

Evidence of a rearrangement of the surface structure in titanium phthalocyanine sensors induced by the interaction with nitrogen oxides molecules

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Thin-film samples of titanium phthalocyanine, a sensor of environmental pollutants, were studied by time resolved energy-dispersive x-ray reflectivity (EDXR). This original method demonstrated to be an ideal tool to follow the evolution of the films morphology upon gas exposure, *in situ*, also allowing an unexpected response of the sensors to be detected. Indeed, while the increase in thickness showed the characteristic feature of a "breathing-like" expansion, already observed in other metal-Pc, the curve of roughness versus exposure time exhibited a peak. This effect, in some cases evident by observation with the naked eye the EDXR data, was attributed to a surface structure rearrangement process. © 2005 American Institute of Physics. [DOI: 10.1063/1.2119429]

The discovery that phthalocyanines films act as *p*-type semiconductors,¹ have indicated that this material as a suitable candidate for gas detection.² Indeed, it has been observed³ that acceptor gases such as nitric oxide and nitrogen dioxide (NO_x) cause a large increase in phthalocyanine conductivities and decreases of activation energies. In particular, titanium phthalocyanine [Ti(Pc)₂] was recently proposed as a potential transducer for optical detection. This is due to the dramatic change of its visible absorption spectrum during exposure to NO_x,⁴ which is characterized by very high selectivity versus NO_x (Ref. 5) and good reversibility.

A systematic energy-dispersive x-ray reflectivity (EDXR) study on a large number of Ti(Pc)₂ films of different thicknesses was performed. Indeed, x-ray reflectometry is sensitive to surface and interface morphology at the angstrom resolution.⁶ The method is based on the optical properties of x rays⁷ (Snell rule). In the energy dispersive mode,^{8,9} the experimental geometry remains unchanged during data collection,¹⁰ which is a fundamental advantage for *in situ* studies.¹¹

A series of Ti(Pc)₂ films of various nominal thicknesses, determined by an oscillating quartz crystal balance (Edwards FTM5 Film Thickness Monitor), were grown by sublimation of Ti(Pc)₂ powder¹² on a Si wafer in a vacuum chamber.

In order to monitor the overall characteristics of the film-gas interaction process, a first cycle of time resolved EDXR investigations were performed submitting a series of samples to a flux ϕ of 20 nmol/s of NO_x (i.e., [NO₂/N₂O₄]=50 ppm) in a N₂ (450 ppm) stream. As a result, we were able to monitor the overall response of the morphological parameters of the films during exposure to the

gas. Further investigations concerned the effect of the sensor recovery on film morphology. Indeed, the optical/conductometric properties of the TiPc based sensors are known to be reversible by means thermal or light treatment. Therefore, the previous films were removed from the setup and submitted (*ex situ*) to thermal treatment performed under vacuum (at a temperature of 200 °C for 30') and then measured once more by EDXR.

As an example of the results obtained, in Fig. 1, the EDXR spectra collected *in situ* in the case of a film having a nominal thickness of 91 nm (a) are reported. The change in

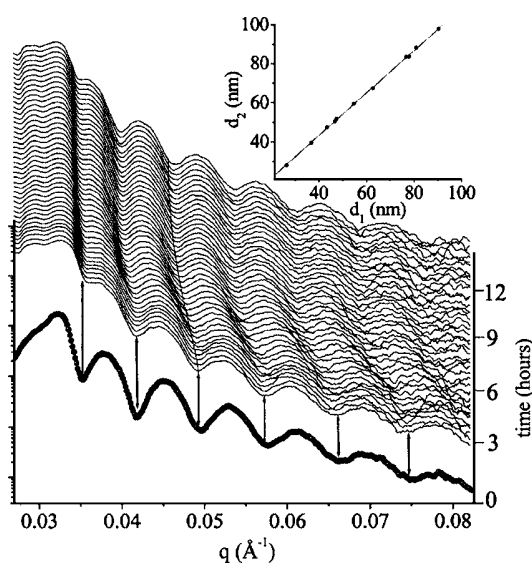


FIG. 1. Sequences of time-resolved EDXR spectra for a 91 nm film exposed to a gas flux of 20 nmol/s. The EDXR profile collected after the film had been reset is also reported (bottom spectrum). The inset shows the final thickness vs the initial thickness for all the films studied.

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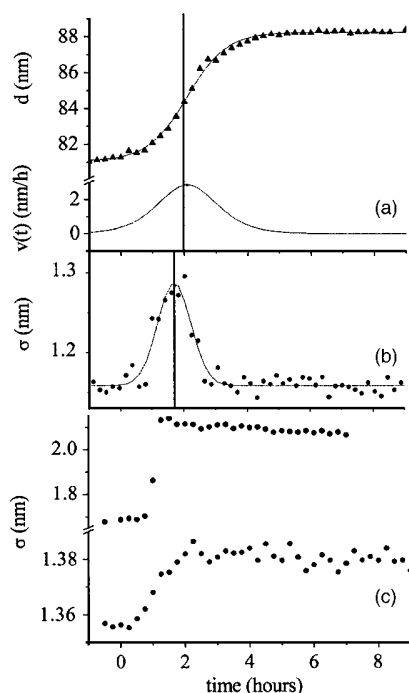


FIG. 2. (a) Time dependence of the Ti(Pc)_2 film thickness d obtained by analyzing the EDXR spectra recorded in real time and derivate of the $d(t)$ curve, $v(t)$. In (b) the roughness time dependence for the same sample is shown. (c) Roughness curves obtained for a $(\text{RuPc})_2$ and a CuPc film. They both show a step growth until a plateau is reached, the final value being slightly higher than the initial value.

the period of oscillations and in their damping are related to the variation of film thickness d and of its roughness σ , respectively.^{13,14} In the bottom of Fig. 1 the EDXR spectrum collected after the film had been submitted to thermal treatment, which is known to cause the reset of the film sensor properties,⁶ is also plotted. Comparing the spectra, it appears that the oscillations of the latter EDXR pattern are in phase with those of the first pattern collected during gas exposure. Therefore, the film returned to its original thickness as a consequence of heating, showing that the reversibility of the sensor is related to the recovery of the initial film thickness.

Analyzing the sequences of spectra relative to the various films, according to Parrat's theory for x-ray reflectivity,¹⁵ the general trend for the morphological evolution was revealed. The overall increase of the thickness of each film turned out to be proportional to its initial value, as can be seen in the inset of Fig. 1, where all the points plotted lie on a straight line crossing the axis origin. Moreover, the shape of the thickness versus time curves [$d(t)$] are similar for all the samples. As an example, the d and σ vs t curves obtained by processing the spectra in Fig. 1, are plotted in Fig. 2(a). The "breathing-like" process accounting for the $d(t)$ trend can be easily interpreted considering the $d(t)$ derivative, namely the film growth speed $v(t)$ [continuum line in Fig. 2(a)]. As the gas starts flowing in the cell, the film bulk response is not immediate: at the beginning the $d(t)$ profiles remains almost flat, so that $v(t)$ is small (induction time of about 1 h). Then $v(t)$ starts increasing rapidly, until it reaches a maximum value. In the following stage, the process slows down and, finally, $v(t)$ approaches zero, indicating that the film thickening has concluded. This film expansion is similar to that observed in other metal-phtalocyanine (MPc) films

(with $M=\text{Ru, Cu, Pb}$) when exposed to the same gas.¹⁶ However, the roughness evolution [Fig. 2(b)] shows a completely different behavior with respect to the other MPc. Indeed, the surface response usually consists of a monotonic increase of roughness during the first part of the exposure to the gas, followed by a plateau, when the saturation is reached, as can be seen in Fig. 2(c). On the contrary, the $\text{Ti(Pc)}_2\sigma(t)$ curve exhibits a peak, i.e., after a normal initial rise, it reaches a maximum value and, then, begins to decrease until a final constant value is reached. This is comparable with the initial value or only slightly higher. Observing Fig. 2(b), it is evident that the time t_2 at which the surface roughness reaches its maximum value coincides approximately with the time t_1 of maximum growth speed. The coincidence of t_1 and t_2 was demonstrated to be a general characteristic of the Ti(Pc)_2 films upon (NO_x) gas exposure, i.e., the time t_2 at which the surface roughness is maximum always coincides with the time t_1 of the maximum growth speed, within the error bar.

Two different explanations may be proposed: the first is the attribution of such behaviour to a thermodynamic effect, the other is its attribution to a kinetic effect.

In the case of a thermodynamic effect, the $\sigma(t)$ peak would represent the transformation from an initial arrangement of the layer formed by the $\text{NO}_x\text{-Ti(Pc)}_2$ molecules interacting at the film surface to a final arrangement, passing through an intermediate phase. In this case, the transformation might be described as a transition from the original structure of the film surface, consisting of a progressive increase of the roughness due to the appearance of a new surface structure represented by a $\text{NO}_x\text{-Ti(Pc)}_2$ layer, up to a threshold value. After this value, the layer relaxes to a second phase, which exhibits a roughness comparable with that of the original film surface. Alternatively, in terms of a kinetic explanation it is assumed that the interaction layer does not possess a regular structure but represents only the molecules statistical occupancy of the receptive sites at the film surface. In this case, the increase of $\sigma(t)$ (left side of the peak) would correspond to the random deposition of an increasing number of gas molecules that, by interacting with the surface film molecules, induces a consequent increase of roughness. Since the penetration inside the film (diffusion) takes a certain time, the "crowding" of the molecules at the surface augments progressively. In this kinetic model, the crowding of the molecules on the surface must reach a critical concentration before the diffusion can occur, which implies a progressive increase of roughness. When the diffusion mechanism becomes effective, the molecules penetrate inside the film, whose thickness rapidly increases. In the case of a thermodynamic effect, the $\sigma(t)$ peak height should not be influenced by the deposition rate of the molecules, i.e., the gas flux, as long as the quasiequilibrium conditions are preserved. On the contrary, in the case of a kinetic effect, the crowding should be a function of the deposition rate, since the more intense ϕ is, the more rapid the increase of $\sigma(t)$ should be and, as a consequence, the higher the $\sigma(t)$ peak.

In order to discriminate between these two hypotheses, the gas sensing films were therefore submitted to a NO_x gas flux of various intensities (Fig. 3). The spectrum recorded after 30 min (fourth spectrum) is characterized by a much larger damping of oscillations (i.e., a much larger surface roughness of the film) with respect to both the first and the last ones shown in the figure. In the earlier example (Fig. 2),

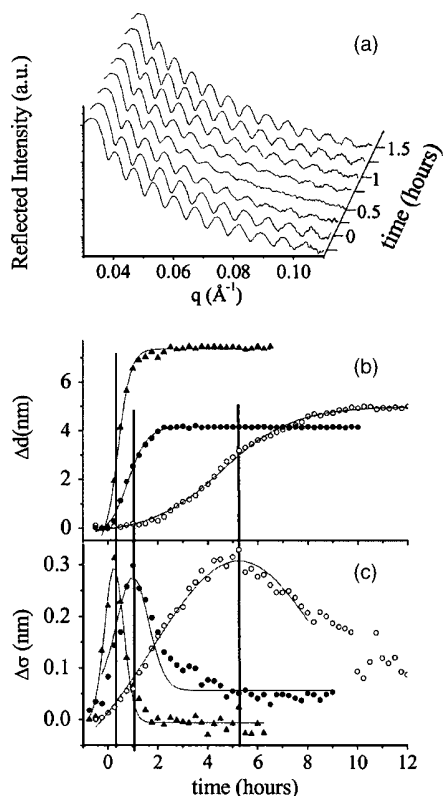


FIG. 3. (a) Sequences of EDXR spectra for a 91 nm film exposed to a gas flux of 30 nmol/s. (b) Comparison of the relative variation of the $\text{Ti}(\text{Pc})_2$ film thickness over time: 91 nm film exposed to a gas flux $\phi=30$ nmol/s (triangle), 57 nm film exposed to a gas flux $\phi=20$ nmol/s (circle), and 71 nm film exposed to a gas flux $\phi=10$ nmol/s (open circle). (c) The relative variation of the $\text{Ti}(\text{Pc})_2$ layer roughness over time for the same films as in (b).

the σ vs t curve obtained by analyzing this sequence of spectra [line with triangles in Fig. 3(c)] will exhibit a maximum in correspondence with the spectrum recorded after 30 min. In Fig. 3(b), a selection of curves describing the relative increase in thicknesses, $[(\Delta d(t)=d(t)-d_1)]$, are shown. In Fig. 3(c) the relative roughness variation [i.e., the $\Delta\sigma(t)=\sigma(t)-\sigma_1$ curves, where σ_1 is the initial value the $\sigma(t)$ curve] of the same films are reported. As expected, as the gas flux intensity ϕ increases, the position of the maximum of the $\Delta\sigma(t)$ curves shifts to lower time values. Of great importance is the fact that the $\Delta\sigma(t)$ peak height is independent of the gas molecules deposition rate and indicates that the phenomena responsible for the anomalous behavior of the films surface roughness is, indeed, a thermodynamic effect. However, to confirm that the results are reliable and not dominated by saturation effects, due to the excessive abundance of stimulating agent, further measurements were performed by exposing the films to a 20 nmol/s NO_x flux and to a pure N_2 flux alternatively.

Moreover, in the case of a kinetic crowding effect of the NO_x gas flux, the observed roughness behavior would be present only during the exposition of the film to the gas flux containing NO_x molecules. Figure 4 shows that this is not the case: in Fig. 4(a) the film, submitted to NO_x gas, shows the same thickness and roughness evolution observed previously. Then, before the gas absorption process is completed the NO_x gas flux is interrupted, and the film is exposed to the flux of N_2 gas only [Fig. 4(b)]: the film thickness decreases

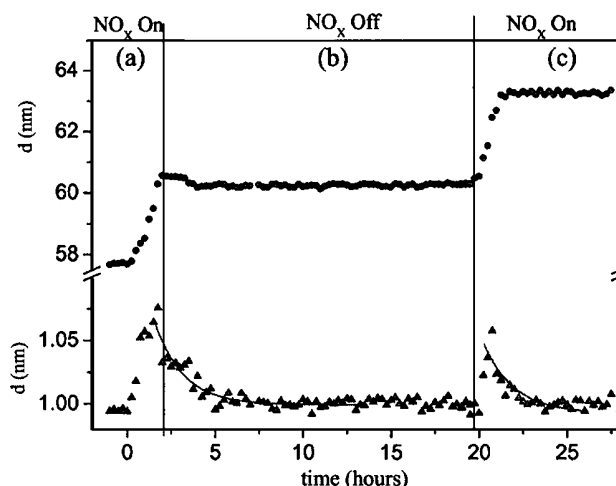


FIG. 4. Time dependence of the $\text{Ti}(\text{Pc})_2$ film thickness d and the roughness σ , during the exposition of the film alternatively to NO_x [(a),(c)] and N_2 (b) gas fluxes.

slightly as expected,¹⁷ while its roughness does not return to the original value instantaneously but, rather, it takes about 3 h (similarly to what observed in the previous case). As the film is kept under the N_2 flux for long times, the film morphology is stable. Since the gas absorption process was not concluded, when the NO_x is fluxed again on the film [Fig. 4(c)], the film thickness and roughness evolution is completed. It must be noticed that the roughness, after having reached its maximum, decreases following the same trend both when the gas flux contains NO_x molecules and when it is formed by N_2 molecules only.

The study provides the first experimental evidence for a structural surface rearrangement in $\text{Ti}(\text{Pc})_2$ gas sensing films induced by interaction with NO_x molecules. Further investigations are needed to clarify if the observed structural changes possess the characteristics of a surface phase transition.

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