

# Iodine doped polyaniline and cobalt-phthalocyanine as sensitive layers for ammonia detection via surface acoustic wave sensor

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## Abstract

We report here the detection of aqueous ammonia using cobalt phthalocyanine (CoPc) and iodine doped polyaniline (I-PANI) as active layers associated to surface acoustic wave (SAW) sensor. Cobalt phthalocyanine films were deposited on the gold sensing layer of SAW sensor platform by molecular beam epitaxy (MBE), while iodine doped polyaniline films were elaborated by Plasma Enhanced Chemical Vapor Deposition (PECVD). The functionalized SAW surfaces have been characterized by means of atomic force microscopy and by X-ray fluorescence. The two realized chemsensors have been tested and compared in terms of sensitivity and detection limit. This work demonstrates successful strategies for the fabrication of a reliable SAW sensor able to detect small molecules.

## 1. Introduction

Ammonia exists at various concentrations in ambient polluting aerosols and in aquatic environment, mainly due to intensive use of nitrogenous materials in agriculture. At high concentration, it may cause diseases to humans and aquatic fauna. Therefore, the detection of both gas and aqueous ammonia is an important task for industrial and environmental applications, which explains the wide development of large varieties of ammonia chemsensors [1, 2]. We will report here the development of two ammonia-SAW sensors. The main difference between them is related to the sensing layer type: iodine doped polyaniline (I-PANI), elaborated by Plasma Enhanced Chemical Vapor Deposition (PECVD) for one, and a 100 nm thick cobalt phthalocyanine (CoPc), deposited by molecular beam epitaxy (MBE) for the other [3,4]. The active chemical interfaces have been characterized by atomic force microscopy and/or by X-ray fluorescence, before being tested to detect ammonia at different concentrations.

## 2. SAW sensor and instrumentation

The developed sensor consists of a dual delay line fabricated on a 36° rot lithium tantalate (LiTaO<sub>3</sub>) piezoelectric substrate. Interdigital transducer (IDT) electrodes, the transmitter and the receiver, were of the same design and fabricated from evaporated chromium/gold (20 nm/80 nm) layers with a periodicity of  $\lambda = 40 \mu\text{m}$ , which corresponds to an operating frequency of about 104 MHz. The dual-delay-line was inserted in a pulse mode system with two independent paths. Thus, any perturbation (i.e. chemical recognition) in the medium close to the sensing area can be monitored by recording the variations of the output signal (phase and amplitude) versus time [5, 6].

## 3. Results and discussions

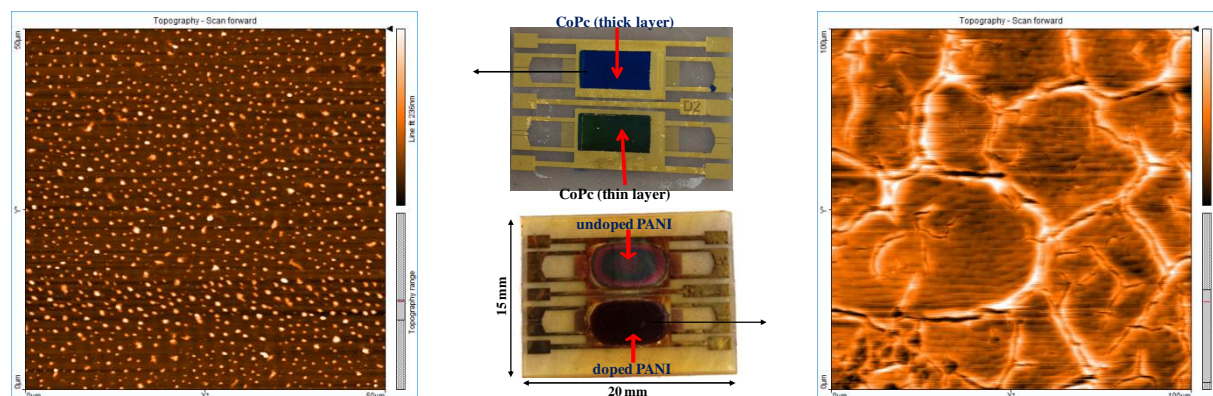
### 3.1. SAW sensor functionalization and physicochemical characterisation

The sensitive layers, I-PANI or CoPc, are elaborated over the SAW sensors' sensing area. Their quality is the key factor to enhance a chemsensor's sensitivity, that's why surface characterization before any use is of primordial. Atomic force microscopy (AFM), a suitable tool for surface metrology and topography imaging, has been used to compare surface topography of the two elaborated films. The obtained images are gathered on figure 1.

For CoPc film, the AFM image shows regularly spaced quasi circular shape over smooth background morphology. Three dimensional AFM image (not shown) reveals that these regularly spaced grains are basically protruding out of the substrate plane, like nanobrushes. Their heights vary between 60 and 130 nm, while their widths spacing vary between 300 and 650 nm.

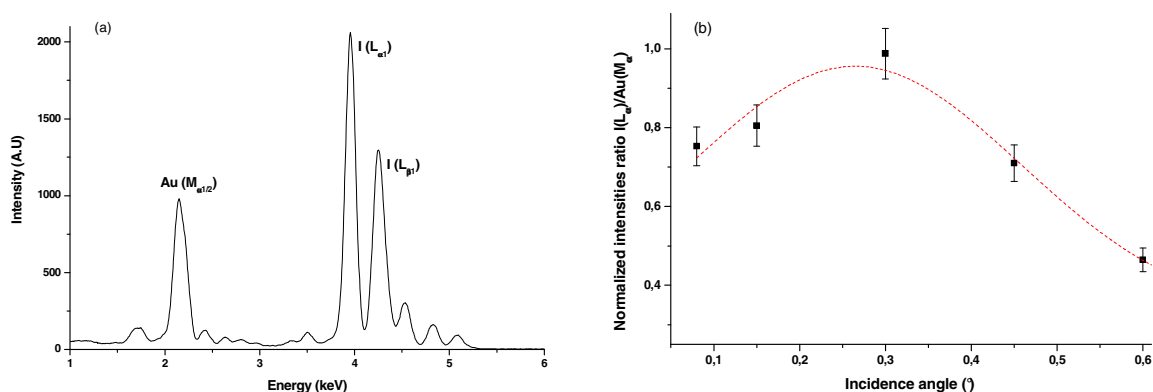
For the I-PANI layer, the AFM image shows the existence of a large rounded structure, of which the 3D representation highlights crater-like shapes with a mean diameter and height of order of 35  $\mu\text{m}$  and 0.9  $\mu\text{m}$  respectively. Within these

shapes a small periodic structure, of mean periodicity of order of  $2.5 \mu\text{m}$ , is observed. This specific form, if mastered, can lead to a significant increase of the active surface and consequently enhances the sensor sensitivity.



**Figure 1.** Photographs of two dual delay lines SAW sensors functionalized with either PANI or CoPc (middle); and AFM images of elaborated films on sensitive area of SAW sensor: CoPc films (left) and iodine doped PANI layer (right).

Fluorescence spectra of iodine doped PANI, have been recorded for various incidence angles. Figure 2a represents, in a restricted interval of energies, a typical X-ray spectrum which displays multiple peaks, mainly  $M$ -lines of gold substrate and  $L$ -lines for iodine. According to the fact that X-rays penetration depth in materials increases when the incidence angle of X-rays raises, normalized intensities ratio  $I(L_{\alpha})/Au(M_{\alpha})$  versus incidence angle, gives information about the doping profile of iodine into the PANI film (fig 2b). The obtained results show an almost Gaussian profile where iodine is mostly present in the superficial layers.



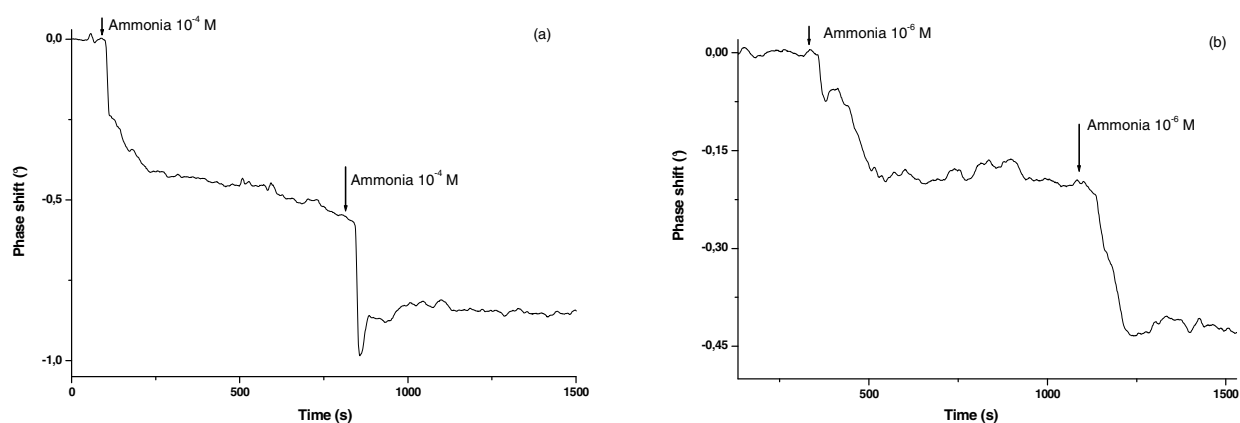
**Figure 2.** a) Fluorescence spectra of iodine doped PANI at grazing incidence of  $0.6^\circ$ ; (b) variation of the doping amount versus incidence angles.

### 3.2. Ammonia detection

Two different solutions were investigated in this study: ammonia in methanol solution where only  $\text{NH}_3$  is existent and aqueous ammonia where both  $\text{NH}_3$  and  $\text{NH}_4^+$ ,  $\text{OH}^-$  are present. In fact, in water, the ammonia is in equilibrium with the ammonium ion. This equilibrium depends largely on the pH and, in a less extent, on the temperature. In slightly acid solution, the balance favors the ammonium ion.

Different concentrations of aqueous ammonia and methanol solution have been considered to check both sensitivity and the detection limit of the CoPc based SAW sensor. Figure 3, presents two examples where phase variation of the sensors' output signal, is recorded versus time, to follow ammonia detection with CoPc film. The injection of a  $10^{-4}$  M ammonia in methanol solution led to a phase shift of about  $0.48^\circ$  (Fig.3a), while the detection of  $10^{-6}$  M aqueous ammonia is accompanied with around  $0.2^\circ$  phase shift (Fig.3b). These results show that the CoPC functionalized SAW sensor is sensitive to ammonia, either in gas or ionic form. The better sensitivity of CoPc film based SAW sensor was of  $0.26^\circ/\mu\text{M}$ , and the limit of detection (LOD) was estimated to be  $0.115 \mu\text{M}$  (around 2 ppb). This value is lower than the Minimal Risk Level of 0.1 ppm or the Reference Exposure Level of 0.29 ppm [7]. Notice that even if some earlier works present LOD as low as  $0.054 \mu\text{M}$  (1 ppb) or  $0.0175 \mu\text{M}$ , using optical [8] and electrical [9] transductions respectively, more recent works reported LOD of ammonia of order of few ppm only (around its permissible maximum concentration of 50 ppm) [10-12]. This highlight the continuing interest in ammonia sensors development and shows that LOD is one

of some criteria to be considered in this research area for practical uses in environment and industries, such as versatility, fast response, reusability, robustness...



**Figure 3.** Phase variation versus time for 100 nm thick CoPc film-based ammonia SAW sensor following injection of a) ammonia in methanol; b) aqueous ammonia.

For the iodine doped PANI based SAW sensor, we have noticed that gold sensitive area maybe etched by iodine in the case of not sufficiently thick PANI films. This fact alters considerably the metrological performance of the sensor. Optimization of the amount and time of doping in relation to the chosen PANI film thickness, become thus imperative before to envisage further experimentations. Nevertheless, we tested the feasibility with small amount of iodine doping, in a thick layer (about 1  $\mu\text{m}$ ), which limits the use of the realized sensor for high concentrations only. Various concentrations in the interval 0.1 M – 0.7 M have been tested. Important phase shifts ( $3.76^\circ$  to  $4.36^\circ$ ) were recorded, showing the potential of the iodine doped PANI in sensing ammonia and the significance of optimizing such sensitive layer. The obtained results show equally that in comparable conditions, except for concentration of ammonia solutions, the recognition kinetics is concentration dependent: the detection is faster for higher concentrations.

## 4. Conclusion

We have shown the potential of functionalized surface acoustic wave devices SAW sensor in chemical detection. Among the various interfaces associated to chemosensors, we have chosen cobalt phthalocyanine (CoPc) and Iodine doped polyaniline as active layers associated to surface acoustic wave (SAW) sensor. The sensor functionalization being the key step in successful realization of sensitive and selective sensors, the SAW surface has been characterized by means of atomic force microscopy and by X-ray fluorescence. The topography of the two films showed different features, with columnar-like shapes for CoPc while I-PANI highlights crater-like shapes. In both cases, these particular shapes enhance drastically the active surface area, leading to an augmentation of the interface solution/sensitive layer, and thus to an improvement of the sensor sensitivity. The two realized chemosensors have been tested in terms of sensitivity and of detection limit. For the I-PANI, the Iodine diffusion in the PANI film up to the gold surface considerably decreases the metrological performance of the realized sensor, because of gold maybe etched by iodine. To overcome this difficulty, some other configurations, such as a tampon layer, or chlorine doping are envisaged. This work demonstrates successful strategies for the fabrication of a reliable SAW sensor, which can be potentially used for practical applications in chemical detection.

## 5. References

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