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Abstract

Investigation on the Development, Stabilization and Impact of Thermally Induced Oxygen Vacancies on the Chemoresistive Sensing Properties of MOX †

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Abstract: Gas sensors based on metal oxide (MOX) semiconductors doped with oxygen vacancies (VO) have many advantages over stoichiometric MOX, such as higher surface reactivity and lower operating temperature. However, preparing reduced MOX is challenging, and the impact of different VO types and concentration on sensing performance is still unclear. In this work, we developed a tailored reducing thermal treatment for creating controlled VO in MOX. The effect of the length and temperature of the treatment was investigated using several characterization methods. Finally, measurements were performed to evaluate the impact of VO type and concentration on reduced MOX sensing performance.

Keywords: chemoresistive gas sensors; reduced MOX; oxygen vacancies; low-working temperature

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1. Introduction

Chemoresistive gas sensors are the most widely used solid-state devices because of their small size, sensitivity, and low cost [1]. However, the most widely used sensing materials, nanostructured MOX, lack selectivity and show high power consumption, which limits their effective and widespread adoption. To address these limitations, recent research has focused on developing new sensing materials with improved chemoresistive properties, particularly modified MOX (doped or functionalized) that combine MOX stability with enhanced selectivity through surface sensitization, as well as lower working temperature. One area of interest has been intrinsic dopants, including V_O, which have a significant impact on MOX electrical properties and surface reactivity [2]. However, a lack of stable and repeatable methods for preparing reduced MOX and a limited understanding of the impact of different types and concentration of V_O on gas-sensing performance have hindered the development of sensors based on these materials [2]. This study aimed to investigate the development of reduced WO_3 and SnO_2 nanoparticles with controlled V_O concentration, obtained through a tailored thermal reducing treatment. Impact of the thermal treatment length and temperature on the type and concentration of V_O developed, as well as their influence on the gas-sensing performance of reduced MOX, were investigated.

2. Materials and Methods

To synthesize stoichiometric WO_3 and SnO_2 nanoparticles, simple sol–gel syntheses were used with precursors tungsten hexachloride and tin(II) ethylhexanoate. The reagents were dissolved in 2-propanol at specific temperatures, and deionized water was used to obtain MOX colloids, which were then separated by filtration and calcinated at 650 °C in air. The resulting nanoparticles were reduced at different temperatures (300–800 °C)

using a rapid thermal processing instrument (RTP, Annealsys sas, Montpellier, France) in an N_2/H_2 (96%/4%) environment. Different treatment lengths were explored to investigate the effect of process time and temperature on the V_O type and concentration. The elemental (XPS, EDX), optical (UV-vis spectroscopy), and structural (XRD) properties of the reduced powders were characterized. Finally, both stoichiometric and reduced WO_3 and SnO_2 nanopowders were deposited onto silicon substrates, and their sensing performance was tested towards different target gases in a gas test bench.

3. Discussion

The XPS analysis showed that different oxidation states were present for W (5+, 4+ and 3+) and Sn (1+ and 0) in the WO_3 and SnO_2 reduced powders. These were caused by the formation of surface V_O resulting from reducing thermal treatments. Increasing the reducing thermal treatment temperature increased the surface V_O concentration and produced both in-plane and bridging V_O. XRD and optical characterizations revealed that V_O was also present in the bulk of the samples, resulting in changes to the crystal lattice dimensions and a reduction in the band gap compared to the stoichiometric WO_3 and SnO_2. The sensing characterization revealed a strong increase in the sensing performance in the detection of NH_3 and NO_2 for reduced WO_3 (Figure 1a) and reduced SnO_2 (Figure 1b), respectively, compared to the stoichiometric powders. A decrease in the working temperature of reduced SnO_2 and WO_3 compared to stoichiometric powders was observed as well. A proposed explanation for the role of surface V_O in the sensing mechanism is also presented.

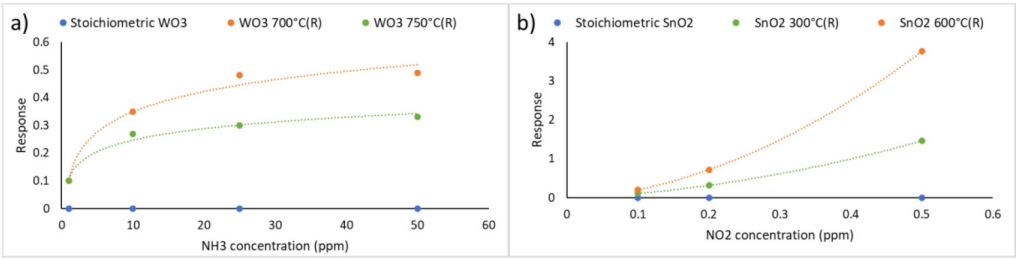

Figure 1. (**a**) Sensing responses, at a working temperature of 70 °C, of (**a**) stoichiometric and reduced (R) WO_3 powders vs. NH_3 and (**b**) stoichiometric and reduced (R) SnO_2 powders vs. NO_2.

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