Morphological variations as nonstandard test parameters for the response to pollutant gas concentration: An application to Ruthenium Phthalocyanine sensing films

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A systematic time-resolved energy dispersive x-ray reflectometry study was performed *in situ* on Ruthenium Phthalocyanine thin fims to estimate the morphological detection limits of this material as NO_2 transducer and the influence of the gas concentration on the gas-film interaction mechanisms. The work validates the use of this unconventional method—based on the observation of the morphological parameters change—for evaluating the response of novel sensing materials in alternative to more standard procedures. Indeed, the *morphological monitoring* is shown to be sensitive to the gas concentration in a range comparable to the usual electroresistive measurements. Moreover, while the latter is only able to give the information on whether the gas is interacting with the sensor, the former is also able to discriminate among interaction processes of a different nature (in the present case the interaction limited to the film surface and the one involving the material bulk). [DOI: 10.1063/1.2183817]

Metal Phthalocynines (MePc) are *p*-type organic semiconductors[1] sensitive to gases, such as NO_2 or ammonia, even at low concentrations.[2–6] Their mean detection limit ranges from 10 ppm down to 500 ppm, depending on the sensor design more than on the material itself.[7,8] Previous studies[9] have demonstrated that morphological changes are correlated to the electrochemical response of the MePc thin films[10–12] An important information in the understanding of its two step gas-film interaction[11] would come from correlating the morphological changes experienced by the sensing film with the gas concentration.

In this work, a quantitative evaluation of morphological changes occurring in the films during their exposure to the oxidating gas NO_2 in dependence of its concentration is reported. The study has two main goals. First, it is crucial to determine whether the mechanisms involved in the film morphological evolution upon gas exposure are somehow dependent on the NO_2 concentration or not. Second, we aim to test the use of this *morphological monitoring* method for evaluating the response of novel sensing materials, as an alternative to standard measurements. As the result, the detection limits of the $(RuPc)_2$ device—from the viewpoint of the morphological parameters—was obtained, and the sensitivity of such parameters to the gas interaction was tested. As such, it represents an alternative to the measurements of the electrical conductivity, which is the standard control parameter for gas sensors. In order to study in real time the morphological changes during the exposure to NO_2 at different concentrations, the *in situ* energy dispersive x-ray reflectometry (EDXR) (Refs. 9 and 10) was used.

X-ray reflectometry is a technique utilized to study surfaces and interfaces morphology at the Angstrom resolution.[12–14] If the sample is a film deposited on a substrate, both the air-film and the film-substrate interfaces reflect the incident x-rays. The interference between the two resuting reflected beams contains morphological information about the roughness σ and the distance (i.e., film thickness d) of the reflecting interfaces. The evaluation of these quantities is made by a fitting procedure based on the Parratt model.[15] In our case, according to previous tests, we assumed the film-substrate interfacial roughness being much smaller than the film-surface one.[16,17]

A $(RuPc)_2$ powder[18] was sublimated under a vacuum (10^{-6} mbar) upon Si [111] substrates by an Edwards Auto 306 vacuum coater and various films with different thicknesses were obtained. In this paper, a noncommercial x-ray reflectometer[19] was used to study the real-time evolution[20–24] of the morphology of these films while exposed to an NO_2/N_2 flux into the experimental chamber. Two series of *in situ* experiments were performed.

As a first step, a 30 ppm NO_2 gas was fluxed upon a 50 nm nominally thick $(RuPc)_2$ film. The sequence of reflectivity patterns, collected every 15 min in these conditions, is shown in Fig. 1. The shift of the oscillations toward lower q values is evident even from these row data, prior to any processing, which indicates that the film is getting thicker, as a consequence of the gas-film interaction. Such morphological evolution must be compared with the electroresistive response, representing the standard parameter to define the device activity. Therefore, a new $(RuPc)_2$ film was deposited

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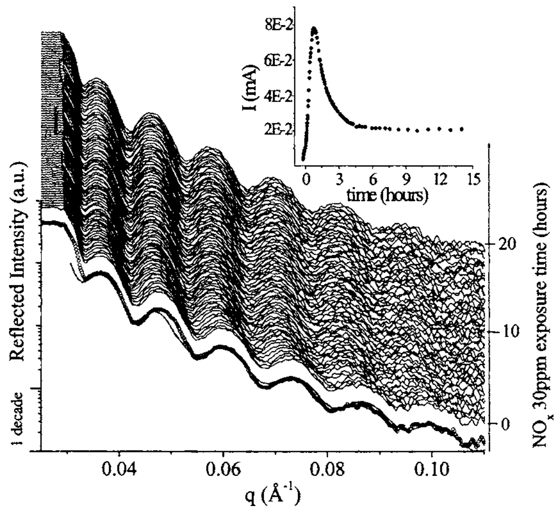

FIG. 1. Sequence of reflectivity patterns collected during the exposure of a $(RuPc)_2$ thin film to an NO_2 [30 ppm] gas flux. In the inset, the electroresistive response measured during the exposure of the thin film to the NO_2 gas flux is plotted as a function of the exposure time.

on an Au electrode and measured during the exposure to a gas flux of the same concentration (30 ppm). The so obtained electrical behavior, is plotted as a function of time in the inset of Fig. 1. Such measurement was performed applying a 0.8 V voltage to the device and monitoring the circuit electroresistive variations. A sudden change is visible as the gas is introduced into the experimental chamber, while the overall electrical evolution (interaction between the Pc's π electrons and NO_2) takes 4 h until a saturation is reached.

The first reflectivity spectra (dots), collected before the NO_2 gas flux was opened, is shifted in Fig. 1 together with its Parratt fit (line). Fitting in this way every pattern of the sequence, the real-time changes of the morphological parameters d and σ were obtained with the following uncertainties: $\Delta d_{\max}=\pm 2$ Å and $\Delta\sigma_{\max}=\pm 0.5$ Å. The same experimental procedure was applied to a series of samples, while exposed to NO_2/N_2 gas mixtures at different NO_2 concentrations, from 5 ppm up to 60 ppm. Since an expansion of the time scale was expected at the lower concentrations (and a compression at the higher ones), the patterns were collected every 15 min for $[NO_2]\leqslant 30$ ppm, and every 5 min for $[NO_2]>30$ ppm. In Fig. 2, the time evolution of the thicknesses of the $(RuPc)_2$ films is presented as a function of time, corresponding to various NO_2 concentrations. In Fig. 3, an analogous plot for surface roughness is shown. As a result, the experimental detection limit was found to be equal to 10 ppm. Two steps in the film growth are evident by following the $d(t)$ curve (dots Fig. 2), corresponding to two independent processes. The observation of the surface roughness (Fig. 3) evolution is a further confirmation of this two-step model. Once these general features of the interaction process are defined, the question of the influence of both the film (initial) thickness and the NO_2 gas concentration can be faced. A first observation is that the characteristic time of the surface process [i.e., of the low t branch of $d(t)$ and $\sigma(t)$ curves] corresponds to $t^*=(2.50\pm 0.25)$ h, independent of the film thickness and gas concentration (line Fig. 3). Therefore, by fitting the $d(t)$ curves, the characteristic times, τ_1 and τ_2, of the two steps of the process can be quantified. The first time τ_1 must be, independent of both the film thickness and the gas concentration. As a consequence, similar values of τ_1 are expected from all the curves. However τ_2, the characteristic time of the bulk-related process, depends on both the film thickness and gas concentration which are not constant in the experiments performed.

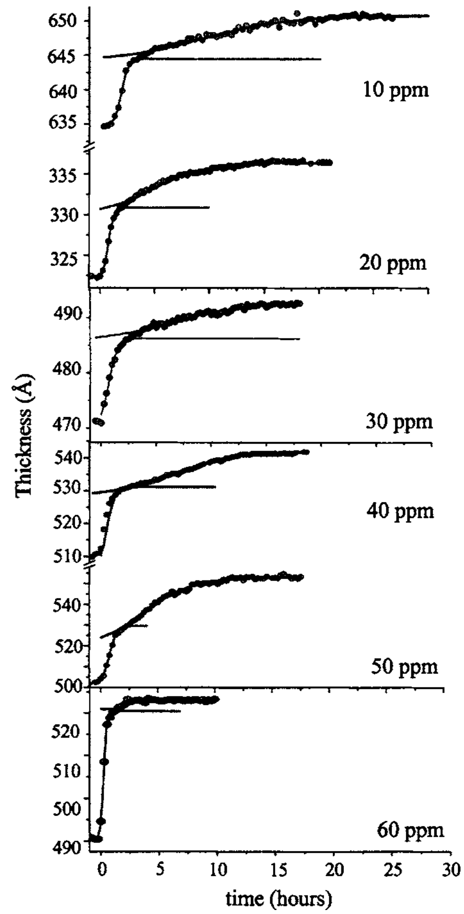

FIG. 2. Time evolution of the thickness d (dots).

In order to study the influence on τ_2 of the two parameters separately, a new series of EDXR time-resolved measurements was carried out at a fixed concentration of NO_2, 50 ppm. As shown in Fig. 4, when the NO_2 concentration remains unchanged, the first interaction mechanism is characterized by a constant characteristic time τ_1 regardless the film thickness (as expected), while τ_2 results to be approximately proportional to the initial thickness d_0: τ_1 (h) $=(0.70\pm 0.10)$ and τ_2 (h)$=(2.40\pm 0.15)+(0.03\pm 0.01)\ d_0$ [Å].

Indeed, now it is possible to rescale τ_2 with respect to the film thickness, isolating its dependence on the concentration only. The plot of τ_2 as a function of the concentration (Fig. 5) can be fit by using a sigmoidal curve. τ_2 varies from 7.90 h to 0.78 h passing from 10 ppm to 60 ppm, which seems to indicate that the bulk diffusion velocity tends to become constant below a 10 ppm NO_2 concentration (lower detection limit) and saturates above 60 ppm NO_2 (upper detection limit). Moreover, the characteristic time $\tau_2=0.78$ h, for $[NO_2]=60$ ppm, is very close to the $\tau_1=0.70$ h, characteristic time of the surface interaction mechanism, which explains why the two steps of the process appeared to be almost simultaneous at this concentration. At concentrations higher than 60 ppm, the former mechanism hides the morphological evolution due to the latter, since $\tau_2<\tau_1$. This represents the intrinsic detection limit of this sensing materials

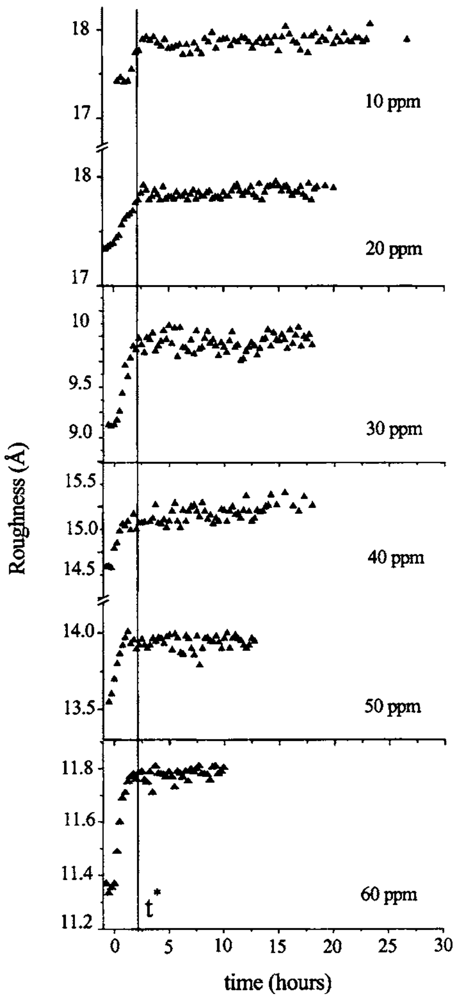

FIG. 3. Time evolution of the surface roughness σ (triangles).

response to the oxidizing gas NO_2 when the two interaction mechanisms have to be distinguished.

In conclusion the *in situ* time-resolved EDXR technique was able to determine the detection limits of NO_2 uptake into a $(RuPc)_2$ thin film from the morphological point of view. The lowest $[NO_2]$ concentration detectable was found to be 10 ppm. At concentrations higher than 60 ppm, the surface absorption hides the diffusion mechanism of the NO_2 into the film bulk, since the characteristic reaction time of the former process becomes higher than the latter. Despite this, the concentration ranges—in which the morphological monitoring is sensitive to—are comparable to that of the more common electroresistive measurements. The reported results validate the use of the *in situ* EDXR technique as a powerful nondestructive tool to investigate the response of novel sensing materials (via the observation of the morphological parameters change) providing, at the same time, the general features of the gas-film interaction.

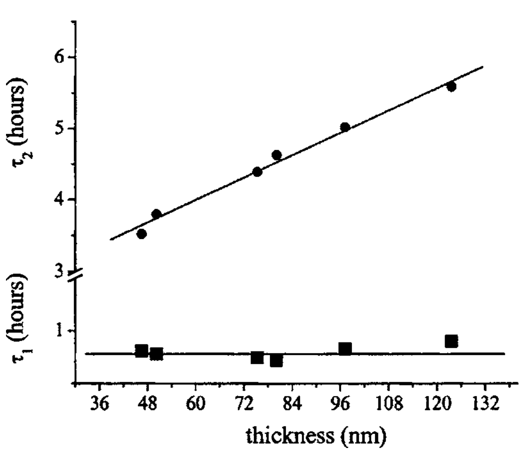

FIG. 4. The characteristic times, τ_1 and τ_2, of the two interection mechanisms as a function of the initial film thickness d_0 in the case of a 50 ppm NO_2 gas flux.

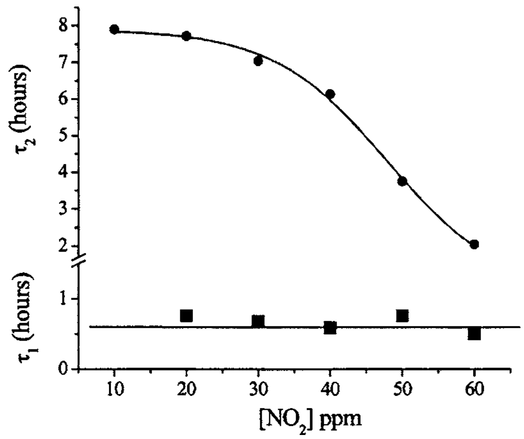

FIG. 5. The characteristic times, τ_1 and τ_2, of the two interection mechanisms as a function of the NO_2 concentration.

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