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CdO-based nanostructures as novel CO₂ gas sensors

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Abstract

Crystalline Cd(OH)₂/CdCO₃ nanowires, having lengths in the range from 0.3 up to several microns and 5–30 nm in diameter, were synthesized by a microwave-assisted wet chemical route and used as a precursor to obtain CdO nanostructures after a suitable thermal treatment in air. The morphology and microstructure of the as-synthesized and annealed materials have been investigated by scanning electron microscopy, transmission electron microscopy, x-ray diffraction and thermogravimetry–differential scanning calorimetry. The change in morphology and electrical properties with temperature has revealed a wire-to-rod transformation along with a decreases of electrical resistance.

Annealed samples were printed on a ceramic substrate with interdigitated contacts to fabricate resistive solid state sensors. Gas sensing properties were explored by monitoring CO₂ in synthetic air in the concentration range 0.2–5 v/v% (2000–50 000 ppm). The effect of annealing temperature, working temperature and CO₂ concentration on sensing properties (sensitivity, response/recovery time and stability) were investigated. The results obtained demonstrate that CdO-based thick films have good potential as novel CO₂ sensors for practical applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Gas sensors based on semiconducting oxide nanostructures have been widely investigated. It has been demonstrated that reduction in crystal size, leading to a large surface-to-volume ratio, significantly increase the sensor performance [1]. This is because nanosized grains of metal oxides are almost depleted of carriers (most carriers are trapped in surface states), hence, when exposed to target gases, they exhibit greater conductance changes as more carriers are activated from their trapped states to the conduction band. In particular, one-dimensional (1D)

structures such as nanowires, nanorods or nanobelts are the subject of extensive interest due to their great potential for gas sensing by means of conductometric solid state sensors [2].

One-dimensional oxide nanostructures, such as crystalline nanowires/nanobelts, can be easily synthesized via the vapor transport and vapor–liquid–solid (VLS) methods [3, 4]. In addition, they can also be synthesized by a number of wet chemical methods, so that the production of such materials is inexpensive and easily scalable [5]. Among them, cadmium oxide (CdO)-based nanostructures have interesting optical and electrical properties and find important applications in optical and electronic devices [6, 7].

Different wet chemical approaches have been followed for the synthesis of one-dimensional (1D) CdO structures [8–12]. For example, Guo *et al* reported the hydrothermal preparation of porous CdO nanowires from mixed cadmium hydroxide ($\text{Cd}(\text{OH})_2$) carbonate nanowires. The wire-like morphology was retained after the thermal treatment [10].

Following this approach, we tried to synthesize CdO 1D structures by heat treatment of $\text{Cd}(\text{OH})_2$ nanowires previously prepared by a microwave-assisted synthesis method [13]. Several papers deal with the synthesis of $\text{Cd}(\text{OH})_2$ one-dimensional structures by different methods; for example, Yang *et al* synthesized $\text{Cd}(\text{OH})_2$ nanowires using $\text{Cd}(\text{NO}_3)_2$ as a precursor by a hydrothermal method at 150 °C for 48 h [14], while Ye *et al* used $\text{Cd}(\text{CH}_3\text{COO})_2$ and $\text{C}_6\text{H}_{12}\text{N}_4$ as precursors in aqueous solution at 95 °C for 16 h [12]. Microwave-assisted synthesis has more advantages with respect to more conventional methods, that is very short reaction times, production of small particles with a narrow particle size distribution, and high purity [15]. Furthermore, it allows the controlled synthesis of particular nanostructures, a theme of utmost importance due to recent interest in the search of nanomaterials with peculiar size and shape-dependent properties [15, 16].

The sensing characteristics of synthesized CdO-based nanostructures for the detection of carbon dioxide (CO_2) were then investigated. Monitoring CO_2 concentration is of great importance in many fields such as in the chemical industry, agriculture, biotechnology, the environment and medicine [17]. Carbon dioxide is a greenhouse gas, which traps heat near the earth's surface and prevents it from being radiated back into space. Carbon dioxide is also an important indicator for indoor air quality. Due to its inert character, it is used in food packaging, where CO_2 considerably extends the storage and shelf life of meat and cheese, as well as fruit and vegetables [18]. The measurement of CO_2 levels in breath is a standard procedure during intensive care and anesthesia and is a primary tool in the diagnosis and management of respiratory function [19].

For measuring the CO_2 concentration in these various matrices, the prevailing technology relies on bulky and expensive non-dispersive infrared absorption (ND-IR) sensors [20]. ND-IR sensors are commercially available and have a very stable accuracy over their long-term operation but they are very expensive, restricting their use only to some specific, high value applications in controlled environments such as surgical wards.

The development of CO_2 sensors based on semiconductor gas sensor technology, enabling a reduction in both size and costs, has been widely pursued [21]. Metal oxide-based films compatible with solid state-based gas sensor technology, such as lanthanum doped tin oxide and $\text{BaTiO}_3/\text{CuO}$, have been well investigated as CO_2 sensors [22, 23]. However, the development of these sensors is a difficult and challenging task, and a number of questions have still to be answered before they can be proposed as a reliable alternative for practical applications. The activation of metal oxide-based sensors by silver nanoparticles or UV light [24, 25] has been proposed for improving their features for the monitoring

of CO_2 . Also mixed metal hydroxyl/carbonates have been investigated, showing very good sensitivity [26].

Regarding cadmium-based sensors, nanostructured CdO has been reported to have a high sensitivity, specially for liquefied petroleum gas and NO_2 [27, 28]. However, to the best of our knowledge, no study on CO_2 detection has been reported so far.

2. Experimental details

2.1. Materials synthesis

The synthesis of CdO nanostructures was carried out as follows. First a 0.1 M solution was prepared by dissolving cadmium nitrate in distilled water. The solution was neutralized with ammonia, and maintained at $\text{pH} = 10$. The above solution was transferred into a microwave oven (power up to 1 kW) and microwave irradiated for 5 min in microwave with convection mode. The precipitate was taken out, washed with bi-distilled water and again microwave irradiated for 5 min in a microwave with convection mode, giving a white product. The 'as-prepared' sample is referred to as CdAP. Two further samples were prepared by calcining the precursor at 250 °C (Cd250) and 350 °C (Cd350).

2.2. Characterization

The morphology of the samples was investigated by a FEI (model XL-30) scanning electron microscope (SEM), equipped with an energy-dispersive x-ray (EDX) microprobe. Transmission electron microscope (TEM) images were recorded on a Technai G20-Stwin TEM using an accelerating voltage of 200 kV.

The microstructure of the synthesized sample was analyzed by x-ray diffraction (XRD) (Bruker AXS D8 Advance) using the $\text{Cu K}\alpha$ wavelength of 1.5405 Å. The average crystalline size of the crystallites was evaluated using Scherrer's formula, $d = \frac{K\lambda}{\beta \cos \theta}$, where d is the mean crystalline size, K is a grain shape-dependent constant (0.9), λ is the wavelength of the incident beam, θ is a Bragg reflection angle, and β is the full width at half maximum of the main diffraction peak. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained in air, at 4 cm^{-1} resolution, on a Nicolet 380 Thermo Fisher spectrophotometer, equipped with a DTGS detector.

Thermal analysis was carried out by using a thermogravimetric and differential scanning calorimeter apparatus (TG-DSC; Netzsch, model STA 409PC). The analyses were carried out with a heating rate of 10 °C min^{-1} in static air up to 600 °C.

2.3. Sensor fabrication and electrical tests

The devices for electrical and sensing tests were fabricated as follows. The CdO-based samples were mixed with water to form a paste, which was screen-printed on alumina substrates (6 × 3 mm^2) with Pt interdigitated electrodes and a Pt heater located on the backside. Then, the devices were stored at room temperature. Before any measurements they were heated *in situ*, and maintained for 30 min in a synthetic air flow at the working temperature to attain baseline stabilization.

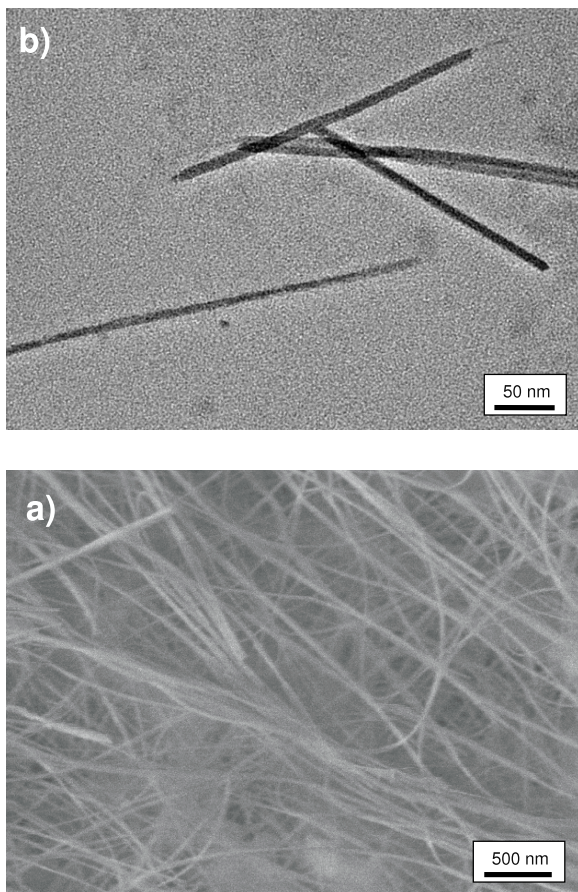


Figure 1. (a) SEM image of as-prepared nanowires. (b) TEM of as-prepared nanowires.

The experimental bench for the electrical characterization is the same as previously described [29]. Electrical measurements were carried out in the temperature range from room temperature (RT) to 350 °C under a synthetic dry air total stream of 100 sccm. A multimeter data acquisition unit (Agilent 34970A) was used for this purpose, while a dual-channel power supplier instrument (Agilent E3631A) was employed to bias the built-in Pt heater.

Gas sensing tests were carried out inside a stainless-steel chamber under a controlled atmosphere in a home-made apparatus [13]. Mass flow controllers were used to adjust the desired concentrations of CO₂ in nitrogen coming from a certified bottle. The sensor response was measured as change in resistance in four point mode using the Agilent 34970A multimeter. The sensor's response to CO₂, S , is defined as $S = (R_{\text{air}} - R_{\text{CO}_2}/R_{\text{air}})100$ where R_{CO_2} is the electrical resistance of the sensor at different CO₂ concentrations and R_{air} is the baseline resistance in synthetic dry air. Response time τ_{res} is defined as the time needed to reach 90% of the response signal, whereas τ_{rec} is the time required until 90% of the original baseline signal is recovered.

3. Results and discussion

3.1. Synthesis and characterization

Cd-based nanowires, synthesized through the reaction of cadmium nitrate with ammonia assisted by microwaves, were

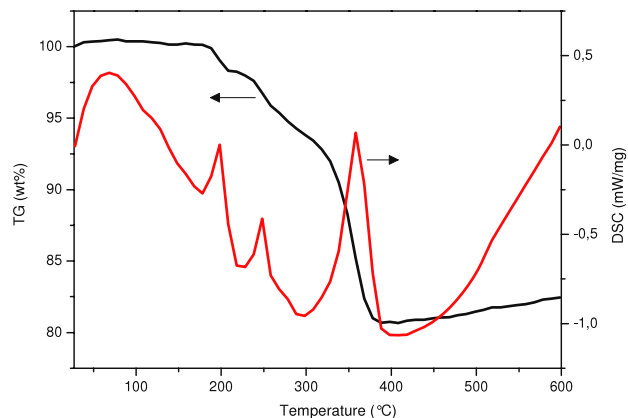


Figure 2. TG-DSC analysis of as-prepared nanowires.

used as a precursor material for the preparation of CdO nanostructures. A detailed description of the synthesis conditions and characterization of the precursor material has been reported elsewhere [13]. It must be mentioned that the experiments described here were carried out on real samples, i.e. stored in air after the synthesis and/or thermal treatments. Therefore, carbonation processes with CO₂ of the ambient air can occur to a some extent, depending on the temperature and ageing time, leading to materials with modified characteristics with respect to freshly prepared samples.

Figure 1 reports the SEM and TEM images of the CdAP sample, showing the presence of nanowires with an almost smooth surface and a high aspect ratio, the length being in the range from 0.3 up to several microns and the diameter in the 5–30 nm interval.

The characteristics of as-prepared nanowires subjected to a successive thermal treatment were first investigated by TG-DSC (figure 2). Different weight losses were observed in the temperature range from RT to 600 °C. Such losses are associated with endothermic processes at 70, 199, 247 and 358 °C resulting from DSC analysis and are probably due to desorption of humidity and other volatile materials [13]. Specifically, in addition to the release of adsorbed water at 70 °C, peaks at 199 and 247 °C, showing a total weight loss of about 5%, appear to be due to prolonged ageing in air which can cause carbonation of the sample with the formation of cadmium carbonate, CdCO₃. The formation of mixed cadmium hydroxide carbonates has already been reported [10]. CdCO₃ decomposes during heating releasing CO₂ as follows:



At a temperature of 358 °C, a weight loss is observed, corresponding to the release of one water molecule from Cd(OH)₂ to give CdO, according the following process:



Then, as-prepared nanowires stored in air appear to have a mixed Cd(OH)₂/CdCO₃ composition, as suggested in a previous report [13].

To analyze the morphological and microstructural modifications induced by the thermal treatment, electron

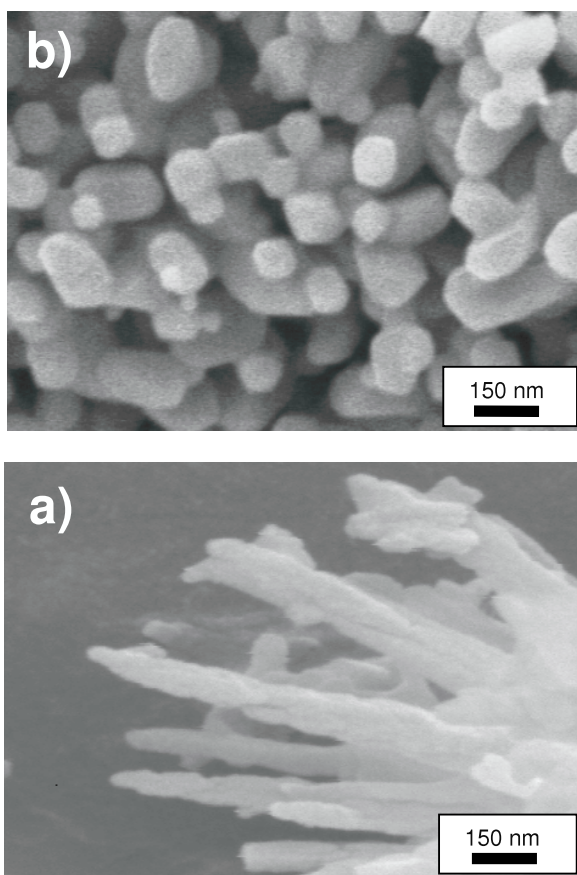


Figure 3. SEM image of samples annealed at different temperatures: (a) Cd250, (b) Cd350.

microscopy and XRD analyses were carried out on samples heated at the two representative temperatures of 250 and 350 °C. Morphological modifications are accompanied by color changes of the samples, going from white (CdAP), light yellow (Cd250) to brown (Cd350). SEM micrographs reported in figure 3 show the morphological characteristics of the samples obtained after thermal treatments. Nanowires imaged on sample Cd250 appear shorter and present a rougher surface with respect to the untreated sample. On increasing the annealing temperature, a wire-to-rod morphological transformation occurred. The rod-like structure is clearly visible on sample Cd350. On the basis of the above results, the nanowire structure appears to collapse at a lower temperature than the cadmium hydroxide carbonate nanowires synthesized by Guo *et al* [10], which were stable at temperatures up to 600 °C.

Figure 4(a) shows the TEM micrograph of sample Cd250, showing a single nanowire. The HRTEM image (figure 4(b)), with clearly visible very small crystallites and lattice fringes, provides evidence of the polycrystalline structure of the nanowires. The measured d -spacing (0.29 nm) in the HRTEM micrograph agrees very well with that of the (104) plane of CdCO_3 (d -spacing = 0.295 nm).

The XRD results are reported in figures 5(a)–(c). The diffraction pattern of the as-synthesized CdAP sample shows the characteristic diffraction peaks of CdCO_3 and Cd(OH)_2 . A

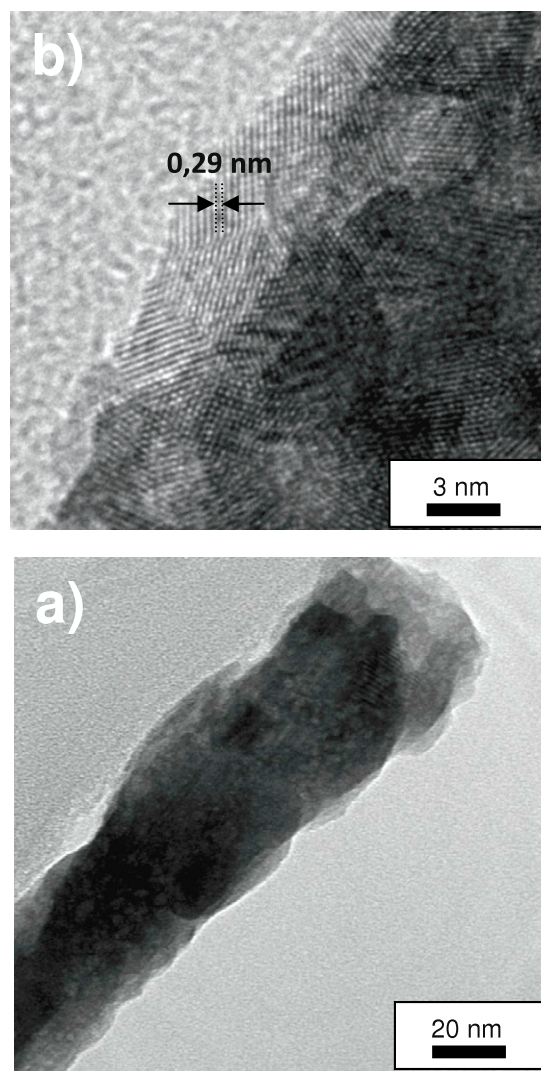


Figure 4. (a) TEM image of the Cd250 sample showing an individual nanowire. (b) HRTEM image showing lattice fringes coming from a nanowire.

similar pattern was registered for sample Cd250, while only the diffraction peaks of a new phase, identified as CdO, are present in the pattern relative to sample Cd350, indicating that the precursor nanowires were completely transformed into the oxide phase. These results are in agreement with the change of precursor color (CdO is brown in color) and thermogravimetric (TG) data. Line broadening analysis of the diffraction peaks carried out with the Scherrer equation indicated that the grain size increases with temperature, from about 18 nm for CdAP, to 21.5 nm (Cd250), and to 26.6 nm for Cd350.

Figure 6 shows the Fourier transform-infrared (FT-IR) spectra of the precursor nanowires heated to different annealing temperatures. The DRIFT spectrum of precursor nanowires shows the characteristic IR absorption peaks corresponding to OH^- , CO_3^{2-} (deriving from Cd(OH)_2 and CdCO_3 , respectively) and H_2O species [13]. DRIFT measurements made on the annealed samples indicate that OH^- and CO_3^{2-} species persist up to 250 °C and finally disappear with the further increase in annealing temperature, in full agreement with the XRD analysis.

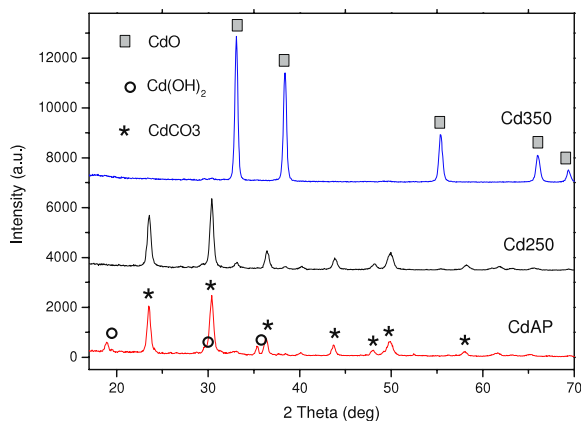


Figure 5. (a) The XRD pattern of as-prepared nanowires sample. (b) XRD of samples annealed at different temperatures.

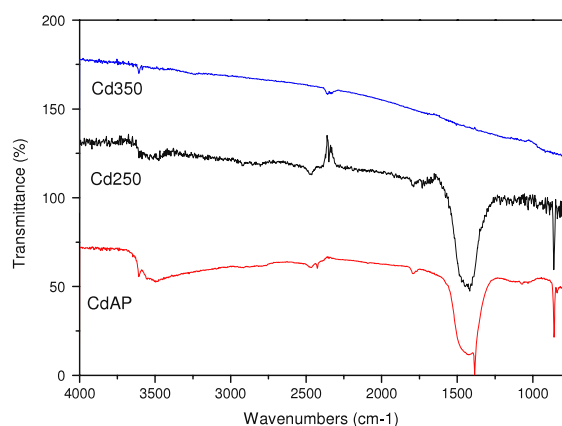


Figure 6. DRIFT of samples annealed at different temperatures.

3.2. Electrical and sensing tests

To assess the suitability of the synthesized materials as a sensing layer for CO₂ resistive sensors, their electrical characteristics have been evaluated. The variation of resistance of the as-synthesized CdAP film with temperature, during a heating and cooling cycle, was previously investigated [13]. The initial very high baseline resistance decreases strongly around 150–160 °C to a value of few tens of ohms or less. This behavior can be attributed to the occurrence of several processes during the heating treatment, as documented by the characterization measurements presented above, and precisely: (i) removal of water vapor, dehydroxylation and/or elimination of (surface)carbonates; (ii) formation of the CdO phase.

In full agreement with our previous report and literature data, the resistance of films based on the calcined samples is much lower than that of as-synthesized one. This high electrical conductivity has been related to the formation of non-stoichiometric, n-type semiconductor CdO having high carrier concentration [30–32].

For CO₂ sensing tests, resistance measurements were made maintaining the Cd250 and Cd350 sensors under a controlled stream of synthetic dry air, and pulsing different CO₂ concentrations (0.2–5 v/v%). The sensors were tested at different temperatures to evaluate the best working conditions

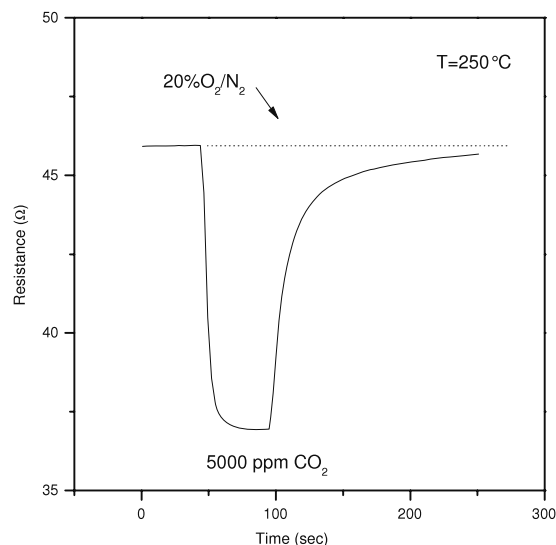


Figure 7. Dynamic response of the Cd250 sensor operating at a temperature of 250 °C.

in terms of sensitivity, response/recovery time and stability. The conductivity of both Cd250 and Cd350 films is reversibly modified when exposed to CO₂ at a concentration of 0.5%. Figure 7 shows the typical transient response of the Cd250 sensor operating at a temperature of 250 °C. A fast decrease of resistance was noted when the sensor was exposed to CO₂. However, sending successive pulses of CO₂ in the sensor chamber, a progressive reduction of the signal with time (figure 8(a)) is noted. On the contrary, the Cd350 sensor is very stable (figure 8(b)), even if it turns out to be much less sensitive of the Cd250 one.

The observed behavior can be interpreted recalling the characterization results reported above. The progressive increase in grain size and consequent loss of surface area of the sensing material with the annealing temperature appears to be the main factor contributing to the decreased response. The higher response of sample Cd250 could also be linked to a specific interaction between CO₂ and OH⁻ species on the surface (see discussion below) and considering the larger availability of OH⁻ species on this sample with respect to Cd350. In agreement with this latter hypothesis, the gradual decrease of the response with time (figure 8(a)) could be explained considering the progressive dehydroxylation of the sample during the sensor operation at high temperature, and the absence of water that hindered the replace of OH⁻ species.

Due to its better stability, further investigations were continued with the Cd350 sensor. Figure 9(a) shows the response of the Cd350 sensor operating at different temperatures. The measurements were performed at 50 °C intervals between 250 and 350 °C. The CO₂ concentration was fixed at 5000 ppm. The maximum response is observed at 250 °C. The response and recovery times of the sensor as a function of the temperature are also reported in figures 9(b) and (c). Even if the response/recovery times substantially decrease with the temperature, their values (about 200 and 300 s, respectively) are still sufficiently fast for many practical applications, also at the lowest temperature tested (250 °C).

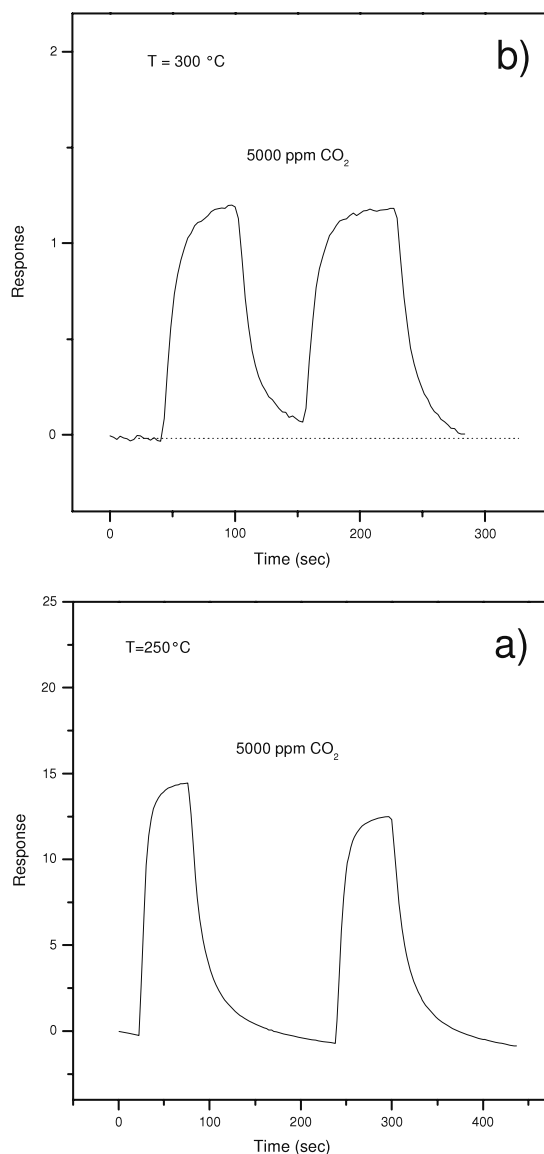


Figure 8. Response of the sensors investigated to successive pulse of CO₂: (a) Cd250, (b) Cd350.

The response of the sensing layer as a function of CO₂ concentration ranging from 0.2 to 5% was then studied at the optimum temperature of 250 °C (figure 10). The signal remains significant even for the lowest CO₂ concentration (2000 ppm). At high CO₂ concentrations the response time is much longer, not allowing signal stabilization to be reached within the programmed time; the recovery time seems instead to be little influenced by CO₂ concentration. The calibration curves referred to this sensor are reported in figures 11(a) and (b), indicating that CO₂ concentrations in the range investigated can be easily monitored and quantified.

3.3. Sensing mechanism

On the basis of characterization and sensing tests reported, we describe a plausible CO₂ sensing mechanism for the investigated sensors. Metal oxide-based resistive sensors have been previously investigated as CO₂ sensors and the related

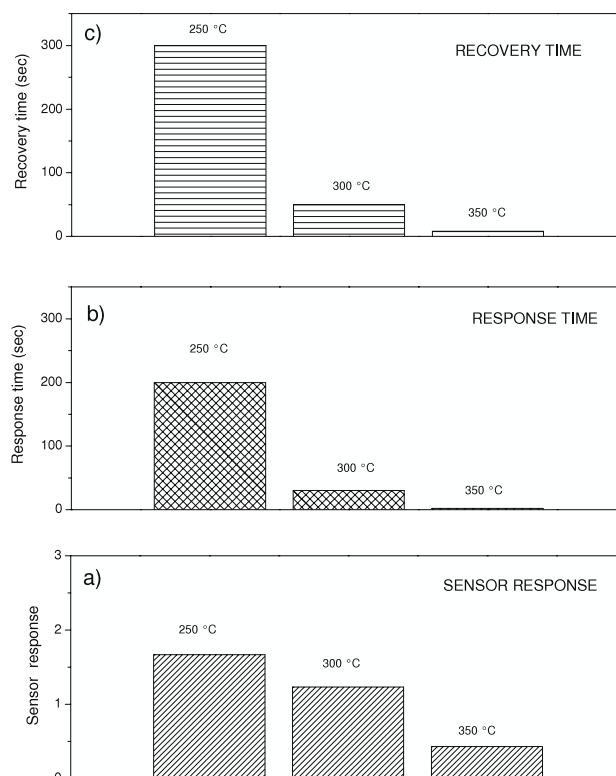


Figure 9. Response, response time and recovery time of the Cd350 sensor operating at different temperatures: (a) sensor response, (b) response time, and (c) recovery time.

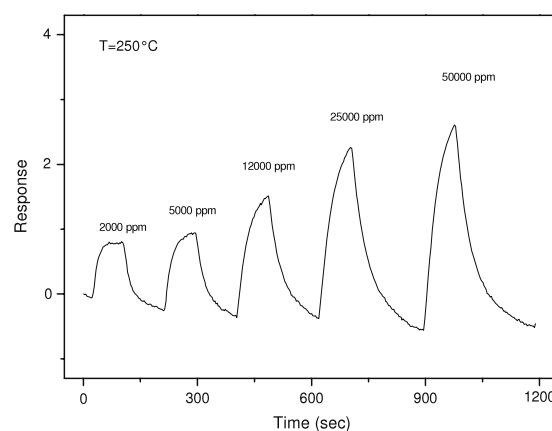
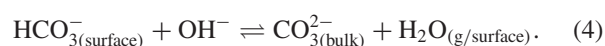


Figure 10. Response of the Cd350 sensor as a function of CO₂ concentration. The operating temperature is 250 °C.

sensing mechanism has been studied [21–25]. On addition of CO₂ in the ambient surroundings the sensor, the following chemical reactions at low operating temperature have been proposed by Ostrick *et al* [33]:



Major adsorption products were hydrogen carbonate and carbonates. At higher operating temperatures, surface

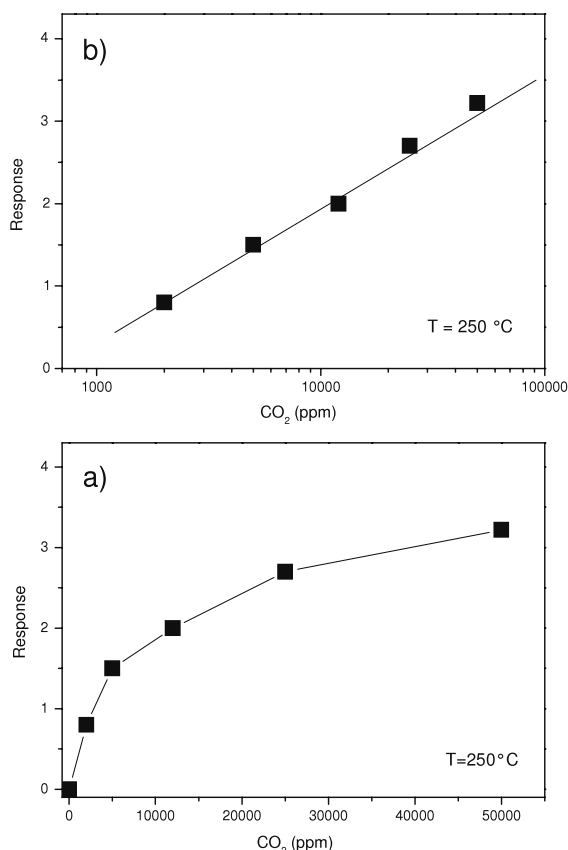
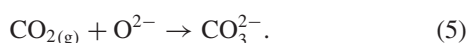


Figure 11. Calibration curves of the Cd350 sensor at a temperature of 250 °C. (a) Response–CO₂ concentration plot. (b) Semi-logarithmic plot.

carbonates can be formed, through the participation of surface oxide ions [34]:



As a result, a negative charge is moved from the surface to the bulk, decreasing the bulk resistance, as experimentally observed when our CdO sensors are exposed to CO₂.

The CO₂ sensing mechanism involved in these metal oxide-based resistive sensor devices relies then on the metal bicarbonate/carbonate \leftrightarrow CO₂ equilibrium. This suggests that easy metal hydrogen carbonate/carbonate formation at the operating temperature of the sensor is a pre-requisite for applying a specific metal oxide as sensing layer in resistive CO₂ sensors. Recently, Weimar and co-workers, pointed out that the condition for CO₂ sensing in dealing with rare earth hydroxide-based sensor is the formation of the rare earth oxycarbonate [35]. The formation of mixed phases of variable composition Cd₂(CO₃)_x(OH)_{2(3-x)} has been reported when Cd precursors are in contact with CO₂ during the synthesis of Cd hydroxide/oxide [10]. The observations reported in the present study confirm that a carbonate phase is formed in the presence of CO₂ on Cd(OH)₂ nanowire-based samples. The decomposition of the CdCO₃ phase occurs at a lower temperature with respect to other metal carbonates, and this feature could favor the sensing properties toward CO₂.

To better elucidate the sensing mechanism, other parameters should however be investigated. Sensing tests were carried out here in dry air, but real sensors should operate in humid environments. Adsorbed water plays an important role in the sensing mechanism of CO₂ on metal oxide surfaces. Indeed, chemical processes (3) and (4) need OH⁻ groups on the surface, which can be provided by the interaction of moisture with the semiconducting oxide. These aspects are outside the scope of the present study. Further work is in progress to investigate the behavior of our sensor under humid conditions.

The nanostructure also plays an important role. Compared with bulk and thin film materials, the enhanced sensitivity of 1D systems with respect to the chemical environment is usually interpreted as a result of the large surface-to-volume ratio [2]. With a large surface-to-volume ratio and a Debye length comparable to the nanowire radius, the electronic property of the nanowire is strongly influenced by surface processes, yielding superior sensitivity to its thin film counterpart. Thus, compared with characteristics of many solid state resistive CO₂ sensors, the presented sensor exhibits shorter response/recovery times, as a consequence of its 1D nanostructure.

4. Conclusion

A microwave-assisted heating method was used to successfully prepare Cd(OH)₂/CdCO₃ nanowires. By annealing this precursor material in air, CdO nanostructures were obtained. The change in morphology and electrical properties with temperature has revealed a wire-to-rod transformation along a strong decreases of electrical resistance.

We have shown that resistive sensor devices based on CdO thick films represent a suitable detection platform for CO₂ monitoring in air. These sensor devices have a number of key features, including fast response/recovery times, low electrical resistance and low noise, making their integration with commercial and low cost electronic instrumentation easy for a large-scale production.

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