Hydrogen Interactions with Nanostructured Metal Oxide Thin Films Prepared by Reactive Magnetron Sputtering Technique

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Abstract

In this paper, we demonstrate the advantages of two advanced sputtering techniques for the preparation of nanostructured thin films of metal oxides. We combined tungsten oxide (WO_3) thin films with other materials to tune the composition, electrical, and structural properties. Thin films of WO_3 were prepared using the DC and HiPIMS technique, which allowed us to tune the phase composition and crystallinity of the oxide by changing the deposition parameters. The second material was then added on top of these films. We prepared nano-islands of copper tungstate ($CuWO_4$) by reactive rf sputtering and Pd particles formed during conventional dc sputtering. The specimens were tested for their conductive response to a hydrogen concentration in synthetic and humid air at various temperatures. The performance of the individual films is presented as well as the details of the synthesis. These nanostructured materials prepared using magnetron sputtering are very suitable for use in miniaturized energy production/storage devices, PEC, PVC, sensing applications etc.

Keywords: Metal Oxides, $CuWO_4$, Magnetron Sputtering, Hydrogen, and HiPIMS.

INTRODUCTION

Nanostructured metal oxides are the most used materials for various applications such as photovoltaic cells, photoelectrochemical cells, water splitting, and other electronic devices due to their tunable bandgap, diverse composition, and high chemical and thermal stability[1], [2].

A variety of methods were used to prepare the metal oxide nanostructured films. Magnetron sputtering is one of the promising preparation methods that provide easy control of the microstructures, structure, and other physical properties.

In this work, we demonstrate magnetron-based techniques which are used to tune the stoichiometry, structural, and electrical properties of sputter (DC) deposited WO_{3-x} films combined with CuO ($CuWO_4$) and Pd/PdO nanoparticles. The electrical properties of as-prepared metal oxide combinations were studied on the surface interaction with H_2 in the synthetic and humid air.

MATERIALS AND METHODS

All the films were deposited by the reactive sputtering technique. Two types of WO_{3-x} films were deposited from a metallic target using reactive dc magnetron sputtering and HiPIMS in the mixture of oxygen and argon gases. The dc sputtering deposited 20 nm WO_{3-x} films were then covered by 5 nm CuO (using rf sputtering deposition) which leads to the formation of $CuWO_4$ nano-islands on the surface of WO_3 due to the higher deposition temperature of CuO film [3]. The three-layered system is prepared by the three-step deposition process where 5 nm WO_3 thin films were deposited on 20 nm CuO films to form $CuWO_4$/CuO. The $CuWO_4$ bilayers were then decorated by 0.8 nm Pd nanostructures.

The HiPIMS deposited WO_{3-x} films were decorated by Pd nanoparticles using rf magnetron sputtering followed by heating up to 350 °C. For more details see Ref. [4].

RESULTS AND DISCUSSION

The SEM micrographs of the combinations of the metal oxides can be seen in Figure 1. The formation of Pd nanoparticles over HiPIMs deposited WO3-x films is shown in Figure 1a. The formation of $CuWO_4$

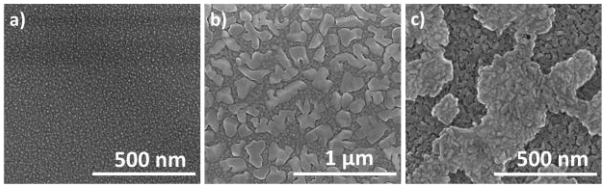

Figure 1 SEM micrographs of a) Pd loaded WO_{3-x} prepared by HiPIMS, b) $CuWO_4/WO_{3-x}$ prepared by rf/dc reactive magnetron sputtering, and c) three layered Pd/$CuWO_4$/CuO system prepared by magnetron spuutering technique

nanoislands over WO_3 and CuO are shown in Fig 1b and Figure 1c. also exhibits the formation of Pd nanoparticles on CuO and PdO nano-islands on $CuWO_4$.
Figure 1
Figure 1c also exhibits the formation of Pd nanoparticles on CuO and PdO nano-islands on $CuWO_4$.
On the basis of the XRD pattern and the SEM analyses, a simple description of the growth process can be formulated. Sputtering of a W target in an Ar and O_2 working gas mixture leads to the deposition of a dense and smooth WO_{3-x} layer. Subsequently, the top-most part of this film reacts with the arriving adatoms during the sputtering of a Cu target in a similar gas mixture leading

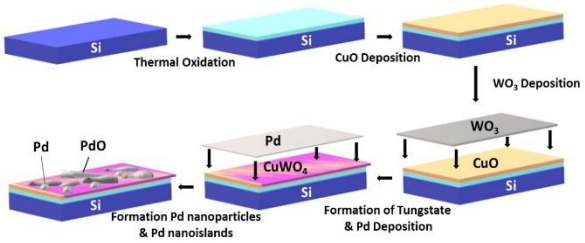

Figure 2 A scheme and description of the deposition process for three-layered system Pd/$CuWO_4$/CuO

to the formation of the $CuWO_4$ islands [3], [5]. The sketch of the process is in Figure 2.

The composition and structure of metal oxides can easily be tuned by varying the HiPIMS deposition parameters as can be seen in Table 1.

Table 1 The stoichiometry and structure of the HiPIMS deposited WO_{3-x} at various voltage pulse lengths. The Sheet resistance is measured at 190 °C

Voltage Pulse Length	Crystalline Phases	Resistance (Ω/sq)	As-Deposited Stoichiometry
500 µs	Monoclinic (triclinic)	3.4 x 10^8	2.76
50 µs	Tetragonal + monoclinic	7.3 x 10^6	3.01
DC	Tetragonal + monoclinic	1.2 x 10^6	2.94
100 µs	Tetragonal + triclinic	1.7 x 10^5	3.07
200 µs	Triclinic (monoclinic)	2.0 x 10^5	2.92
800 µs	Triclinic (monoclinic)	6.3 x 10^2	2.15

The relative response of hydrogen interaction on the corresponding materials is shown in Table 2.
The baseline resistances of as-prepared metal oxides and the resistance in presence of hydrogen (R_{H2}) are measured at higher temperatures (in a range of 200-350 °C) by the four-point probe method. The value of the resistance signaificantly changes with the introduction of the hydrogen.

Table 1 Baseline Resistances of the metal oxides and their combinations in the absence and presence of hydrogen gas.

Specimens	Baseline Resistance	R_{H2}
WO_3 (DC)	1.2 x 10^6	9.7 x 10^5
WO_{3-x} (HiPIMS)	3.4 x 10^5	2.0 x 10^5
Pd/WO_{3-x}	3.4 x 10^8	2.04 x 10^3
$CuWO_4$/WO_{3-x}	1.1 x 10^7	4.5 x 10^6
$CuWO_4$/CuO	5.0 x 10^8	2.0 x 10^8
Pd/$CuWO_4$/CuO	6.0 x 10^{11}	2.6 x 10^{12}
CuO	3.4 x 10^5	8.2 x 10^5

The values of the resistance for the metal oxide combinations are relatively higher than that for the pure metal oxide (WO_3 and CuO). The explanation is based on the formation of the heterojunction at the interface materials. While Pd nanoparticles behaved as the catalyst for the base metal oxide films to improve the variation in resistance even at lower temperatures at a humid environment. The value of the resistance was found to be constant at 0, 30, 60, and 95% of the relative humidity in the synthetic air.
The reaction mechanism for the hydrogen interaction with metal oxide[6], [7] is as follows.
In dry conditions, the surface adsorbed O species react with hydrogen which leads to change (increase or decrease depends on the type of metal oxide semiconductor) in the baseline resistance by changing the depletion layer near the surface (described by green arrows in Figure 3).

$$\frac{1}{2}O_2 + 2e^- \rightarrow O_{ads}^{2-} \quad (1)$$

$$H_{2\,ads} + O_{ads}^{2-} \rightarrow H_2O + 2e^- \quad (2)$$

In humid environment the adsorption of water molecules is described by one of the following mechanisms:

$$H_2O + M + O_O \rightarrow (M^+ - OH^-) + (OH)_O^+ + e^- \quad (3)$$

Or

$$H_2O + 2M + O_O \rightarrow 2(M^+ - OH^-) + V_O^{2+} + 2e^- \quad (4)$$

However, when the Metal oxides are exposed to hydrogen in a humid environment, the water molecules react with adsorbed oxygen species on the surface, leading to an increase in the baseline resistance of the metal oxides. At the same time, hydrogen cannot find the oxygen species to react with and the interchange of electrons, and thus the change in the resistance is reduced (red arrows in Figure 3).
Both involve the formation of OH^- groups on the surface that is bonded to the metal ion M^+. According to the first mechanism, Eq. (3), the other hydrogen from the water molecule forms a rooted hydroxyl group $(OH)_O^+$ with the lattice oxygen O_O.

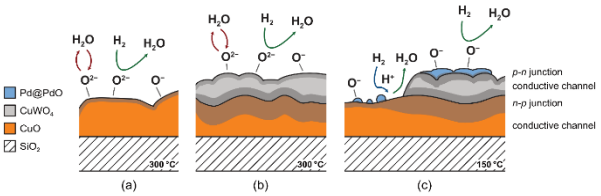

Figure 1 Scheme of synthesized structures with indicated reactions on the surface.

In the other proposed mechanism, Eq. (4), the lattice oxygen forms another adsorbed OH^- bonded to M^+ while leaving an oxygen vacancy $(V)_O^{2+}$.

To overcom the issue of the reduction of the response, the films were decorated with 0.8 nm of Pd. According to Raman spectroscopy, XRD, and other published works on similar systems [8], [9] Pd particles/objects are covered with PdO on their surfaces. Pd and PdO play several important roles in the reaction,:

i) Pd promotes the selectivity towards hydrogen and, at the same time, reduces the response temperature by facilitating the dissociation of H_2 [10] (blue arrow in Fig 3.
ii) PdO favors the adsorption of oxygen over the hydroxyl groups [9].
iii) PdO forms another heterojunction (*p–n)* with the topmost layer of copper tungstate.

See ref. [5] for more details.

CONCLUSION

The synthesis of multilayered thin-film materials using the sputtering technique is demonstrated. The variation in the resistivity of the combined materials is relatively better than the pure material. The structure and composition of the metal oxides are easily controlled by the deposition parameter in the HiPIMS method. resistive response in presence of hydrogen is significantly enhanced just by playing the stoichiometry and structure of the films. Also. by adding Pd particles to the three-layered system the influence of relative humidity was reduced.

These kinds of materials are quite promising for Photovoltaic cells, Solar cells, Gas sensing, Photoelectrochemical cell, energy production, and energy storage devices.

REFERENCES

[1] P. T. Moseley, “Progress in the development of semiconducting metal oxide gas sensors: A review,” *Measurement Science and Technology*, vol. 28, no. 8. Institute of Physics Publishing, Jun. 28, 2017. doi: 10.1088/1361-6501/aa7443.

[2] G. Korotcenkov and B. K. Cho, “Metal oxide composites in conductometric gas sensors: Achievements and challenges,” *Sensors and Actuators, B: Chemical*, vol. 244. Elsevier B.V., pp. 182–210, 2017. doi: 10.1016/j.snb.2016.12.117.

[3] N. Kumar, J. Čapek, and S. Haviar, “Nanostructured CuWO4/WO3-x films prepared by reactive magnetron sputtering for hydrogen sensing,” *International Journal of Hydrogen Energy*, vol. 45, no. 35, pp. 18066–18074, Jul. 2020, doi: 10.1016/j.ijhydene.2020.04.203.

[4] N. Kumar, S. Haviar, J. Rezek, P. Baroch, and P. Zeman, “Tuning stoichiometry and structure of Pd-WO3−x thin films for hydrogen gas sensing by high-power impulse magnetron sputtering,” *Materials*, vol. 13, no. 22, pp. 1–12, Nov. 2020, doi: 10.3390/ma13225101.

[5] N. Kumar, S. Haviar, and P. Zeman, “Three-layer PdO/CuWO4 /CuO system for hydrogen gas sensing with reduced humidity interference,” *Nanomaterials*, vol. 11, no. 12, Dec. 2021, doi: 10.3390/nano11123456.

[6] J. Miao, C. Chen, and J. Y. S. Lin, “Humidity independent hydrogen sulfide sensing response achieved with monolayer film of CuO nanosheets,” *Sensors and Actuators, B: Chemical*, vol. 309, Apr. 2020, doi: 10.1016/j.snb.2020.127785.

[7] B. Urasinska-Wojcik and J. W. Gardner, “H2S Sensing in Dry and Humid H2 Environment with p-Type CuO Thick-Film Gas Sensors,” *IEEE Sensors Journal*, vol. 18, no. 9, pp. 3502–3508, May 2018, doi: 10.1109/JSEN.2018.2811462.

[8] Y. Cao, C. Zhou, Y. Chen, H. Qin, and J. Hu, “Enhanced CO Sensing Performances of PdO/WO3Determined by Heterojunction Structure under Illumination,” *ACS Omega*, vol. 5, no. 44, pp. 28784–28792, Nov. 2020, doi: 10.1021/acsomega.0c04137.

[9] S. Ma, M. Hu, P. Zeng, M. Li, W. Yan, and Y. Qin, “Synthesis and low-temperature gas sensing properties of tungsten oxide nanowires/porous silicon composite,” *Sensors and Actuators, B: Chemical*, vol. 192, pp. 341–349, Mar. 2014, doi: 10.1016/j.snb.2013.10.121.

[10] F. E. Annanouch *et al.*, “p-Type PdO nanoparticles supported on n-type WO3 nanoneedles for hydrogen sensing,” *Thin Solid Films*, vol. 618, pp. 238–245, Nov. 2016, doi: 10.1016/j.tsf.2016.08.053.

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