

W-Sn Mixed Oxides for Selective Detection of NO₂

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Abstract:

Tungsten-tin mixed oxides at increasing Sn molar fraction (0.1, 0.3 and 0.5) were synthesized by sol-gel co-precipitation route. The prepared powders were characterized by electron microscopy (SEM and TEM), X-ray diffraction, specific surface area measurements (BET), UV-Vis-NIR and IR spectroscopies. It turned out that the mixed materials W-Sn(0.1) and W-Sn(0.3) form a solid solution with WO₃ crystal structure without phase segregation, achieving the goal to reduce the WO₃ grain growth with temperature. The prepared powders were deposited to produce gas sensors in form of thick films through screen-printing technology. The gas sensing measurements highlighted that the mixed oxide sensors offer a better response with respect to pure WO₃, at the same time maintaining the characteristics of almost complete insensitivity to carbon monoxide and benzene.

Key words: W–Sn mixed oxides, nanomaterials, UV-Vis-NIR and FT-IR spectroscopies, thick film gas sensors, NO₂ detection

Introduction

Despite several European and worldwide regulations limit anthropogenic emissions of air pollutants, a significant proportion of the urban population are still experiencing pollutant concentrations above limit values. NO₂ is certainly the pollutant gas of greatest concern mainly due to aged diesel vehicle fleet. Thereby, the atmospheric pollutants monitoring is of strong interest, especially if implemented through portable and versatile devices as thick film gas sensors.

In this work, mixed oxides of tungsten and tin were characterized and taken into account to detect NO₂. Indeed, mixed metal oxides and solid solutions have been usually considered for the superior performances shown in comparison to the single oxides. In this context, we attempted to join advantages of the better characteristics of both materials: high sensitivity toward oxidizing gases for WO₃ and SnO₂ with the aim to reduce the WO₃ grain growth with temperature. As a matter of fact, WO₃ suffers from exaggerated grain coalescence assisted by crystalline phase transition.

Experimental

Sol-gel co-precipitation method has been used to synthesize W-Sn oxide materials with Sn molar fraction of 0.1, 0.3 and 0.5. Required stoichiometric proportions of Tin(II) 2-ethylhexanoate in a proper amount of 1-butanol and WCl₆ have been dissolved in absolute ethanol. Diluted HNO₃ solution was added to catalyze the hydrolysis process. The resulting yellowish powder was calcined at 550°C for 2 h.

All materials were characterized through SEM and TEM electron microscopy, BET and XRD analysis. Diffuse reflectance UV-Vis-NIR and absorbance FT-IR spectroscopies, in situ and operando conditions, were employed to characterize surface and electronic properties of the materials. These techniques are suitable to put in evidence the presence of both bonded electrons with energy levels in the band gap and free carriers in the conduction or valence band. In particular, the influence of NO₂ on the concentrations of bonded and free carriers, which are at the base of the sensing mechanisms, were elucidated. Moreover, the surface species formed by the surface reactivity that influences the carrier concentration were determined. Screen printing technique has been used to deposit the sensing layers and the

corresponding thick films were tested for sensing in a sealed test chamber using the flow-through technique.

Results and Discussion

The addition of Sn successfully reduced the coalescence of WO_3 grains during the firing treatment of the thick films, as shown in Fig. 1.

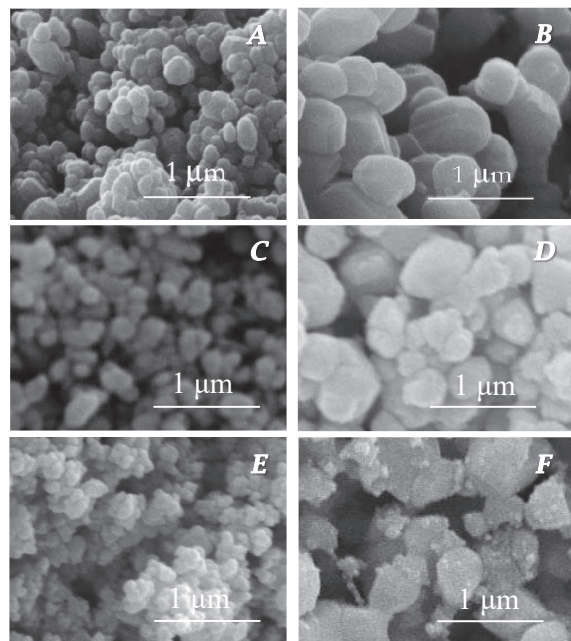


Fig. 1. SEM images of thick films based on pure WO_3 (A, B), $\text{W-Sn}(0.1)$ (C, D), and $\text{W-Sn}(0.3)$ (E, F) at different firing temperatures: 650 °C (A, C, E) and 750 °C (B, D, F).

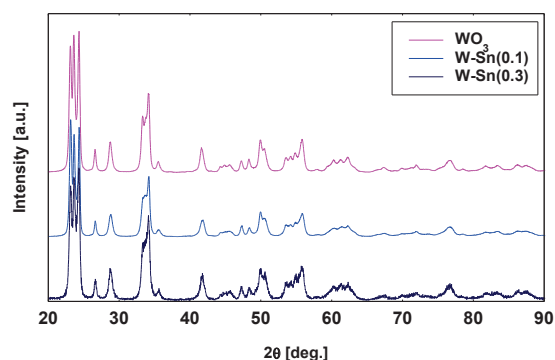


Fig. 2. XRD pattern of pure WO_3 powder compared with the solid solutions with molar ratio 0.1 and 0.3.

As shown in Fig. 2, the XRD patterns of the pure WO_3 , $\text{W-Sn}(0.1)$ and $\text{W-Sn}(0.3)$ powders correspond to the monoclinic crystal structure (space group $\text{P}2_1/n$) of polycrystalline WO_3 without any other phases. No change in the $\text{W-Sn}(0.1)$ and $\text{W-Sn}(0.3)$ unit cell parameters and unit cell volume was observed with respect to pure WO_3 . As proof of solid solution creation, a decrease of the W sites occupancy in the

crystal structure with increasing of Sn content was observed, thus confirming the substitution of W with Sn atoms.

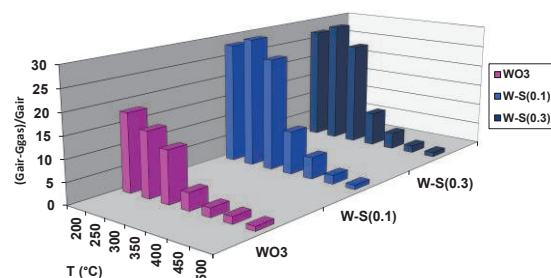


Fig. 3. Magnitude of response to 200 ppb of NO_2 for pure WO_3 compared with those offered by $\text{W-Sn}(0.1)$ and $\text{W-Sn}(0.3)$ films, all fired at 750 °C.

Like SnO_2 , WO_3 behaves as a n-type semiconductor because of lattice defects. In SnO_2 , oxygen vacancies act as electron donor levels, while WO_3 is characterized by polarons as evidenced by spectroscopic analysis. The conductivity value of WO_3 in air is almost two orders of magnitude higher than that of SnO_2 . Both materials exhibit three regions of conductivity and of the surface energy barrier toward temperature (not shown for sake of brevity), but with a very low value in the case of WO_3 . Mixed W-Sn specimens show conductivity and energy barriers modulated by Sn molar ratio and peculiar spectroscopic features in terms of band gap values and defect levels inside the band gap.

It is well known the ability of WO_3 based gas sensors to detect oxidizing gases like NO_2 [1]. This can be seen also in [2] in which the addition of 1 or 5% of W in SnO_2 , progressively modifies the sensing properties from the detection of reducing to that of oxidizing gases. In particular, pure WO_3 sensor is insensitive to CO and almost to benzene. In Fig. 3 a comparison between the responses in dry air to 200 ppb of NO_2 for WO_3 , $\text{W-Sn}(0.1)$ and $\text{W-Sn}(0.3)$ is shown. It can be observed that the mixed sensors offer a better response with respect to pure WO_3 , so improving the performance for NO_2 sensing.

References

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