

Time-resolved energy dispersive x-ray reflectometry measurements on ruthenium phthalocyanine gas sensing films

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The energy dispersive (ED) variant of the conventional x-ray reflectivity (XR) provides an atomic scale determination of the morphological characteristics of thin films, such as their thickness and surface roughness. We report on the *in situ* EDXR measurements of the (minimal) morphological changes of ruthenium phthalocyanine gas sensing thin films. A series of reflectivity spectra have been collected, during the exposure of the films to a gas flux of nitrogen oxides (NO_x) molecules. The measurements allowed a very high density time sampling of the evolution of the two morphological parameters, providing important information on the gas-film interaction. © 2003 American Institute of Physics. [DOI: 10.1063/1.1579868]

The interaction process between metal-phthalocyanines (MPc) and gases is currently under intensive investigation in view of the use of MPc films as optical/conductimetric sensors, for their electronic properties change remarkably upon exposure to gases such as nitrogen oxides NO_x .^{1,2}

It is known³ that films of different MPc are characterized by different packing and long-range structures (i.e., available lattice spaces), inducing a different behavior towards the interacting gas diffusion.

The interaction mechanisms are not yet well understood and a deeper insight into the modifications occurring in the film morphology is needed.⁴ Therefore, it appears extremely useful to monitor *in situ* the changes experienced by parameters as the film thickness and roughness, which are very sensitive to the interaction process.

When the sensing film is exposed to the gas, the formation of a charge transfer-complex between phthalocyanine and NO_x is expected.³ The produced holes are responsible for the transfer of the electric charges along the phthalocyanine matrix, so that the molecular arrangements and morphology play an important role in the film's electrical response to the gas exposure. Furthermore, properties such as reversibility, response time, and recovery rates, which represent fundamental aspects of the sensor performance, are also strongly affected by the film morphology. In particular, the process of gas absorption and diffusion can influence the velocity of response and the strength of the film-gas interaction and/or the possible occurrence of chemical reactions determining whether the sensor is reversible or not. Several authors have studied, by different methods, the mechanism of gas diffusion in a thin/thick film sensor, especially of semiconducting oxide thin films.⁴ A diffusion-reaction model

was found to satisfactorily interpret the various performances of gas-sensing devices, together with the changes in thickness, roughness, or crystallinity of the films.^{5,6} Nevertheless, the reported measurements were focused on the devices electrical response, while the structural and morphological changes, accompanying the exposition to the gas, were not investigated.⁷

An appropriate tool for evaluating the latter is x-ray reflectometry. This technique is commonly utilized to probe the properties of surfaces and interfaces of layered samples, like films deposited on substrates, multilayers, superlattices, etc.⁸ The method is based on the Snell rule applied to x rays⁹ that, near the critical angle ϑ_c , can be summarized as $\vartheta/\lambda = \text{constant}$, where λ is the x-ray wavelength. At small angles, $\vartheta/\lambda \approx \sin \vartheta/\lambda \propto E \sin \vartheta$ ($E = \text{radiation energy}$), so that the ϑ/λ is practically proportional to the scattering parameter q , that is to say, to the same quantity on which the x-ray intensity depends in a diffraction measurements.

Hence, in analogy with diffraction,¹⁰ there are two ways of performing the q scan, namely either using a monochromatic beam and executing an angular scan (angular dispersive mode) or using a polychromatic x-ray beam at a fixed angle and carrying out an energy scan [energy dispersive (ED) mode].

The advantages of the ED technique on the angular dispersive counterpart¹⁰ are connected to the immobility of the experimental apparatus during data collection and are particularly useful in reflectometry. Indeed, in the grazing geometry required for this kind of measurements, any minimal misalignments of the sample may induce relevant relative errors during the angular scan. Moreover, if many scans have to be carried out consecutively, as in the present case, reproducibility problems may arise because of the mechanical movements of the diffractometer arms.

The application of the x-ray reflectometry technique to a

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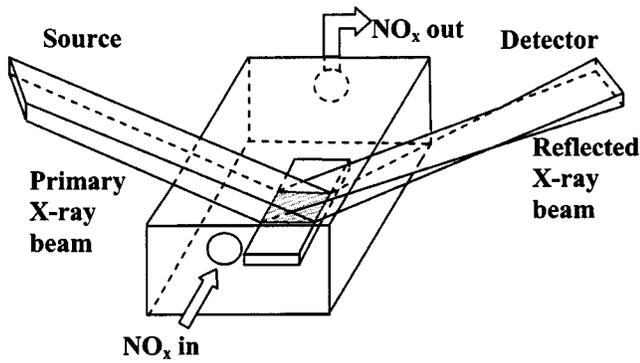


FIG. 1. Sketch of the experimental chamber.

thin film sensor *ex situ*, consisting in comparing the spectra collected before and after the exposure to the gas, can give some hints on the mechanism of the process, but can hardly be conclusive.¹¹ Furthermore, the removal of the sample from the diffractometer after the first measurement and its repositioning to perform the second may induce serious systematic errors, compromising, as mentioned earlier, the reliability of the results. The use of ED x-ray reflectivity EDXR *in situ* prevents this problem and allows the evolution of the film morphology to be followed with extreme accuracy.^{12,13} This enables to discriminate among the proposed models ac-

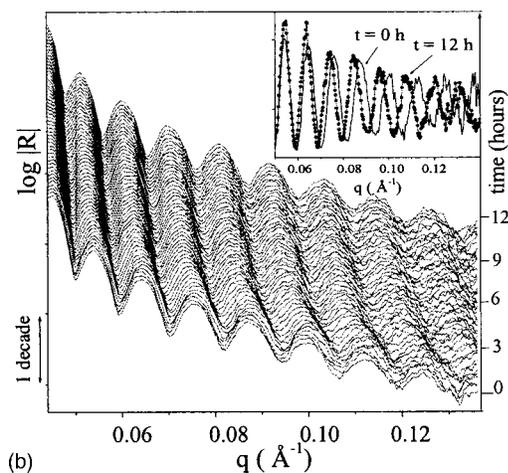
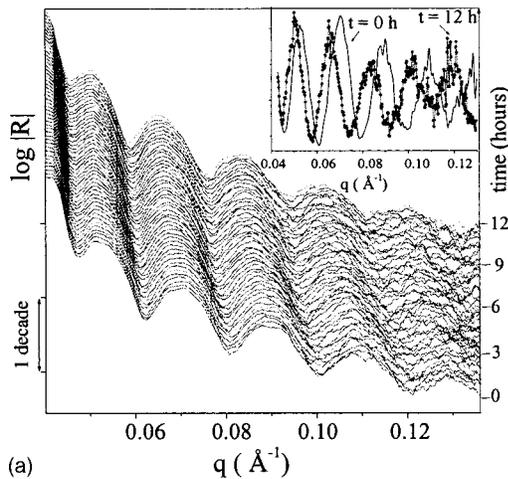


FIG. 2. Plot of the real time evolution of the x-ray reflectivity spectra: (a) for the 300 Å and (b) for the 500 Å films. In the insets: the oscillating contribution to the reflectivity (at the beginning and after 12 h of exposure to the NO_x gas) is isolated.

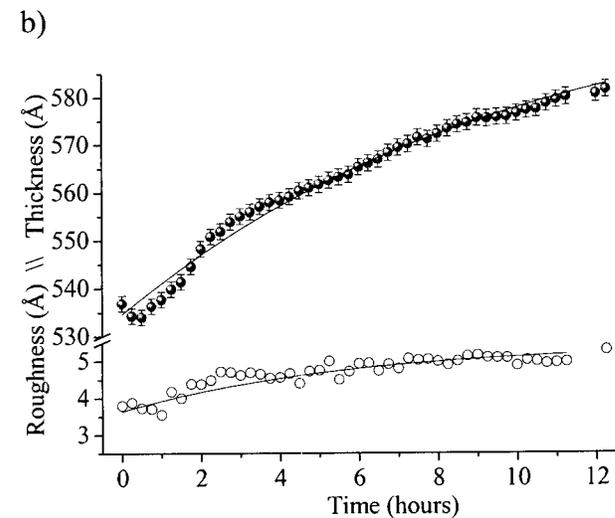
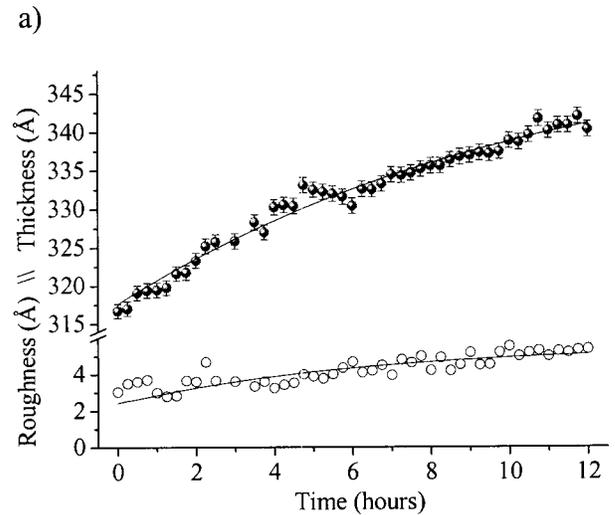


FIG. 3. Curves of the films thickness (full dots) and roughness (open dots) as a function of time, obtained by fitting the spectra of Fig. 2 using Parrat's model, for the 300 Å (a) and for the 500 Å (b) films, respectively. The solid lines represent the fit of the data points according to an upper-limited exponential function describing the saturation process.

counting for the different processes that occur during the absorption of the film and the diffusion of the gas. Indeed, the real time evolution of the morphological parameters described by any realistic model is to be consistent with the x-ray reflectometry results.

The present work studies the kinetics of interaction between the NO_x gas and two ruthenium phthalocyanine (RuPc)₂ films. The films were grown by sublimation of a (RuPc)₂ powder¹ on a Si wafer in a vacuum, their nominal thickness were 300 and 500 Å, as measured by an oscillating quartz crystal device (Edwards FTM5 film thickness monitor).

The experiment consisted of collecting some 50 x-ray reflection spectra, each acquired for 15 min, over a total observation time of about 12 h. The film under measurement, having a surface of about 1 cm², was placed in the experimental chamber shown in Fig. 1 and exposed at room temperature to a NO_x gas flux of 20 nmol/s. Preliminary trials showed that, after this time, the films are completely saturated with NO_x molecules and a stationary condition is

TABLE I. Values of the EDXR measurements fit parameters.

Nominal thickness (Å)	Initial thickness d_1 (Å)	Asymptotic thickness d_2 (Å)	Characteristic time τ_d (h)	Initial roughness σ_1 (Å)	Asymptotic roughness σ_2 (Å)	Characteristic time τ_σ (h)
300	318(1)	352(1)	10.7(0.5)	2.4(3)	5.6(3)	6.2(0.5)
500	534(1)	603(1)	9.9(0.5)	3.6(3)	5.5(3)	5.9(0.5)

reached, so that the reflection spectrum does not change any longer.

The two sequences of the reflected intensity spectra, relative to the two samples, are plotted in Fig. 2, after being normalized to the energy-dependent primary beam. A progressive dephasing of the spectral oscillations is clearly observable. In particular, a continuous shift of the minima towards lower q values as a function of time is evident in Fig. 2(b). Since the film thickness 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. In the insert, the first and the last spectra are compared after the subtraction of the Fresnel reflectivity contribution. The latter operation is equivalent to the subtraction of the form factor from the x-ray diffraction pattern of an amorphous sample in order to isolate its oscillating part (static structure factor).

The slight change in the period of the oscillations and in their damping are related to the increase of the film thickness (d) and roughness (σ).^{14,15} The changes experienced by the two parameters are quantified, in more rigorous terms, by fitting the XR spectra according to Parrat's formula for x-ray reflectivity.¹⁶

The d and σ vs t curves are plotted in Fig. 3. In order to estimate the characteristic times of the overall process, the curves were fitted with an upper-limited exponential function, $x(t) = x_1 + (x_2 - x_1)[1 - \exp(-t/\tau)]$, describing the case of a progressive increase of a given parameter x , from its initial value x_1 till its asymptotical value x_2 (saturation) in a characteristic time τ . In the previous formula, $x(t)$ represents the evolution over time of the film thickness as obtained from the d vs t curve, and the evolution over time of the surface roughness from the σ vs t curve. The film-substrate interfacial roughness is assumed to be negligibly small, since the Si substrate is practically flat, if compared to the film surface.

Comparing Figs. 3(a) and 3(b), it can be noticed that the data (both thickness and roughness) related to the 500 Å sample are of higher quality with respect to those of 300 Å. This is due to the fact that the spectra [see Fig. 2(a) versus Fig. 2(b)] of a thicker sample are characterized by a higher number of oscillations, which allows a better fit.

The values of the fit parameters are reported in Table I. The increase in the thickness is of the order of 10%, in both the samples (11% for the 300 Å film and 13% for the 500 Å), namely the increase is proportional to the original thickness. Instead, the roughness value experiences a growth that is independent of the film thickness. The two characteristics times, τ_d and τ_σ of the two processes are about the same for the 300 and the 500 Å film: τ_d is approximately 10 h and τ_σ approximately 6 h for the two samples, respectively. These considerations confirm that the interaction with the gas involves both the surface and the bulk of the film: the surface

interaction between the gas and $(\text{RuPc})_2$, inducing the increase in roughness, is more rapid and not influenced by the underlying bulk. However, the bulk process, involving the intercalation of the gas molecules inside the film, needs a longer time.

A last comment regards the actual shape of the d vs t curves. In Fig. 3(b), thanks to the high statistical accuracy of the data, a more complex behavior than that described by the exponential function used in the fit can be noticed in the initial part of the curve (say for $t < 6$ h). This sort of modulation is due to the actual response of the film bulk to the interaction with the gas molecules, suggesting that the thickness and roughness increase is more rapid in the first 3 h than in the following stage. This seems to indicate that, in an early stage of the process, a cooperative phenomenon occurs while, the morphological parameters progressively approach their saturation values only in the subsequent stage, in different times for thickness and roughness. A possible interpretation of this kind of behavior is that the initial uptake of the gas into the film facilitates the subsequent penetration: either due to the increase of the free space inside the film matrix or to the increase of the number of reactive sites.

In conclusion, we present an *in situ* study of the morphological change of gas-sensing thin films upon working, by time-resolved EDXR measurements. The results reported demonstrate that this technique, allowing us to perform long lasting time resolved measurements, can be an effective tool to retrieve information on the interaction process between such films and an interacting gas.

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