Information Text S1

The overview spectra corresponding to ZnO:Eu columnar thin films with increased Eu-doping concentration are shown in **Figure S1a**. For both spectra the presence of Zn, Eu, O and C is clearly observed and the direct comparison indicates that the signal corresponding to Eu is stronger for the ZnO:Eu(4) thin film (blue line, top) than the ZnO:Eu(2) thin film (red line, bottom). The signal corresponding to Zn, Eu and O is attributed to the thin film while the signal of C originates from surface adsorbates such as atmospheric carbohydrates. For a more detailed comparison of the two ZnO:Eu thin films, the C-1s, Eu-3d and Zn-2p lines are depicted in **Figure S1b**. The different level of doping reflects on the europium signal and accordingly the corresponding Eu-3d lines are more pronounced for the ZnO:Eu(4) thin film than for the ZnO:Eu(2) thin film. However, the peak position of the Eu-3$d_{5/2}$ and Eu-3$d_{3/2}$ lines are identical for both thin films. The location of the Eu-3$d_{5/2}$ line centred around 1134.6 eV corresponds well with Eu^{3+} in Eu_2O_3 [1]. In contrast, for metallic Eu a peak located around 1126 eV is typically reported [2]. Accordingly, in the europium doped ZnO thin films the Eu is most likely present as Eu^{3+} like in Eu_2O_3. The closer evaluation of the Zn-2p lines yields information about the oxidation state of Zn in the ZnO:Eu thin films. For both thin films, the Zn-2$p_{3/2}$ line is located with a peak around 1021.7 eV, which corresponds well with Zn^{2+} in ZnO (commonly reported between 1021.40 eV and 1022.50 eV) [1].

In order to indicate the doping level in both thin films with increased Eu-doping, an exemplary quantification was conducted. The quantification of the europium doped ZnO thin films was performed based on the Zn-2p and Eu-3d lines (see **Figure S1b**) for the sample ZnO:Eu(4) and ZnO:Eu(2). The Eu/Zn ratio in this XPS spectra quantification is roughly 1.11 and 0.67 respectively, which in turn corresponds to a Eu- doping surface concentration of about 53 % in case of ZnO:Eu(4) and 40 % in case of ZnO:Eu(2). Some details on sample SCS preparation can be found in other work too [3-4].

Supporting Information Text S2

After surface relaxation, the top and bottom surfaces were not equivalent and therefore we also needed to consider the unrelaxed surface energy (γ_u) in order to calculate the final surface energy of the relaxed surface. The unrelaxed surface energy is defined as the surface energy before any surface optimization and is calculated as:

$$\gamma_u = \frac{E_{slab,u} - nE_{bulk}}{2A} \tag{1}$$

where $E_{slab,u}$ is the energy of the unrelaxed slab, nE_{bulk} is the energy of an equal number of bulk atoms, and A is the surface area of one side of the slab. Using this value, it is then possible to calculate the relaxed surface energy (γ_r) from the total energy of the relaxed slab.

The relaxed surface energy, γ_r, is given by:

$$\gamma_r = E_{slab,r} - nE_{bulk} - \gamma_u \tag{2}$$

where $E_{slab,r}$ is the energy of the relaxed slab.

Bader charges were calculated using a developed by Henkelman and co-workers [5-6].

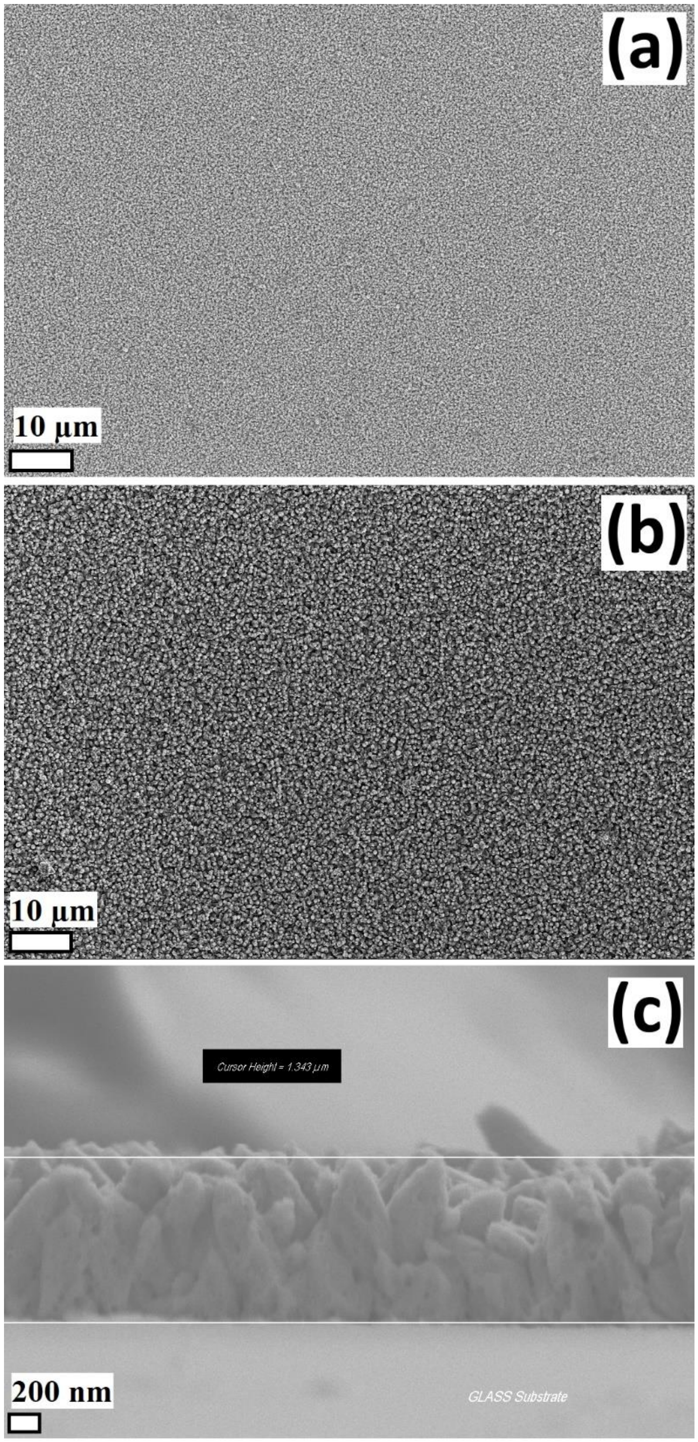
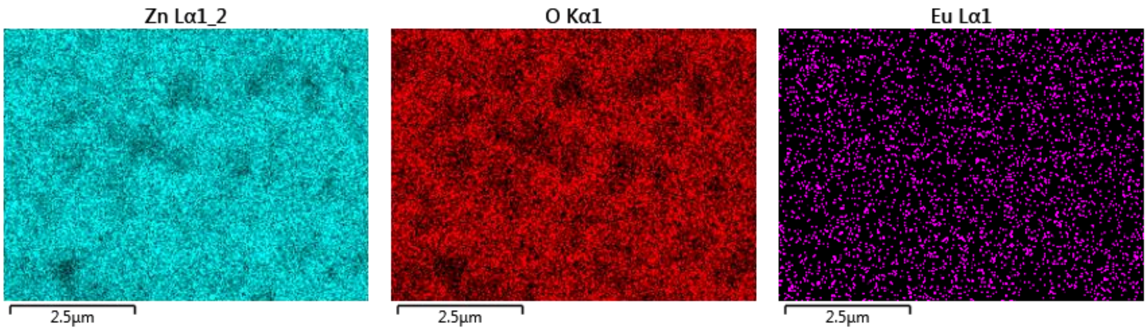
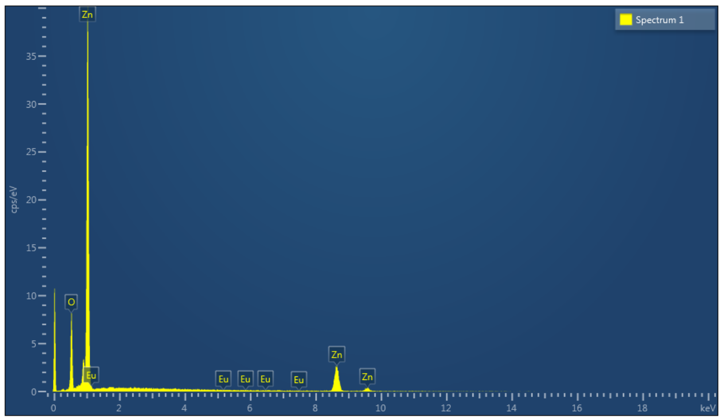


Figure S1. SEM images of ZnO:Eu films thermal annealed at: (a) 650 ºC for 2 h, with about 0.1 at. % Eu; (b) 650 ºC for 2 h with about 0.15 at% Eu and Pd-functionalized; (c) 650 ºC for 2 h with about 0.2 at. % Eu in sectional-view showing a thickness of about 1.35 µm.





Sample ZnO:Eu2T650C

Result Type	Atomic %

Spectrum Label	Spectrum 1
O	49.30
Zn	50.60
Eu	0.10
Total	100.00

Statistics	O	Zn	Eu
Max	49.30	50.60	0.10
Min	49.30	50.60	0.10
Average	49.30	50.60	0.10
Standard Deviation	0.00	0.00	0.00

Figure S2. Compositional images taken by EDX elemental mapping at the microstructural level of columnar ZnO:Eu2 films thermal annealed at 650 ºC for 2 h, with about 0.1 at. % Eu and EDX spectra below, respectively.

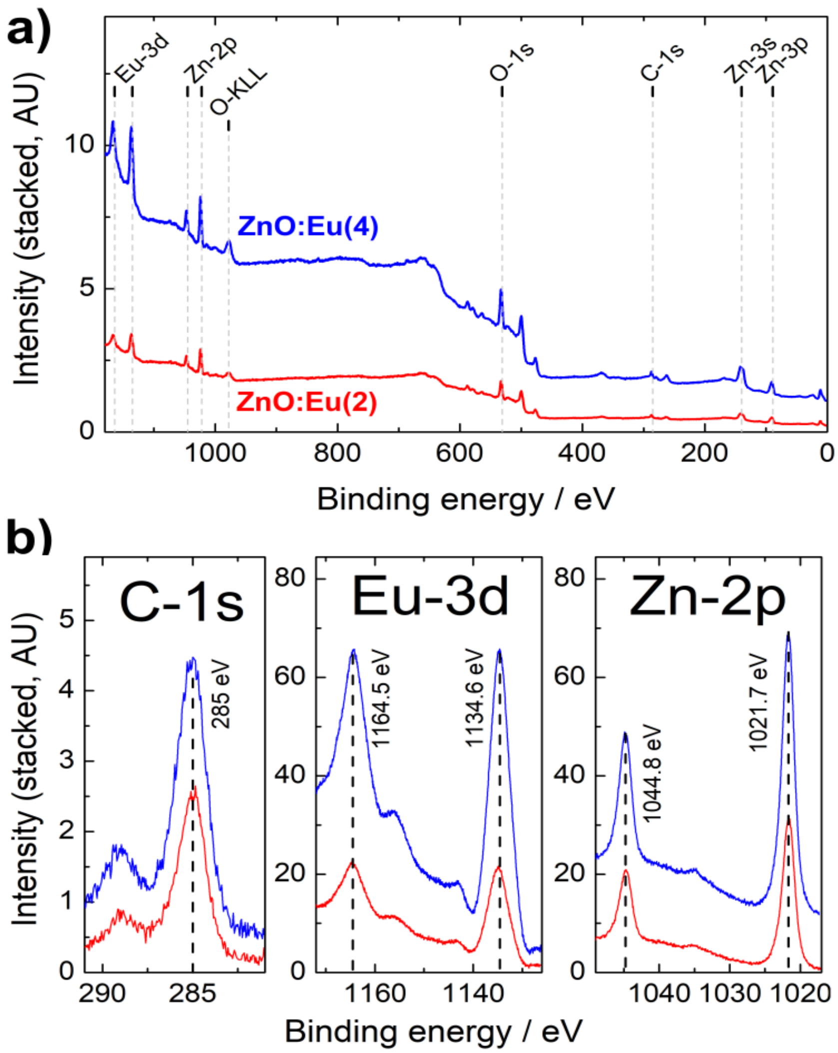


Figure S3. XPS spectra of ZnO:Eu columnar thin films with different doping concentrations. The overview spectra (a) reveal the presence of Eu, Zn, O and C for both ZnO:Eu thin films. The high resolution spectra (b) of the C-1s line, Eu-3d lines and Zn-2p lines indicate that there is no difference in peak positions between both samples. The peak location of Eu-3d and Zn-2p lines correspond to Eu^{3+} in Eu_2O_3 and Zn^{2+} in ZnO respectively.

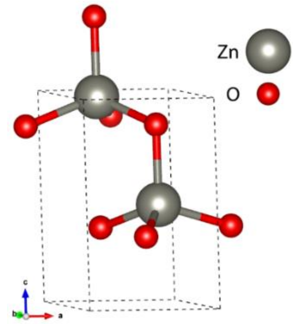


Figure S4. Bulk structure of ZnO.

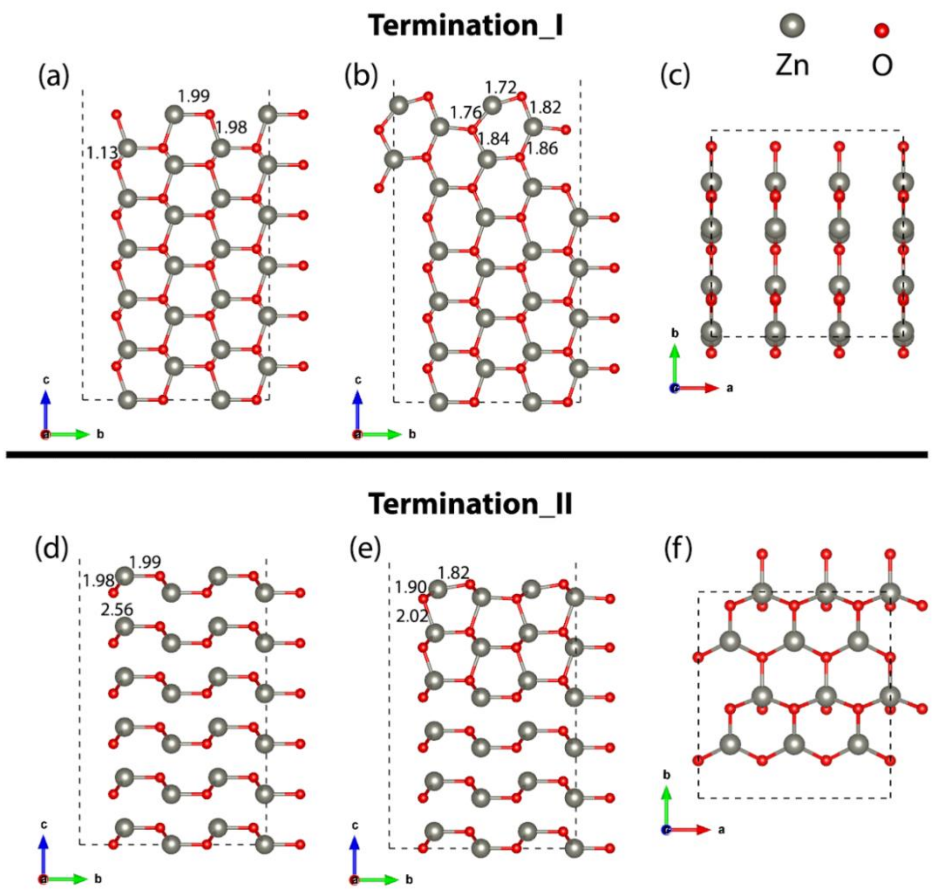


Figure S5. Two possible ZnO (1 0 $\bar{1}$ 0) surface terminations. (a, b, and c): Termination_I (side view of un-relaxed structure, side view of relaxed structure, and top view of relaxed structure. (d, e, and f): Termination_II (side view of un-relaxed structure, side view of relaxed structure, and top view of relaxed structure.

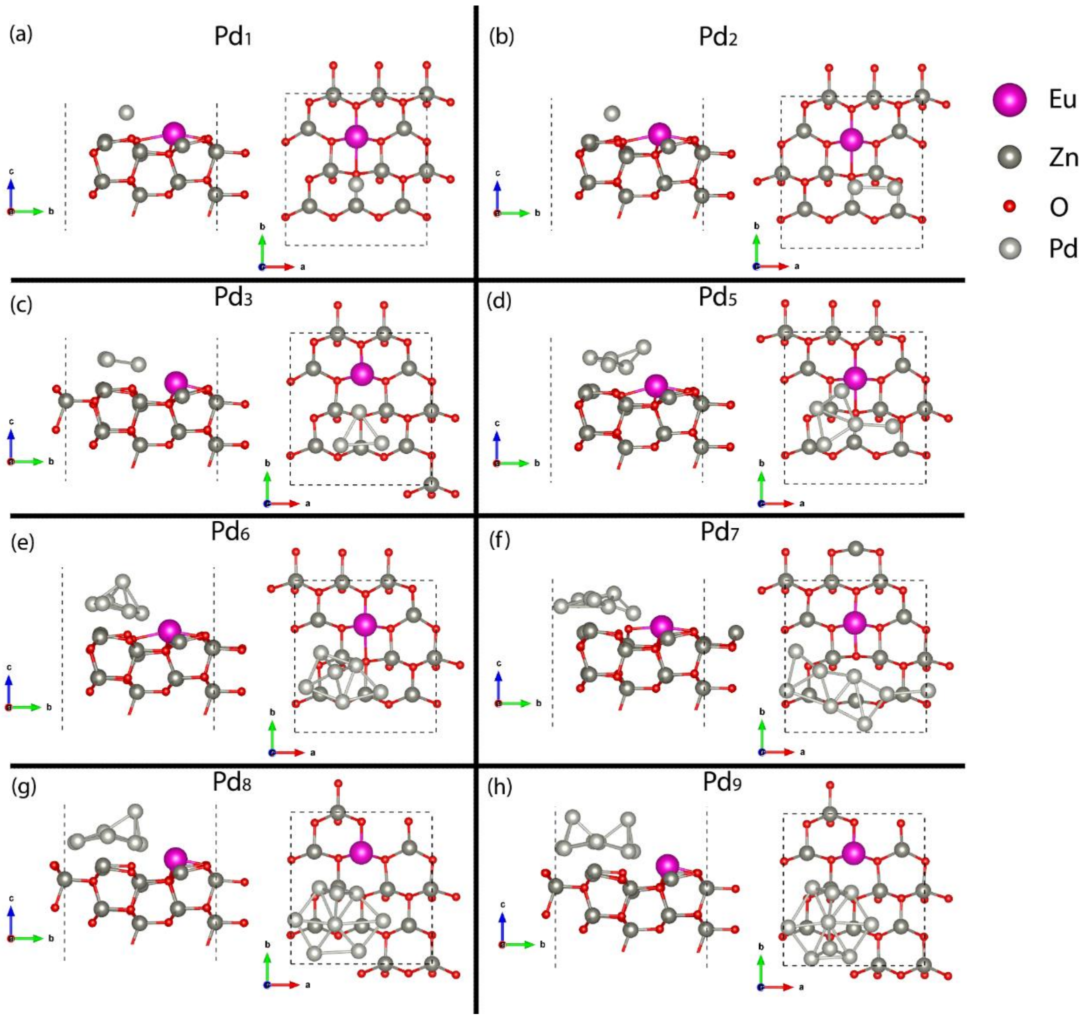


Figure S6. Top and side views of Pd_n (n=1 to 9] clusters adsorbed on Eu:ZnO($10\overline{1}0$) surface: (a, b, c, d): Pd_1, Pd_2, Pd_3 and Pd_5 cluster over Eu:ZnO($10\overline{1}0$) surface. (e, f, g, h): Pd_5, Pd_6, Pd_7, Pd_8, and Pd_9 cluster over Eu:ZnO($10\overline{1}0$) surface.

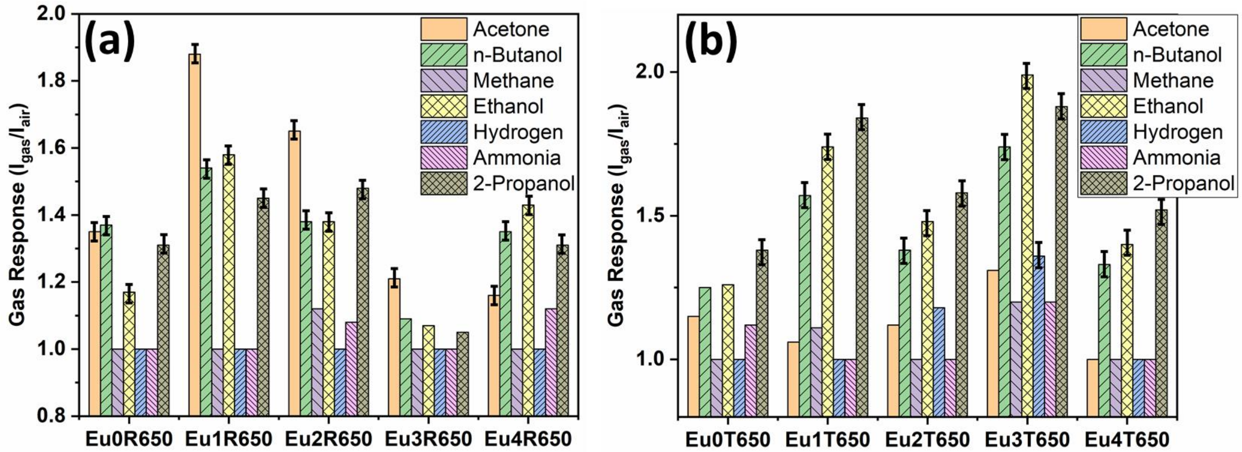


Figure S7. The gas response of pristine ZnO:Eu columnar films with different content of Eu (0.00 at. % Eu – Eu0; ~0.05 at. % Eu – Eu1; ~0.10 at. % Eu – Eu2; ~0.15 at. % Eu – Eu3 and ~0.20 at. % Eu – Eu4) to 100 ppm of different gases at operating temperature of 350 ºC: (a) samples RTA-treated at 650 ºC for 60 s; and (b) samples TA-treated at 650 ºC for 2 h.

Figure S7a presents the gas response of pristine ZnO:Eu columnar films RTA-treated at 650 ºC for 60 s and with different content of Eu (0.00 at. % Eu noted as Eu0; ~0.05 at. % Eu noted as Eu1; ~0.10 at. % Eu noted as Eu2; ~0.15 at. % Eu noted as Eu3 and ~0.20 at. % Eu noted as Eu4) to 100 ppm of different gases at operating temperature of 350 ºC. **Figure S7**b presents the gas response of sample sets with different content of Eu as noted above, but TA-treated at 650 ºC for 2 h. It can be clearly seen that at higher operating temperature (350 ºC) both types of annealed sample sets do not show selectivity and proves that sensor function is perfect at 350 ºC.

Figure S8 shows dynamic response of Pd-functionalized ZnO:Eu columnar films for 100, 200 and 300 ppm of hydrogen measured at room temperature. It clearly proves that by Eu-doping of columnar ZnO films followed by Pd-functionalization it is possible to decrease the operating temperature of the sensing material versus H_2 gas.

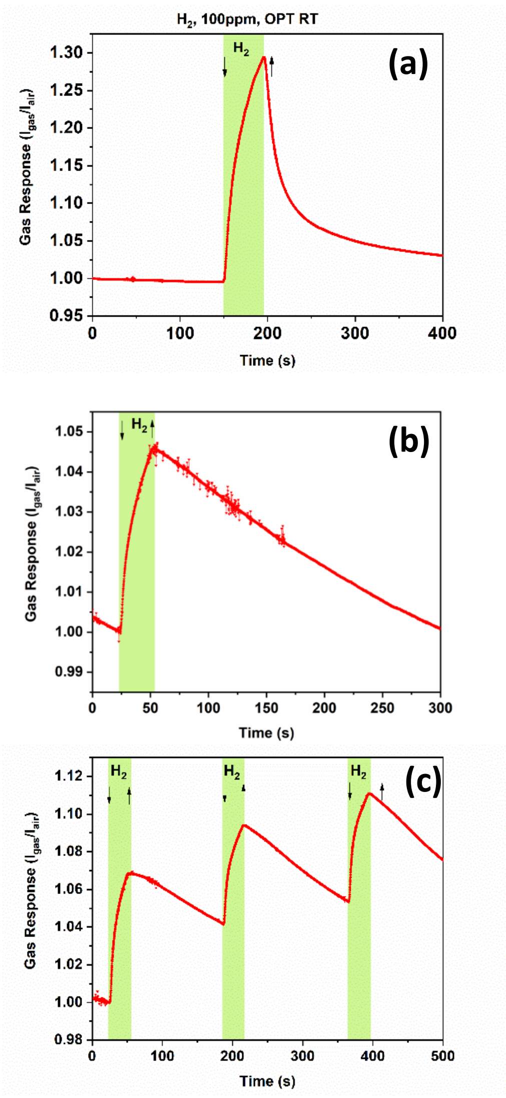


Figure S8. Dynamic response of Pd-functionalized ZnO:Eu columnar films for: (a) 100 ppm of hydrogen measured at room temperature; (b) 200 ppm of hydrogen measured at room temperature, sample with 0.05 at. % Eu subjected to TA550, sample set Eu1T550; (c) 300 ppm of hydrogen measured at room temperature, sample with 0.1 at. % Eu after TA550.

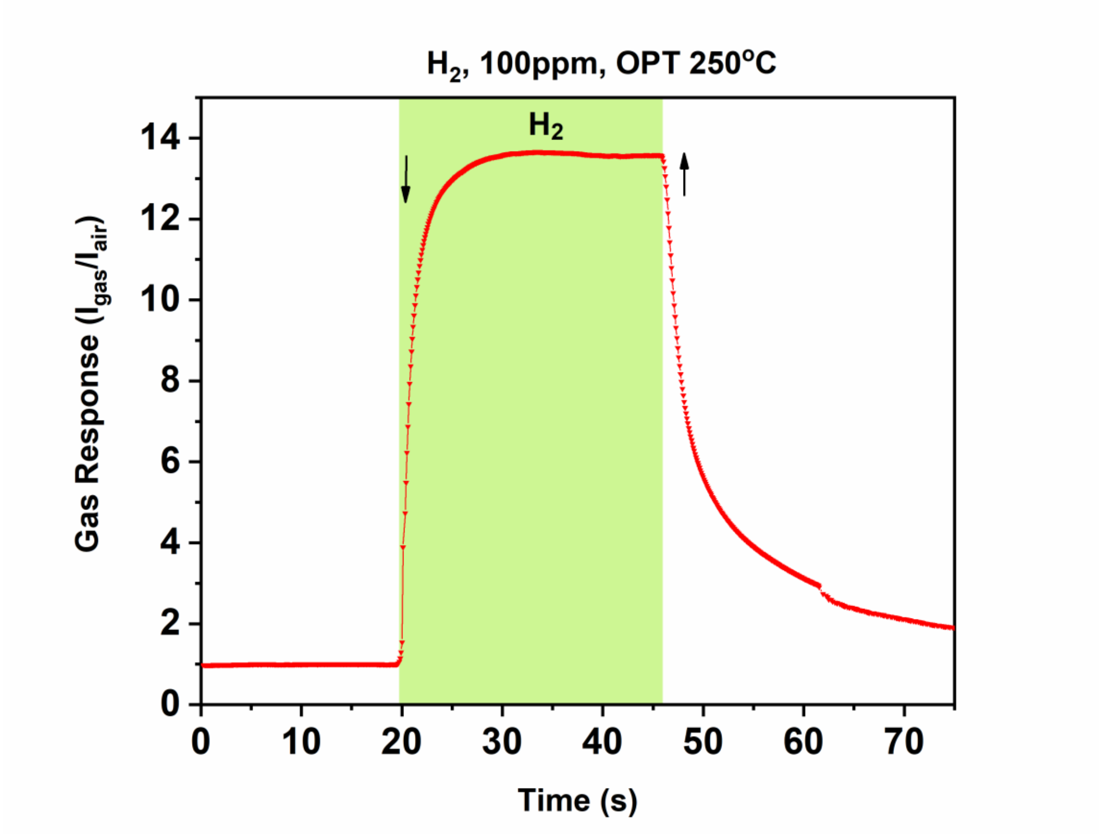


Figure S9. Dynamic response of ZnO with about 0.05 at. % Eu – Eu1T650; Pd-functionalized columnar films for 100 ppm of hydrogen gas at operating temperature of 250 ºC.

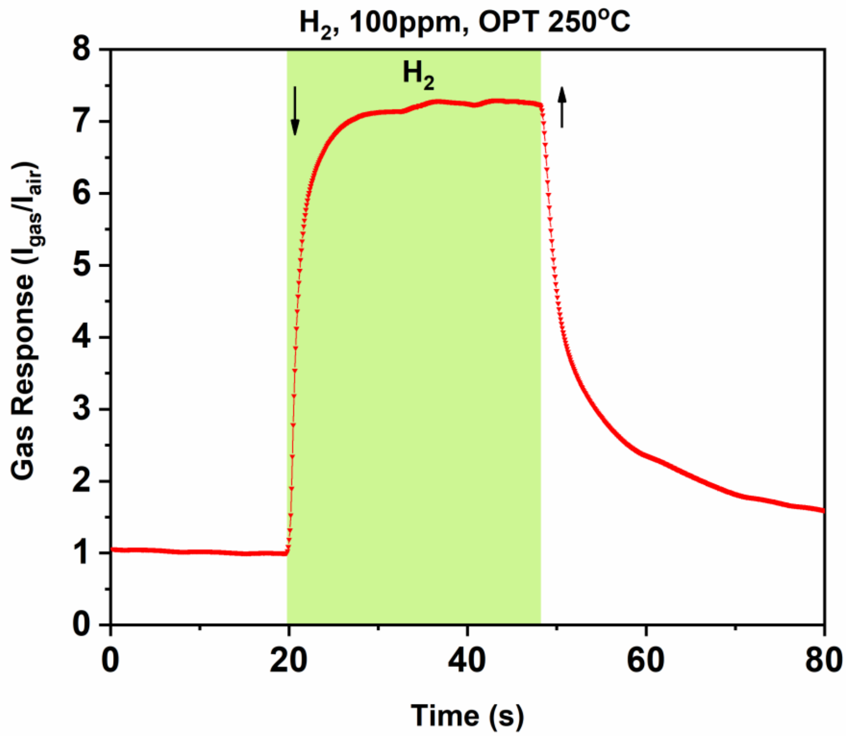


Figure S10. Dynamic response of ZnO:Eu with about 0.2 at. % Eu –Eu4T650; Pd-functionalized columnar films for 100 ppm of hydrogen gas at operating temperature of 250 ºC.

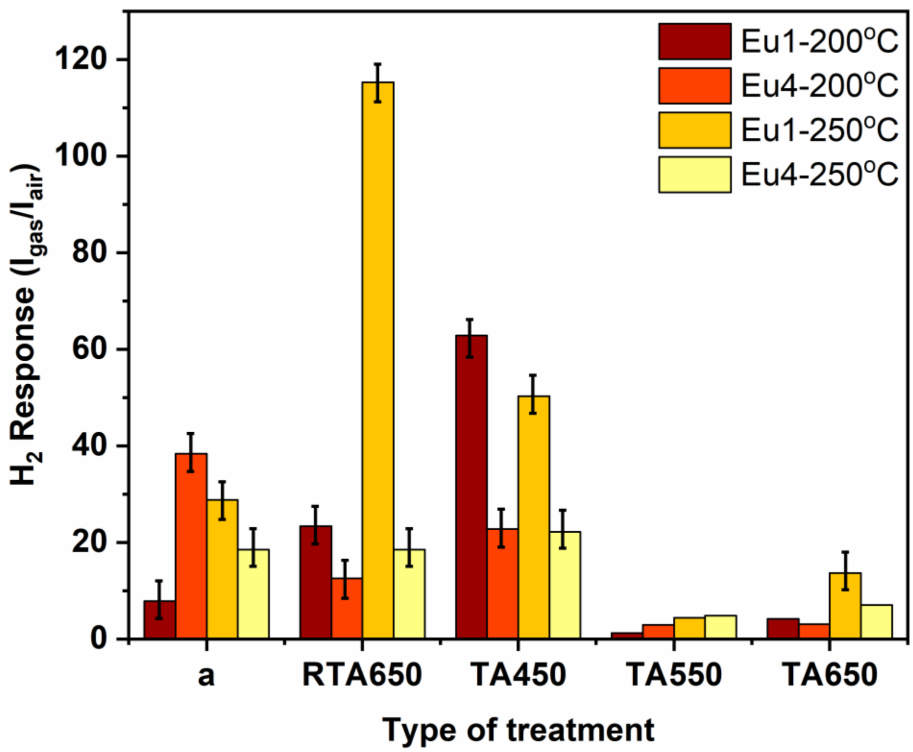


Figure S11. Response of Pd-functionalized ZnO:Eu columnar films to 100 ppm hydrogen versus treatment type (TA or RTA), noted as Eu1(~0.05 at. % Eu), Eu4(~0.2 at. % Eu) at operating temperatures of 200 °C and 250 °C. Type of treatment: **a** - as grown; RTA650-rapid thermal annealing; TA450,TA550,TA650 - thermal annealing at 450, 550, 650 °C, respectively.

Table S1. Calculated adsorption energies (E_{ads}) (in eV), shortest Pd-Zn (d_{Zn}^{s}) and Pd-O (d_{O}^{s}) distances (in Å) of the Pd_n cluster with the first atomic layer of the ZnO slab for different Pd_n/ZnO ($10\overline{1}0$) systems.

	Pd_1	Pd_2	Pd_3	Pd_5	Pd_6	Pd_7	Pd_8	Pd_9
E_{ads}	-1.65	-2.89	-5.35	-6.97	-7.05	-6.98	-7.83	-8.15
d_{Zn}^{s}	2.533	2.542	2.657	2.543	2.627	2.641	2.679	2.635
d_{O}^{s}	2.149	2.168	2.218	2.101	2.109	2.101	2.063	2.061

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