Title
Optical Hydrogen Sensing Based on Hybrid 2D MoO3/Au Nanoparticles

Authors
Angiola, M
Alsaif, M MYA
Kalantar-zadeh, K
et al.

Publication Date
2015

DOI
10.1016/j.proeng.2015.08.830

Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 120 (2015) 1141 – 1144

Procedia Engineering

www.elsevier.com/locate/procedia

EUROSENSORS 2015

Optical hydrogen sensing based on hybrid 2D MoO_3/Au nanoparticles

M. Angiola[a], M. MYA Alsaif[b], K. Kalantar-zadeh[b], A. Wisitsoraat[c], W. Wlodarski[b], A. Martucci[a,*]

[a]*Unviersità di Padova, Dipartimento di Ingegneria Industriale, Via Marzolo, 9, 35131 Padova, Italy*
[b]*School of Electrical & Computer Engineering, RMIT University, Melbourne, Australia*
[c]*Nanoelectronics and MEMS Laboratory, National Electronics and Computer Technology Center Pathumthani, Thailand*

Abstract

In this work for the first time, we report the use of molybdenum oxide (MoO_3) nanoflakes on gold as active material for plasmonic optical gas sensor. The MoO_3 flakes were deposited over a monolayer of gold nanoparticles, chemically attached to a functionalized fused silica substrate. The coupling between MoO_3 and gold nanoparticles led to reversible optical changes of the localized surface plasmon resonance of gold nanoparticles upon exposure to H_2.

Peer-review under responsibility of the organizing committee of EUROSENSORS 2015

Keywords: molymdenum oxide; gold nanoparticles; surface plasmon resonance; optical sensor

1. Introduction

Among the two dimensional (2D) transition metal oxides, molybdenum trioxide (MoO_3) is one of the most studied gas sensitive material. 2D α-MoO_3, which is the layered crystal phase of this compound, can be useful especially for H_2 gas interaction since the small H_2 molecules can interact on its surface, diffuse across the layers, spill over and readily intercalate into the layers [1,2]. MoO_3 is an *n*-type semiconductor with a relatively wide

* Alessandro Martucci. Tel.: 0039 0498275506; fax: .: 0039 0498275505.
E-mail address: alex.martucci@unipd.it

Peer-review under responsibility of the organizing committee of EUROSENSORS 2015
doi:10.1016/j.proeng.2015.08.830

bandgap energy of ~3.2 eV [3]. As a low cost and chemically stable compound, nanostructured MoO_3 also plays an important part in many industrial applications. This material has been integrated into a wide range of transducing platforms [4], such as electrochromic [5], photochromic [6], surface acoustic wave (SAW) [7] and conductometric [8].

In order to demonstrate the high efficiency of using 2D MoO_3 as an optical sensor, nanoflakes have been coupled with Au nanoparticles (NPs). Au NPs have been widely used as optical probe thanks to their Localized Surface Plasmon Resonance (LSPR). Recently, we demonstrated the possibility to fabricate optical gas sensor combining graphene oxides flakes with an Au monolayer [9]. Here we extend such a strategy to 2D MoO_3.

2. Experimental

A detailed description of the MoO_3 nanoflakes synthesis is reported in [8]. The obtained 2D MoO_3 dispersed in an ethanol/water mixture and was drop casted (300 µl of solution for two times) on previously prepared Au monolayer deposited on pure silica glass slides from colloidal gold of 15 nm diameter as reported in [10]. A sample was also made of the pure 2D MoO_3 film obtained with the same drop casting procedure but on bare silicon substrate as a reference. The obtained films were heat treated at 400 °C in air for one hour.

Optical absorption spectra were obtained in the 200-900 nm wavelength range using a UV-Vis dual-beam spectrophotometer. Crystalline phases were assessed using glancing angle X-ray diffraction (GAXRD), using a 1° incidence angle and CuKα radiation at 30 kV and 40 mA. The films microstructures were examined using field emission scanning electron microscopy (FESEM) operated at 30 kV.

Optical gas sensing tests were performed on samples deposited on pure silica glass slides (with and without the gold layer) with optical absorption measurements in the 200-900 nm wavelength range using a Harrick gas flow cell (with 5.5 cm path length) coupled with a UV-Vis spectrophotometer. The substrate dimensions were reduced to 10 mm × 20 mm by scoring the substrate and breaking it to this size. The standard operating temperature (OT) was set at 300°C and gases at concentrations of 1 vol% CO or H_2 in dry air at a flow rate of 0.4 L/min were used. The incident spectrophotometer beam was normal to the film surface and illuminated an area of 9 mm × 1.5 mm.

3. Results and discussion

Figure 1a shows the GAXRD pattern of the Au monolayer coated with the MoO_3 annealed at 400 °C. It is possible to appreciate the presence of orthorhombic MoO_3 crystalline phase (JCPDS No. 050508) as well as the Au diffraction peaks (JCPDS No. 040784) of the underneath gold monolayer. Looking at the relative intensities of the MoO_3 diffraction peaks it is possible to note a preferred orientation along the (040) plane. The film microstructure is presented in figure 1b, with MoO_3 flakes of dimensions in the 200-300 nm range.

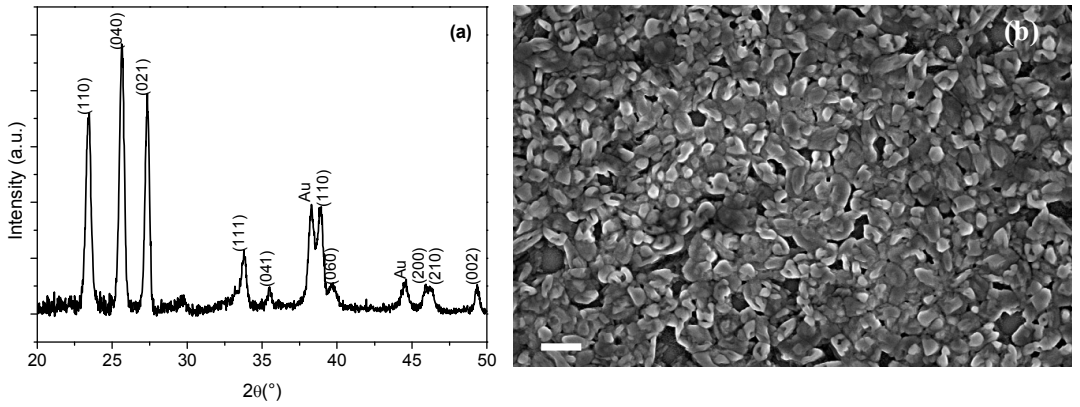

Figure 1 (a) GAXRD pattern of Au monolayer coated with the MoO_3 annealed at 400 °C. (b) FESEM image of MoO_3 film drop casted on silicon substrate (with Au underneath layer) and annealed at 400 °C. The bar correspond to 1 µm.

The absorption spectra of bare Au monolayer and Au monolayer covered with MoO_3 nanoflakes are presented in figure 2a. For the bare Au monolayer, it is possible to note the Au LSPR peak centred at 538 nm. The deposition of the MoO_3 nanoflakes induces a general increase in absorbance, probably due to an increase of the scattering, as well as a shift of the LSPR peak to a longer wavelength due to the higher dielectric contact of the MoO_3 nanoflakes with respect to air. It is also possible to note the absorption in the area of less than 450 nm due to the MoO_3 nanoflakes.

The effect of the target gas on the absorbance has been monitored both for the Au monolayer coated with MoO_3 and for the reference pure MoO_3. The sensing performances were monitored using the Optical Absorption Change parameter, defined as the difference in absorbance during target gas exposure and during air exposure (OAC = A_{gas}-A_{Air}). Figure 2 shows the OAC after the H_2 exposure for both the Au monolayer coated with MoO_3 and pure MoO_3. It is evident that the presence of Au NPs is essential for having a gas response. The larger variation in the absorbance can be detected after the 570 nm region, corresponding to the position of the Au LSPR peak, and in the near infrared region. The prepared sensor did not respond to CO.

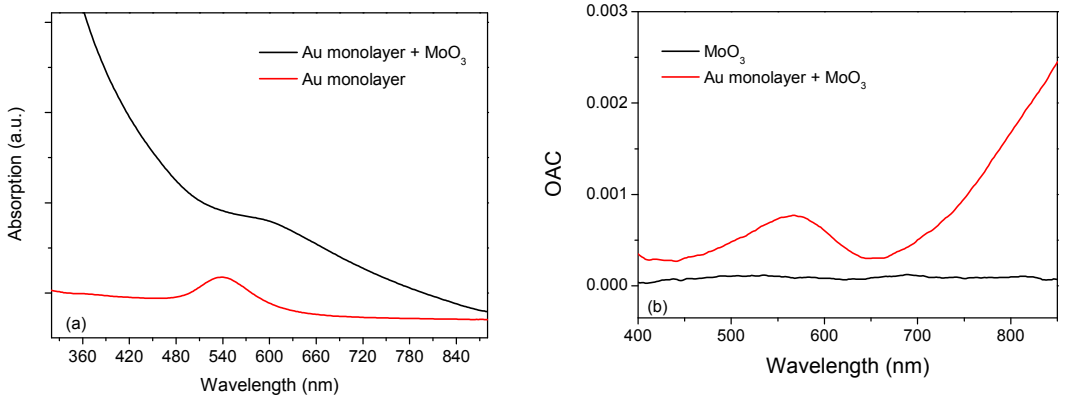

Figure 2 (a) Absorption spectra of Au monolayer (red line) and Au monolayer coated with MoO_3 nanoflakes (black line) annealed at 400 °C. (b) OAC curves (OAC = A_{H2}-A_{Air}) for Au monolayer coated with MoO_3 (red line) and for the pure MoO_3 (black) under 1vol% H_2 exposure at 300 °C OT.

The samples show good dynamic behavior after repeated exposures to H_2 as reported in Figure 3: the response time is short, while the recovery time is slightly longer but still satisfactory. It is worth noting that at 570 nm the dynamic measurements are not as stable as those at 800 nm.

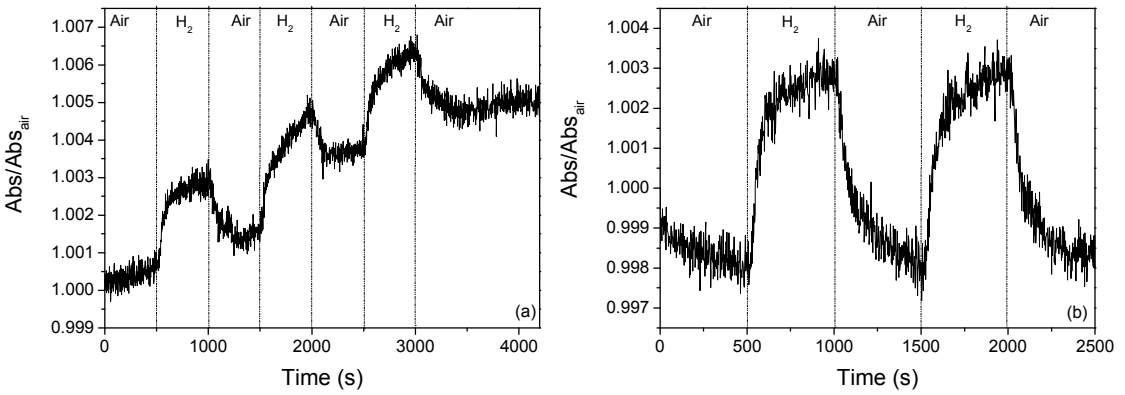

Figure 3 Dynamic response of the Au monolayer coated with MoO_3 nanoflakes at 300 °C OT, during exposure to different air-H_2-air cycles at (a) 570 nm and (b) 800 nm.

The sensing mechanism may be interpreted considering the interaction of H_2 with the oxygen adsorbed on the MoO_3 surface which leads to the formation of H_2O and the release of electrons, as already reported in [5]. This charge injection can be monitored looking at the LSPR peak of Au NPS which is in contact with the MoO_3 film, as alredy reported for other transition metal oxide – Au NPs composites [12]. It is worth noting that pure MoO_3 films did not show any appreciable variation of the absorbance when exposed to H_2, demonstrating the importance of the coupling with the Au NPs.

4. Conclusions

2D MoO_3 has been successfully used as a sensitive layer for LSPR based optical sensor. While bare MoO_3 was not sensitive to the target gas, the coupling between MoO_3 nanoflakes and Au NPs is effective for the realization of sensitive H_2 optical gas sensor. The plasmonic presented sensor has a good potential for future H_2 sensing applications.

Acknowledgements

M. Angiola gratefully acknowledges the financial support from the CARIPARO Foundation for the project “Dottorati di ricerca”.

References

[1] A. Kaniyoor, R.I. Jafri, T. Arockiadoss, S. Ramaprabhu, Nanostructured Pt decorated graphene and multi walled carbon nanotube based room temperaturehydrogen gas sensor, Nanoscale 1 (2009) 382–386.
[2] R. Arsat, M. Breedon, M. Shafiei, P.G. Spizziri, S. Gilje, R.B. Kaner, K. Kalantar-zadeh, W. Wlodarski, Graphene-like nano-sheets for surface acoustic wave gas sensor applications, Chem. Phys.Lett. 467 (2009) 344–347.
[3] W.S. Kim, H.C. Kim, S.H. Hong, Gas sensing properties of MoO_3 nanoparticles synthesized by solvothermal method, J. Nanopart. Res. 12 (2010) 1889–1896.
[4] C. Imawan, H. Steffes, F. Solzbacher, E. Obermeier, Structural and gas-sensing properties of V_2O_5–MoO_3 thin films for H_2 detection, Sens. Actuators B 77(2001) 346–351.
[5] M.B. Rahmani, S.H. Keshmiri, J. Yu, A.Z. Sadek, L. Al-Mashat, A. Moafi, K. Latham, Y.X. Li ,W. Wlodarski, K. Kalantar-zadeh, Gas sensing properties of thermally evaporated lamellar MoO_3, Sens. Act. B145 (2010) 13–19.
[6] J. Scarminio, A. Lourenc, A. Gorenstein, Electrochromism and photochromismin amorphous molybdenum oxide films, Thin Solid Films 302 (1997) 66–70.
[7] A. Kaniyoor, R.I. Jafri, T. Arockiadoss, S. Ramaprabhu, Nanostructured Pt dec-orated graphene and multi walled carbon nanotube based room temperaturehydrogen gas sensor, Nanoscale 1 (2009) 382–386.
[8] M.M.Y.A. Alsaif, S. Balendhran, M. R. Field, K. Latham,W. Wlodarski, J. Z. Ou, K. Kalantar-zadeh, Two dimensional MoO_3 nanoflakes obtained using solvent-assisted grinding and sonication method: application for H_2 gas sensing, Sens. Act. B 192 (2014) 196-204.
[9] M. Cittadini, M. Bersani, F. Perrozzi, L. Ottaviano, W. Wlodarski, A. Martucci, Graphene oxide coupled with gold nanoparticles for localized surface plasmon resonance based gas sensor, Carbon 69 (2014) 452-456.
[10] C. Imawan, H. Steffes, F. Solzbacher, E. Obermeier, Structural and gas-sensingproperties of V_2O_5–MoO_3 thin films for H_2 detection, Sens. Act. B 77 (2001) 346–351.
[11] E. Della Gaspera, M. Karg, J. Baldauf, J. Jasieniak, G. Maggioni, A. Martucci, Au nanoparticle monolayers covered with sol–gel oxide thin films: optical and morphological study, Langmuir (2011) 27, 13739-13747.
[12] E. Della Gaspera, M. Bersani, G. Mattei, T.-L. Nguyen, P. Mulvaney, A. Martucci, Cooperative effect of Au and Pt inside TiO_2 matrix for optical hydrogen detection at room temperature using surface plasmon spectroscopy, Nanoscale (2012) 4, 5972-5979.