Highly Responsive Pd-Decorated MoO$_3$ Nanowall H$_2$ Gas Sensors Obtained from In-Situ-Controlled Thermal Oxidation of Sputtered MoS$_2$ Films

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ABSTRACT: Among transition metal oxides, MoO$_3$ is a promising material due to its layered structure and different oxidation states, making it suitable for different device applications. One of the methods used to grow MoO$_3$ is radio frequency magnetron sputtering (RFMS), which is the most compatible method in industry. However, obtaining nanostructures by RFMS for metal oxides is challenging because of compact morphology film formation. In this study, $\alpha$-MoO$_3$ with vertical nanowalls is obtained by a two-step process; deposition of magnetron-sputtered MoS$_2$ vertical nanowalls and postoxidation of these structures without changing the morphology. In situ transmittance and electrical measurements are performed to control the oxidation process, which shed light on understanding the oxidation of MoS$_2$ nanowalls. The transition from MoS$_2$ to $\alpha$-MoO$_3$ is investigated with partially oxidized MoS$_2$/MoO$_3$ samples with different thicknesses. It is also concluded that oxidation starts from nanowalls perpendicular to the substrate and lasts with oxidation of basal planes. Four different thicknesses of $\alpha$-MoO$_3$ nanowall samples are fabricated for H$_2$ gas sensors. Also, the effect of Pd deposition on the H$_2$-sensing properties of sensors is deeply investigated. An outstanding response of $3.3 \times 10^4$ as well as the response and recovery times of 379 and 304 s, respectively, are achieved from the thinnest Pd-loaded sample. Also, the gas-sensing mechanism is explored by gasochromic measurements to investigate the sensor behaviors under the conditions of dry air and N$_2$ gas as the carrier gas.

KEYWORDS: thermal oxidation, RF-magnetron sputtering, MoO$_3$, MoS$_2$, H$_2$ gas sensor, gasochromism

1. INTRODUCTION

Transition metal oxides such as WO$_3$, MoO$_3$, and V$_2$O$_5$ are functional materials that has been attracting the attention of scientists in the last few years due to their wide and tunable band gaps, variable electronic and optical properties due to reduction and oxidation properties, as well as their layered structure in hydrate or anhydrate crystal phases.$^1$ Among them, MoO$_3$ and its substoichiometric forms have a wide range of applications such as in electrochromic devices,$^{2-6}$ gas sensors,$^7$ optoelectronics,$^8$ catalysis,$^9$ supercapacitors,$^{10}$ and solid lubricants.$^{11}$ Stoichiometric MoO$_3$ is a wide band gap semiconductor ($\sim$3 eV) that might be narrowed by reduction into MoO$_2$ ($2 < x < 3$)$^{12,13}$ In the reduction process, oxygen defects introduce more electrons into the conduction band. This presents itself as the narrowed band gap and better conductivity, which become possible by Mo$^{6+}$ reduction to Mo$^{5+}$ and finally to Mo$^{4+}$ to achieve semimetal MoO$_2$.$^{13}$ Through this process, the optical properties of MoO$_3$ change significantly. Therefore, it is among the most studied materials for various devices, especially electrochromic and gasochromic devices.

MoO$_3$ has two thermodynamically stable common crystal phases, stable orthorhombic $\alpha$-MoO$_3$ and metastable monoclinic $\beta$-MoO$_3$.$^{12}$ The $\alpha$-phase attracts much attention due to its layered crystal structure and its ability to form two-dimensional (2D) atomically thin morphologies, which is a state-of-the-art material after discovering graphene.$^{13}$ The fundamental building blocks of both $\alpha$-MoO$_3$ and $\beta$-MoO$_3$ crystal structures are MoO$_6$ octahedrons that bond differently.$^{14}$ In orthorhombic $\alpha$-MoO$_3$, distorted MoO$_6$ octahedrons link with edge-sharing zigzag rows and are corner-sharing along [001] and [010] directions, respectively, to form planar double-layer sheets by weak van der Waals force between them.$^{15,16}$ Unlike the $\alpha$-phase, monoclinic $\beta$-MoO$_3$ does not form a layered crystal structure, and MoO$_6$ octahedrons only share corners to form a ReO$_3$-like crystal structure by corner-sharing.$^{13,15}$ Depending on the applications, $\alpha$-MoO$_3$ and $\beta$-MoO$_3$ have their own advantages and disadvantages. The transition from the $\beta$-phase to the $\alpha$-phase at temperatures above 350 °C has been reported.$^{17}$

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Understanding the shape and size effects of materials on their properties and tracing their behaviors in contact with the environment around them have enabled scientists to fabricate different nanostructures with improved optoelectronic properties, which led to the fabrication of materials with a high aspect ratio. In the case of MoO$_3$, nanostructures such as nanosheets, nanorods, nanowires, quantum dots, nanotubes, and nanoparticles have been reported so far via different material growth methods such as chemical vapor deposition, radio frequency (RF)/DC magnetron sputtering, thermal evaporation, electron beam evaporation, spray pyrolysis, hydrothermal synthesis, electrochemical anodization, electrochemical deposition, and exfoliation. All the material growth methods mentioned above have their advantages and disadvantages. However, the sputtering method has some advantages that distinguish it from the growth methods mentioned above, such as its compatibility with industry, large area coatings, and the possibility of mass production. In addition, it is easy to control growth parameters to perform uniform and repeatable depositions. On the other hand, it is also inexpensive compared to other high vacuum-required growth methods. Besides these advantages, it is challenging to grow nanostructures by tuning the controllable growth parameters in magnetron sputtering. It is common that sputtered materials form a compact thin film morphology. In order to achieve nanostructures via the magnetron sputtering method, some extra post-treatments, usage of catalysts, and substrate treatments might be required. For example, Zhang et al. prepared monolayer hollow spherical tungsten oxide films by combining magnetron sputtering with the colloidal crystal template. Instead of growing MoO$_3$ nanostructures by the methods mentioned above, there are also some reports on the full or partial oxidation of MoS$_2$ to achieve MoO$_3$ or MoS$_2$/MoO$_3$ hybrid composite structures. In one of them, 2D MoO$_3$ nanosheets were synthesized by chemical oxidation of exfoliated MoS$_2$. Similarly, MoS$_2$/MoO$_3$ heterostructures were prepared by plasma oxidation of MoS$_2$ layers. On the other hand, the thermal oxidation method is preferred by some researchers. However, most of them did not successfully preserve the morphology during the conversion from MoS$_2$ to MoO$_3$ material.

One of the most used applications of MoO$_3$ materials is the gas sensor devices. Metal oxide semiconductors are preferred because of their resistance to a harsh environment, ease of production, low cost, and repeatability. Also, due to the ease of production and the ability to miniaturize, chemiresistive semiconducting metal oxide gas sensors and their heterostructures attract much attention among other types of gas sensors. In particular, materials for H$_2$ gas sensing have gained importance because they are supposed to be one of the materials with the highest potential as alternative energy sources. Increasing the usage of H$_2$ gas as an alternative to fossil fuels and considering its explosive potential, detecting H$_2$ gas sensors have become a promising material among the metal oxide semiconductor gas sensors for detecting H$_2$ gas due to the chromic nature of MoO$_3$ and its ability to undergo reversible reduction and oxidation reactions by ion injection and extraction.

Here, we report thermal oxidation of sputtered MoS$_2$ to achieve α-MoO$_3$ without a morphological change of the film to use in highly responsive H$_2$ gas sensors. In situ conversion of MoS$_2$ to MoO$_3$ was performed through optical and electrical measurements. Furthermore, the potential of the converted materials was explored by fabricating H$_2$ gas sensors with different thicknesses to study the effect of thickness and nanostructures on the gas-sensing properties of achieved MoO$_3$. An outstanding sensitivity of 3.3 × 10$^4$ for 1000 ppm was achieved from the thinnest MoO$_3$ sample, one of the highest reported responses for MoO$_3$-based H$_2$ gas sensors at a relatively low operating temperature (100 °C). Furthermore, the effect of Pd deposition on H$_2$ gas-sensing performance is discussed in depth in the H$_2$ Gas-Sensing Performances and Mechanism section.

2. EXPERIMENTAL SECTION

The Experimental Section in this study is divided into four parts: (a) film deposition, (b) dynamic in situ transmittance and electrical measurements during the oxidation process, (c) film characterization, and (d) H$_2$ gas sensor measurements.

2.1. Film Deposition. MoS$_2$ nanowalls were deposited via a RF magnetron sputtering (RFMS) system using a MoS$_2$ target with a diameter of 2 in. and a purity of 99.999%. Quartz and ITO-coated glasses with a sheet resistance of 20 Ohm/cm were used as substrates for gas sensor measurements and material characterizations. Both quartz and ITO substrates were cleaned ultrasonically in isopropanol, ethanol, and deionized water (10 min for each step) and dried under N$_2$. The distance between the target and substrates was about 7 cm, and the gus position was fixed perpendicular to the substrates. The chamber was evacuated to a base pressure of 2 × 10$^{-6}$ Torr. Sputtering was performed at a substrate temperature of 300 °C and an argon pressure of 16 mTorr with a sputtering power of 120 W. Four different thicknesses of MoS$_2$ were sputtered. Depending on the growth time, films were labeled Z$_{0.5}$, Z$_{2.5}$, Z$_{7.5}$, and Z$_{30}$, corresponding to 30 s, 2.5 min, 7.5 min, and 30 min growth time with thicknesses of 40, 115, 370, and 1440 nm, respectively, as shown in the cross-sectional field emission scanning electron microscopy (FSEM) images presented in Supporting Information, Figure S1.

2.2. In Situ Transmittance and Electrical Measurements. The dynamic in situ transmittance and two-probe electrical measurements were performed during the oxidation process in a chamber having an optical window. A tungsten−halogen lamp was used as the light source. MoS$_2$ samples to be oxidized were heated up to 380 °C, and oxygen gas was let in during preheating up to 380 °C and during the oxidation process. For two-probe electrical measurements, interdigitated electrode (IDE) contacts (Pt contacts deposited with a RF-magnetron sputter) with a 400 μm distance between them were used.

2.3. Film Characterization. A Zeiss Sigma 300 field emission scanning electron microscope was used to investigate the morphological characteristics of MoS$_2$ and MoO$_3$ films. A WITec alpha 300R was used for micro-Raman measurements of MoS$_2$, MoS$_2$/MoO$_3$, and MoO$_3$ films. For crystal structure characterization of films, a PANalytical Empyrean X-ray diffraction (XRD) system was used. X-ray photoelectron spectroscopy (XPS) measurements for determining the material composition were performed with a Specs Flex-Mod XPS system equipped with a 150 mm radius hemispherical energy analyzer with a 2D charge-coupled detector. The measurements were current values in the case of chemiresistive gas sensors. The oxide-based sensors generally operate at relatively high temperatures with low sensitivity. Pd-decorated MoO$_3$ has become a promising material among the metal oxide semiconductor gas sensors for detecting H$_2$ gas due to the chromic nature of MoO$_3$ and its ability to undergo reversible reduction and oxidation reactions by ion injection and extraction.
performed using an Al anode with a \( K_\alpha \) energy of 1486.71 eV. The depth profile measurements were conducted by 3 keV Ar\(^+\) ion sputtering with 300 s of etching for each cycle.

2.4. \( \text{H}_2 \) Gas Sensors (Sample Preparation and Performance Measurements). For \( \text{H}_2 \) gas sensor measurements, Pt IDE contacts were deposited first on a quartz substrate by sputtering using a shadow mask. Then, MoS\(_2\) films with different thicknesses were deposited on contacts. Next, oxidation of samples of different thicknesses was performed in tube furnaces for 2 h. At the final step of the device fabrication, sample surfaces were activated by Pd deposition under 27 mTorr and 25 W power conditions for 7 s by RFMS. Gas sensor measurements were performed using a homemade gas sensor system with a chamber of 0.5 L volume. All the samples were held under an applied voltage of 0.5 V using a KEITHLEY 487 picoammeter/voltage source. \( \text{H}_2 \) gas with various standard cubic centimeters per minute (sccm) was mixed with 500 sccm of dry air to achieve the desired \( \text{H}_2 \) part per million (ppm) levels between 100 and 1000 ppm at three different measurement temperatures (100, 200, and 300 °C), which were set before the gas-sensing measurements. Measurements between 10 and 90 ppm were performed for sample \( \text{Z}_{0.5} \) at an operating temperature of 200 °C.

3. RESULTS AND DISCUSSION

3.1. In Situ Measurements. The thermal oxidation process was used to convert sputtered nanowall morphology MoS\(_2\) films into MoO\(_3\) without changing the surface morphology to take advantage of the large surface-to-volume ratio of the films in sensor applications. After many trials to keep the surface morphology with no change (Supporting Information, Figure S2), it has been realized that certain oxidation conditions are needed to control during the thermal oxidation, such as the oxidation temperature and time. It has also been confirmed that these parameters depend on the MoS\(_2\) thickness. Therefore, it is decided to control the oxidation process by in situ transmittance and two-probe electrical measurements. These in situ measurements allow us to trace the sulfur-to-oxygen ratio by simply checking the samples’ opaqueness because the decreasing sulfur to oxygen ratio presents itself as increasing transparency and decreasing conductivity. The predictable chemical equation for the thermal oxidation process of MoS\(_2\) is shown below.
\[ 2\text{MoS}_2 + 7\text{O}_2 \rightarrow 2\text{MoO}_3 + 4\text{SO}_2 \]

In some applications, it is inevitable to use transparent conductive oxides (TCOs) as a substrate for MoO$_3$ films, that is, electrochromic devices, in which the transparency and conductivity of electrodes are essential parameters. Moreover, a longer oxidation time means the disappearance of oxygen vacancies in TCO, which presents itself as a decrease in conductivity.\textsuperscript{53,54} Therefore, for such situations, controlling the oxidation time might be an important parameter.

MoS$_2$ films with two different thicknesses, namely, Z$_{2.5}$ and Z$_{30}$, were used for in situ measurements. Changes in optical and electrical properties of MoS$_2$ films with the transmittance during the oxidation process are shown in Figure 1a,b. The data collection time for the transmittance change is every 60 s. In order to avoid crowd plots, sparse data is used in the plot. As seen in Figure 1a,b, there is a significant change in the transparency of the films, which turned from opaque to transparent (see the inset image). This indicates that the oxidation process is successful. Figure 1c shows the transmittance change of films versus time monitored at a wavelength of 550 nm. As seen from the figures, both samples’ transparency increase as the oxidation time gets longer. The films’ starting transmittance values change due to the thickness differences in the samples. This is so crucial for the research that we have conducted because it allows us to find approximate oxidation time. The term approximation is used here because finding the exact oxidation time from the graph is hard. The change in transmittance becomes slower after some duration, as seen from the plot. At this point, it is not easy to understand whether all sulfurs are gone or some remain. On the other hand, this plot, in its way, gives a strong idea about the approximate oxidation time. As seen from Figure 1c, the oxidation times for Z$_{2.5}$ and Z$_{30}$ are about 13.2 and 23.0 min, respectively. The differences in oxidation times between Z$_{2.5}$ and Z$_{30}$ are predictable due to the thickness differences between the films. It can be seen that the slope of Z$_{30}$ is greater than that of Z$_{2.5}$, which means faster oxidation. In addition, the tendency of dynamic transparency of Z$_{30}$ gives rise to flattening quicker than that of the sample Z$_{2.5}$, but transmittance of Z$_{30}$ still increases very slowly.

Figure 1d shows the current versus time changes of MoS$_2$ films during the oxidation process. It can be noted that the graph is semilogarithmic. As seen from the plot, the current value decreases as the oxidation time gets longer, which shows basically that converted MoO$_3$ films have a larger resistance than MoS$_2$. As seen from the figure for sample Z$_{2.5}$, current increases from 1.2 to 12.0 μA. The increase in the current value in this interval is related to the increase in the temperature from RT to 380 °C. However, the temperature reached at the maximum point of the current is 375 °C. The current starts to decrease rapidly at a temperature of 375 °C, indicating that the oxidation process has started handling the current decrease. After 586 s, the current value reaches 1.7 nA for the sample Z$_{2.5}$. For sample Z$_{30}$, the current starts from 1.2 μA and reaches a value of 14.2 μA. Unlike the sample Z$_{2.5}$, the current starts to decrease for Z$_{30}$ at a temperature of 360 °C. The Z$_{30}$ sample takes about 890 s to achieve a current value of 1.7 nA. This experiment proves a successful oxidation process with the in situ measurements and gives some information about the conductivity of the samples. It also allows us to stop the oxidation process by checking the sample’s transparency or conductivity to obtain a semioxide composite of MoS$_2$/MoO$_3$.

### 3.2. Material Characterization

In situ optical and electrical measurements confirm the successful thermal oxidation process of MoS$_2$ into MoO$_3$. In order to follow the morphology, as well as the structural and optical properties after the MoS$_2$–MoO$_3$ conversion, Raman, XRD, and the FESEM measurements were performed on the end materials together with the MoS$_2$/MoO$_3$ composite materials in which the thermal oxidation process was completed at some point. Figure 2a–h shows the results of these measurements. However, before we elaborate on how oxidation takes place in MoS$_2$ nanowalls, first, we offer a glimpse on the growth mechanism of MoS$_2$ nanowalls. Figure 2a,b presents FESEM images of 15 and 30 s grown MoS$_2$ films on the ITO substrate. As seen from Figure 2a, no vertically grown MoS$_2$ nanowall-shaped morphology is seen in 15 s of deposition, but ITO film grains can be seen. The result is because of horizontally grown MoS$_2$ with a 2D-like morphology at the first step of deposition. As the growth time continues, the nanowall-like vertical structures start to appear, as seen in 30 s grown MoS$_2$. The appearance of 3D structures might be due to accruing stress between boundaries of grown sheets or defect sites that start during the first steps of deposition. After a while, it appears to be the beginning of vertical growth.\textsuperscript{55} A detailed study of transition from 2D to 3D growth forming nanowalls in the WS$_2$ film deposited by RFMS, which was predicted to be the same for MoS$_2$, was reported in our previous study.\textsuperscript{55}

Figure 2c shows the XRD graphs of MoS$_2$, partially oxidized MoS$_2$/MoO$_3$, and MoO$_3$ films of Z$_{2.5}$ and Z$_{30}$ samples. The (002) plane peak intensity, related to basal planes oriented parallel to the substrate, has decreased with a longer deposition time. However, the peak intensity of the (100) plane, which is related to edge planes perpendicular to substrates, increases as the deposition time gets longer.\textsuperscript{56} This might also prove the 2D and 3D growth stages in sputtered MoS$_2$. A similar observation of 2D and 3D growth stages has been reported earlier.\textsuperscript{57} This structural anisotropy in MoS$_2$ films also gives rise to anisotropic oxidation. It is known that oxidation of MoS$_2$ starts from edge crystal planes, and oxidation is very easy for these planes compared to the basal planes.\textsuperscript{58} The (002) basal plane is more protected against oxidation. However, as already reported, the edge plane, that is (100), is in more contact with the environment and is more reactive to oxidation.\textsuperscript{59} As shown in Figure 1c, there is no linear change in the oxidation time with increasing thickness. The oxidation time for Z$_{2.5}$ is 13.2 min, while it is 23.0 min for Z$_{30}$.

This result is because of the formation of the same (002) basal plane in both thin and thick films, where the first nanowalls are extremely fast oxidized, followed by very slow oxidation of the (002) basal plane. As shown in Figure 2e,g, the thickness of walls is approximately about 10 nm making oxidation easier. In addition, sputter-grown MoS$_2$ films are highly sulfur-deficient,\textsuperscript{60} and this might be helpful for the oxidation process. XRD patterns show that the edge plane (100) is almost diminished in the partially oxidized MoS$_2$/MoO$_3$ sample. However, the (002) plane can still be observed, belonging to the MoS$_2$ basal plane, which indicates that the oxidation starts from the edge planes. Furthermore, it can be seen that MoO$_3$-related XRD peaks start to appear. Overall, all the MoS$_2$-related XRD peaks entirely disappear, and the appearance of the (020) peak and several other XRD peaks belonging to the oxide indicates the successful transformation into α-MoO$_3$.\textsuperscript{55}
Figure 2d shows the Raman spectra of MoS$_2$, MoS$_2$/MoO$_3$, and MoO$_3$. Both E$_{2g}^1$ and A$_{1g}$, which are related to in-plane and out-of-plane Raman optical phonon modes of MoS$_2$, respectively, appear for each different thickness. B$_{1g}$ and A$_{1g}$ modes of $\alpha$-MoO$_3$ start to appear for the partially oxidized MoS$_2$/MoO$_3$ structure. After oxidation, all the MoS$_2$-related Raman peaks disappear, indicating that fully oxidized $\alpha$-MoO$_3$ is achieved. The primary purpose of this study is to investigate the oxidation of MoS$_2$ nanowalls without changing the morphology of films. Figure 2e–h shows the FESEM images of 2.5 and 30 min grown MoS$_2$ and MoO$_3$ after thermal oxidation. The FESEM images of MoS$_2$ show the homogeneous distribution of nanowalls throughout the substrate. It is also seen from FESEM images that increasing the deposition time gives rise to extra branches growing on nanowalls. Cross-sectional SEM images also show vertically grown nanowalls (for cross-sectional FESEM images of Z$_{2.5}$, Z$_{7.5}$, Z$_{10}$, and Z$_{30}$, see Supporting Information, Figure S1). From transmission electron microscopy images of obtained MoO$_3$, it can be seen that the Mo to Mo distance between two layers is about 1.37 nm (Supporting Information, Figure S3) which is close to the theoretical value of 1.4 nm. Figure 2f,h shows the FESEM images of thermally oxidized MoO$_3$ grown for 2.5 and 30 min. As seen from FESEM images, there is no significant change in the morphology of oxide films compared to the sulfide films.

Figure 3a shows the XPS survey spectra of 30 min grown MoS$_2$, fully oxidized $\alpha$-MoO$_3$, as well as the partially oxidized MoS$_2$/MoO$_3$ sample. The figure shows only peaks belonging to the C, O, S, and Mo elements. The C element peak is
attributed to surface contamination. This adventitious C–C binding energy is used to correct the spectra obtained. The inset figure shows the energy regions of O and S elements in the survey spectra. The intensity of the O element peak is the weakest in the MoS$_2$ sample, which is due to the surface oxidation, and it is increased for the oxidized samples. On the other hand, the S element peak is the maximum for the MoS$_2$ sample, as shown in the inset and the high-resolution spectra in Figure 3b, while it diminishes for the fully oxidized $\alpha$-MoO$_3$ sample. The partially oxidized MoS$_2$/MoO$_3$ sample shows minimal S element peak intensity as seen in the spectra, although we tried to obtain a more significant intensity by taking out the sample from oxidation in a few minutes. Nevertheless, it is realized that the surface is fully oxidized upon starting the oxidation because the nanowall morphology of MoS$_2$ is highly active for oxidation, which is already discussed in the XRD analysis. The calculated atomic percentages of the elements are given in the inset table. This data clearly shows the successful oxidation of the sputtered MoS$_2$ samples. Figure 3c shows the high-resolution Mo 3d region spectra of the three samples investigated in the study. An S 2s peak is seen for the MoS$_2$ sample, while no signal appears for the fully and partially oxidized samples. It is apparent in the figure that the Mo binding energy peak appears

| Sample Name | Mo (%) | S (%) | O (%) |
|-------------|--------|-------|-------|
| MoS$_2$     | 28.6   | 56.5  | 15.0  |
| MoS$_2$/MoO$_3$ | 27.2   | 2.2   | 70.5  |
| MoO$_3$     | 25     | 0     | 75.0  |
on the lower energy side, indicating the Mo$^{4+}$ oxidation state of the MoS$_2$ sample. This confirms the formation of MoS$_2$. On the other hand, partially and fully oxidized samples show similar binding energy peaks, shifting to a higher binding energy corresponding to the Mo$^{6+}$ oxidation state. This confirms the formation of MoO$_3$ after thermal oxidation.

Figure 3d−f shows the depth profile of the 30 min partially oxidized sample, which shows how the oxidation process occurs. The Mo 3d high-resolution depth profile is obtained for a total of 30 cycles of measurements. The Mo 3d binding energy peaks appear at 233.1 and 236.1 eV, which are similar up to the sixth etch cycle. These binding energy values correspond to the Mo$^{6+}$ oxidation state, confirming the formation of MoO$_3$ after thermal oxidation.

Figure 3d−f shows the depth profile of the 30 min partially oxidized sample, which shows how the oxidation process occurs. The Mo 3d high-resolution depth profile is obtained for a total of 30 cycles of measurements. The Mo 3d binding energy peaks appear at 233.1 and 236.1 eV, which are similar up to the sixth etch cycle. These binding energy values correspond to the Mo$^{6+}$ oxidation state, confirming the formation of MoO$_3$. As seen in Figure 3e, the Mo peak displays a binding energy shift as the etch cycle number increases. At a lower binding energy, the shoulder starts to appear at the sixth etch cycle. The evolution of the shoulder peak can be clearly seen in the spectra in which it first appears as a shoulder, then becomes more prominent in terms of intensity, and finally becomes a separate dominant peak. Although some reports show the reduction of MoO$_3$ to lower oxidation states with Ar$^+$ ion sputtering, it can be seen in the S element depth profile in Figure 3f that the S element appears at the sixth cycle and becomes highly dominant as the number of etch cycles is increased. These two Mo and S elements’ depth profiles indicate that oxidation of MoS$_2$ starts from the surface and continues for the entire depth of the sample, as previously discussed in the XRD data. It is clear that oxidation did not definitely occur beyond the 14th etch cycle for the partially oxidized MoS$_2$/MoO$_3$ beyond that cycle, bare, not oxidized MoS$_2$ is present, which is confirmed by the Mo 3d and S 2p photoelectron binding energy peaks.

3.3. H$_2$ Gas-Sensing Performances and Mechanism. MoO$_3$ films with four different thicknesses corresponding to their deposition times of 0.5, 2.5, 7.5, and 30 min, indicated as Z$_{0.5}$, Z$_{2.5}$, Z$_{7.5}$, and Z$_{30}$, respectively, are studied. Figure 4a−e shows dynamic responses, response, and recovery times, and response (I$_{H2}$/I$_{air}$) of MoO$_3$ sensors at different operating temperatures and for different H$_2$ gas concentrations. Figure 4a shows dynamic responses of MoO$_3$ nanowalls for 1000 ppm H$_2$ gas operating at a temperature of 100 °C. It can be observed that the sensor responses decrease as the thickness increases. At a lower binding energy, the shoulder starts to appear at the sixth etch cycle. The evolution of the shoulder peak can be clearly seen in the spectra in which it first appears as a shoulder, then becomes more prominent in terms of intensity, and finally becomes a separate dominant peak. Although some reports show the reduction of MoO$_3$ to lower oxidation states with Ar$^+$ ion sputtering, it can be seen in the S element depth profile in Figure 3f that the S element appears at the sixth cycle and becomes highly dominant as the number of etch cycles is increased. These two Mo and S elements’ depth profiles indicate that oxidation of MoS$_2$ starts from the surface and continues for the entire depth of the sample, as previously discussed in the XRD data. It is clear that oxidation did not definitely occur beyond the 14th etch cycle for the partially oxidized MoS$_2$/MoO$_3$ beyond that cycle, bare, not oxidized MoS$_2$ is present, which is confirmed by the Mo 3d and S 2p photoelectron binding energy peaks.
sensors used in the current study. The highest response is $3.2 \times 10^7$ for sensor Z2.5, followed by Z7.5 with a $2.2 \times 10^6$ response, as seen in Figure 4e. However, as shown in Figure 4a, the maximum current value reached for Z7.5 is smaller than that for Z0.5, which shows a response of $3.3 \times 10^5$. The difference comes from the conductivity change of the samples with the thickness, which leads to different $I_{\text{air}}$ values. Apparently, this value is minimum for the thicker samples, which is on the order of picoamperes, while it is on the order of nanoamperes for the thinnest sample. Although Z2.5 displays the highest response, it should be noted that the responsivity and recovery times should also be considered. Therefore, sensor Z0.5, with the response and recovery times of 379 and 304 s, respectively, shows the best sensing performance at a temperature of 100 °C for 100 ppm H2 gas. It should be kept in mind that the recovery current could not reach the starting current value, $I_{\text{air}}$, at an operating temperature of 100 °C. The starting current value of the Z0.5 sensor is $2.0 \times 10^{-9}$ A, while after recovery, it reaches a current value of $3.6 \times 10^{-7}$ A. Although the difference is about 2 orders between the starting and recovery values, this recovery value seems negligible when it is considered that the response of the sensor is more than $\sim 10^5$.

The dynamic responses of four sensors are demonstrated at an operating temperature of 200 °C in Figure 4b. Sensor Z0.5 shows the highest response of $2.4 \times 10^4$, followed by Z2.5 with a response of $1.8 \times 10^4$ under 1000 ppm H2 gas conditions. In addition, the figure shows that the Z0.5 sensor reaches the highest current value in the presence of H2 gas. It is preferable for a gas sensor to reach the current value as high as possible, and the Z0.5 sensor is therefore even better due to the ease of detection of higher current values. Sensor Z0.5, due to its responsivity and recovery times of 633 and 224 s, respectively, shows the best performance among other sensors. In addition, Z0.5 shows the maximum response for 100 ppm at an operating temperature of 200 °C. For that reason, measurements of H2 concentrations under 100 ppm were performed for the Z0.5 sensor as shown in Figure 4f. At a temperature of 200 °C, a response of 0.84 (84%) for 10 ppm H2 gas is measured for Z0.5. Figure 4c indicates the dynamic response of sensors for 100, 500, and 1000 ppm at an operating temperature of 300 °C. Z0.5 demonstrates a maximum response of $7.4 \times 10^4$ in comparison with other sensors. However, as shown in Figure 4b,c, the maximum current value that the Z0.5 sample reaches at 200 °C is about 3 times larger than that at 300 °C. Regarding the
recovery point, the dynamic responses at a temperature of 300 °C show the best recovery. The sensors recover fully and reach the starting current before H2 is introduced into the chamber, as seen in the inset figure of semilogarithmic plots for 500 ppm H2 gas. Figure 4g shows the 11-cycle sensor response for sample $Z_{0.5}$ at 300 °C for 1000 ppm H2 gas and the repeatability of the sensor. As seen in the figure, the response does not change significantly after 11 cycles of measurements.

Further experiments were conducted to study the hydrogen-sensing mechanism and the effect of Pd catalysis on H2-sensing performances of MoO3 nanowalls. The H2 gas-sensing mechanism of metal oxide-based gas sensors is generally explained as follows: oxygen molecules get adsorbed on the surface of metal oxide, which extract electrons from the conduction band of the semiconductor and reduce the conductivity of the material, resulting in the formation of negatively charged oxygen species at different operating temperatures including O$_2^-$, O$^-$, and O$^{2-}$. In the case of n-type semiconductors, this reduction in conductivity is reversed by exposure to reducing gases such as NH$_3$ or H2. Hydrogen bonding with oxygen species that are adsorbed on the semiconductor surface removes surface-adsorbed oxygens that introduce electrons into the conduction band and lead to an increase in the conductivity of metal oxide. The formation process of negatively charged oxygen ions can be summarized as follows:

\[ \text{O}_2\text{ (gas)} \leftrightarrow \text{O}_2\text{ (ads)} \text{ (100 °C)} \]
\[ \text{O}_2\text{ (ads)} + e^- \leftrightarrow \text{O}_2^-\text{ (ads)} \text{ (100 – 300 °C)} \]
\[ \text{O}_2^-\text{ (ads)} + e^- \leftrightarrow 2\text{O}^-\text{ (ads)} \text{ (>300 °C)} \]

Depending on the nature and structure of materials and the behavior with different target gases, each gas sensor material has a different optimum operating temperature. The H2 gas-sensing mechanism of chromogenic materials such as MoO3 cannot be explained just by the oxygen adsorption model because H2 molecules and H+ ions not only incorporate with adsorbed oxygens but also attack different coordinated oxygens in the structure of the material in order to reduce MoO3 to MoO3-x. In order to improve the gas-sensing properties of metal oxide semiconductors, there have been different approaches applied so far. One of them is decorating or doping with noble metals such as Pt, Pd, or Au, which act as catalysts. To find out whether noble metals change the work function of metal oxide, there are two approaches, which are “chemical sensitization” and “electronic sensitization.” Chemical sensitization is the disassociation of the target analyte molecule called the spillover effect. In this case, the deposition of metal catalysts does not change the conductivity of the sensing material. Electronic sensitization refers to the temporary oxidation of a catalytic metal, which gives rise to the formation of a depletion layer. This depletion layer reduces the conductivity of the sensing material. Oxygens on the surface of the catalyst metal are removed when the H2 gas is introduced. This appears as thinning of the depletion layer, which increases material conductivity.

Gasochromic measurements have been designed to determine the sensing mechanism related to hydrogen intercalation. The inset in Figure 5 shows the schematic illustration of the sensor materials, explaining the sensing mechanism of gas sensors produced in the study. Black dots on the surface represent the Pd nanostructures as a catalytic material. FESEM images of Pd-decorated MoO3 nanowalls are shown in Figure S5. The left side of the figure represents the sensing mechanism at 100 °C, while the right side shows that at 300 °C. Figure 5a,b shows the transmittance changes of samples $Z_{2.5}$ and $Z_{30}$ at a wavelength of 700 nm for 1000 ppm H2 gas at operating temperatures of 100 and 300 °C, respectively. There are no significant changes in transmittance for both sample measurements performed at 300 °C; however, significant changes of 25.5 and 15.0% transmittance are observed for samples $Z_{2.5}$ and $Z_{30}$ respectively, at 100 °C. These results show similarity to those of the electrical sensor measurement in which the sensor response at 100 °C is higher than that at 300 °C. Gasochromic measurements indicate that more H+ ions intercalate at 100 °C temperature than those at 300 °C. There might be a couple of reasons for this to observe. First of all, it might be possible with more H2 gas desorption from the surface at higher temperatures by removing the active number of H2 gas molecules, as seen in the inset figure circle number 2. For this reason, the spillover zone at 300 °C is smaller than that at 100 °C, as seen in the schematic illustration. On the other hand, the MoO3 sites reduced by the H2 gas are oxidized easily by the oxygen molecules in dry air with rising temperature because 300 °C is very close to the oxidation temperature of MoS2, as it is shown by the oxidation at around 380 °C from the in situ measurements. Actually, there is a trade-off between the oxidation of the sites by the oxygen in dry air and reduction by H2 gas. It is this trade-off that creates an equilibrium slab of active thickness, which basically determines the conductivity change of the sensors. In order to confirm this hypothesis, gasochromic measurements under H2 gas mixed with N2 were performed. As seen in Figure 5c, the transmittance change of $Z_{30}$ under 1000 ppm H2 at a temperature of 100 °C and under N2 conditions at a wavelength of 700 nm is more than 70.0%, which is about 4.8 times higher than that of H2 mixed in the air. The inset figure shows the colored state of the sample. The response is much higher under N2 gas compared to that under dry air. It is known that N2 itself removes surface-adsorbed oxygen species, which boosts the reduction of MoO3, and in the case of the nanostructure, this effect is stronger than that on compact films because more surface is exposed to N2 gas. This also indicates that the equilibrium slab thickness is not well enough to change the conductivity of the thick sensors compared to that of the thinner samples, indicating the higher response in the thinner samples such as $Z_{2.5}$ and $Z_{0.5}$.

In order to understand the effect of Pd catalysis, sensor measurements were performed for the sample $Z_{0.5}$ without Pd loading. Figure 5d shows the dynamic sensor responses of $Z_{0.5}$ with and without Pd catalysis at 100 °C temperature. Sensor responses obtained for $Z_{0.5}$ under 1000 ppm H2 in air without Pd loading are 4074, 114, and 98 fold at 100, 200, and 300 °C operating temperatures, respectively. These values are 79.7 (at 100 °C), 207 (at 200 °C), and 754 (at 300 °C) times smaller than that obtained at the same operating temperature (see Supporting Information, Figure S4) for Pd-loaded samples. This indicates that the spillover effect occurs at different temperatures and boosts the sensor sensitivity and response time. At all operating temperatures for Pd-loaded samples, sensor responses increase significantly compared to those of bare samples. On the other hand, the sensor responsivity of Pd-loaded sample with considering temperature, shows a
similar trend to that without Pd catalysis. Figure 5e shows the average current change rates of Pd-loaded Z0.5 sample at different operating temperatures for different time intervals of sensing times. As shown in Figure 5e, for the first 100 s of gas sensing, the average current change rate for 300 °C operating temperature is 2 nA/s, and it reaches the maximum value of 31 nA/s between 200 and 250 s. The current variation by time is almost constant through 50–400 s time intervals. However, the average current change rate starts with 150 pA/s for the first 100 s and then it reaches the maximum value of 6.5 μA/s at a time interval of 250–300 s. The rate variation is much higher than the result obtained at 300 °C. These different current change rates at different temperatures at the beginning and in the middle of the gas-sensing process can be explained by the following steps of sensing mechanism: H2 molecules first reach the surface, then H+ ions are formed by the spillover effect, these ions play a role in removing adsorbed surface oxygens, causing the conductivity change which is relatively small at the beginning of the process. Then, more H+ ions are formed due to the spillover effect, and the H+ intercalation begins in the inner sections of MoO3 due to the field-effect caused by the H+ in contact with each other at the spillover intersection zones, as seen in the schematic representation of the gas sensor in Figure 5. The reduction of MoO3 starts at the bulk, forming water vapor that leaves the structure, causing a dramatic increase in the current change rate as illustrated in the inset figure circle number 3 of Figure 5. Room-temperature (RT) H2 gas-sensing measurement for sample Z0.5 for 1% H2 gas concentration is shown in Supporting Information, Figure S6. A response of 7.5 × 107 was achieved at RT. The data are included in the Supporting Information due to the long sensing and recovery times.

4. CONCLUSIONS

In conclusion, MoS2 nanowall films with four different thicknesses (40, 115, 370, and 1440 nm) deposited by RFMS were successfully turned into α-MoO3 by thermal oxidation without changing the morphology of the films, which are confirmed by XRD, Raman, FESEM, and XPS measurements. In situ measurements during the oxidation process were performed to control the oxidation. They also show that the nanowalls perpendicular to the substrate turn to the oxide material faster than the basal planes. It is concluded from the depth profile XPS measurement that the oxidation starts from the nanowalls found on the surface and continues through the depth of the material. The conversion from MoS2 to MoO3 is also confirmed by Raman and XRD measurements. H2 gas-sensing performances of MoO3 films were determined on films with different thicknesses at 100, 200, and 300 °C operating temperatures. The thinnest sample with a thickness of ~40 nm shows the outstanding performance with a response of 3.3 × 109-fold. Response and recovery times of 379 and 304 s, respectively, are achieved at an operating temperature of 100 °C. In addition, gaschromatic measurements were performed to explain the H2-sensing mechanism of MoO3 at 100 and 300 °C. Transmittance changes of about % 25.5 and % 15.0 are achieved for samples with thicknesses of 115 and 1440 nm, respectively, at a temperature of 100 °C. Also, a further gaschromatic experiment was performed for 1000 ppm H2 in a N2 atmosphere to understand the intercalation mechanism of the H+ ions. Elimination of the H+ ions by dry air is also confirmed.
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