Experimental evidence of a two-step reversible absorption/desorption process in ruthenium phtalocyanine gas sensing films by *in situ* energy dispersive x-ray reflectometry

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An *in situ* energy dispersive x-ray reflectivity technique was used to study the morphological changes of gas sensing thin films of ruthenium phtalocyanine $(RuPc)_2$ induced by gas absorption/desorption processes. The time-resolved collection of reflectivity spectra during the exposure of each film to a gas flux of nitrogen oxides provided the evolution of the morphological parameters (thickness and roughness). The gas absorption process develops in two stages: The first induces morphological changes characteristic of a surface (adsorption) process, while the second is dominated by a bulk effect. This two-step behavior is also observed in the desorption process: When the thermal treatment is performed at 130 °C, the gas is released from the bulk only. Conversely, at higher temperatures, the gas is fully released, i.e., also from the surface, and the initial film thickness is regained. Finally, a further *in situ* study upon a second absorption treatment was carried out: In this case, only the film bulk diffusion process takes place. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1874311]

Metal-Phthalocyanines (MPc) are currently under intensive study due to their prospective applications as optical/conductometric sensors of environmental pollutants. Indeed, the electronic properties of these flexible and environmentally stable materials undergo rapid changes in the presence of gases, such as nitrogen oxides.[1–3] Up until now, despite the wide characterization of the changes in their electrical transport properties, only preliminary investigations of the morphological changes have been reported.[4–7] The aim of the present letter is to follow these changes in real time in order to retrieve information on gas-film interactions during the exposure of the $(RuPc)_2$ films to NO_x (i.e., $[NO_2/N_2O_4]$ =50 ppm, $[N_2]$=450 ppm) gas. Previous studies have demonstrated that energy dispersive x-ray reflectivity (EDXR) is the appropriate tool for very accurate morphological measurements.[8–10]

The x-ray reflectivity technique is based on the optical properties of x-rays,[11] namely the Snell rule applied to these energy ranges.[12] The energy dispersive (ED) mode makes use of a polychromatic x-ray beam and the reflection spectra are collected at a fixed angle by scanning the energy of the reflected x-ray beam.[13]

The present letter focuses on two fundamental aspects of the interaction between the NO_x gas and ruthenium phtalocyanine $(RuPc)_2$ films. The experimental procedure adopted is as follows: A first exposure of the samples to NO_x gas (Step 1), an *ex situ* thermal treatment (Step 2), and a second exposure to NO_x gas (Step 3). In Step 1, the absorption ki-

netics of the films on first exposure to the gas was studied. In Step 2, recovery of film morphology is induced by thermal treatment, two different results being obtained (depending on the temperatures applied): Either the films return to their original condition (total recovery) or to a well-defined intermediate state (partial recovery). Finally, in Step 3, the kinetics of a second absorption process is recorded and compared to the first.

The method mentioned above was applied systematically to study a large number of films (their nominal thickness ranging from 20 nm to 120 nm, as measured by an oscillating quartz crystal device). The films were grown by sublimation under a vacuum of $(RuPc)_2$ powder[14,15] on a Si wafer. In the following account, in order to show all phases of the EDXR analysis, attention will be focused on two samples that are representative of the whole set.

(1) **Step 1.** The films under measurement were exposed at room temperature to a gas flux of NO_x molecules (20 nmoles/s) until a stationary condition was reached, i.e., the reflection spectra did not show any further changes. Such a time-resolved collection of reflectivity spectra provided a very accurate description of the evolution of morphological parameters upon the first gas treatment. The sequence of the EDXR spectra reported in Fig. 1 corresponds to the two representative samples: Sample 1 having a nominal thickness of 50 nm [Fig. 1(a)] and Sample 2 of nominal thickness 100 nm [Fig. 1(b)]. The actual thickness values, as obtained by EDXR, were found to be 44 nm (Sample 1), and 76 nm (Sample 2). In the two figures, the change in the oscillation periods and in their damping are related to the variation of the film thickness d and of its roughness σ, respectively.[16,17]

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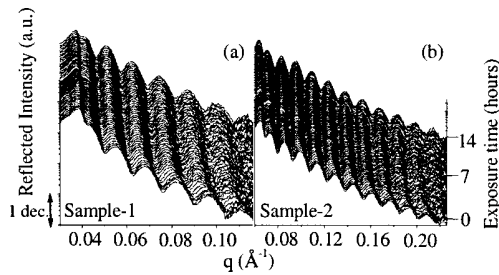
FIG. 1. Time-resolved EDXR spectra: (a) Sample 1 and (b) Sample 2.

FIG. 2. Sample 1 (a) $d(t)$ curve of the $(RuPc)_2$ layer (full dots) and its derivative $v(t)$ (open dots). (b) sigma (t) curve (full dots). (c) Reflectivity profiles relative to the d_2, d^*, and the d_1 values recorded *in situ*. (d) The bottom spectrum is recorded *ex situ* after heat treatment at $T = 130 \,^\circ C$.

A qualitative picture of the modifications occurring in the film thicknesses can, therefore, be obtained by preliminary observation of the row spectra. Indeed, a progressive compression of the curves, corresponding to a shift toward lower q values as a function of time, is evident. Since d is connected to the oscillation period Δq by the approximate relation $d = 2\pi / \Delta q$, this shift witnesses the increase of d as a consequence of the exposure to the gas. To quantify the change of d and σ, the spectra were fitted according to Parrat's model.[18] The d and σ versus t curves for the two samples are plotted in Figs. 2(a), 2(b), 3(a), and 3(b), respectively. They are characterized by a first rapid increase from the initial value d_1 up to a crossover value d^*, followed by a slower growth to reach the final plateau at d_2.

This two-fold response upon gas exposure is peculiar to the $(RuPc)_2$ samples and has no equivalent in the other MPc studied,[10] whose increase in thickness can be reproduced by a simple Boltzmann growth.

(2) **Step 2.** In order to test possible reversible behavior of the phenomena described above, the samples were removed in order to undergo thermal treatment for 30 min in a vacuum at 10^{-2} Torr, the heating temperature being 130 $^\circ C$ (Sample 1) and 200 $^\circ C$ (Sample 2), respectively.

(3) **Step 3.** The samples where placed back and measured again by EDXR. The reflection spectra corresponding to the three characteristic points of the $d(t)$ curve obtained during the first exposure, namely d_1, d^*, and d_2, are reported in Fig. 2(c) for Sample 1 and in Fig. 3(c) for Sample 2. The above spectra must be compared with the spectra collected after the thermal treatment, in Figs. 2(d) (Sample 1) and 3(d) (Sample 2). In both cases, the oscillations of the spectra recorded after the thermal treatment are characterized by longer q periods, with respect to the spectra obtained at the end of the gas exposure. This indicates that the gas desorption due to heating always induced a reduction of the film thickness that is different for the two samples. Indeed, in the first case [Fig. 2(d), Sample 1, reset at 130 $^\circ C$], the oscillations of the spectrum collected after the thermal treatment are in phase with those of the spectrum relative to the value d^* while, in the second case [Fig. 3(d), Sample 2, reset at 200 $^\circ C$], they are in phase with those of the spectrum relative to d_1. On the basis of EDXR data, several pieces of experimental evidence demonstrate the occurrence of two distinct and independent mechanisms in the gas-film interaction. They are summarized as follows.

(1) As mentioned previously, the increase in film thickness as a function of time, reported in Figs. 2(a) and 3(a), cannot be represented by a simple exponential growth or by a Boltzmann curve, which usually fit reaction processes. Rather, it seems that the $d(t)$ curves are composed of two distinct branches: A rapid increase from the initial value d_1 to
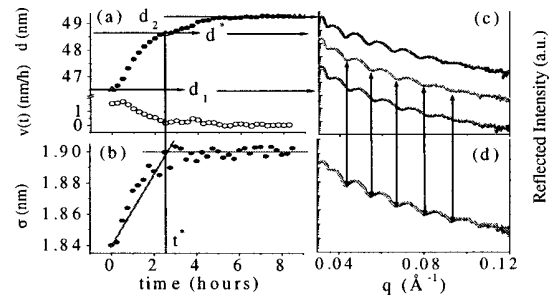
a crossover value d^*, followed by a slower growth up to the final plateau at d_2. This double trend is more evident when the $d(t)$ derivative, namely the film growth speed $v(t)$, is plotted [Figs. 2(a) and 3(a), open circles]. As the gas starts flowing in the cell, the increase of d is very rapid. Then it slows down until the derivate approaches a constant value, corresponding to d^*, indicating that the first (rapid) part of the film "growth" is concluded. Subsequently, a second "slower" increase in d takes place from d^* to d_2.

(2) Keeping the working conditions (namely the temperature and gas flux) unchanged, the first part of the increase in thickness (i.e., from d_1 to d^*) has the same duration regardless of the initial thickness of the film, the time t^* at which $d(t)$ reaches its crossover value d^* being about 3 h. The second part, on the other hand, has a duration that is proportional to the initial thickness.

(3) Another notable point that emerges from *in situ* EDXR measurements is the shape of the curve of the film surface roughness as a function of the exposure time [$\sigma(t)$ curve]. In the case of $(RuPc)_2$ samples, see Figs. 2(b) and 3(b), this $\sigma(t)$ curve increases (linearly) until time t^* (defined in Point 2) and, then it remains stationary. This behavior demonstrates that the surface morphology evolves only until t^*, with no further modifications being detected.

Points 1 to 3 are indicative of the fact that the first part of the film growth upon gas absorption is dominated by a surface process (adsorption), which is not influenced by the amount of underlying material. The second part, however, appears to be essentially connected with the interaction between the gas molecules and the film bulk.

(4) More evidence is obtained from further EDXR measurements, performed after the film was treated thermally. Indeed, depending on the temperature at which the samples had been heated, only two results were obtained: The thickness can either go back to the intermediate d^* value (inter-
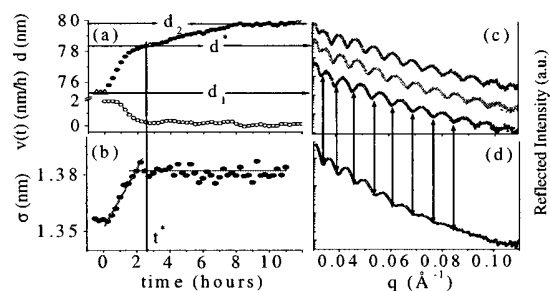
FIG. 3. (a)–(c) The same sequence of graphs as in Fig. 2 is reported for Sample 2. (d) Spectrum recorded *ex situ* after heat treatment at 200 $^\circ C$.

mediate recovering), or to the original d_1 value (total recovering), with no other values being observed. This indicates that the removal of the gas molecules trapped in the film is a two-step process ruled by two different activation energies E_1 at $T \leqslant 130\ °C$ and E_2 in the temperature region $130\ °C \leqslant T \leqslant 200\ °C$. From the above considerations, attributing the decrease in thickness to the release of the molecules trapped in the film is straightforward, the first part of the process being essentially due to the release from the film bulk and, the second, from the film surface.

(5) Finally, more information on the surface versus bulk interaction mechanisms was obtained from the *in situ* collection of reflectivity spectra during a new exposure of the samples to NO_x (Step 3): The resulting $d(t)$ curves are compared with those obtained during the first gas exposure in Fig. 4(a) for Sample 1, and in Fig. 4(b) for Sample 2. As discussed above, the starting values are d^* for the partially recovered samples (case of Sample 1) and d_1 for the totally recovered samples (case of Sample 2). It is remarkable that the $d(t)$ curve for both samples reproduces the same behavior as the second part of the curve observed during the first absorption: A simple Boltzmann growth, consistent with a pure bulk absorption process, the final value being d_2 for Sample 1, and about $d_1 + d_2 - d^*$ for Sample 2. Moreover, the shape of the $\sigma(t)$ curve [Figs. 4(a) and 4(b)] is different with respect to that of the first exposure: The rapid σ increase, which reveals a drastic change of the surface morphology during the first exposure to the gas, is no longer present. It is worth noticing that the initial roughness value at the second exposure is higher with respect to the final value of the first exposure. This effect, although always present, is much more evident in the case of the samples reset at $200\ °C$, indicating that the thermal treatment at a higher temperature has increased the surface roughness.

Therefore, during the second exposure of the films to the gas, the morphological evolution of the films can be regarded as a pure bulk absorption process, similar to the second part of the process present in the first exposure. On the other hand, the fact that the surface layer was preserved in the case of Sample 1 (and not in Sample 2) does not affect the bulk diffusion process and the final thicknesses of the films, confirming that the two processes occurring in the first cycle are independent. This implies that the second bulk absorption treatment always provides a response similar to that in the first gas exposure.

In summary, the EDXR data demonstrate that the response of the film when it is exposed to the gas is characterized by a first fast increase in thickness, reversible at $200\ °C$, that can be attributed essentially to a surface adsorption, and a second slower one, reversible at $130\ °C$ that shows the morphological characteristics of a bulk absorption process. A possible explanation is that the former process induces the formation of a layer, whose thickness is $(d^* - d_1)$, on the film surface, persisting also when the gas flux is interrupted and that can be removed only by heating the sample to a temperature close to $200\ °C$. This behavior is different from the other Pc systems investigated and, in principle, could be associated with the interaction of the NO_x molecules with the Ru metal atoms. Moreover, the microstructural characterization of these films reveals a peculiar packing and long-range structure,[14] possibly inducing a different behavior in gas diffusion. However, since the difference is essentially restricted
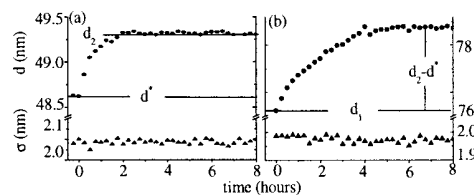

FIG. 4. Time dependence of the $(RuPc)_2$ layer thickness (full dots) and roughness (triangles) at the second submission to the gas.

to the interaction at the film surface, it seems more likely that the metal, rather than the film packing, is responsible. The observation that the two steps of gas desorption require rather different energies (desorption is fully accomplished only at higher temperatures), suggests that gas diffusion is mediated by strong interactions.

In addition, the clarification of the mechanisms involved in the film/gas interaction, the importance of this unexpected result lies in the great technological relevance given by the possible use of these films as optical/conductometric sensors. The reported measurements are experimental evidence of the reversibility of the bulk absorption process for a $(RuPc)_2$-based sensing film that provides the dominant contribution to the optical/conductometric response of a chemical sensor.

In conclusion, we present experimental evidence of a total reversible absorption/desorption process in $(RuPc)_2$ gas sensing films, obtained by combined *in situ* and *ex situ* studies of the film morphology by (time-resolved) EDXR measurements. The technique demonstrated itself as a powerful tool for following the morphological variations of gas sensing films during the absorption and after desorption of gases. The results reported provide experimental evidence for the understanding of the interaction process between $(RuPc)_2$ films and NO_x gas, and indicate that such films are suitable candidates to be used as detectors of environmental pollutants.

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