Single-Crystal Pt-Decorated WO₃ Ultrathin Films: A Platform for Sub-ppm Hydrogen Sensing at Room Temperature

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**Supporting Information

ABSTRACT: Hydrogen-related technologies are rapidly developing, driven by the necessity of efficient and high-density energy storage. This poses new challenges to the detection of dangerous gases, in particular the realization of cheap, sensitive, and fast hydrogen sensors. Several materials are being studied for this application, but most present critical bottlenecks, such as high operational temperature, low sensitivity, slow response time, and/or complex fabrication procedures. Here, we demonstrate that WO₃ in the form of single-crystal, ultrathin films with a Pt catalyst allows high-performance sensing of H₂ gas at room temperature. Thanks to the high electrical resistance in the pristine state, this material is able to detect hydrogen concentrations down to 1 ppm near room temperature. Moreover, the high surface-to-volume ratio of WO₃ ultrathin films determines fast sensor response and recovery, with characteristic times as low as 1 s when the concentration exceeds 100 ppm. By modeling the hydrogen (de)intercalation dynamics with a kinetic model, we extract the energy barriers of the relevant processes and relate the doping mechanism to the formation of oxygen vacancies. Our results reveal the potential ofsingle-crystal WO₃ ultrathin films toward the development of sub-ppm hydrogen detectors working at room temperature.

KEYWORDS: hydrogen sensing, ultrathin films, room temperature gas detection, WO₃ single crystals, kinetics of intercalation and deintercalation

INTRODUCTION

Transition metal oxides are a class of materials whose properties can be tuned by several external parameters, such as heteroepitaxial strain, electrostatic doping, intercalation of other species, or oxygen vacancies. This versatility recently triggered a broad technological interest, which goes beyond the use in oxide-based fuel cells, memristive systems, neuromorphic architectures, chemical actuators, and gas sensors. In this framework, oxide compounds are of particular interest for building high-performance hydrogen sensors, motivated by the growing demand for using H₂ gas to transport and store energy and to reduce the safety risks imposed by this explosive gas. Several oxide materials have been employed for resistive hydrogen sensing, with TiO₂, SnO₂, VO₂, and WO₃ being among the most prominent ones. WO₃, in particular, is regarded as a very promising candidate because incorporation of hydrogen changes its electrical resistance by several orders of magnitude. As summarized in Table 1, hydrogen sensing has been demonstrated with various forms of WO₃ such as amorphous layers and nanostructured materials. These sensors, however, usually require a high operational temperature, resulting in high power consumption and poor long-term stability, and have a sensitivity limited to hydrogen concentrations of hundreds of ppm.

In this work, we show that single-crystal WO₃ ultrathin films with a Pt catalyst can detect H₂ concentrations down to 1 ppm, with a fast response time, while working at or nearby room temperature. We show that hydrogen intercalation in the WO₃ crystal lattice determines changes of more than 5 orders of magnitude in the electrical resistivity of the material and that...
this fully reversible process is mediated by a small amount of platinum catalyst. Response time and lower detection limit can be tuned by temperature, which are reduced by an order of magnitude at a slightly elevated temperature of 65 °C. We study the hydrogen dynamics by modeling the intercalation and deintercalation processes with a series of coupled kinetic equations and extract the characteristic energy scales related to H₂ dissociation, incorporation, and recombination phenomena. We also demonstrate that hydrogen doping is a powerful control parameter to modulate the physical state of WO₃, which can be stabilized in kinetically arrested configurations just below room temperature. Our results show that single-crystal WO₃ ultrathin films are strong candidates for next-generation hydrogen sensing devices, combining high sensitivity, fast response, and device scalability.

RESULTS AND DISCUSSION

WO₃ Material Preparation. We grow a 24 unit cell (uc) crystalline WO₃ film on a SrTiO₃ (001) substrate by pulsed laser deposition (growth details in the Experimental Section and ref 31). The WO₃ structural properties are investigated by X-ray diffraction (XRD) and presented in Figure 1a, where finite size oscillations indicate high crystalline quality and confirm the expected film thickness of 9 nm. The reciprocal space map in Figure 1b shows that the material is a single crystal, coherently oriented to the substrate lattice. Surface topography, investigated by atomic force microscopy (AFM) in Figure 1c, shows a step and terrace structure which mimics the underlying substrate morphology. The hydrogen reaction is made possible by the presence of a catalyst, whose function is to facilitate the splitting of H₂ molecules from gas phase into atomic hydrogen, which is absorbed into the WO₃ lattice. In this work, we use platinum, which has the advantage of a high catalytic efficiency together with a low reactivity with oxide materials. A Pt layer having nominal thickness of 1 nm is deposited at room temperature by evaporation in vacuum (Figure 1d). Deposition of this low amount of material is expected to form sparse droplets of a few nanometers, and their catalytic activity is confirmed by the data discussed in the following section. Electrical measurements are performed on 50 μm × 50 μm patterned squares measured in van der Pauw configuration, as shown in the optical image of Figure 1e (details in the Experimental Section). The experimental setup is sketched in Figure 1f. We mount the sample in a vacuum chamber (base pressure p < 1 × 10⁻⁴ mbar), which is placed in a dark environment. Mixtures of H₂ in Ar carrying gas, with concentration C₉₂ ranging from 20% down to 1 ppm, are prepared in a series of preparation chambers before exposing the sample. The system also allows to regulate the total pressure of the gas mixture from 1 bar down to 1 mbar.

WO₃ Response to Hydrogen. The high crystal quality of the WO₃ material determines a high electrical resistance of the pristine device R = 400 MΩ at room temperature. This corresponds to a resistivity of 360 Ω cm, consistent with previous reports of high quality WO₃ thin films with negligible amount of oxygen vacancies. In Figure 2 we show that upon exposure to a high hydrogen concentration (C₉₂ = 5%, 1 bar total pressure) at room temperature the resistance drops by 5 orders of magnitude, and after a few minutes it saturates to a constant value. When the sample chamber is evacuated, the resistance stays approximately constant, indicating that the doped state is stable over time. When the doped device is exposed to air, the electrical resistance increases over time, recovering more than 3 orders of magnitude in the first 10 min and reaching the initial state after several hours.

Figure 1. Characterization and preparation of WO₃ thin films. (a) θ–2θ X-ray diffraction scan showing the (001) and (002) peaks of the WO₃ thin film with finite size oscillations around the sharp peaks of the SrTiO₃ substrate. (b) Reciprocal space map around the (103) peak. (c) Atomic force microscopy of the WO₃ surface. (d) Schematic of the WO₃/SrTiO₃ heterostructure after the evaporation of the Pt catalyst. (e) Optical image of the WO₃ sample patterned in van der Pauw geometry (the image is taken before the removal of the resist for better contrast). (f) Schematic of the experimental setup comprising the sample anchored on a Peltier element (red), the vacuum chamber SC1, the four-probe configuration used for resistive readout, the series of preparation chambers (PC1, PC2), gas bottles, pressure sensors, and vacuum pumps used to prepare the gas mixture (details in the Experimental Section).

Figure 2. Room temperature electrical and optical changes with hydrogen gas. The WO₃ thin film is exposed to different environmental conditions: 1 bar of air, 1 bar of hydrogen mixture, and vacuum. Both electrical resistance and sample color (optical images) change upon exposure to H₂ and recover their initial state once in air (see also the video in the Supporting Information).
During the electrical measurement, we took a series of photographs of an unpatterned WO₃ region which is presented in Figure 2 at the corresponding time. The material color changes, switching to blue upon the introduction of the gas (doped state), and going back to the initial transparency when the resistance progressively recovers its original value (see also the video in the Supporting Information). This color change is a well-known effect of hydrogen doping of WO₃, consistent with previous reports.²⁶,³⁴,³⁵ Both the resistance and optical data indicate that the measured changes in the sample properties are due to hydrogen intercalation and deintercalation into the WO₃ lattice.³⁶ Moreover, the data show that hydrogen doping is a reversible process and that the deintercalation is facilitated by the presence of air. Although a precise description of the doping mechanism is still a matter of debate, several reports show that the incorporation of atomic hydrogen determines electron doping of WO₃.²⁴,³⁷,³⁸ The Pt catalyst plays a primary role in the intercalation process, as without it the resistance of WO₃ remains constant upon exposure to H₂ (Figure S1). Increasing (decreasing) the amount of Pt catalyst, the material response to hydrogen can be made faster (slower), as discussed in Figure S2. In our experiments, the hydrogen is diluted in a carrier gas. We tested different inert gases (Ar, N₂, and He) and observed similar responses, indicating they have a negligible contribution in the intercalation process (Figure S3). While still showing a good response, a slower intercalation rate is observed when the carrier gas is air. We attribute this difference to the presence of O₂ molecules that can react with H atoms to form water.³⁶ The intercalation rate is also reduced when no carrier gas is used, even if the H₂ partial pressure is the same. The rate of the deintercalation process is quite slow both in a vacuum and in an inert gas atmosphere, while it is significantly enhanced in the presence of O₂ molecules (further details in Figure S4).

Hydrogen Sensing. The strong and fast response of single-crystal WO₃ ultrathin films to H₂ makes them appealing candidates to develop hydrogen gas sensors. For this purpose, we characterize in Figure 3a the resistive changes of WO₃ for different values of C₇H₂. The measurements are performed with the following experimental procedure: (i) evacuation of the sample chamber (p < 1 × 10⁻⁴ mbar), (ii) exposure to the H₂/Ar mixture for 1 min, (iii) chamber evacuation, and (iv) exposure to air for 10 min. The curves are measured at a sample temperature of 25 °C (solid blue) and 65 °C (dashed red). (b) Percentage resistive variation at 1 s after exposure to H₂ and (c) corresponding response time. (d) Recovery time upon exposure to air. The dotted lines are linear fits to the solid markers, while the grayed-out data points are either below the sensor detection limit (low ppm) or in its saturation regime (high ppm).
at 1 s after the introduction of H2 gas. This analysis is reported in Figure 3b, where we show that at intermediate concentrations (solid markers) the response depends on C(H2) according to the power law $\Delta R/R_0 \sim (C(H2))^\alpha$. We find $\alpha = 1.3$ at 25 °C and $\alpha = 1.5$ at 65 °C, indicating that a similar relationship regulates the trend at both temperatures. The onset of the saturated response of the WO3 device (shaded markers in Figure 3b) depends on its operational temperature. At 25 °C the response follows the power law in the range 10–1000 ppm, while at 65 °C this window is shifted to lower concentrations in the range 1–100 ppm. This indicates that by increasing the sensor temperature by a few tens of degrees, it is possible to lower the detection limit by 1 order of magnitude or, in other words, that the sensitivity range can be tuned by controlling the sample temperature.

To evaluate the response time of WO3, we consider a simplified model describing the time-dependent resistance change as $\Delta R/R_0 \sim e^{-\tau/\tau_f}$, where the response time $\tau$ is the fitting parameter. We find a lower $\tau$ for higher hydrogen concentration and sample temperature in step (ii), reaching $\tau = 1$ s for C(H2) = 100 ppm at 65 °C (Figure 3c). We note that independently of the value of $\tau$ and in the whole range of explored parameters, the presence of hydrogen is always detectable within the 1 min time frame used in the experiments. Figure 3d shows the recovery time of doped WO3 after exposing the device to air in step (iv). Again, lower $\tau$ is measured at higher temperature and higher initial hydrogen concentration in WO3. Finally, we note that the sensor response is independent of the initial resistance value $R_0$ (Figure S5), meaning that in the explored range of parameters WO3 works as a differential sensor, with a response depending only on C(H2) and not on the doping state of the material. In addition, the sensor preserves its functionality in a low-pressure H2 atmosphere, demonstrating its operability also as possible detector for pure H2 gas (Figure S6). These characteristics make WO3 an interesting material for H2 sensing that can be used in a large variety of environments.

Kinetic Model. To obtain an insight into the mechanism regulating the doping of WO3 thin films, we study the intercalation and deintercalation kinetics in a controlled atmosphere. For this purpose, we consider the minimal model of two-step reactions schematically illustrated in Figure 4a, where each step is described by a rate constant $k_{1,i}$ and its reverse by $k_{-1,i}$. We describe the intercalation and deintercalation processes by the balance equations

$$\begin{align*}
H_2 & \xrightarrow{k_{1,0}} 2H_2(\text{Pt}) \xrightarrow{k_{-1,0}} 2H_2(\text{bulk}) \\
2H_2(\text{bulk}) & \xrightarrow{k_{-2,0}} H_2(\text{surf.}) \xrightarrow{k_{-1,0}} H_2
\end{align*}$$

(1a) (1b)

where with $H_2(\text{Pt})$ we indicate a hydrogen atom on a catalyst site, with $H_2(\text{surf.})$ anywhere on WO3 or Pt surface, and with $H_2(\text{bulk})$ intercalated in the WO3 lattice. Our model describes the intercalation and deintercalation considering different initial conditions. The intercalation experiment starts with undoped WO3 and an infinite reservoir of H2 in gas phase, allowing to consider the dissociative adsorption ($k_{1,i}$) of H2 on Pt as an irreversible process. The subsequent hydrogen exchange between WO3 surface and WO3 bulk is an equilibrium reaction, regulated by rate constants $k_{1,i}$ and $k_{-1,i}$. The deintercalation experiment is modeled considering an initial condition where WO3 is in a state of saturated doping and in a vacuum atmosphere. Hydrogen atoms in the crystal lattice migrate toward and from the surface (rate constants $k_{1,i}$ and $k_{-1,i}$) where they can recombine to form H2. Differently from the intercalation process, in this step the hydrogen recombines in a spontaneous reaction that does not require a catalyst. H2 molecules can thus form anywhere on WO3 surface. Subsequently, hydrogen molecules desorb and are pumped away in an irreversible process ($k_{1,0}$).

Hydrogen intercalation is experimentally studied starting from an undoped, low-conductance state. In Figure 4b we show intercalation curves performed in a low-pressure (5 mbar) gas mixture with C(H2) = 20% at different sample temperatures. Higher temperatures determine faster intercalation, with the conductance reaching a saturation value after a few tens of minutes. The deintercalation process in Figure 4c is studied starting with WO3 in a high-conductance state. At the beginning of the measurement, WO3 is exposed to a vacuum atmosphere, and the conductance decreases over time, with a faster rate at higher temperature. We note that in vacuum the
deintercalation process is much slower than in air, so that the curves do not reach full saturation in the duration of the experiment (2 h), in agreement with our interpretation of the role played by oxygen in accelerating the desorption process (Figure S4).

The kinetic equations associated with the reactions in eqs 1a and 1b (see also the Supporting Information) are solved numerically to fit the experimental data (dashed lines in Figures 4b and 4c). Our model shows good agreement with the measurements and allows us to extract the rate constants of the different processes (Figures 4d to 4g). We find that $k_{1,i}$ is at all temperatures 1 order of magnitude larger than $k_{1,i}$, signaling a faster rate of H\textsubscript{2} splitting compared to its recombination. This difference supports our choice to consider the dissociative adsorption of H\textsubscript{2} an irreversible process during the intercalation experiment (i.e., $k_{-1,i} \ll k_{1,i}$). In the deintercalation experiment, instead, $k_{-1,i}$ becomes important because the vacuum atmosphere hinders the H\textsubscript{2} splitting reaction by carrying away the H\textsubscript{2} molecules as soon as they recombine. This difference supports our choice to consider the dissociative adsorption of H\textsubscript{2} an irreversible process during the intercalation experiment (i.e., $k_{-1,i} \ll k_{1,i}$).

Previous experimental and density functional theory calculations have shown that H\textsubscript{2} splitting can only happen on the WO\textsubscript{3} surface.42,43 However, the diffusion of H\textsubscript{2} from the Pt sites to WO\textsubscript{3} surface,42,43 is only related to the hydrogen diffusion in WO\textsubscript{3} bulk because recombination can happen anywhere on the WO\textsubscript{3} surface, with lower values expected for smaller particles.39,40

Similarly, recombinitive desorption at oxide surfaces entails activation energies in the range 0.05–0.9 eV depending on the hydrogen binding energy at the adsorption site.41

The surface-to-bulk diffusion rate constants $k_{1,i}$ show a weak temperature dependence (Figure 4f). The bulk-to-surface rates $k_{2,i}$ in Figure 4g, instead, show a linear trend which allows to extract activation energies of 0.43 and 0.24 eV in the intercalation and deintercalation experiments, respectively. The higher activation energy required during deintercalation stems from the fact that hydrogen splitting can only happen on the catalyst particles, so that the hydrogen atoms have to overcome two energy barriers: the diffusion on WO\textsubscript{3} surface and then the diffusion in WO\textsubscript{3} bulk. During deintercalation, instead, $k_{2,i}$ is only related to the hydrogen diffusion in WO\textsubscript{3} bulk because recombination can happen anywhere on the WO\textsubscript{3} surface. Previous experimental and density functional theory calculations reported energy barriers between 0.26 and 0.37 eV for hydrogen migration from the Pt sites to WO\textsubscript{3} surface,42,43 which are compatible with our experimental results.

Electrical Transport. The previous analysis showed that both intercalation and deintercalation are thermally activated processes, so that their rate can be controlled changing the sample temperature. Furthermore, we showed that the room temperature resistivity of WO\textsubscript{3} films can be continuously tuned by H\textsubscript{2} intercalation. As a result, hydrogen kinetics in the WO\textsubscript{3} lattice can be arrested by cooling down the material. This allows to get an insight into the electronic doping mechanism by measuring the transport activation energy of the free carriers induced by hydrogen doping. In Figure 5a, we show a series of resistance versus temperature curves measured on a single WO\textsubscript{3} device under different doping conditions. Before each measurement, we expose the sample to hydrogen gas at room temperature in order to obtain the desired sheet resistance $\rho_{300K}$ after which we evacuate the sample chamber and start a cooling ramp. All curves show a semiconducting trend, where higher doping produces a shallower temperature dependence. We note that the resistance versus temperature curves are similar to what previously reported for WO\textsubscript{3} doped with oxygen vacancies, suggesting the occurrence of a similar mechanism of extrinsic doping. This interpretation is supported by recent experiments on WO\textsubscript{3} nanowires which showed that H\textsubscript{2} intercalation is accompanied by the formation of interstitial H\textsubscript{2}O molecules along with oxygen vacancies.

We consider an Arrhenius mechanism to describe the temperature dependence of the electrical transport $\sigma = 1/\rho = e^{-E_a/kT}$, where $E_a$ is the activation energy. The resulting fits in the high-temperature regime (above 150 K, dashed lines) show good agreement with the experimental data and allow to extract the trend of $E_a$ as a function of $\rho_{300K}$ reported in Figure 5b. The data show the logarithmic dependence $E_a = A \log \rho_{300K} + B$, with $A = 19$ meV and $B = 90$ meV. We show in the Supporting Information that the activation energy can be expressed as

$$E_a = k_B T_{300K} \log \rho_{300K} + \gamma \log C_{1H} + \gamma T_{300K} \Delta S^o$$

where $\gamma$ is related to the extrinsic donor charge, $\Delta S^o$ is the reaction entropy, and $C_{1H}$ is the hydrogen concentration inside the WO\textsubscript{3} lattice. Equation 2 provides a direct relation between $E_a$ and $\rho_{300K}$ through the coefficient $k_B T_{300K} \sim 26$ meV. However, $\rho_{300K}$ is also a function of $C_{1H}$ and by comparing eq 2 with the experimental fit, we find that the resistivity can be expressed as $\rho_{300K} \sim (C_{1H})^{\gamma/0.3}$. We show in the Supporting Information that $\gamma = 1/3$ if the electron donors are oxygen vacancies. Substituting this value, we obtain an almost linear relationship between the conductance and hydrogen concentration in the material $\sigma_{300K} = 1/\rho_{300K} \sim C_{1H}$, in agreement with the assumption we used to treat the experimental intercalation and deintercalation curves with the kinetic model. The linear dependence between hydrogen concentration in WO\textsubscript{3} and electrical conductivity constitutes a powerful transduction scheme for the electrical sensing of H\textsubscript{2} gas.

CONCLUSIONS

To conclude, single-crystal Pt-decorated WO\textsubscript{3} ultrathin films have proven extremely sensitive and fast probes for solid state hydrogen gas sensors. Thanks to the high crystal quality and high surface-to-volume ratio, our devices showed a 5 orders of magnitude change in electrical resistivity upon exposure to H\textsubscript{2} gas at room temperature. The device response can be tuned by...
controlling the temperature, enabling detection of a hydrogen concentration down to 10 ppm at room temperature and down to 1 ppm at 65 °C, where we measured short response times as low as 1 s for concentrations above 100 ppm. We successfully modeled the intercalation and deintercalation of hydrogen in the WO₃ lattice with a kinetic of thermally activated processes. Our analysis allowed to extract the activation energies of the different reactions, which are in good agreement with previous reports based on ab initio calculations. These results show that heteroepitaxial WO₃ films hold great potential for high-performance hydrogen gas sensors, providing high sensitivity, fast response, high dynamic range, and a simple device architecture.

## EXPERIMENTAL SECTION

### Sample Growth

WO₃ thin films were grown by pulsed laser deposition on commercially available 5 mm × 5 mm SrTiO₃ (001) substrates, with TiO₂ surface termination. The laser ablation was performed using a KrF excimer laser (Coherent COMPexPro 205, λ = 248 nm) with a 1 Hz repetition rate and 1 J cm⁻² fluence. The target-to-substrate distance was fixed at 55 mm. The WO₃ films were deposited from a WO₃ sintered target at 500 °C substrate temperature and 8 × 10⁻² mbar oxygen pressure. Film thickness was monitored in situ during growth by intensity oscillations of reflection high-energy electron diffraction (RHEED). At the end of the growth, the films were cooled down to room temperature in the same oxygen pressure used during deposition. Further details on the growth and sample characterization are reported in ref 31.

### Van Der Pauw Geometry Fabrication

Standard e-beam lithography with PMMA resist was used to pattern WO₃ heteroepitaxial films. The metal contacts were deposited by evaporation of 5 nm Ti and 45 nm Au at room temperature, followed by lift-off. Ar ion etching was used prior to metal deposition to etch 5 nm of WO₃ in order to provide edge contacts to the film in an interdigitated pattern, which ensure a low contact resistance. The WO₃ mesa was defined by a subsequent lithographical and etching step which removes the WO₃ material from the regions surrounding the van der Pauw geometry. The etching was performed using a beam current of 2 mA and an energy of 500 eV, corresponding to an Ar ion flux of 0.25 mA cm⁻². These parameters produce etched regions which are insulating at all temperatures.

### Gas Mixture Preparation

To regulate the H₂ concentration with high precision, we used the series of vacuum chambers described in Figure 1f: the preparation chambers PC1, PC2, and sample chamber SC1 having vacuum ratios 1:9:1. Before introduction of the gases, the chambers were evacuated to < 0.1 μm bar. The hydrogen gas was sourced from a bottle of 20% H₂/Ar. This gas blend was introduced in the volume PC1 + PC2, where pure Ar gas was used during deposition. Further details on the growth and sample preparation are reported in ref 31.

### Electrical Measurements

The resistive measurements were performed with a Keithley 6430 sourcemeter using a four-probe configuration and a current bias of 100 nA.

### Air Conditions

Air from the environment (relative humidity 50%) was used in the sensing measurements.

### Numerical Solution of Kinetic Equations

The kinetic model in the Supporting Information was solved using the NDSolve function of Wolfram Mathematica. The resulting fit curves yield a coefficient R² ~ 0.99, indicating that our model is a good approximation of the experimental reactions, although higher-order corrections might be present.

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