DOI 10.5162/EUROSENSORS2025/W8.2.3

Nanosecond Pulsed Laser Annealing of Sol−Gel VO_2 Films for H_2 Sensors

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Summary:

Nanosecond Pulsed Laser Annealing (ns-PLA) is a promising technique to simultaneously crystallize and nanostructure metal oxides films. Here, high nanostructured surface area was achieved on sol-gel VO_2 thin films by ns-PLA. The gas sensing tests showed excellent selectivity toward H_2, low operating temperatures of 150°C, detection limit as low as 2 ppm, and long-term stability over 3 months. Advanced in-operando GIXRD and in-situ XPS proved that the sensing mechanism involves reversible structural and chemical changes, based on reversible variations of V oxidation state and H_xVO_2 bronze formation.

Keywords: vanadium oxide, chemoresistive sensor, optical sensor, hydrogen, laser annealing

Background, Motivation an Objective

Nanosecond Pulsed Laser Annealing (ns-PLA) offers notable advantages for the fabrication of functional thin films, enabling ultrafast and localized heating that promotes crystallization and nanostructuring within a few seconds. Unlike conventional thermal treatments, ns-PLA is energy-efficient, compatible with temperature-sensitive substrates, and can significantly reduce process times and emissions. These features make it a compelling method for scalable and sustainable material processing. In this work, we employed ns-PLA to fabricate nanostructured thin films of vanadium dioxide (VO_2), a transition metal oxide known for its thermally induced, reversible metal-insulator transition (MIT) near 68°C. This phase transition results in abrupt changes in VO_2's optical and electrical properties, which can also be modulated by electric fields or strain.[1] Among its various polymorphs, the monoclinic/tetragonal VO_2 (M1/R) phases are particularly interesting for sensing applications but remain less explored than the VO_2 (B) phase.[2] Using a simple and environmentally-friendly sol-gel approach, we prepared VO_2 (M1/R) films by either ns-PLA or traditional furnace-annealing (FA), to assess the impact of crystallinity and nanostructuring on hydrogen (H_2) sensing performance. Dual-mode optical and chemoresistive sensors offer great advantages for cross-validation, versatility in application to multiple platforms, and better understanding of sensing mechanisms. Therefore, the optical and chemoresistive response to H_2 of the VO_2-based sensors was tested in concentrations ranging from a few ppm up to 50,000 ppm. The films were functionalized with Pt nanoparticles to exploit their catalytic activity in enhancing surface reactions. Selectivity tests were performed to verify NO_2 and humidity cross-sensitivity. The sensing mechanism was investigated through in-operando and in-situ techniques, including grazing-incidence X-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS).

Description of the New Method or System

Sol-gel VO_2 films were crystallized by either ns-PLA or FA. The ns-PLA was performed in air, by irradiating the samples with a KrF excimer laser system for 1 min, while FA was performed under a N_2 flux at 550°C for 1 h.[3]

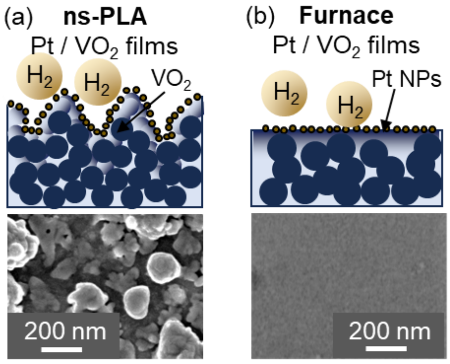

Figure 1. Schematic and SEM images of sol-gel VO_2 films crystallized by (a) ns-PLA or (b) furnace annealing, and decorated by Pt nanoparticles.

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Ellipsometry analysis revealed an average thickness of ~30 and 50 nm, respectively. Scanning electron microscopy (SEM) revealed the spontaneous formation of nanostructures after ns-PLA (Figure 1a), compared to a smooth flat morphology for FA (Figure 1b). GIXRD and Raman confirmed the successful crystallization into VO_2 (M1) for both samples. The optical transmittance, measured at low (20°C) and high (90-150°C) temperatures, proved the presence of a reversible MIT (Figure 2, black/blue lines).

Results

Initially, we investigated the chemoresistive response of both ns-PLA and FA samples to H_2 (5−500 ppm) at 150°C operating temperature (OT) in dry air background. Both samples show an *n*-type behavior, with the electrical resistivity decreasing upon H_2 exposure, coupled with an excellent recovery of the baseline resistance. Both samples sustained over 3 months under working conditions, confirming an excellent long-term stability, and were highly selective towards H_2, as no response was shown upon exposure to NO_2 (400 ppb-2 ppm) or humidity (20-80% at 25°C).

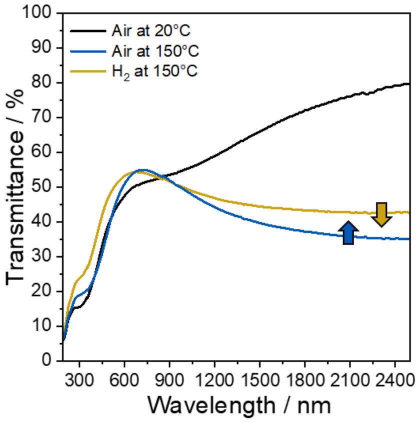

Figure 2. Optical transmittance of the FA sample in air at 20°C (black line) and 150°C (blue line).[3] H_2 sensing response of the FA sample at 150°C OT with dry air background (yellow line).

In addition, both ns-PLA and FA samples show a fully reversible modulation of the optical properties upon H_2 exposure within the entire UV-vis-NIR range (Figure 2). Both sensors display an H_2 response at OTs below 150°C, down to room temperature.

The overall gas sensing mechanism is explained by considering the concurrent role of both Pt nanoparticles (NPs) and VO_2 films. Pt NPs favorably induce the catalytic dissociation of molecular H_2 into atomic H on the surface of VO_2. The H spillover leads to its diffusion within the bulk of the VO_2 films, and results in the formation of the H_xVO_2 bronze (Eq. 1). The latter reacts with adsorbed oxygen, which results in a decrease in resistance due to the electron release (Eq. 2):

$$VO_2 + H \rightleftharpoons H_xVO_2 \quad (1)$$

$$4H_xVO_2 + O_2^- \rightleftharpoons 4VO_2 + 2H_2O + e^- \quad (2)$$

The reversible bronze formation, coupled with the reversible variations in the V oxidation states, were proved by in-operando GIXRD and in-situ XPS. As shown in Figure 3, the appearance of the H_xVO_2 diffraction (yellow pattern) can be seen upon sample exposure to H_2, which is found to be fully reversible, confirming the chemoresistive and optical gas sensing tests.

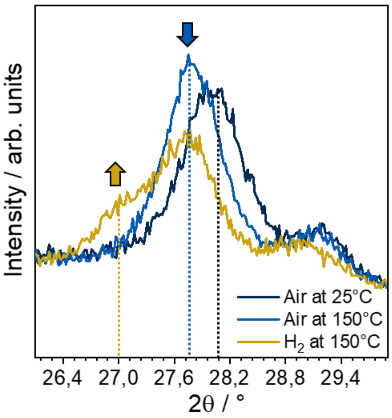

Figure 3. GIXRD of the FA sample in air at 20°C (black pattern), showing the principal monoclinic M1 diffraction, and 150°C (blue pattern), showing the rutile diffraction.[3] GIXRD of the FA sample upon exposure to 5% H_2 at 150°C (yellow pattern), showing the formation of the H_xVO_2 bronze.

Coherently, in-situ XPS highlights the changes in V oxidation state upon H_2 exposure.

In conclusion, we successfully fabricated H_2 sensors via ns-PLA, offering a dual chemoresistive and optical mode, selectivity towards H_2, excellent baseline recovery, and long-term stability.

References

[1] Zhang, Y. et al. Recent Progress on Vanadium Dioxide Nanostructures and Devices: Fabrication, Properties, Applications and Perspectives. *Nanomaterials* 2021, 11, 338. doi.org/10.3390/nano11020338.

[2] Liang, J. et al. High-Sensitivity NH3 Gas Detection at Room Temperature Using In2O3 Nanoparticles-Modified VO2(B) Nanorods Heterojunction. *Appl Surf Sci* 2024, *649*, 159170. doi.org/10.1016/j.apsusc.2023.159170.

[3] Basso, M., et al. Sol-gel Pt-VO_2 films as selective chemoresistive and optical H_2 gas sensors. *ACS Appl. Mater. Interfaces* 2024, 16, 42, 57558–57570. doi.org/10.1021/acsami.4c13003.