



Optical gas sensing through nanostructured ZnO films with different morphologies

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ABSTRACT

We report on nitrogen dioxide (NO₂) sensing measurements by means of zinc oxide films presenting different morphologies. The variation in the photoluminescence emission of the films is employed as transduction mechanism to detect the presence of NO₂ gas molecules at room temperature. The significant role of film morphology on the sensing properties is presented and possible limits in the use of ZnO nanostructures for NO₂ detection at high gas concentration (>20 ppm) and low gas flow (50 ml/min), where a worsening of the sensor response is observed, are discussed. These features are ascribed to a likely incomplete reversibility of the NO₂ adsorption process and examined in connection with the mechanisms of interaction between NO₂ molecules and ZnO.

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1. Introduction

Thanks to their distinctive properties, semiconductor nanostructures are subject of intense studies for applications to chemical and biological sensors [1,2]. In particular, metal oxide semiconductors are very significant materials in this technological field, due to their chemical stability, low cost and low power consumption [3]. Zinc oxide and in particular its nanostructures are extensively investigated as active material for gas sensors, as demonstrated by the great number of tested gases and vapours, like hydrogen, ammonia, carbon monoxide, ethanol, methanol, acetone, butane etc. (see e.g. [4–9]). In addition, ZnO is also studied for applications to biosensors, for species like e.g. glucose [10], cholesterol [11], uric acid [12] and lactic acid [13].

When gas molecules or biological species interact with the surface complexes (e.g. O[−], O₂[−], H⁺, and OH[−]) of the active material of the sensor, they can induce a change in several physical properties of the material, such as the charge-carrier density, inducing variations in the electrical conductance and/or optical emission. As a consequence, different transduction mechanisms can be exploited in order to reveal the presence of the analyte in the environment. Dealing with ZnO as active material, the analyte can be detected,

for example, by measuring the variations of ZnO electrical resistance [4,5] or the frequency shift in ZnO-based Love mode SAW devices [14]. Gas sensing tests making use of ZnO can be performed by means of optical measurements too, for example by the *m*-line method [8], the surface plasmon resonance (SPR) technique [9], the use of optical fibres [15], or the variations of the photoluminescence (PL) emission [6,7].

In particular, sensors based on the variations of the PL emission in presence/absence of gas molecules are attractive because they can provide high responses at room temperature (in opposition to resistive sensors, usually working at temperature of about 300 °C or more) and result stable with a rapid, reproducible and reversible response and good sensitivity. A possible drawback could be the difficulty to realize this kind of sensors in a cheap way and in compact structures, since they require, apart from the sensing material, at least a light source exciting the material, a PL detection system and some integration procedures. However these problems can be overcome, indeed compact and simple PL-based sensors have been recently realized [16,17]. Also other alternative optical approaches, for example based on optical absorption measurements, can be exploited for gas sensing applications [18,19].

Summarizing the mechanism leading to the PL variations during the interaction between nitrogen dioxide (NO₂) molecules and the ZnO active material, it can be observed that ZnO has an intrinsic n-type doping due to native lattice defects, like oxygen vacancies and zinc interstitials, and when the molecules of an oxidizing gas, like NO₂, bind to its surface, they act as electron trappers, thus decreasing the number of charge-carriers which can radiatively recombine

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(the mechanisms of interaction between NO₂ and ZnO are examined in more details in Section 3). As a consequence the NO₂ adsorption process on the ZnO surface induces a quenching of the PL intensity. By a real-time monitoring of the integrated PL intensity in a fixed emission wavelength range, it is then possible to reveal the presence/absence of the gas through the decrease/increase of the PL signal.

In this paper we focus on the role of surface morphology of a set of ZnO samples in the PL quenching mechanisms when the films are exposed to nitrogen dioxide (NO₂), one of the major toxic air pollutants. In the literature, some reports show the comparison of different annealing conditions on ZnO samples for NO₂ resistive gas sensing measurements [27], or the comparison of different active materials for NO₂ detection through PL measurements (e.g. SnO₂ and ZnO in [7]). But, to the best of our knowledge, there is no report in literature about the comparison of different morphologies on NO₂ gas sensing properties through ZnO PL measurements. In particular, in this study the sensitivity to NO₂ gas molecules is examined in different films, grown by pulsed laser deposition (PLD) and showing various morphological features. Low NO₂ gas concentrations (down to 3 ppm) are detected at room temperature and without the aid of any catalyst promoting the surface kinetics. The significant role of film morphology on the sensing properties and some possible effects of an incomplete sensor recovery are discussed. Possible limits in the use of ZnO nanostructures for NO₂ detection at high gas concentration (>20 ppm), where a worsening of the sensor response is observed, are pointed out. The responses when using two different gas flows (50 and 100 ml/min) are compared and the higher gas flow is shown to promote faster sensing response and recovery and lesser effects of surface contamination.

2. Experimental

Details about the growth by pulsed laser deposition of the ZnO films employed in this work and about their morphological characterization by scanning electron microscopy (SEM) were previously reported in Refs. [20,21]. Briefly, the films were deposited on Si (1 0 0) substrates by KrF (248 nm) or ArF (193 nm) laser ablation in oxygen background atmosphere. By changing the substrate temperature in the range 500–700 °C and the oxygen pressure in the range 1–100 Pa, smooth and rough films as well as nanostructures were obtained.

For the optical gas sensing measurements the samples were excited by a cw He–Cd laser (325 nm). The laser beam was collected by an UV optical fibre (400 µm, Avantes FC-UV400-2) and split in two branches: a branch of the fibre was sent to a silicon photodiode (properly shielded from the light of the outside environment) connected with a pico-ammeter, in order to take into account the fluctuations of the laser power during the sensing measurements; the second branch directed the laser beam onto the sample, with a focus spot of about 3 mm². The sample was placed inside an aluminium sealed chamber where it was exposed to dry air or to a proper mixture of NO₂ and dry air. The chamber was provided with four apertures: two of them were used for gas inlet and outlet respectively; the others were connected with the excitation and collection optical fibres. The PL emission collected through the second optical fibre was sent to a spectrometer (Avantes MC2000) with a 75 mm focal length, a 600 lines/mm grating, 200 µm slit, a 2048 pixels CCD linear array detector, and a spectral resolution of 4 nm. It should be noticed that a high spectral resolution was not required in this kind of measurements because the integrated luminescence signal in a wide spectral range was used for the sensing measurements. The software (Avantes SpectraWin 5) used to analyze the sample luminescence allowed to periodically acquire the integral of the PL spectrum in a fixed wavelength range at fixed time intervals (each 3 s in our mea-

surements). The desired gas concentration in the chamber was obtained by mixing different flows of dry air and NO₂ through a bank of three mass flow controllers (Brooks Instrument 5850S). Each controller could operate in the flow range ~2.5–50 ml/min with an accuracy of ±0.2%. Two different total flows (50 and 100 ml/min) were used. The maximum used NO₂ concentration in dry air was 114 ppm, while the minimum obtainable concentration was about 5 ppm with a total flow of 50 ml/min and 3 ppm with 100 ml/min.

Before each measurement, the tested samples were exposed for 15 min in dry air flux in order to get a stabilization of the surface dynamics between the active material and the incoming flux. Then, for each selected NO₂ concentration, an exposure of 5 min to the gas flux was followed by a recovery of 5 min in dry air flux. These periods were long enough to get detectable sensor response and sensor recovery for the probed samples.

3. Results and discussion

Fig. 1 displays the SEM images of the five ZnO samples selected for the present study. By properly changing the deposition parameters, many different kinds of structures were realized. By KrF laser ablation, at a substrate temperature of 600 °C a rough film (sample 1) grew at low oxygen pressure of 5 Pa (Fig. 1(a)), whereas an aligned rod-array, perpendicular to the substrate surface and with column diameters in the range ~100–400 nm (sample 2), was obtained at high oxygen pressure of 100 Pa (Fig. 1(b)). By ArF laser ablation, at low oxygen pressure of 1 Pa hexagonal hierarchical nanostructures grew with increasing sizes when increasing the substrate temperature from 550 °C (sample 3, Fig. 1(c)) to 600 °C (sample 4, Fig. 1(d)). Finally, at 600 °C and high oxygen pressure of 100 Pa, an array of misaligned pencils, with diameters in the range ~80–500 nm (sample 5), was obtained (Fig. 1(e)). Further details about the sample growth and characterizations can be found in Refs. [20,21].

These films were exposed to dry air and to NO₂, and the variations of their PL emission due to these exposures were investigated as explained in Section 2.

The high crystal quality of the films considered in this work induces the PL signal in the ultraviolet (UV) range, resulting from band-edge excitonic emission, to be very intense, and the defect-related PL emission in the visible range, usually observed in ZnO materials, to be very low or almost totally absent, as noticeable in Fig. 2, where a representative PL spectrum showing the room temperature PL emission of sample 5 is reported as example. As a consequence, in our sensing measurements, the integrated area in the excitonic range, i.e. 360–420 nm (filled area in Fig. 2), was monitored. The weak peaks observed around 443, 507 and 540 nm were only due to light scattered inside the experimental set up and they were not considered.

During the sample exposure to the NO₂ gas, the only significant effect observed in the emission spectrum was a reduction of the PL intensity, while no shift of the emission peak or change in its lineshape were observed.

This decrease of the PL intensity can be related to the interaction between the NO₂ molecules and the ZnO surface as briefly mentioned in Section 1. In order to give a more detailed explanation, we can observe that the interaction between NO₂ molecules and ZnO is not a simple matter, since several adsorption processes can occur [22–24]. Indeed, when an NO₂ molecule interacts with an n-type material, it can be adsorbed capturing an electron from the material in different ways.

For example, NO₂ can be directly adsorbed on the ZnO surface according to the reaction:



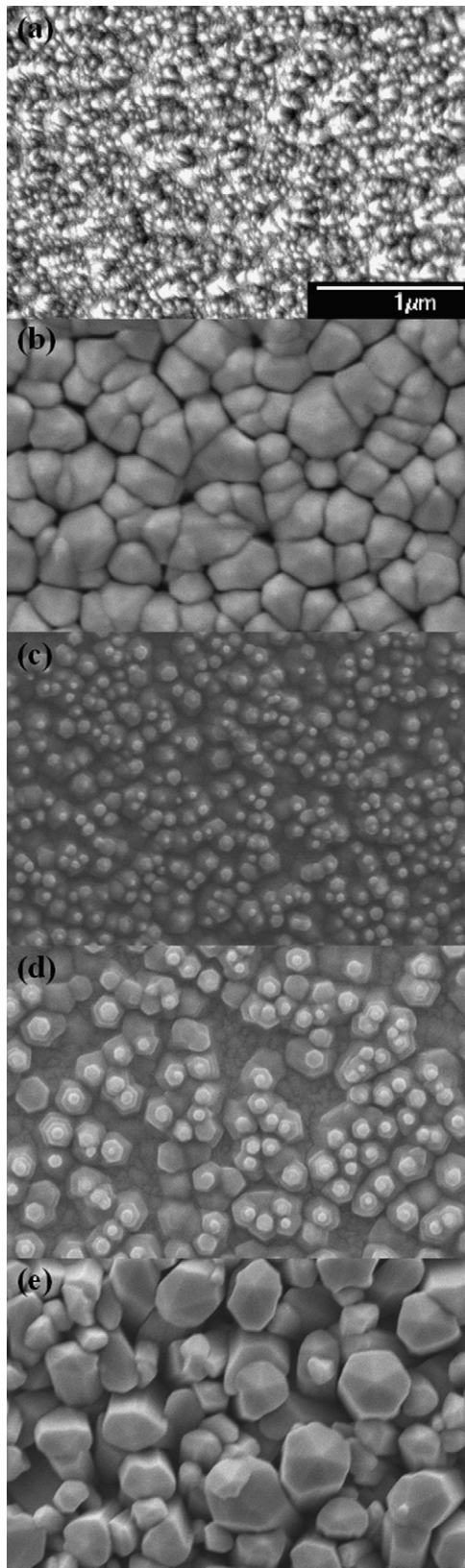


Fig. 1. SEM images of ZnO samples grown by PLD. The samples in (a) and (b) were deposited by KrF laser ablation at substrate temperature of 600 °C and oxygen pressure of 5 and 100 Pa respectively. The samples in (c–e) were deposited by ArF laser ablation: (c) and (d) at oxygen pressure of 1 Pa and substrate temperature of 550 and 600 °C respectively; (e) at substrate temperature of 600 °C and oxygen pressure of 100 Pa. The marker is the same for all pictures.

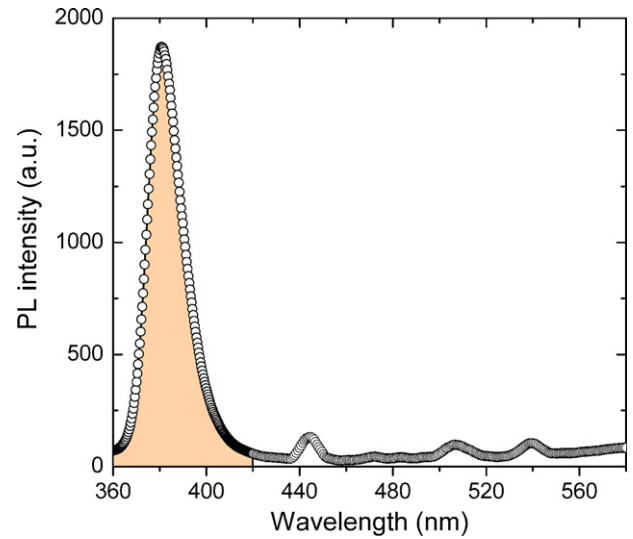


Fig. 2. Room temperature PL spectrum of sample shown in Fig. 1(e). The shaded area indicates the range considered for the sensing measurements.

Additionally, NO_2 can dissociate producing a nitrogen monoxide (NO) molecule and an oxygen atom which is adsorbed on the ZnO surface capturing an electron:



NO molecules, naturally present in a NO_x atmosphere or deriving from reaction (2), can be adsorbed on the ZnO surface as well, thus trapping other electrons from the material. As for NO_2 , also NO molecules can be directly adsorbed or can dissociate through the following reactions, respectively:



All reactions (1)–(4) involve the trapping of ZnO electrons in the bonds with the adsorbed species. This means that a depletion layer for charge-carriers is created on the ZnO surface due to gas adsorption. As a consequence, the number of electrons which can radiatively recombine is decreased during the ZnO exposure to NO_2 , thus explaining the reduction of the PL signal in NO_2 atmosphere with respect to its initial value when the material is exposed to dry air. If the adsorption processes are reversible then, after the active material is exposed to air again, the adsorbed molecules should leave the surface, allowing the de-trapping of electrons and the consequent recovery of the PL signal.

Apart from the PL quenching due to gas absorption by the ZnO surface, we have to consider another factor which could cause a reduction of the measured PL intensity, namely the direct interaction between the NO_2 molecules and the UV photons. In fact, NO_2 can undergo photodissociation under UV illumination with photon wavelengths lower than ~ 415 nm, following the photochemical dissociation [25,26]:



where $h\nu$ is the energy of the photon absorbed by the NO_2 molecule to promote the molecule decomposition. Since the photon wavelength of the laser beam used for the sample photo-excitation (see Section 2) and most of the ZnO PL emission in our experiments (see Fig. 2) are below 415 nm, the possible influence of light absorption related to NO_2 photodissociation in our measurements should be considered. In order to exclude significant effects of a direct absorption of the laser beam by the NO_2 molecules photodissociating according to reaction (5), the sample in the measurement

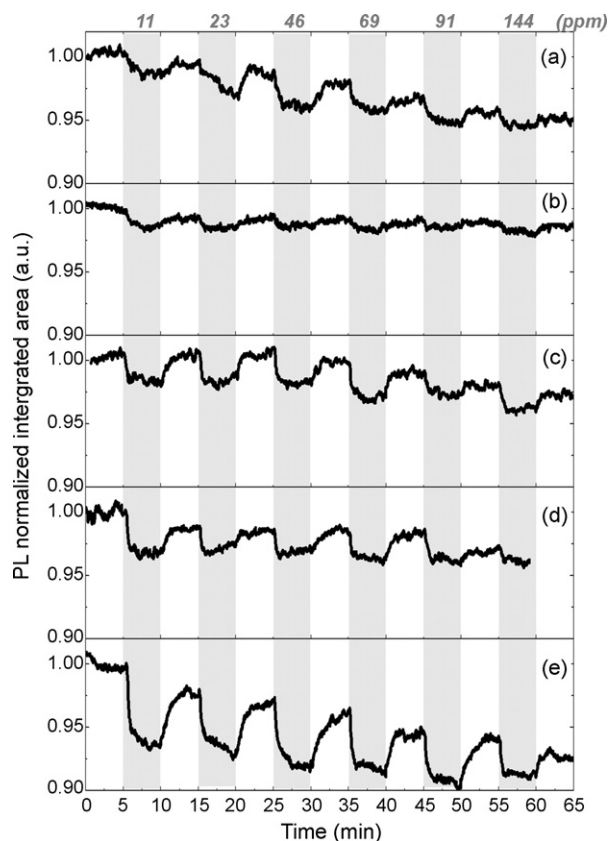


Fig. 3. Room temperature NO_2 optical sensing measurements for samples shown in Fig. 1 at gas concentrations from 11 to 114 ppm, with a gas flow of 50 ml/min. The time intervals of NO_2 exposure are grey-shaded and the corresponding gas concentrations are reported on the top of the graph.

chamber was replaced by a mirror and the intensity of the reflected laser beam was measured in absence or presence of NO_2 : no variation of the signal was observed by our detection system when the gas was introduced inside the chamber, thus allowing to exclude any significant direct absorption of the laser photons. At the same time, also a direct absorption of the sample PL at wavelengths lower than ~ 415 nm by the NO_2 molecules can be excluded in our measurements because, if the PL was absorbed by the gas, then:

1. The sensor responses should depend only on the gas concentration, regardless of the sample properties. On the contrary, as evident in the measurements presented later, the response was strongly dependent on the sample features.
2. No effect of saturation or of irreversibility of gas adsorption should be observed. On the contrary these effects, described in details later, were observed in our measurements.

All the discussions above indicate that the PL quenching is attributable to the electron trapping caused by the actual interaction between the ZnO surface and the NO_2 molecules, and not to the other factors.

Fig. 3(a)–(e) shows the integrated area of the PL emission vs. time, during the sensing measurements, for samples 1–5 respectively. Six different NO_2 concentrations, from 11 to 114 ppm, were tested with a total flow of 50 ml/min. The concentrations are indicated on the top of the graph and the time intervals of exposure to NO_2 are evidenced by the grey shading, while the white regions indicate the exposure to dry air. The signals were corrected for the main laser power fluctuations as explained in Section 2 and they were normalized assuming a value of 1 for the integrated area at

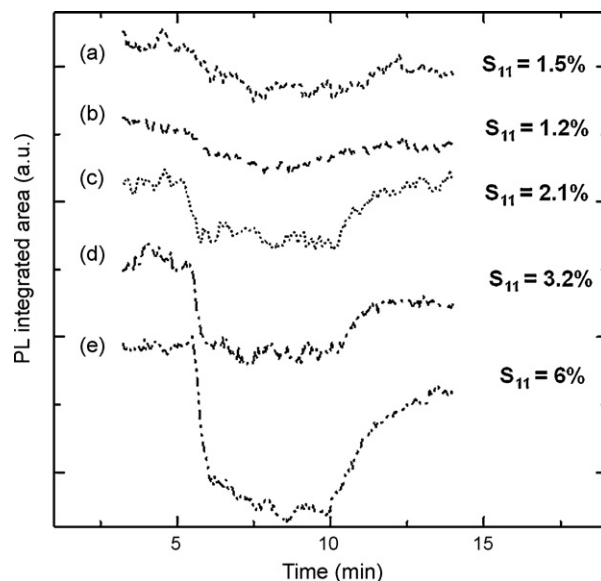


Fig. 4. Magnification of the decrease and subsequent recovery of the PL integrated area at the first NO_2 concentration (11 ppm) reported in Fig. 3. The spectra are vertically translated for clarity. The sensor response S_{11} measured for each sample is reported next to the corresponding spectrum.

the beginning of the measure. All the graphs are reported with the same scale on the Y-axes in order to make a comparison of the different samples. When NO_2 was introduced into the chamber the PL integrated intensity sharply decreased, reaching a rather stable value after about 2 min. When dry air was flowed again, the integral partially recovered its initial value.

In more details, we can define the sensor response S_C , at a fixed gas concentration C, as the percentage variation of the PL integrated area with respect to the initial value, namely:

$$S_C = \frac{I_a - I_g}{I_a} \% = \frac{\Delta I}{I_a} \%$$

where I_a and I_g are the values of the PL integrated area when the sensor was exposed to dry air and to the gas respectively. The values of I_a and I_g were the average values of the PL integrated area resulting after the stabilization.

Fig. 4 shows a magnification of the decrease of the PL integrated area value at the lowest NO_2 concentration (11 ppm) and the subsequent recovery in air. The corresponding values of the response S_{11} are reported in the figure for each sample.

Figs. 3 and 4 clearly evidence that the response to the gas is different for the various samples. The responses of the nanostructured samples 3, 4 and 5 result better than those of samples 1 and 2, due to their higher total exposed surface deriving from the highly nanostructured morphology. Furthermore we observe that, although sample 2 was constituted by a rod-array, thus having a high surface-to-volume ratio and a high total surface, it presented the worse response to the gas. This can be explained observing that the rods are tightly close one each other, thus allowing only a small fraction of the incoming molecules to bind to their surface. A low response was also revealed for sample 1. In fact the sensing measurement of this sample presented a quite broad variation of the PL integrated area in dry air/ NO_2 switching, having this sample a non-nanostructured surface although quite rough. On the contrary, the response was better in the last three signals of Figs. 3 and 4, and the highest response (about 6% at 11 ppm) was obtained for the pencil-array (sample 5). This behaviour is due to the sample surface, which is constituted by well separated pencils, so resulting in a very high aspect ratio and very wide total surface available for gas molecule adsorption.

However, apart from film morphology, the response could be influenced also by other factors, such as the different crystallographic orientation or atomic termination of the faces exposed to the gas, and different sample composition or lattice defects. For example, the bonding interactions of NO₂ molecules with Zn-terminated faces, which contain tri-coordinated Zn atoms missing one neighbour, are stronger than those with O-terminated faces [24]. Concerning our samples, XRD measurements (not shown here) indicated that all samples are preferentially oriented along the *c*-axis of the ZnO wurtzite structure (some XRD spectra can be found in Refs. [20,21]). Only for the last sample also some small contribution of other crystallographic planes, other than the (002) and (004) ones, can be observed in the XRD spectra, as expected due to the slight misalignment of the pencils. This suggests that the contribution of other crystallographic planes to the adsorption mechanisms can also help to improve the sensing response in sample 5 with respect to the other samples. Dealing with the influence of lattice defects, it has been sometimes reported that the presence of oxygen vacancies can increase the ZnO sensor sensitivity [27]. On the contrary, in our study the highest sensitivity is obtained for sample 5, which, among all the probed films, presents the lowest oxygen-related defect emission, as reported in our previous studies [20]. So these observations point out the fundamental importance of sample morphology on the gas sensing performances.

As observable in Fig. 3, the quenching of the PL integrated area, or in other words the response, decreases as the gas concentration increases in the range 11–114 ppm for all the samples. A possible explanation of this counterintuitive behaviour is that: (i) the 11 ppm NO₂ concentration was high enough to almost saturate the available adsorption molecular sites; (ii) the process of NO₂ adsorption was not fully reversed during the sample recovery in dry air. In other words, after the 11 ppm exposure and the following recovery in dry air, the adsorption sites on the sample surface were not all released of the adsorbed species, hence in the subsequent measurements at higher gas concentrations the incoming molecules found fewer available adsorption sites, thus inducing a weaker PL quenching despite the higher gas concentration. This incomplete reversibility of NO₂ adsorption was also suggested by another feature, present in all the sample responses in Fig. 3: beside the sharp variations of the PL integrated area, the sample radiative emission continuously decreased during the experimental run-time (with a final reduction of about 3–7%), indicating again that probably not all the adsorbed molecules were released during the recoveries in dry air and that consequently a complete retrieval of the initial PL integral value was not allowed. We also observed similar features in sensing measurements by using other ZnO nanostructures obtained by different growth techniques and presenting different morphologies [28].

In order to examine the responses at lower NO₂ gas concentrations and to check the effects of gas flux in the sensing measurements, sample 5, which showed the highest sensitivity, was tested at lower gas concentrations (from 3 to 20 ppm) and at a higher gas flux (100 ml/min). Fig. 5(a) shows the sensing measurements at NO₂ concentrations in the range 5–20 ppm with a total flow of 50 ml/min, and in the range 3–20 ppm with a total flow of 100 ml/min.

The first fundamental remark is the very low response: at 50 ml/min the response value is about 0.7% and 0.9% at 10 and 15 ppm NO₂ concentrations respectively, far lower than the 6% value observed in the previous measurement at 11 ppm (Fig. 4(e)). Anyway, in spite of these low responses, the variations of the PL integrated area when switching between NO₂ and dry air resulted to be still sharp, also at the lowest tested NO₂ concentrations. In order to exclude a possible evident deterioration of the sample morphology causing this worsening of the sensor response, the

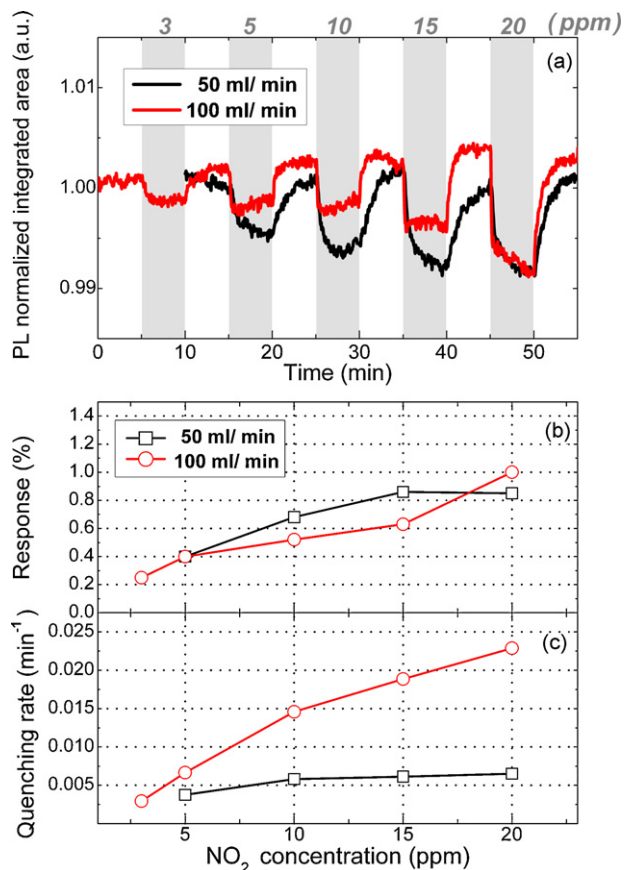
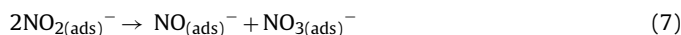


Fig. 5. (a) Room temperature NO₂ optical sensing measurements for sample shown in Fig. 1(e) at gas concentrations from 3 to 20 ppm, with gas flows of 50 ml/min (black line) and 100 ml/min (red line). (b) Response values and (c) quenching rates measured from Fig. 5(a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

sample was investigated again by SEM inspections and no significant differences were observed by comparison with the previous SEM images. Therefore this decrease is supposed to derive from the incomplete release of NO₂ molecules adsorbed in the previous measurements. After this observation, the sample was heated at 50 °C for 15 min in order to favour the desorption of the weakly bonded species adsorbed in the previous tests, and, after cooling, the sensing measurements were repeated, but no significant improvement was obtained. This result suggests that most of the adsorbed species remain strongly bonded on the ZnO surface, most probably on the Zn sites as explained above, thus occupying the adsorption sites, avoiding further gas adsorption and worsening the sensor response. This suggestion is also confirmed by results indicating that, besides the species shown in reactions (1)–(4), also other species can be formed on the ZnO surface and can be strongly chemisorbed, thus requiring high temperatures to be released. For example in Ref. [24] the authors found no evidence of a full decomposition of NO₂ on the ZnO surface at room temperature, while the presence of adsorbed NO₂, NO and NO₃ was detected. The formation of NO₃ species, which are adsorbed as nitrate ions (NO₃⁻), is considered the consequence of the following possible reactions:



These two reactions do not induce any further change in the number of trapped charge-carriers, hence they do not contribute to the PL quenching. But, on the other hand, the formation of dif-

ferent adsorbed species plays an important role in the desorption processes, since the different species can be desorbed with different ease according to their bonding energies with the ZnO surface, thus having different desorption dynamics and affecting the sensor recovery. Indeed, as reported in Ref. [24], the adsorbed NO₂ species are desorbed after an annealing at ~130 °C, while NO₃ is desorbed at ~430 °C, thus explaining the lack of any improvement of the sensor response at lower heating temperatures.

Fig. 5(b) displays the response values corresponding to the NO₂ concentrations reported in Fig. 5(a). The values ranged from ~0.4% at 5 ppm to ~0.85% at 20 ppm with a flow of 50 ml/min, and from ~0.25% at 3 ppm to ~1% at 20 ppm with a flow of 100 ml/min. An important feature inferred from Fig. 5(a) and (b) is that, contrary to what observed for the measurements at the higher concentrations reported in Fig. 3(e), in this case the sensor response followed a “more ordinary” trend with gas concentration, since it increased with increasing NO₂ concentrations. This denotes that, in this case, the effects of the incomplete reversibility of NO₂ adsorption are reduced, as expected due to the lower tested NO₂ concentrations. Furthermore Fig. 5(b) shows that the sample responses in the range 5–15 ppm at a total flow of 50 ml/min were slightly higher than those with 100 ml/min, reasonably due to the fact that the measurement at 100 ml/min was performed after that one at 50 ml/min and thus after a slight worsening of the sample sensitivity. However it is important to notice that at 50 ml/min the response increased as the gas concentration increased up to 15 ppm, then it reached a plateau, suggesting that at this NO₂ gas concentration the effects of incomplete recovery started to become significant. On the contrary, at a flow of 100 ml/min, the sensitivity increased with the increasing NO₂ concentration in the whole examined range of Fig. 5. This can be attributed to a better desorption of the NO₂ molecules induced by the higher flow, thus allowing a better recovery of the PL integrated area.

Moreover from Fig. 5(a) it can be observed that at a total flow of 100 ml/min the decreases and the following recoveries of the PL integrated area during the exposure to NO₂ and dry air respectively are faster than those at 50 ml/min. In order to verify this aspect, the slopes of the signals were measured by linear fittings in the regions of decrease and recovery of the PL signal. The quenching rate, defined as the modulus of the slope during the PL decrease, is reported in Fig. 5(c) as a function of the NO₂ concentration. As expected, for both gas flows the rate increased with the gas concentration and, as previously suggested, the rates at 100 ml/min were much higher and increased more rapidly with the gas concentration than those at 50 ml/min. Analogously, the slopes during the PL recoveries (not shown) are higher at 100 ml/min (~0.004–0.006 min^{−1}) with respect to those at 50 ml/min (~0.002–0.004 min^{−1}). In other words, the sample response and recovery are faster at higher flow. This behaviour is explained since a higher velocity of the incoming gas molecules allowed a faster occupation of the available adsorption sites and thus a faster PL quenching. Analogously a higher dry air flow permitted a faster unbinding of the adsorbed molecules and thus a faster recovery of the PL integral signal.

As previously stated, PL-based sensors have usually the advantage to work at low temperatures, but we observed that, in our case, maybe high temperatures are required to promote the desorption of strongly bonded species, thus partially reducing this advantage. As a possible solution, the sensor can be heated only in limited time intervals in order to remove the surface contamination and to obtain a sensor recovery. Another possible solution is to make the sensor work at higher gas flows, in order to take advantage of the better sensor performances (faster responses and better recovery) observed at a higher gas flow. Analyses concerning this subject will be the object of our further studies.

4. Conclusions

Nitrogen dioxide sensing tests were performed by means of measurements of PL quenching in nanostructured ZnO films with different morphologies. The influence of film morphology was examined, showing an improvement of the sensing responses for nanostructures with high aspect ratio and wide total surface exposed to gas adsorption. The sample constituted by pencil-like structures showed the highest sensitivity and was able to detect NO₂ concentrations as low as 3 ppm at room temperature.

Some features attributable to an incomplete reversibility of NO₂ adsorption and to a possible irreversible worsening of the sensor response were observed, particularly at high gas concentration (above 10–15 ppm) and low gas flow (50 ml/min). These features suggest possible limitations in exploiting these films for the detection of high NO₂ concentrations (10–15 ppm), even if it must be underlined that NO₂ concentrations of the order of 10–15 ppm are higher than those ones usually measured in environmental pollution. Finally we observed that a higher gas flow (100 ml/min) promoted faster response and recovery, and reduced the effects of the incomplete reversibility.

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References

- [1] F. Patolsky, C.M. Lieber, Nanowire nanosensors, *Mater. Today* 8 (2005) 20–28.
- [2] X.-J. Huang, Y.-K. Choi, Chemical sensors based on nanostructured materials, *Sens. Actuators B* 122 (2007) 659.
- [3] Z.L. Wang, Novel nanostructures of ZnO for nanoscale photonics, optoelectronics, piezoelectricity, and sensing, *Appl. Phys. A* 88 (2007) 7–15.
- [4] J.X. Wang, X.W. Sun, Y. Yang, H. Huang, Y.C. Lee, O.K. Tan, L. Vayssieres, Hydrothermally grown oriented ZnO nanorod arrays for gas sensing applications, *Nanotechnology* 17 (2006) 4995–4998.
- [5] C.C. Li, Z.F. Du, L.M. Li, H.C. Yu, Q. Wan, T.H. Wang, Surface-depletion controlled gas sensing of ZnO nanorods grown at room temperature, *Appl. Phys. Lett.* 91 (2007) 032101.
- [6] G. Sberveglieri, C. Baratto, E. Comini, G. Faglia, M. Ferroni, A. Ponzoni, A. Vomiero, Synthesis and characterization of semiconducting nanowires for gas sensing, *Sens. Actuators B* 121 (2007) 208–213.
- [7] A. Bismuto, S. Lettieri, P. Maddalena, C. Baratto, E. Comini, G. Faglia, G. Sberveglieri, L. Zanotti, Room-temperature gas sensing based on visible photoluminescence properties of metal oxide nanobelts, *J. Opt. A: Pure Appl. Opt.* 8 (2006) S585–S588.
- [8] T. Mazingue, L. Escoubas, L. Spalluto, F. Flory, G. Socol, C. Ristoscu, E. Axente, S. Grigorescu, I.N. Mihailescu, N.A. Vainos, Nanostructured ZnO coatings grown by pulsed laser deposition for optical gas sensing of butane, *J. Appl. Phys.* 98 (2005) 74312.
- [9] C. de Julián Fernández, M.G. Manera, G. Pellegrini, M. Bersani, G. Mattei, R. Rella, L. Vasanelli, P. Mazzoldi, Surface plasmon resonance optical gas sensing of nanostructured ZnO films, *Sens. Actuators B* 130 (2008) 531–537.
- [10] J.X. Wang, X.W. Sun, A. Wei, Y. Lei, X.P. Cai, C.M. Li, Z.L. Dong, Zinc oxide nanocomb biosensor for glucose detection, *Appl. Phys. Lett.* 88 (2006) 233106.
- [11] S.P. Singh, S.K. Arya, P. Pandey, B.D. Malhotra, S. Saha, K. Sreenivas, V. Gupta, Cholesterol biosensor based on rf sputtered zinc oxide nanoporous thin film, *Appl. Phys. Lett.* 91 (2007) 063901.
- [12] F. Zhang, X. Wang, S. Ai, Z. Sun, Q. Wan, Z. Zhu, Y. Xian, L. Jin, K. Yamamoto, Immobilization of uricase on ZnO nanorods for a reagentless uric acid biosensor, *Anal. Chim. Acta* 519 (2004) 155–160.
- [13] B.H. Chu, B.S. Kang, F. Ren, C.Y. Chang, Y.L. Wang, S.J. Pearton, A.V. Glushakov, D.M. Dennis, J.W. Johnson, P. Rajagopal, J.C. Roberts, E.L. Piner, K.J. Linthicum, Enzyme-based lactic acid detection using AlGaIn/GaN high electron mobility transistors with ZnO nanorods grown on the gate region, *Appl. Phys. Lett.* 93 (2008) 042114.
- [14] K. Kalantar-Zadeh, A. Trinchi, W. Wlodarski, A. Holland, M.Z. Atashbar, A novel Love mode device with nanocrystalline ZnO film for gas sensing applications, in: *Proceedings of the 1st IEEE Conference on Nanotechnology IEEE-NANO 2001*, 2001, pp. 556–561.
- [15] A.O. Dikovska, P.A. Atanasov, A.T. Andreev, B.S. Zafirova, E.I. Karakoleva, T.R. Stoyanov, ZnO thin film on side polished optical fiber for gas sensing applications, *Appl. Surf. Sci.* 254 (2007) 1087–1090.
- [16] V. Savvate'ev, Z. Chen-Esterliit, J.W. Aylott, B. Choudhury, C.-H. Kim, L. Zou, J.H. Friedl, R. Shinar, J. Shinar, R. Kopelman, Integrated organic light-emitting

- device/fluorescence-based chemical sensors, *Appl. Phys. Lett.* 81 (2002) 4652–4654.
- [17] B. Choudhury, R. Shinar, J. Shinar, Glucose biosensors based on organic light-emitting devices structurally integrated with a luminescent sensing element, *J. Appl. Phys.* 96 (2004) 2949–2954.
- [18] J.M. Pedrosa, C.M. Dooling, T.H. Richardson, R.K. Hyde, C.A. Hunter, M.T. Martín, L. Camacho, The optical gas-sensing properties of an asymmetrically substituted porphyrin, *J. Mater. Chem.* 12 (2002) 2659–2664.
- [19] A. Gulino, T. Gupta, P.G. Mineo, M.E. van der Boom, Selective NO_x optical sensing with surface-confined osmium polypyridyl complexes, *Chem. Commun.* (2007) 4878–4880.
- [20] D. Valerini, A.P. Caricato, M. Lomascolo, F. Romano, A. Taurino, T. Tunno, M. Martino, Zinc oxide nanostructures grown by pulsed laser deposition, *Appl. Phys. A* 93 (2008) 729–733.
- [21] D. Valerini, A.P. Caricato, A. Creti, M. Lomascolo, F. Romano, A. Taurino, T. Tunno, M. Martino, Morphology and photoluminescence properties of zinc oxide films grown by pulsed laser deposition, *Appl. Surf. Sci.* 255 (2009) 9680–9683.
- [22] E. Comini, Metal oxide nano-crystals for gas sensing, *Anal. Chim. Acta* 568 (2006) 28–40.
- [23] O. Lupan, S. Shishiyau, L. Chow, T. Shishiyau, Nanostructured zinc oxide gas sensors by successive ionic layer adsorption and reaction method and rapid photothermal processing, *Thin Solid Films* 516 (2008) 3338–3345.
- [24] J.A. Rodriguez, T. Jirsak, J. Dvorak, S. Sambasivan, D. Fischer, Reaction of NO₂ with Zn and ZnO: Photoemission, XANES, and density functional studies on the formation of NO₃, *J. Phys. Chem. B* 104 (2000) 319–328.
- [25] C.H. Wu, H. Niki, Methods for measuring nitrogen dioxide photodissociation rate. Application to smog chamber studies, *Environ. Sci. Technol.* 9 (1975) 46–52.
- [26] M. Wojciechowska, S. Lomnicki, Nitrogen oxides removal by catalytic methods, *Clean Prod. Process.* 1 (1999) 237–247.
- [27] M.-W. Ahn, K.-S. Park, J.-H. Heo, J.-G. Park, D.-W. Kim, K.J. Choi, J.-H. Lee, S.-H. Hong, Gas sensing properties of defect-controlled ZnO-nanowire gas sensor, *Appl. Phys. Lett.* 93 (2008) 263103.
- [28] A. Creti, A. Taurino, D. Valerini, C. Martucci, F. Quaranta, M. Lomascolo, P. Siciliano, R. Rella, NO₂ optical sensing in ZnO nanostructures, in: *SENSORS*, 2008 IEEE, 2008, pp. 309–312.

Biographies

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Anna Paola Caricato graduated cum laude in physics in 1996 at the University of Lecce. She took her Ph.D. in physics in 2000 at the University of Modena and Reggio-Emilia. Since 2005 she has been working as researcher at the Physics Department of the University of Lecce. Her current interests involve studying laser–material interactions. In particular she is involved in studying the deposition of optical materials, like silicates, tellurites and chalcogenide glasses as thin films by pulsed laser deposition. Very recently she is working on the deposition of polymer (PFO), organic material (Ge-TTP, BSA) and colloidal nanoparticles (TiO₂, SnO₂) by a new laser-based technique (Matrix-Assisted Pulsed Laser Evaporation) for sensor applications.

Mauro Lomascolo is senior researcher and permanent scientific staff member of the Institute for Microelectronics and Microsystems IMM-CNR (National Council of Research) Unit of Lecce since 1999. In particular he has been involved in the study and in the electro-optical characterization of low dimensional heterostructures for photonic and optoelectronics applications. His current scientific interest is the physics of nanoscale structured materials, and in particular, colloidal semiconductor nanocrystals studied by advanced characterization techniques such as femto-second optical spectroscopy.

Roberto Rella, physicist, senior researcher, received his degree in Physics in 1985 from the University of Lecce. His initial research activity, developed at the Department of Materials Science of Lecce University, was focused on the growth of bulk and thin film semiconductor materials and their optical and electrical characterization for optoelectronic devices. Actually, he is a senior researcher at the Institute for Microelectronic and Microsystems of the National Council of Research in Lecce and his research interests include molecular electronics, self assembled systems, chemical and bio-chemical sensors, conducting polymers. He is involved in different national and international projects regarding the development of resistive opto- and bio-chemical sensors based on organic, inorganic and hybrid sensing layers. He is author of more than 200 publications. Actually, he is responsible of the sensor laboratory at the IMM-CNR Institute.

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