proceedings

Abstract

Two-Dimensional Layered Amorphous Metal Oxide Gas Sensors (LAMOS) Perspectives and Gas Sensing Properties †

Valentina Paolucci [1,*], Jessica De Santis [1], Vittorio Ricci [1], Giacomo Giorgi [2,3] and Carlo Cantalini [1,*]

1 Department of Industrial and Information Engineering and Economics, University of L'Aquila, UdR INSTM of L'Aquila, 67100 L'Aquila, Italy
2 Department of Civil & Environmental Engineering, Università Degli Studi di Perugia, 06125 Perugia, Italy
3 CNR-SCITEC, 06123 Perugia, Italy
* Correspondence: valentina.paolucci2@univaq.it (V.P.); carlo.cantalini@univaq.it (C.C.)
† Presented at the XXXV EUROSENSORS Conference, Lecce, Italy, 10–13 September 2023.

Abstract: Two-dimensional Layered Amorphous Metal Oxide Sensors (LAMOS) represent a new class of 2D amorphous oxide (*a*-MOx) interfaces with unveiled properties in gas sensing applications. Herein, we report the humidity and gas sensing response of *p*- and *n*-type chemoresistive few-layered (2D) amorphous *a*-SnO_2, *a*-In_2O_3, and *a*-Cr_2O_3, discussing their reaction mechanisms using DFT modelling and electrical tests. LAMOS interfaces can be easily prepared by controlled oxidation in air of a large class of exfoliated 2D TMDs, MCs, and TMTH (Transition Metal Dichalcogenides, Chalcogenides, and Trihalides) like WS_2, MoS_2, $SnSe_2$, In_2Se_3, $NiCl_2$, and $CrCl_3$, yielding 2D amorphous *a*-MOx interfaces. LAMOS platforms preserving all the surface-to-volume advantages of their 2D precursors show excellent gas sensing properties representing a new class of material for gas sensing applications.

Keywords: 2D; amorphous metal oxides; oxidation; TMDs; MCs; TMTH

check for updates

Citation: Paolucci, V.; De Santis, J.; Ricci, V.; Giorgi, G.; Cantalini, C. Two-Dimensional Layered Amorphous Metal Oxide Gas Sensors (LAMOS) Perspectives and Gas Sensing Properties. *Proceedings* **2024**, 97, 190. https://doi.org/10.3390/proceedings2024097190

Academic Editors: Pietro Siciliano and Luca Francioso

Published: 17 April 2024

1. Introduction

The intrinsic thermodynamic instability ($\Delta G < 0$) of 2D exfoliated TMDs/MCs/TMTHs (Transition Metal Dichalcogenides/Metal Chalcogenides/Transition Metal Trihalides), demonstrated by their spontaneous oxidation in dry/wet air laboratory conditions, represents a great opportunity to develop, via suitable thermal treatment, template-self-assembled, amorphous-metal-oxide (*a*-MOx) skin layers over crystalline 2D exfoliated TMDs/MCs/TMTH.

Departing from liquid-phase exfoliated TMDs/MCs/TMTHs, annealing in air at temperatures below the crystallization temperature of the native oxide, either amorphous/crystalline 2D heterostructures of *a*-MO/TMDs [1,2], or fully oxidized amorphous 2D *a*-MOx interfaces can be prepared [3] with unexploited surface properties.

Herein, we demonstrate that the oxidation/amorphization process can be extended to a large variety of exfoliated TMDs (WS_2), MCs ($SnSe_2$), and TMTH ($CrCl_3$) where sulfur, selenium, or chlorine atoms can be easily displaced by O_2 atoms under controlled oxidation conditions, producing 2D layered *n*-type *a*-WO_3, *a*-SnO_2, and *p*-type *a*-Cr_2O_3 2D flakes spin-coated as thin films, with excellent sensing properties to H_2, NH_3, H_2S, and NO_2, and long-term stability properties. This research opens new perspectives for a novel generation of layered interfaces (LAMOS), exploiting new interaction mechanisms of these van der Waals amorphous semiconductor interfaces with the environment.

2. Materials and Methods

Liquid-phase exfoliated commercial SnSe2, WS2, and CrCl3 powders were annealed in air at different temperatures (180 °C–300 °C) and times (24–70 h), and spin-coated over interdigital electrodes provided with platinum electrodes and a back side heater. Platforms have been tested to sub ppm H2, NH3, H2S, NO2 gases and humidity at a 100 °C operating temperature.

3. Discussion

Figure 1a shows the SEM picture of a spin-coated thin film over interdigitated electrodes (light regions) of 2D *a*-SnO2 flakes of around 300 nm lateral size (Figure 1b,c), with a vertical height of approximately 20 nm, forming localized inter-sheet junctions between the flakes. Figure 1d shows the HRTEM of exfoliated flakes of 2D SnSe2 exhibiting a fully crystalline and ordered 2D texture extending up to the edge of the flake (see electronic magnification, Figure 1d). After annealing, the 2D SnSe2 is transformed in *a*-SnO2, whose amorphous structure is shown in Figure 1e. Grazing incidence XRD and XPS analysis of the annealed SnSe2 flakes confirms the formation of the fully amorphous *a*-SnO2 layer with a chemical composition matching that of SnO2.

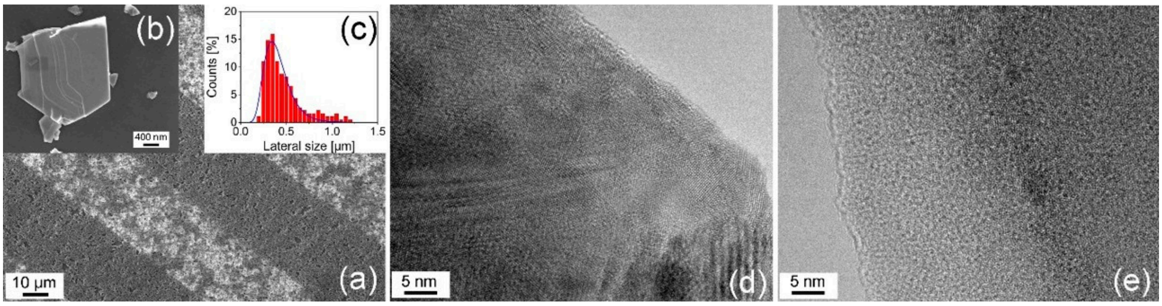

Figure 1. (**a**) SEM picture of *a*-SnO2 spin-coated flakes over Si3N4 substrates with Pt-finger-type electrodes; (**b**) high-magnification SEM of terraced as-exfoliated $SnSe_2$ flake; (**c**) lateral size distribution of exfoliated $SnSe_2$; (**d**) HRTEM of the as exfoliated crystalline 2D-SnSe2; (**e**) HRTEM of the *a*-SnO2 flake after oxidation of the 2D-SnSe2.

Considering humid air as a natural background in practical gas sensing applications, we preliminary applied combined density function theory and ab initio molecular dynamics, demonstrating that a dissociative water mechanism occurs over *a*-MOx surfaces, leading to the formation of chemisorbed hydroxyls, as shown in Figure 2a. Experiments that aimed to investigate the humidity cross-response on NO2 and H2 sensing highlighted that increasing the relative humidity increases the degree of hydroxylation, resulting in an increase/decrease in the sensor signal response (i.e., Rg/Ra or Ra/Rg) to 1 ppm NO2 and 100 ppm H2, as shown in Figure 2b,c, respectively.

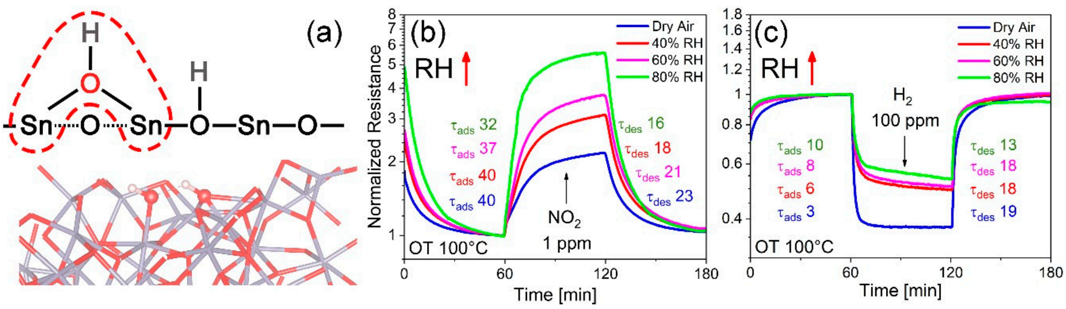

Figure 2. (**a**) Schematization of H2O dissociative chemisorption mechanism over *a*-SnO2 at a 100 °C operating temperature; (**b**,**c**) adsorption/desorption responses to 1 ppm NO2 and 100 ppm H2 with increasing RH.

Adsorption/desorption mechanisms of water and gases over amorphous interfaces (*a*-MOx), investigated via theory and experiments, resulted in being congruent with those of crystalline metal oxides. Long-term stability properties of the electrical response to humidity and different gases, over a period of one year, exhibit no remarkable fluctuations in the base line resistance (BLR) or the sensor's signal response (i.e., RRs), demonstrating that the amorphization/oxidation strategy effectively passivates the material from further degradation, while preserving an excellent gas sensing response.

Author Contributions: Conceptualization, C.C. and V.P.; methodology, C.C.; software, G.G.; validation, C.C. and V.P.; formal analysis, V.P., J.D.S., V.R. and G.G.; investigation, V.P., J.D.S., V.R. and G.G.; data curation, V.P., J.D.S., V.R., G.G. and C.C.; writing—original draft preparation, C.C. and V.P.; writing—review and editing, C.C. and V.P.; supervision, C.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Paolucci, V.; D'Olimpio, G.; Kuo, C.N.; Lue, C.S.; Boukhvalov, D.W.; Cantalini, C.; Politano, A. Self-Assembled $SnO_2/SnSe_2$ Heterostructures: A Suitable Platform for Ultrasensitive NO_2 and H_2 Sensing. *ACS Appl. Mater. Interfaces* **2020**, *12*, 34362–34369. [CrossRef] [PubMed]
2. Paolucci, V.; De Santis, J.; Lozzi, L.; Giorgi, G.; Cantalini, C. Layered amorphous *a*-SnO_2 gas sensors by controlled oxidation of 2D-$SnSe_2$. *Sens. Actuators B Chem.* **2022**, *350*, 130890. [CrossRef]
3. Paolucci, V.; De Santis, J.; Ricci, V.; Lozzi, L.; Giorgi, G.; Cantalini, C. Bidimensional Engineered Amorphous *a*-SnO_2 Interfaces: Synthesis and Gas Sensing Response to H_2S and Humidity. *ACS Sens.* **2022**, *7*, 2058–2068. [CrossRef] [PubMed]