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NO_x Sensing with n-type WO₃ – CuWO₄ Composites

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Thin-films of WO₃ : CuWO₄ composites were used as sensing materials for NO monitoring. The thin-films were prepared by the pulsed laser deposition technique using formulations with molar ratio spanning from 1 to 0. The sensing films were characterized by depth-profilometry, X-ray diffraction (XRD) and electron transport measurements. The transduction mechanism and its relation to the chemical surroundings, including temperature effects, were studied by monitoring the changes in electronic conductance (resistance) with temperature, gas-phase analyte chemical nature and concentration. Sensor performance studies were carried out. It was found that the best sensing material was composed of a nanometric layer of CuWO₄. This formulation offers fast response and short recovery times towards both O₂ and NO, with a response proportional to analyte concentration and excellent reproducibility.

Introduction

Nitrogen oxide species (NO_x) comprise a particularly noxious family of gas-phase pollutants. Nitrogen monoxide (NO) and nitrogen dioxide (NO₂) are primarily formed from fossil fuel combustion. In diesel engines, the lean nature of the combustion mixture (lower hydrocarbon concentration and O₂ concentration above the stoichiometric ratio for full combustion) promotes the formation of nitrogen oxides, specifically NO and NO₂. The increasing popularity of diesel vehicles given the superior power and higher efficiency per fuel volume has produced a fast increment of the atmospheric levels of NO_x species (N₂O, N₂O₃, N₂O₄, N₂O₅) and other associated such as ozone (O₃), acidic species including HNO₃ and HNO₂, and particulate matter.(1) Naturally, given the strong possibility of a catastrophic scenario with the increment of operating diesel automobiles, government institutions around the globe have produced regulatory legislations to control NO_x emissions and protect both public health and public welfare. The enforcement of these legislations (with periodic adjustments lowering the legal levels of permissible NO_x emission) has pressured the automobile industry to start the quest for more reliable, selective and robust NO_x sensors.(2,3)

The conductometric sensor is a well-established prototype for monitoring gas-phase species.(4,5,6) The sensing mechanism is based on physical-chemical interactions between metal oxide semiconductor surface states (*e.g.* free electrons, vacancies, empty orbitals or holes) and a gas-phase analyte. The effect of such interactions on the sensing material electron transport properties is interpreted and quantified through the monitoring of changes in the conductivity (or resistivity) behaviour.

Previous studies have shown that WO_3 is a material used for the real time monitoring of some gas-phase pollutants (*e.g.* conductometric sensor prototype), and particularly for NO_x monitoring technology.⁷ Specifically, two major strategies have been used to improve WO_3 conductometric sensor performance, *i)* in combination with catalytic metals (8,9,10,11) and *ii)* composite formulations with other semiconductor oxides. (7,12,13,14,15,16) The present work reports the latter as the experimental strategy to complement the sensing profile of WO_3 , increasing by this means the range of sensing functionality for NO_x species.

For this study, thin-films with composition $\text{WO}_3 : \text{CuWO}_4$ with varying molar ratio were prepared using the pulsed laser deposition technique (PLD). The crystallographic and structural features of the thin-films are discussed. The temperature effect on the electron transport properties of the thin-films was investigated and the sensing performance towards O_2 and NO was evaluated.

Experimental

Materials

CuWO_4 was prepared *in situ* in presence of an excess of WO_3 by a solid-state reaction between WO_3 and CuO at high temperature. The reagents were used as received, WO_3 (Alfa Aesar, 99.998%) and CuO (Alfa Aesar, 99.995%). Mixtures with different W : Cu molar ratio, were placed in alumina crucibles and annealed in two steps under oxygen. First, the metal oxides were allowed to react at 600 °C for 12 hours. Prior to a second thermal treatment, the resulting material was thoroughly ground and the resulting powder sintered at 750 °C for 24 hours under O_2 .

Laser targets were prepared in the form of compact pellets using the powders resulting from the thermal treatments described above. The pellets were sintered at 680 °C for 24 hours in O_2 . A pellet of CuWO_4 (T-6) was prepared by annealing a $\text{CuO} : \text{WO}_3$ mixture in a 1:1 stoichiometric ratio. The laser target compositions are listed in **Table I**.

TABLE I. Pulsed Laser Deposition Target Composition (Molar Ratio)

Target	$\text{CuWO}_4 : \text{WO}_3$ Molar Ratio
T-1	0 : 1
T-2	1.2 : 41.3
T-3	6.3 : 34.5
T-4	12.5 : 26.1
T-5	25.1 : 9.3
T-6	1 : 0

Thin-films from targets in **TABLE I** were produced by the pulsed laser deposition technique (PLD) using a Lambda Physik LPX305i laser (Kr-F excimer laser with $\lambda = 248$ nm, ablation energy 600 mJ/pulse, pulse rate 8 Hz, pulse time 20 ns). Thin-films were deposited on single crystal sapphire substrates ($\alpha\text{-Al}_2\text{O}_3$, 1" 1 02) in an isothermal regime. Thin-films were produced by target laser ablation (20 minutes) at 600 °C in 100 mtorr O_2 atmosphere. Following deposition, the chamber pressure was increased to 400 mTorr (O_2) and the films were allowed to stand at 600 °C for 15 minutes. Finally, the thin-films were allowed to cool to 25 °C at a temperature rate of ~ 8 °C/minute.

Physical-chemical Characterization

Laser targets and thin-films were characterized by powder-X-ray diffraction (P-XRD) using a Bruker-D8 diffractometer with parallel beam geometry and a sample holder kept stationary with both the XR-source tube and detector arms mobile. The XR-source was a cobalt tube ($\text{Co } \lambda \text{ K}\alpha_1 = 1.78897 \text{ \AA}$). No monochromator or filter were used. The crystallographic studies of the PLD thin-films were done by spinning the sample at 15 rpm. XRDs for laser targets (pellets) were obtained with a stationary sample holder. The fingerprint methodology (Phase-ID, Search/Match routine) was used as a diagnostic tool for the identification of crystal phases and analysis of reaction products. The reference patterns used for the structural analysis were provided in the ICDD Powder Diffraction File (PDF) database (supplied as PDF-2 and compiled into DIFFRACTplus Reference Database format, release in 2002).

Thin-film thicknesses were measured using an XP-2TM profilometer (XP Series Stylus Profilometer, Ambios Tecnology, Inc.).

The system for evaluating the sensing performance consisted of computer operated elements with a heater (powered using a Xantrex HPD 60-5 power supply), gas-supply manifold (MKS Type 1479A, Mass-Flo[®] controllers), sensing electrodes (gold electrodes connected to a sourcemeter, Keithley 2400) and a custom feedback temperature controller equipped with a K-type thermocouple. For sensing studies, gold electrodes were deposited onto the thin-films using a thermal vacuum procedure. Conductance (resistance) was monitored to detect changes in electron transport properties with changes in experimental conditions (*e.g.* temperature effects, interaction with gas-phase species, *etc.*). In order to assure proper ohmic contacts, two small pads of gold were placed between the sensing electrodes and the film electrodes. For the experiments, the total gas flow rate was kept at 250 cm³/minute. The temperature range for the sensing functionality studies was between 100-500 °C.

Results and Discussion

Structural Characterization

Formation of CuWO_4 was confirmed by comparing the XRD laser target reflections with database standards (DIFFRACT^{plus} Reference Database). The limiting reagent within the molar ratio used for laser targets was CuO. In accordance with this, no reflections from CuO were observed. **Figure 1** shows the XR-diffractogram for PLD targets containing pure samples, **Figure 1a** shows the XRD for CuWO_4 XRD and **1b**. WO_3 XRD. Excellent match for reflections were found for the targets (standards provided by the DIFFRACTplus Reference Database format, 2002). WO_3 features a monoclinic unit cell (17,18,19) while CuWO_4 is triclinic.

Figure 1. XRDs for PLD Targets. Figure 1a. WO_3 XRD and 1b. CuWO_4 XRD.

The XRD for the targets showed weak reflections arising from Co- $\text{K}\beta$ wavelengths. For instance, for WO_3 (**Figure 1a**) the corresponding XR-diffractogram shows a small triplet centered at 24.9° . Calculation of d-spaces using the corresponding 2θ angles and the wavelength for Co- $\text{K}\beta$ line produced identical lattice parameter (**d**) values as for the triplet centered at 27.7° . This is consistently the case, allowing to exclude the presence of impurities. The XRD of the targets for remaining formulations reflected the increasing content of CuWO_4 . The 2θ angles for both phases remained at the same position as for the pure material pellets (XRD targets).

TABLE II lists the films thicknesses as measured using profilometry, film composition, rate of thin-film growth, and deposition temperature. The values reported in **TABLE II** corroborated the nanoscopic nature of the films. For some compositions, the film deposition was carried out at both 600 °C and 20 °C. This was done to evaluate the effect of deposition temperature on lattice parameters. Material transfer from pellet to substrate surface (α -Al₂O₃) was considered to be nearly stoichiometric as it is often found for this technique.⁽²⁰⁾ The thin-film composition in **TABLE II** (molar ratio Cu : W) reflects the latter assumption.

TABLE II. Thin-film Thickness Estimated by Profilometry, Laser Deposition Parameters and Corresponding Film Composition (Cu : W molar ratio).

Film ID	Molar Ratio Cu : W	Deposition Temperature (°C)	Thin-Film Thickness (nm)	Deposition Rate (nm/minutes)
F-1	0:1	600	264	13
F-2	0:1	20	276	18
F-3	1.2 : 42.5	600	343	17
F-4	6.3 : 40.8	600	333	17
F-5	12.5 : 38.6	600	358	18
F-6	25.1 : 34.4	600	295	15
F-7	25.1 : 34.4	20	225	15
F-8	1 : 0	600	280	14

Figure 2 shows the XRDs for studied thin-films. The films prepared at room temperature (F-2 and F-7, **TABLE II**) did not show reflections other than those due to the α -Al₂O₃ substrate. Further characterization of these films, shown by XRD to be amorphous, was not carried out. As expected, the thin-film XRDs showed the substrate reflections. Note that both the substrate (α -Al₂O₃) and the thin-film material (WO₃ and CuWO₄) display XRD patterns with reflections within similar 2 θ angles. For instance, for F-1 (**Figure 2**), overlap at 2 θ $\approx$ 55.38 ° occurred. This fact is supported by the change in the observed order for relative intensity at the 2 θ angles where the substrate reflections appeared (both arising from K α ₁ and K β X-ray radiation). The thin-film XRDs display a reduced number of reflections compared with the bulk material. The WO₃ thin-film XRD (F-1) revealed a preferential orientation for the PL deposited film along the (0, 0, 2n) axes (monoclinic WO₃). For instance, the WO₃ thin-film (F-1) displayed a medium to low intensity reflection centered at 55.477 °, this reflection corresponds to the [0,0,4] plane, and a reflection at 26.932 ° corresponds to the [0,0,2] plane both in a WO₃ monoclinic unit cell.

Comprehensive phase and composition identification based on the thin-film XRDs was not possible due to the preferential orientation and limited number of reflections. For instance, the F-1 XRD (WO₃ thin-film XRD) shows reflections that can be assigned to monoclinic WO₃ (2 θ = 26.932 ° and 55.477 °),²¹ while the reflection at 2 θ =24.375 ° does not correspond to WO₃ (WO₃ monoclinic unit cell). The WO₃ thin-film (F-1) produced in this study displayed a pale-blue color with a grayish tone. This colour is characteristic of oxygen-depleted tungsten oxides (WO_{3- δ}).^(17, 18, 19) In particular, WO_{2.90} has been reported to be dark blue coloured. Based on the film colour, it is likely that there has been a formation of a non-stoichiometric tungsten oxide phase (WO_{3- δ}). The reflection at 2 θ $\approx$ 24.38 ° supports this assumption (XRD for F-1). Phases with oxygen-to-tungsten ratio (3- δ) = 2.9 have been reported before for WO₃-based thin-films. ^(22, 23, 10, 24, 25)

Figure 2. XRDs for Representative Thin-Films of $\text{CuWO}_4 : \text{WO}_3$

Thin-film Sensing Performance Characterization

For the conductivity measurements, all the thin-film formulations displayed a change in charge carrier behaviour with both temperature and gas-phase analyte exposure to O_2 and NO . Thin-films with a WO_3 excess did not show sensing properties suitable for sensing applications. Although all the films containing WO_3 displayed short response times, a long time for signal stabilization upon analyte exposure (during and after gas exposure) and long recovery time were common features; *e.g.* in the case of the WO_3 thin-film, for NO sensing study at 500°C , the time elapsed for signal recovery was about 8 hours. In contrast, the thin-film with composition CuWO_4 (F-8) showed excellent sensing parameters for O_2 and NO . Given the excellent sensing profile displayed by the CuWO_4 thin-film (F-8), the sensing performance discussion will focus on the results obtained for this material.

For many semiconductor metal oxides, the sensing mechanism for gas-phase species is based on physical-chemical changes that interacting gas-phase species produce within the outer layer of sensing materials (*e.g.* electronic origin, change of composition and structure, *etc.*). **Equation 1** summarizes the fundamental process that renders CuWO_4 thin-film (F-8) suitable for sensing redox gas-phase species; that is, gas-phase species that undergo a redox change upon interaction with surface states within the semiconductor surface such as O_2 .(3, 4, 5, 7, 8)

Interaction of reactive gas-phase species with semiconductor metal oxides at high temperature ($T > 100^\circ\text{C}$) modifies the surface electron transport properties through a change in surface defect concentration (chemisorption processes). Formation of ionized oxygen species at the semiconductor surface, at the expense of the removal of charge diffusion electrons, changes the physical–chemical properties of the surface (effect of gas-phase species on energy and chemical nature of surface states, band bending, formation of new species through chemisorption, segregation of both ionized oxygen adsorbates and oxygen-vacancies into deeper layers, *etc.*). (3, 4, 5, 7, 26) Monitoring changes in the charge carrier behaviour with temperature and gas-phase analyte using properties associated with the electron transport properties behavior (*e.g.* conductance / resistance) provides information that allows the evaluation of sensing potential.

Temperature Effect on the Electron Transport Properties

Figure 3 shows the temperature effect on the F-8 conductance σ (CuWO_4 thin-film) in the $200\text{--}500^\circ\text{C}$ range. As expected for semiconductor materials, the σ for this thin-film increased with temperature (**Figure 3**), which agrees with the intrinsic, activated nature of electron mobility and conductivity for metal oxide semiconductors. (27, 28, 29, 30, 31)

Figure 3. Thermal Stability and Reference State (20 % O_2 in N_2) Conductance Reproducibility with Temperature for F-8 (CuWO_4 Thin-Film).

Despite the cyclical thermal stress promoted by regular temperature changes, the film showed good reproducibility for σ in the reference gas (20 % O₂ in N₂). This indicates that the film possesses good mechanical endurance and suitable thermal stability.

Effect of Oxygen Concentration on the Electrical Properties of F-8 (CuWO₄ thin-film)

The decrease in conductance σ for the monitored metal oxide surface with increasing O₂ concentration is a suitable evidence to establish the semiconductor nature.(32) Hence, it is shown that CuWO₄ behaved as an n-type semiconductor. Since n-type semiconductor metal-oxides are characterized by the presence of oxygen vacancies, an increment in O₂ concentration will promote the reduction of this type of surface state. This process is confirmed by a change (reduction) in thin-film conductance. **Equation 2** represents the process that controls the electronic behavior of CuWO₄ thin-film (F-8) at high temperature. Several measurements of σ profile vs. [O₂] were done in order to study the effect of [O₂] at 300 and 500 °C. **Figure 4** shows the effect of oxygen concentration on the F-8 electrical transport properties at 500 °C. The electrical conductance σ at 300 ° displayed a similar behavior. The changes for σ at the latter temperature were less pronounced than for σ vs. [O₂] at 500 °C. As expected, σ decreased with increasing O₂ concentration, in accord with the expected behaviour for n-type semiconductor metal oxides ([O₂] increases → σ decreases).

Figure 4. Sensor Response for F-8 (CuWO₄ Thin-Film) to O₂ Exposure, T=500 °C.

Reproducibility tests were performed in order to test the accuracy of the material response to O_2 at 300 ° and 500 °C. **Figure 5** shows the effect of cyclic O_2 exposures on the σ values at 500 °C.

Figure 5. Reliability Tests for F-8 (CuWO₄ Thin-Film). The Plots Show the Change of Resistance Values (R) with $[O_2]$, T=500 °C.

In general, the F-8 (CuWO₄ Thin-Film) response towards O_2 produced consistent changes in electrical conductivity with oxygen concentration at both working temperatures. The values are reproduced within $\pm 3\%$. The response maxima occurred at exposure periods (~ 5 minutes) within the residence time for the gas flow apparatus used for data collection. For this study, the recovery time was defined as the time required for reaching a stationary state in the reference gas (20% O_2 in N_2) upon a change in $[O_2]$ and was calculated using the relation $\delta R/\delta t$ vs. t (time). At 300 °C, the estimated recovery time was approximately 45 minutes, whereas at 500 °C, a stationary state was reached within 20 minutes. **Figure 6** shows the differential plot ($\delta R/\delta t$ vs. time) for resistance change with both time and $[O_2]$. The recovery time did not show a significant dependence on $[O_2]$.

6a.

6b.

Figure 6. Rates of Response and Recovery for O_2 Exposure (CuWO_4 Thin-Film). Figure 6a shows a derivative plot for R vs. $[\text{O}_2]$ with time at $T=500^\circ \text{C}$. Figure 6b shows an expanded view for the 10 – 40 % $[\text{O}_2]$ range.

Sensing Performance for CuWO₄ Thin-Film (F-8) toward Nitrogen Monoxide NO

The thin-film (F-8, CuWO₄) displayed a change in conductance with gas-phase analyte concentration [NO], as shown in **Figure 7**. NO exposure promoted an enhancement for the electron transport of F-8. This is manifested by the stepwise increase of σ with increasing [NO]. The data profile consisted of a fast response upon initial NO exposure (~ 5 minutes). For the [NO] range investigated, this pattern was consistently observed. The elapsed time period for the latter parameter is consistent also with the estimated residence time (~ 4 minutes) in the measurement flow system, thus the response rate is considered very fast. The response time for the concentration range investigated did not show a significant dependence on [NO].

Figure 7. Sensor Response for F-8 (CuWO₄ thin-film) to NO Exposure, T= 500 °C. [NO] is Indicated in ppm.

The σ profile shows a rather complex behaviour in the [NO] range studied. Upon NO exposure, the conductance underwent a sudden increase proportional to the [NO]. Shortly after the sudden conductance rise, a decrease is observed. This pattern suggests the occurrence of two parallel chemical processes. Commonly, interaction of reactive gas-phase species with semiconductor metal oxides modifies the surface electron transport properties by redox processes. The increase in σ with [NO] indicated that this species promotes the formation of new surface states (*e.g.* oxygen vacancies, surface electrons). For this event, a possibility is the oxidation of NO adsorbates at the material surface resulting in the transfer of charge carriers to the sensing material surface. The increase in resistance after the first stage is in agreement with a removal of charge carriers from the semiconductor surface by a product from the first, faster process. For the latter process, NO₂ resulting from the oxidation of NO through the annihilation of surface O²⁻ oxide species (or O⁻) could promote the resistance increment. Consequently, NO₂ should have undergone a reduction process that produced NO or N₂. **Equations 3 and 4** are proposed to satisfy the dynamics observed for this system.

Conclusions

CuWO₄ thin-films, prepared by the pulsed laser deposition technique, show sensor functionality toward NO and O₂. The thermal stability and consistency of the conductivity with temperature reveal the potential of CuWO₄ thin-films for high-temperature monitoring applications. The material showed satisfactory σ reproducibility, which is a fundamental property for the fabrication of a sensor prototype. The reproducibility for response indicates that the chemistry that controls the sensing mechanism to NO consists of reversible and temperature-dependent chemical interactions consisting of two overlapping processes. The reversible nature of interaction with O₂ suggests that, with appropriate consideration for oxygen partial pressure, the material could be used for NO monitoring applications in oxidizing environments.

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