RESEARCH ARTICLE

Gas Sensing Investigation of Porous Hot-wire Molybdenum Disulphide Thin Films

Giorgos Papadimitropoulos[*,1,2], *Angelika Balliou*[1], *Dimitris Davazoglou*[1] *and Dimitrios N. Kouvatsos*[1]

The gas sensing properties of porous hot-wire MoS_2 ($hwMoS_2$) thin films have been studied. The films were deposited on oxidized silicon substrates by heating a molybdenum filament in a vacuum chamber in H_2S environment. The samples remain at room temperature during the deposition and the grown films are amorphous and porous. Reversible changes of the current values in the $hwMoS_2$ films were observed due to the presence or upon removal of chemical gases such as hydrogen (H_2) and carbon monoxide (CO). The sensitivity, was dependent on the concentrations of the gases and the temperature of measurement. The response time was found to be comparable to the recovery time and of the order of a few seconds. It is important to note that the surface of the $hwMoS_2$ films was not activated with any catalyst, which is a common practice in most thin films used for gas sensing, rendering our process simpler and cheaper.

Introduction

Gas sensing has been increasingly important for modern societies due to the need for fast identification of toxic gases and organic vapours. The detection of hazardous gases finds applications in the industrial and medical sectors for environmental and human security, emission control and medical diagnosis [**1-5**]. A material is appropriate as sensing element in chemical sensors when it is capable to return to its initial properties (e.g., resistance value) upon removal of the cause that induced the change of its properties. Many materials have been used up to now for the formation of chemical sensorsincluding conducting polymers, carbon nanotubes and metal oxides such as WO_3, Ta_2O_5 and MoO_3 [**6**]. Among these materials, metal oxides have shown the best performance, in terms of time response and sensitivity. Metal oxides are widely used in gas sensing devices since they are cost effective materials and can be easily developed [**7-12**]. However, their major drawback for gas sensing applications is that the resistive metal oxide-based sensors typically work at high temperatures (higher than 300 ^oC), consequently leading to high power consumption. In addition, the high operating temperature values results to signal drift due to the formation of metal oxide grains [**13**]. Another drawback of the metal oxide based chemical sensors is the lack of selectivity without activation of their surface with a noble metal [**6,14-15**].

Over the past decade, graphene, molybdenum disulfide, and tungsten disulfide, have been extensively investigated due to their unique thermal, optical, mechanical, and electronic properties [**16,17**]. Transition metal dichalcogenides (TMDs), carbon nanotubes (CNTs), and graphene structures are alternative materials that can be used to replace metal oxide semiconductors [**18**] and consequently, to improve selectivity and sensitivity. Among the TMDs, MoS_2 is widely used as a solid lubricant in solar cells [**19**], resistive random access memory devices (RRAM) [**20**], supercapacitors [**21**], photo detectors [**22**] and as a catalyst in hydrogen evolution [**23**]. Recent reports have proven that MoS_2 is potentially viable in gas sensing [**24,25**] because of its excellent semiconducting properties. In order to improve the sensitivity and reduce the operating temperature, various noble metals such as platinum, gold and palladium have been used as surface additives [**26,27**].

In this work we examine hot-wire molybdenum disulphide ($hwMoS_2$) thin films as sensing materials for gas sensors. The films are deposited very simply compared to other techniques by heating a molybdenum filament under vacuum in H_2S environment. The samples remain at room temperature during the growth of films rendering hot-wire deposition suitable for plastic and polymeric substrates. The deposited films are amorphous, porous and show reversible current changes upon insertion/removal of a gas; this renders them suitable for chemical sensors.

Experimental

The $hwMoS_2$ thin films were deposited on Si (100) wafers covered by a 100 nm thick thermal silicon oxide. Over the

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latter, gold interdigitated electrodes were patterned using e-beam evaporation and the lift-off technique. The samples were placed 5 cm below the molybdenum filament that was fixed between two Cu current leads. First, the chamber pressure was set constant to 1,5 Torr with the aid of a pressure-control system that consisted of a baratron manometer, a butterfly valve and an electronic unit. Afterwards, the filament was heated at 400 ºC. The deposition time was 30 s and resulted to a film of thickness around 60 nm. With this deposition technique the substrate remains at room temperature throughout the whole deposition process.

For their characterization as chemical sensors, the hwMoS_2 films were packed in classic dual in-line packages (DIL) using the wire bonding technique. The interdigitated electrodes were 50 nm thick (46 nm Au and 4 nm Ti as adhesion layer) and with spaces of 2, 4, 10 and 30 um. The sensing properties of the samples were tested using a home-made setup comprised a small volume stainless steel chamber and a heater that was able to reach temperatures up to 500 ºC, with accuracy ±1 ºC. The concentration of the gases that were used to insert into the chamber, was controlled by mass flow controllers. The sensors were first exposed to synthetic air until they could reach a stable signal value. Then the sensors were exposed to controlled concentrations of the analyte gases. The current changes of the sensors were measured with an electrometer connected to a personal computer via a GPIB interface. It is important to mention that the temperature was measured on the heater and not on the sample, therefore, the real temperature value on the sample was smaller than that measured on the heater, since between the heater and the MoS_2 film, were interposed the ceramic package and the silicon substrate. The setup calibration yielded that the real temperature on the sample was lower than that on the heater by a factor of 1.25. Direct measurement of the temperature on the sample is challenging, since it requires the fabrication of micro-thermocouples integrated on it. Moreover, integrated gas sensors require an intimate heating obtained by a micro-heater integrated on the chip.

In our study, we used an external as our aim was the investigation of the sensing capabilities of the hwMoS_2 films and not the testing of integrated sensors. In addition, in this work the surface of the hwMoS_2 films was not activated with any catalyst, which is a common practice in most thin films used for gas sensing. Activation of the surface with gold or another catalytic material is expected to further improve the performance of the sensors.

Results and discussion

The deposition of the hot-wire MoS_2 films profits from the vapours formed from the reaction of the native oxide on the surface of the Mo filament and the H_2S, according to the following reaction:

$$2MoO_3 + 4H_2S \rightarrow 2MoS_2 + 4H_2O + O_2$$

The above reaction is extensively used for the hydrodesulfurization of oil [**28,29**] and has been studied with various experimental methods [**30,31**]. The structure of MoO_3 consists of MoO_3 octahedra that are linked together forming bi-layers, due to van der Waals forces [**32, 33**]. The sulphidation process of MoO_3 starts by substituting the O ions at the outer surfaces of the bi-layers by S ions [**30,31**]. The S ions then diffuse and substitute the internal oxygen ions in the bi-layers. During this procedure small areas of MoS_2 are formed and linked together by Mo-S-Mo bridges [**31**].

Fig. 1 depicts SEM (a, upper) and AFM (b, down) micrographs of the surface of hwMoS_2 sample that was deposited with the filament at 400 ºC. It is observed that the sample exhibits a granular surface morphology with root mean square value 6 nm and voids between grains. The corresponding void fraction is of the order of 40 % as revealed by Spectroscopic Ellispometry measurements (see supporting information). A possible reason for the high void fraction is that the grains are not compact but are composed of smaller grains. This morphology of films is desired in gas sensing applications because increase the active region resulting in better response time values [**34**].

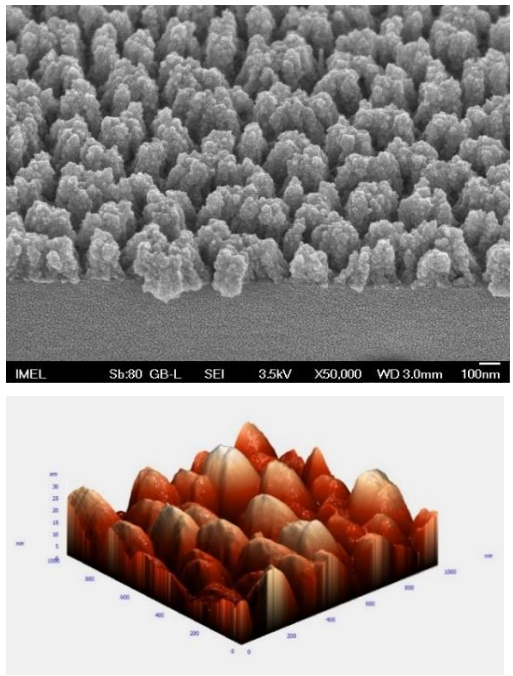

Fig. 1. SEM micrograph (a, upper) and 3D AFM image (b, down) of a MoS_2 thin film.

The deposited films are amorphous as the XRD spectra and UV-vis absorbance measurements revealed (**Fig. 2**). In the XRD spectra there are no crystalline peaks corresponding to MoS_2 while UV-vis absorbance measurements indicate the absence of the excitonic A and B bands at 670 and 610 nm respectively, which are typical of ordered 2H-MoS_2 structures [**35**]. From SE measurements analysis (see supporting information) the band-gap of the deposited films is estimated to be 1.27 eV with no characteristic peaks or features in their spectral

refractive indexes, suggesting an amorphous material with indirect gap.

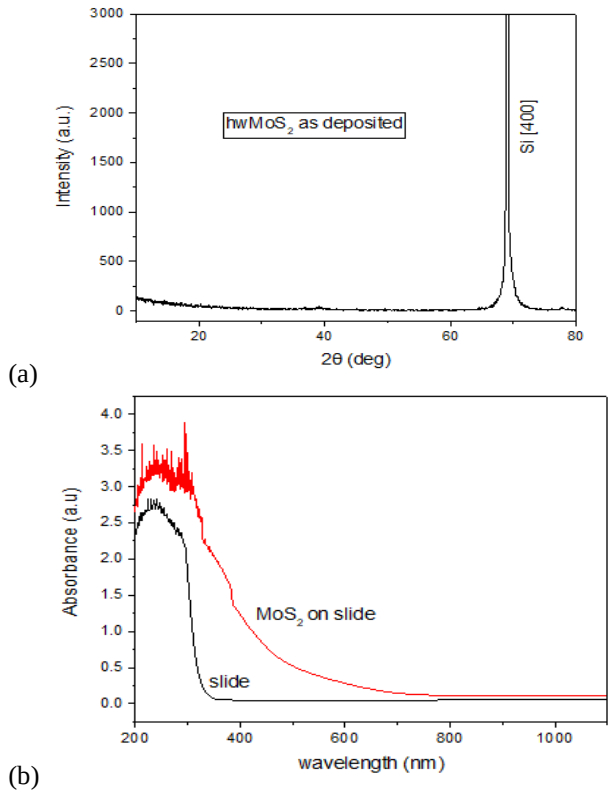

Fig. 2. XRD spectra (a, upper) and UV-vis absorbance (b, down) of as-deposited MoS_2 thin film.

In **Fig. 3**, X-ray microanalysis and Raman spectra indicate the composition of the deposited films. More specifically, X-ray microanalysis reveal that the grown films are composed mostly by Mo and S while Raman pattern indicate the two well-known peaks E_{2g} and A_{1g} at 383,8 cm^{-1} and 408 cm^{-1}, respectively, that are typical for MoS_2 films [**36**].

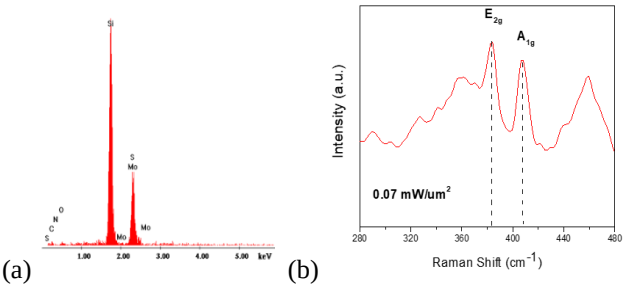

Fig. 3. X-ray microanalysis (a, upper) and Raman spectra (b, down) of hot-wire deposited MoS_2 thin film.

Fig. 4 shows the response-recovery curves for a $hwMoS_2$ sample, at 100 ºC (a, upper) and 200 ºC (b, down), respectively, for H_2 and CO gases at concentrations of 800, 400, 200 and 100 ppm. The measured current increases abruptly when the target gas enters, and then rapidly returns to its initial state when the gas exerts of the testing chamber.

The $hwMoS_2$ gas sensing thin film shows fast response and recovery to CO and H_2. The response time to 100 ppm CO and H_2 at 100 ºC working temperature were recorded as 30s and 37s, respectively. As the gases ppm and the working temperature increase the response and recovery times decrease significantly. These values are relatively small possibly due to the nano-structuring and porosity of the hot-wire MoS_2 thin films.

Repeatability is a significant characteristic to guarantee the reliability and stability of the chemical sensors for long-term operation [**37**]. Thus, the reproducibility of the $hwMoS_2$ thin film gas sensor was tested many times during a period of two months. The $hwMoS_2$ film has stable response to each target gas, indicating the excellent reproducibility of the fabricated gas sensing film.

An explanation of the gas sensing mechanism of the $hwMoS_2$ thin film is that the thin film consists of vertically stacked layers, comprising covalently bonded Mo-S atoms, and each neighbouring layer is connected by van der Waals forces. The relatively weak van der Waals forces enable the infiltration and diffusion of the target gas molecules between the layers. As a result, the resistance of the MoS_2 film drastically changes during the adsorption and diffusion of the gas molecules within its layers.

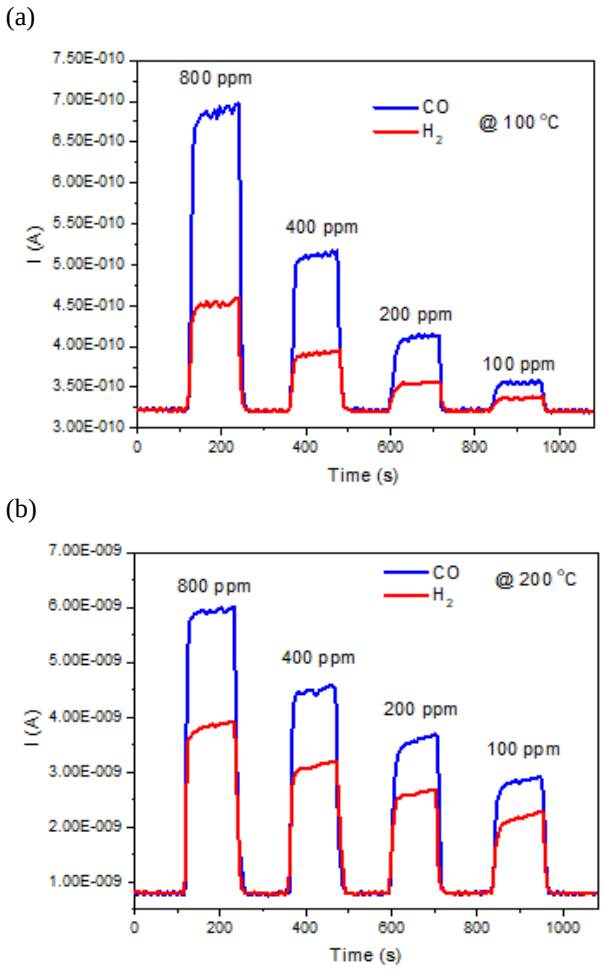

Fig. 4. Time variations of the current at different temperatures.

The dependence of the sensitivity (which is defined as the ratio of the sensor current in air to the sensor current in gases) versus H_2 and CO concentrations is shown in **Fig. 5** (a, upper and b, down) respectively. It is observed that the sensitivity is largely dependent on temperature and there is an almost linear increase of sensitivity with the gas concentration for all the temperatures. With the rise of working temperature values the sensitivity increases. The hwMoS_2 films exhibit better response to CO gas compared to H_2 gas.

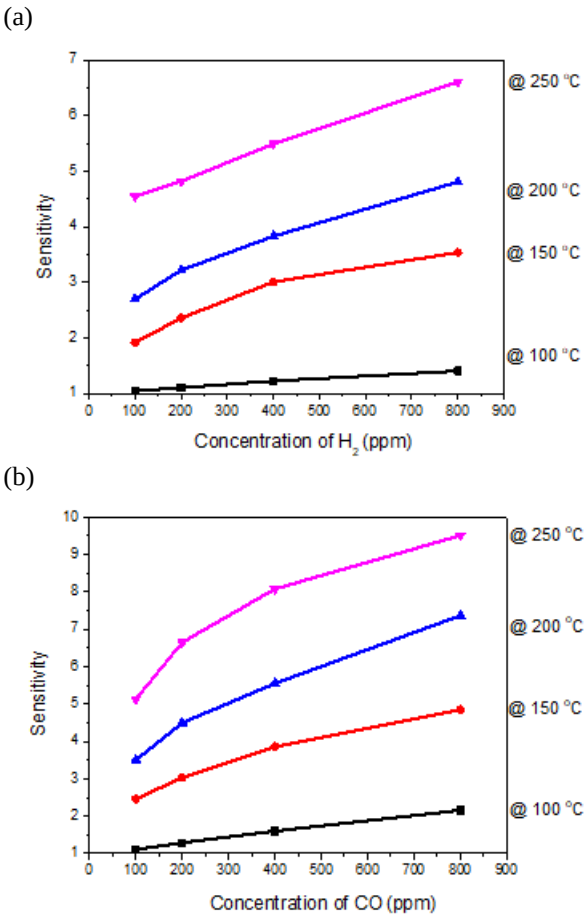

Fig. 5. Variations of sensitivity vs concentration of gases for various temperatures.

In **Fig. 6** the variations of the 90% of the rise time (time interval necessary for the current to rise by 90% of its total variation) as a function of the hydrogen (a, upper) and carbon monoxide (b, down) concentrations at temperature of 150 and 250 °C are shown. It is clear that the carbon monoxide affects more than hydrogen and invokes faster variations in the film resistance. At high gas concentrations it seems that the speed of the current increase becomes less dependent on the nature of the gas and there is saturation of the rise time. This is occurs most likely due to the saturation of all MoS_2 molecules on the surface of the film. The observed rise time values are relatively small and comparable to those mentioned in the literature [**13, 38-40**] due to the nano-structure and porosity of the hot-wire MoS_2 thin films as we mentioned above.

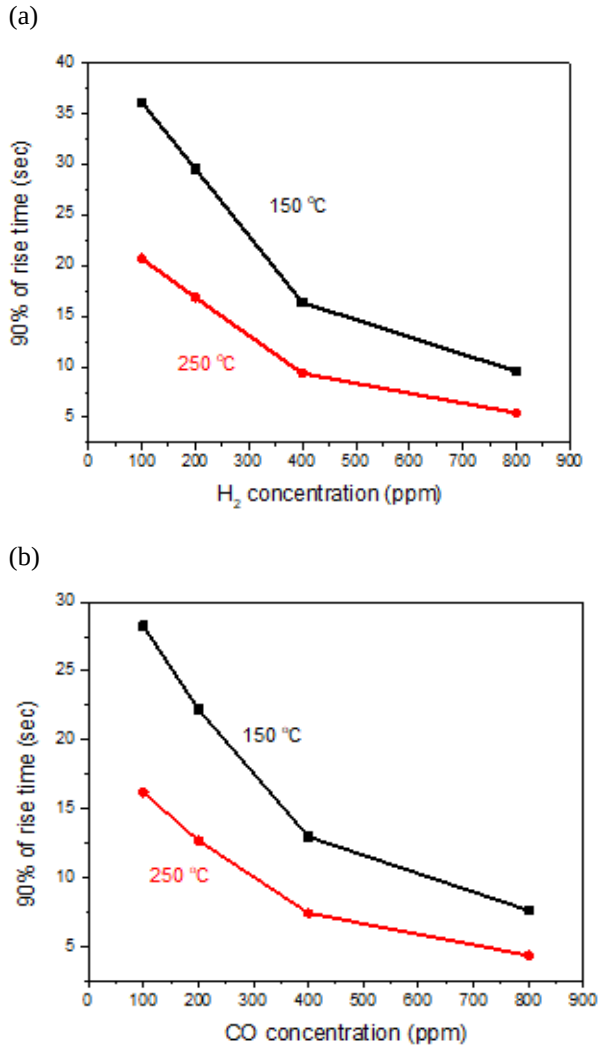

Fig. 6. Variations of 90% of rise time vs concentration of gases for various temperatures.

Conclusions

In this work the sensing capabilities of hwMoS_2 films were presented. It is shown that these films exhibit important changes of their current in various concentrations of hydrogen and carbon monoxide, as well as for various temperatures of heating. The hwMoS_2 films presented satisfactory characteristics with regard to their response time and magnitude, their stability and repeatability. However, the most important fact is that the hwMoS_2 surface has not been activated with any thin metal catalytic layer. The deposition of such layer (usually gold or platinum) is expected to improve further the sensing ability of these films. The detection of hydrogen and carbon monoxide is important for the protection of health and environment. Hydrogen is highly flammable and carbon monoxide is a toxic gas and environmental pollutant. Their

detection and control in residential and industrial environments are necessary in order to avoid potentially severe health and environmental problems.

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Conflicts of interest

"There are no conflicts to declare".

Keywords

hot-wire deposition, porous MoS_2, gas sensing, thin films

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Authors biography

Giorgos Papadimitropoulos received his degree in Physics from the University of Ioannina (2002) and his M.Sc. as well as his Ph.D. from UoA, Department of Informatics and Telecommunications, (2004 and 2009 respectively). He has participated in various national and European programs. He has more than 90 scientific papers and conference proceedings, 16 h index, 21 i10-index and over 1000 citations. His research focuses on thin films for application in microelectronics.

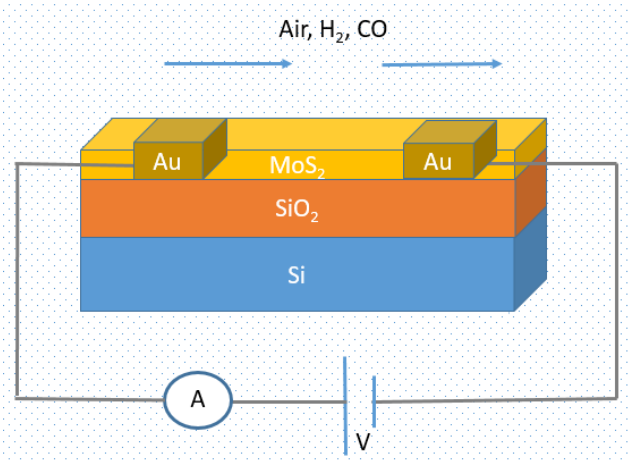
Angelika Balliou is a physicist (NTUA/TU Berlin, 2007) with M.Sc. in Material Science & Technology (NTUA, 2009) and Ph.D. in Molecular Electronics & Nanotechnology (NTUA/NCSR "Demokritos", 2016). She has participated in several EU projects, has published 18 research journal and proceedings papers and has given 12 conferences talks. She has co-organized one international Entrepreneurial Workshop and is currently Post Doc Researcher at NCSR "Demokritos". Her research interests include novel hybrid materials, TFTs and optoelectronic nanodevices.

Dimitris Davazoglou graduated from the Physics Department of Aristotle University of Thessaloniki in 1983 and received his M.Sc. (D.E.A.) and his Ph.D. from the Universite de Montpellier II in 1984 and 1987 respectively. He has been in the NCSR "Demokritos" since 1990 where he now serves as Research Director. His research focuses on thin films for application in microelectronics. He has published more than 130 articles in international journals and more than 2000 citations.

Dimitrios N. Kouvatsos received his Ph.D. (Electrical Engineering) from Lehigh University in 1991, later working as Visiting Research Scientist and Adjunct Lecturer. Since 2009 he is a Research Director at NCSR "Demokritos". He has published 107 research journal and proceedings papers, has given 80 conference presentations and is reviewer in 20 journals. He has directed five international projects and supervised several Ph.D. and M.Sc. theses; research interests include polysilicon or chalcogenide TFTs and integrated microsystems.

Graphical abstract

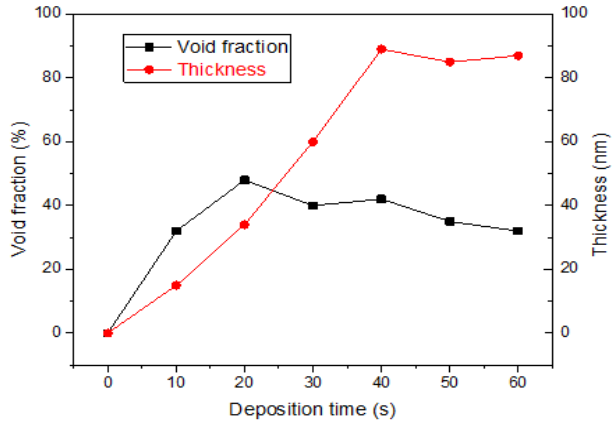
The schematic of the testing structure is shown in the following picture. The hwMoS$_2$ thin films were deposited on Si (100) wafers covered by a 100 nm thick thermal silicon oxide. Over the latter, gold interdigitated electrodes were patterned using ebeam evaporation and the lift-off technique. Reversible changes of current were caused by the presence or upon removal of chemical gases such as hydrogen (H_2) and carbon monoxide (CO).



Supporting information

The results below derived by Spectroscopic Ellispometry analysis.

(a) Void fraction of hwMoS$_2$ film.



(b) Tauc plot with the corresponding band-gap of the hwMoS$_2$ film.