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Comparison study of conductometric, optical and SAW gas sensors based on porous sol–gel silica films doped with NiO and Au nanocrystals

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ABSTRACT

Conductometric, optical and surface acoustic wave gas sensors based on sol–gel silica porous films doped with NiO and Au nanoparticles are studied. The nanocomposite films are characterized by optical absorption in the visible and near-infrared region, spectroscopic ellipsometry, X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) analysis and X-ray photoemission spectroscopy (XPS). They show poor conductometric gas sensing response toward CO and H₂. However, both optical and surface acoustic wave (SAW) responses are reversible and stable to H₂. Moreover, exploiting the wavelength dependence of the optical sensor response it is possible to selective recognition of H₂. Choosing the appropriate wavelength, almost no variation in absorption is observed when introducing different gases into the testing chamber.

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1. Introduction

In the last few years, besides well known gas sensors based on electrochemical and mass spectroscopy platforms, there has been a constant development of different types of gas sensor transducers, aiming at improving sensitivity and selectivity, and to minimize electromagnetic noise dependence, high operating temperature and cumbersome instrumental setup and operation [1].

At the same time, much effort has been directed toward identifying different materials as suitable active layers for toxic gases and organic vapours (VOCs), using metal oxides [2–4], polymers [5], and organic dyes [6].

Solid-state sensors based on semiconductors, especially transition metal oxides, have been widely investigated due to their high temperature and environmental stability compared to polymers and organic dyes, which usually suffer thermal and/or UV degradation.

Films containing NiO, a p-type semiconductor with a wide band gap of 4.2 eV, have been recently proposed as sensitive materials for

chemoresistive [7] and optical gas sensors [8]. The working mechanism of NiO-based platforms consists in a change of the electrical resistance or optical transmittance of the material as a consequence of physisorption/chemisorption and reactions of the measured gas with its surface. The interaction extent with the target gas can be maximized either by increasing the sensor's surface area [9], or by doping the oxide with noble metal nanoparticles (NPs) [10,11]. We have already shown the enhancement of the optical gas sensing response due to the introduction of gold NPs inside a porous sol–gel SiO₂ matrix doped with NiO nanocrystals [12,13]. In fact, the surface plasmon resonance of metal NPs depends strongly upon the surrounding medium properties, particularly refractive index [14–16]. Even a small change of the matrix properties leads to a large variation of the plasmonic frequencies, allowing for detection of the target gas at even lower concentrations. Moreover, because of the Au NPs optical properties, it is possible to tune the response of the sensors, by selecting an appropriate wavelength of analysis [17,18].

In this paper we report electrical, optical and surface acoustic wave based gas sensing properties of sol–gel nanocomposite thin films formed by a porous SiO₂ framework with enhanced surface area, where NiO and Au metal NPs are homogeneously dispersed. The aim of this paper is to compare the response of the three differ-

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ent gas sensor platforms in order to better understand the nature of the gas sensing mechanism.

2. Experimental

The nanostructured thin films were made using the sol–gel technique, mixing together two different solutions: first the SiO_2 matrix solution is prepared by mixing $\text{CH}_3\text{CH}_2\text{OH}$ (ethanol), $\text{Si}(\text{OC}_2\text{H}_5)_4$ (tetraethoxy silane, TEOS), $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ (methyl triethoxy silane, MTES), H_2O (water) and HCl (hydrochloric acid) according to the molar ratios: $\text{EtOH}/\text{TEOS}/\text{MTES}/\text{H}_2\text{O}/\text{HCl} = 4/1/1/2/0.01$. For the Au precursor, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (hydrogen tetrachloroaurate trihydrate) was used, and it was directly added to the matrix solution according to $\text{Ni}:\text{Au} = 5:1$ ratio. The doping solution was made by dissolving $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (nickel chloride hexahydrate) in ethanol, in the presence of $\text{N}[\text{3}(\text{trimethoxysilyl})\text{propyl}]\text{-ethylenediamine}$ (DAEPTMS), keeping the molar ratio $\text{Ni}/\text{DAEPTMS} = 1$. This modified silane was chosen as an appropriate coordinating agent because of its double aminic functionality, which gives the capability to anchor the metal ions to the SiO_2 network, leading to an homogeneous Ni dispersion inside the matrix.

The matrix solution was stirred in a closed vessel for 90 min before being mixed with the doping solution, according to an $\text{Si}/\text{Ni} = 7/3$ nominal ratio, and the final solution was stirred for at least 30 min before film deposition.

The films were deposited either on $\text{Si}/\text{Si}_3\text{N}_4$ substrates patterned with Pt interdigital surface electrodes for conductometric gas sensing measurements, on SiO_2 glass substrates for optical absorbance measurements, or on $\text{La}_2\text{Ga}_5\text{SiO}_{14}$ surface acoustic wave (SAW) transducers. The dip-coating technique was chosen for film deposition with a withdrawal speed between 100 cm/min and 300 cm/min at room temperature (23°C) and at controlled humidity ($\text{RH} = 20\%$). The sample was then dried in air at 60°C for 5 min and then stabilized in air for 30 min at 500°C . Further incremental annealing cycles each of 30 min duration were done at 600°C , 700°C and 800°C in order to finally stabilize the sample and promote both NiO and Au crystallization. Film thicknesses up to 500 nm have been obtained, measured with a profilometer. In a previous work [8] we showed that NiO– SiO_2 nanocomposite films are still porous at 700°C and the porosity of the matrix provides a path for the gas molecules to reach the functional ultrafine particles embedded in the glass matrix.

The films were characterized by X-ray diffraction (XRD) by using a Philips diffractometer equipped with glancing-incidence X-ray optics. The analysis was performed at 0.5° incidence using $\text{Cu-K}\alpha$ Ni filtered radiation at 40 kV and 40 mA. Structural and compositional characterization was performed on cross-sectional samples of the composite films. High Resolution Transmission Electron Microscopy (HRTEM) measurements were taken with a field emission FEI TECNAI F20 SuperTwin FEG–(S)TEM microscope operating at 200 kV and equipped with an energy-dispersive X-ray (EDX) spectrometer for compositional analysis and a Gatan 794 Multiple Scan Camera, allowing digital image recording on a 1024×1024 pixel CCD array.

The surface composition of thin films deposited on a Si wafer (with its native oxide layer) was analyzed by X-ray Photoemission Spectroscopy (XPS) using a modified VG ESCALAB MK II (Vacuum generators, Hastings, England) where a twin (Mg/Al) anode X-ray source, a sputter gun, and a hemispherical electrostatic analyzer with a five channel detector are mounted. The XPS data reported in the present study were obtained using $\text{Mg K}\alpha$ radiation (1253.6 eV) as an excitation source. The charging effect has been compensated by referencing all the binding energies (BEs) to the C 1s peak at 284.8 eV. Photoemission spectra have been obtained at room temperature using a normal emission geometry. Before

taking XPS measurements, the samples were degassed overnight under UHV (pressure lower than 10^{-8} mbar). In order to derive the chemical composition of the films, the theoretical photoemission cross-sections by Yeh and Lindau [19] have been used, while the electron inelastic mean free path has been calculated with the TPP2 algorithm [20].

Transmittance at normal incidence and ellipsometric quantities Ψ and Δ have been measured using a J.A. Woollam V-VASE Spectroscopic Ellipsometer in vertical configuration, at three different angles of incidence (65° , 70° , 75°) in the wavelength range 400–1100 nm. Optical constants n and k have been evaluated from Ψ , Δ and transmittance data using WVASE32 ellipsometric data analysis software.

Optical sensor functionality was studied by making optical absorbance/transmittance measurements over the wavelength range $250 \text{ nm} < \lambda < 800 \text{ nm}$ with sample films mounted on a heater inside a custom-built gas flow cell coupled with a Varian Cary1E spectrophotometer. Films heated at temperatures between room temperature and 330°C were exposed to different concentrations of H_2 and CO in dry air. The substrate size was approximately $1 \text{ cm} \times 2 \text{ cm}$ and the incident spectrophotometer beam was normal to the film surface and covering a $6 \text{ mm} \times 1.5 \text{ mm}$ section area.

The electrical response of films to H_2 and CO gases was measured by an automated system. Dry air was mixed by an MKS147 multi-gas mass controller (MKS Instruments Inc. Massachusetts) with diluted H_2 mixture (1000 ppm in air) and CO mixture (1000 ppm in air) in order to have gas concentrations at the outlet in the range 10–1000 ppm in dry air carrier gas. Electrical measurements were carried out at the operating temperature of the films in the temperature range of $25\text{--}350^\circ\text{C}$ and different gas concentrations. The resistance of the films was measured using a Keithley 2001 multimeter with the 2-wire technique.

The SAW gas sensor device was mounted inside an enclosed environmental cell and exposed to different H_2 and CO gas concentrations in synthetic air at various temperatures between 50°C and 300°C . A Fluke high-resolution frequency counter (PM66860B) was used to measure the resonant frequency changes of the SAW sensor.

3. Results and discussion

3.1. Optical, morphological and surface characterization

Fig. 1 shows refractive index (n) and extinction coefficient (k) in the visible and NIR region for the samples annealed at 500°C , 600°C , 700°C and 800°C . Au NP contribution due to surface plasmon resonance (SPR) around 550–600 nm is evident: the absorption causes higher values of k , but also n is affected, because of the Kramers–Kronig relationship. At $\lambda > 800 \text{ nm}$ the nanocomposite films present a Cauchy dispersion of n and k values, that is a continuous slight decrease of both values with increasing wavelength.

Analyzing the behavior of n (Fig. 1a) away from the SPR region, it is clear that when increasing the annealing temperature, an increase of refractive index is observed. The n value measured at 1000 nm is 1.569 at 500°C , 1.615 at 600°C , 1.628 at 700°C and 1.639 at 800°C . The lower n value observed at low annealing temperature can be ascribed to the residual porosity of the film.

Analyzing the behavior of k (Fig. 1b), it can be seen that there are different featured SPR bands arising from the Au NPs existing inside the SiO_2 matrix at different annealing conditions. The double-featured SPR band for samples annealed up to 700°C and 800°C appears both red-shifted and modified in shape with respect to the usual single-peak shape expected from red colored Au NP dispersions [21] and which is present in the film annealed at 500°C . At

Fig. 1. Refractive index n (a) and extinction coefficient k (b) of the films annealed from 500 °C up to 800 °C.

Fig. 2. TEM results on the nanocomposite film annealed at 700 °C. (a) Bright-field cross-section of the film showing cookie-like nanoparticles embedded in the matrix; (b) one cookie-like nanoparticle at higher magnification (labels 1, 2 and 3 refer to different zones probed by EDX analysis); (c) HRTEM view of the Au–NiO interface.

600 °C an intermediate situation is observed, because of the broadening and small red-shifting of the plasmon peak, suggesting the onset of a structural modification. After the annealing process the films present a homogeneous color that ranges from pink-red to violet-blue tones according to the annealing temperature.

The plasmon absorption wavelength of spherical gold NPs in SiO₂ is around 530 nm, while in 500 °C treated samples the plasmon resonance is slightly red-shifted (around 550 nm, see Fig. 1b) because of the higher refractive index of NiO, homogeneously dispersed into the silica matrix. In addition, during NiO crystallization a coupling between NiO and Au occurs, leading to a double-featured plasmon resonance band of Au NPs. This is due to the two different media that the Au NPs in the cookie-like configuration are in contact with: nickel oxide (higher refractive index with respect to silica so the SPR is red-shifted at around 610 nm) and silica matrix (SPR at around 530 nm, i.e., no shift) [4].

Cross-sectional TEM measurements were performed to study the films morphology and the presence of atypical twofold NPs, so-called cookie-like [13] uniformly dispersed in the film treated at 700 °C has been observed. HRTEM analysis revealed that these structures arise from hetero-epitaxial coupling of crystalline Au (111) and NiO (200) planes, as shown in Fig. 2, which exhibit a modest lattice mismatch. In the film annealed at 500 °C, TEM measurements showed the presence of separate Au and NiO NPs with average diameters of 25 nm and 5 nm, respectively, with no twofold structure.

EDX elemental analysis was performed to further study the nature of the twofold NPs. The beam was centered in three different parts of the sample – each of the two sides of the cookie-like structure and the matrix – confirming the coupling of Au and crystalline NiO NPs.

In Table 1, the label “cluster (1)” refers to the dark side of the structure, while “cluster (2)” refers to the lighter one: cluster (1)

is essentially a Au phase (Ni signal comes from the surrounding matrix), cluster (2) is NiO, while the matrix (3) is composed of SiO₂ and some residual non-crystallized NiO. XRD was performed to follow the evolution after the annealing treatments of the crystalline phases inside the thin film. Fig. 3 shows the XRD data of the samples for the different annealing temperatures. Crystalline fcc Au peaks are evident in all samples at 38.18° and 44.39°, corresponding to (111) and (200) lattice planes, respectively (JCPDS #040714), while crystalline NiO is clearly observed only at high annealing temperature with a shoulder at 37.25° and a peak centered at 43.28°, corresponding to (111) and (200) lattice planes, respectively (JCPDS #471049). The small size and only partially crystalline structure of the corresponding NPs explains why TEM analysis showed NiO NPs in the samples annealed at 500 °C, while no diffraction peaks are present in the XRD data.

The surface composition of the nanocomposite thin films after the heat treatment at 500 °C and 800 °C has been monitored by XPS. Fig. 4 shows the Ni 2p, Au 4f and Si 2p XPS peaks obtained for very thin films (in the 30–40 nm range) deposited on a silicon wafer in order to minimize the film charge build-up during the XPS experiment. Since the surface measurements were finalized to actually determine the effective surface composition of the sensors, the XPS data were taken directly on the as-prepared samples,

Table 1

Atomic percentage values for the main elements present in the film annealed at 700 °C obtained from EDX measurements performed on the different regions reported in Fig. 2b.

Elements	Cluster (1) at%	Cluster (2) at%	Matrix (3) at%	All sample at%
O	48.1	60.0	66.0	60.7
Si	22.3	17.6	28.6	29.3
Ni	3.9	22	5.4	8.0
Au	25.7	0.4	0	2.0

Fig. 3. XRD spectra of nanocomposite films annealed from 500 °C up to 800 °C. The main diffraction line positions of NiO (JCPDS #471049) and Au (JCPDS #040714) are shown at the bottom of the figure.

Table 2

Surface composition of the thin films deposited on a Si wafer after thermal treatments (500 °C and 800 °C). The estimated error in the determination of each component is approximately 10%.

Elements (at%)	500 °C	800 °C
Si	19.3	20.4
O	50.6	54.2
Ni	13.5	11.2
Au	0.1	0.4
C	16.5	13.8

without any sputter cleaning procedure. The corresponding surface stoichiometries are detailed in Table 2.

The analysis of the Ni 2p photoemission region clearly indicates the presence of Ni(II) ions in NiO as confirmed by the BE of the maximum intensity Ni 2p_{3/2} peak (854.4 eV) and by the relative intensity of the satellites. A detailed examination of the low BE side of the Ni 2p_{3/2} peaks (see the inset in Fig. 4) indicates that the sample treated at higher temperature presents a small shoulder, suggesting the presence of some more reduced species either formed by thermal reduction or by the interaction with metal NPs (i.e., formation of the cookie-like structures). The analysis of the Au 4f peak reveals the presence of metallic Au with bulk-like electronic features. It must be noted that the chemical composition determined

on the basis of XPS (and therefore a surface chemical composition) points to a strong Au surface depletion with respect to the nominal value expected on the basis of the preparation procedure. This is in agreement with TEM data showing that the first few nanometers from the surface do not exhibit Au precipitation. Moreover, after increasing the annealing temperature, a higher Au content in the surface region is observed (see Table 2).

In both films, a measurable amount of carbon is observed which could be partially ascribed to adventitious carbon, but probably also to some carbon residue as suggested from the significant decrease of the C content after the annealing at 800 °C with respect to the sample treated at 500 °C. The incomplete elimination of the carbon fraction due to the sol–gel precursors is also evident from the analysis of the Si 2p XPS region (Fig. 4) where it is evident that for the lower temperature treated sample, the Si 2p peak is larger and characterized by a centroid shifted to lower BE [22]. However, the sample treated at 800 °C presents a Si 2p peak maximum at 103.5 eV and a lower full width at half maximum, observations which are compatible with fully oxidized SiO₂.

3.2. Gas sensing characterization

Three different kind of gas sensing measurements were performed in order to evaluate how the same film material reacts when exposed to H₂ and CO. Only samples annealed at 700 °C were tested: this choice comes from the fact that at 700 °C the film presents the cookie-like structures, with more crystalline NiO NPs compared to lower annealing temperatures, but still porous, thus allowing the gas to reach the active NPs inside the porous matrix.

Fig. 5 shows the electrical resistance response of the nanocomposite film at 300 °C operating temperature under CO concentrations ranging from 5 ppm to 300 ppm in air (Fig. 5a) and under H₂ concentrations ranging from 8.5 ppm to 510 ppm in air (Fig. 5b). Conductometric gas sensing measurements showed almost no response towards CO, while a small increase in resistance has been shown only when exposed to 340–500 ppm H₂.

In a previous work [23] it was shown that SiO₂ films containing NiO nanocrystals were excellent candidates for hydrogen and carbon monoxide conductometric sensors; the fact that gold doped SiO₂–NiO films do not show any appreciable conductometric response can be related to the different resistance of the film itself. NiO doped silica films have quite low resistance (around 10⁵ Ω at 300 °C) because NiO NPs overcome the percolation threshold [23], while in the films doped with Au, the NiO NPs are more separated inside the matrix (see Fig. 2a), thus showing very high

Fig. 4. XPS data for the Au 4f, Ni 2p and Si 2p regions of the thin films deposited on a Si wafer after a thermal treatment (500 °C and 800 °C).

Fig. 5. Dynamic changes of the resistance of films annealed at 700 °C: (a) under CO concentrations ranging from 5 ppm to 300 ppm in air; and (b) under H₂ concentrations ranging from 8.5 ppm to 510 ppm in air. Data measured at 300 °C operating temperature.

resistance (around $10^9 \Omega$ at 300 °C) and no appreciable variation in conductivity when exposed to the gas species.

The nanocomposite films exhibited clear and reversible absorbance changes in the visible-NIR wavelength region when exposed to CO and H₂, as it is shown in Fig. 6. 1%v/v CO induced a decrease in absorbance over the whole wavelengths range with the exception of wavelengths near the main SPR band around 613 nm. Even if the variation in absorbance during CO exposure is very small, it is easily detectable with respect to background signal noise with conventional spectrophotometers which have a resolution of $10^{-2}/10^{-3}$, as can be seen in our previous publications [12,17]. The variation in absorbance during 1%v/v H₂ exposure is much higher with respect to CO exposure. Moreover H₂ induced a clear blue-shift of the overall SPR band and a decrease of absorbance level around the plasmon frequencies. As discussed in our previous papers [12,17] the CO sensing behaviors can be related to an increased catalytic activity promoted by gold, closely associated with the catalytic activity of the Au/NiO interface. The large blue-shift and shape modification of the Au plasmon band detected in the presence of H₂ can be related to a variation of the electron density of the Au NPs and/or the dielectric constants of the medium caused by the interaction of the H₂ with the nanocompos-

Fig. 7. Optical change ($\Delta A = [Abs_{Air} - Abs_{Gas}]$) of films annealed at 700 °C after exposure to 1% v/v CO (black line) and 1% v/v H₂ (gray line) at 300 °C operating temperature.

Fig. 8. Relative absorbance change at 640 nm and at 300 °C operating temperature. The sample exposure sequence was: air–1% v/v H₂–air–1% v/v H₂ and 1% CO v/v–air–1% v/v H₂–air.

Fig. 6. Optical absorbance spectra of films annealed at 700 °C measured in air (black line) and during exposure to 1% v/v CO (gray line, left) and 1% v/v H₂ (gray line, right) at 300 °C operating temperature. The figure highlights the effect of gas exposure on the SPR frequencies of Au nanoparticles (450–750 nm region).

Fig. 9. Dynamic response of a nanocomposite film annealed at 700 °C with a $\text{La}_2\text{Ga}_5\text{SiO}_{14}$ SAW sensor towards H_2 at 170 °C operative temperature (left) and towards CO at 210 °C operative temperature.

ite. It has been reported by Kobayashi et al. [18,24] that crystalline NiO promotes a CO sensitive charge carrier density change. The strong wavelength dependence of the optical spectra and the difference between absorption values measured for H_2 and CO exposure allows selectivity of the film response towards each of the two species.

By evaluating the difference in absorption from pure air to air containing the target gas versus the wavelength (Fig. 7) it is possible to appreciate the strong wavelength dependence of the sensor response, especially when exposed to hydrogen. So for each target gas some characteristic wavelengths can be determined which correspond to maximum (negative and/or positive) response, or to null response.

For example, at $\lambda = 660$ nm (maximum positive variation for 1% H_2 exposure) the sensor is showing its strongest response, while at $\lambda = 640$ nm (no variation for 1% CO exposure but still high variation for 1% H_2 exposure) it is possible to selectively sense H_2 . Fig. 8 demonstrates the selectivity towards H_2 with respect the interfering CO gas. Absorbance at $\lambda = 640$ nm is monitored and it shows almost no variation even when introducing 1% CO while detecting a 1% v/v H_2 atmosphere.

Response time of the sensors when exposed to 1% H_2 has been evaluated analysing the time in which the material reaches 90% of the variation in absorbance induced by the gas, and it has been found to be around 1 min.

The films deposited on SAW transducers have been also tested toward CO and H_2 . An ac voltage is applied to the interdigitated transducer, thus creating an oscillating acoustic (mechanical) wave due to the piezoelectric substrate used as a positive feedback element in a closed loop circuit with an amplifier. When a continuous layer is deposited on top of this substrate, changes in the film physical properties, due for example to absorption/desorption processes, or to oxidation/reduction reactions, promote a change in the oscillator frequency [25,26]. A frequency counter was used to measure the operational frequency of the sensor, that was found to be approximately 55 MHz in dry synthetic air at a temperature of 170 °C.

Fig. 9 shows the dynamic responses registered for both gases at the selected operational temperatures. The nanocomposite films have been tested at increasing gases volumetric concentrations in the 0.06–0.5% range. It is evident that only exposure to H_2 gives a significant signal, showing reproducible baseline recovery at all gas exposures cycles and with a response proportional to the gas concentration. The introduction of H_2 to the sensor surface causes an increase in resonant frequency. The sensor response is defined as the variation in operating frequency of oscillation due to the interaction with the target gas. The measured sensor response was approximately 8 kHz toward 0.5% of H_2 at 170 °C operating temperature. The same behaviour has been observed even after repeated cycles of exposure, as can be seen from Fig. 9. The nanocomposite

films show quasi-instantaneous detection time, very fast recovery time and quite good baseline recovery; with a detection time for SAW measurements of around 1 min, comparable with optical results.

However, it was not possible to get a stable baseline signal during CO exposures, as an uncontrolled drift has been observed (Fig. 9 right) even during tests up to 14 h long, which is not acceptable for reliable gas detection. Tests have also been repeated four times during a 7 days test period, and this trend was observed in all experiments.

The response of a SAW sensor coated with a gas sensitive layer can be related to changes of the film physical properties such as mass, electrical conductivity, elastic modulus, viscosity, and permittivity when exposed to a target gas altering the surface acoustic wave propagation parameters. However, the main perturbation mechanisms such as mass-loading, acoustic-electric changes (conductivity) and dielectric properties are generally utilized for sensing applications [27,28].

In the case with the present films, there was no appreciable change in the conductivity of the film, while the optical gas sensing properties may be related to a variation in the dielectric properties of the materials, as evidenced by the large shift and shape change of the SPR band when exposed to H_2 . It is proposed, therefore, that also in the case of the SAW based sensors the sensing mechanism is mainly related to a variation of the dielectric properties of the films when exposed to H_2 .

4. Conclusions

SiO_2 porous film doped with NiO and Au nanoparticles have been synthesized by the sol–gel technique. The films annealed at 700 °C showed the presence of twofold NPs in the so-called cookie-like configuration. By comparing the gas sensing response of the nanocomposite film used as platform for conductometric, optical and SAW based sensors, it is concluded that the sensing mechanism is mainly related to a variation of the dielectric properties of the films when exposed to H_2 . Moreover, by exploiting the wavelength dependence of the optical sensor response it was demonstrated that the films could be used to selectively recognize H_2 in the presence of CO.

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