

## Vapor sensing on bare and modified blue butterfly wing scales

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### Abstract

In butterflies possessing structural color, the scales covering the wing contain a photonic nanocomposite material constituted from chitin (high refractive index) and air (low refractive index). The reflected color is defined by the periodicity and refractive index contrast of the structure. The structural color is altered measurably when its low refractive index component is replaced by an (air + vapor) mixture, resulting in a concentration and vapor species dependent optical reflectivity variation. It is shown that the reflectivity of the nanoarchitecture, its surface chemistry and characteristic pore size can be modified with a high degree of precision by Atomic Layer Deposition (ALD) of Al<sub>2</sub>O<sub>3</sub>. If the thickness of the deposited layer is kept under control with nanometer precision, the spectral position of the reflectance maximum can be finely tuned. The response signal of pristine and ALD modified butterfly wings is compared.

**Keywords:** Gas / vapor sensor; Butterfly wing; Photonic crystal; Nanostructure; Atomic layer deposition

### 1. Introduction

Monitoring the ambient atmosphere inside buildings is becoming more and more important [1]. Selective chemical sensors, capable of making distinction between the vapors of different volatile organic compounds (VOC) for example, are more and more sought after [1,2]. Selective chemical sensors based on naturally occurring photonic nanoarchitectures, like those in the wing scales of butterflies possessing structural color may offer a handy, cheap and environmentally friendly solution to this problem [3,4].

To improve the performance of traditional sensors and eliminating their deficiencies, the focus is on development of new sensors using environmental friendly bionanomaterials with or without functionalization, using various readout methods [1]. These nanomaterials could detect agents from gaseous or liquid samples and work on the principle of interaction (immobilization) of the analytes on nanostructured architectures. If the nanostructure is a photonic crystal type material and the optical reflectance (transmittance) change is to be followed, the readout can be done using optical methods, even possibly in a wireless manner.

The photonic band gap occurring in a photonic crystal is determined by the geometry (size, shape) and refractive index contrast of the building components [5]. In gas / vapor sensing applications one of the components has to perform a proportional change with the concentration of gas / liquid to be measured. Either size variation or refractive index variation is taking place and generating the detected optical signal. Taking into account the price, laboratory instrumentation and know-how needed for the large scale production of photonic crystals, the artificial 3D photonic crystals are not widespread yet. On the other hand, the natural origin photonic nanostructures: mainly chitinous cuticular organizations in beetles or butterflies [6,7] are also capable of color change in response to the modifications of their medium [8]. The efficacy of a sensor

may be enhanced by building sensor arrays of independent sensitivities and processing in parallel the signals to extract as many as possible characteristic features. This fingerprinting technique results in better selectivity if the sensors in the array show characteristic differences in the detected signal. The sensor material surface being the place of primary interaction with the analyte is a crucial point. Chemical, physical or structural (in terms of nanometer size differences) modification of the surface could be a way to enlarge the library of sensors in the array. For example the atomic layer deposition (ALD) method was shown to be effective in color modification of butterfly wings [9], to alter the wettability [10] or wing scale replication for photovoltaic applications [11].

Recently we reported a detailed spectral and structural examination of nine blue lycaenid butterfly species [12] with characteristic pepper-pot structure. This nanoarchitecture is formed by perforated layers which are very convenient from the point of view of color change by penetration and replacement of the air in the voids of the nanoarchitecture with a material with different refractive index. Performing gas sensitivity measurements, we pointed out [13] *Polyommatus icarus* species as one with highest signal and stability. In the present work we chose another blue butterfly, too, the *Morpho aega* because of the well described structure and narrow optical reflectance spectra [14,15]. In these two samples we will investigate the effect of ALD layers on gas / vapor sensing. For a complete surface modification all the pores have to be covered uniformly along the full depth of the layered nanostructure. ALD promises to be an ideal method for this purpose, as it is based on a molecular scale process: the chemisorption and reaction of precursor (gaseous) materials on the substrate surface [16,17]. The method has several advantages, including its conformal and uniform coverage, precise thickness and composition control, and the possibility of low temperature deposition that allows the coating of sensitive and organic materials as well. Due to the

chemisorption as a governing process, this technique is uniquely versatile to coat high aspect ratio structures, the only condition that needs to be fulfilled is to ensure that the gases have enough time to penetrate inside the pores, and in this case a full coverage of the whole surface is possible. It was shown [18] that with proper precursor management even in very high aspect ratio structures the complete coverage can be achieved, so the butterfly wing scale pores cannot represent an obstacle.

## 2. Experimental Details

The investigated butterfly specimens were obtained from the well curated collection of the Hungarian Natural History Museum. Both *Polyommatus icarus* (Lepidoptera: Lycaenidae: Polyommatae) and *Morpho aega* (Lepidoptera: Nymphalidae: Morphinae) specimens were used as sensor material, therefore flat pieces of the wing membrane were cut and were mounted in frames to provide safety in handling during the experiments. The nanostructure of the blue wing scales was investigated by detailed scanning electron microscopy (SEM). To avoid local charging, 15 nm of sputtered gold was deposited onto the butterfly wings. The prepared pieces were attached to the stubs by conducting carbon tape.

The Al<sub>2</sub>O<sub>3</sub> films were grown in a Picosun SUNALE R-100 type ALD reactor. Electronic grade purity trimethylaluminum and H<sub>2</sub>O were used as precursors. The carrier gas and purging medium was 99.999% purity nitrogen. During deposition the pressure in the chamber was 11 mbar. Flow rates of the precursor gases and water were 150 sccm. The pulse and purging lengths were previously optimized so that the precursors would penetrate into the porous structure of the butterfly wing scales and the growing film would cover its inferior walls evenly. This meant 0.5 s pulses, and 15 s purging after the precursor pulses, and 20 s after the water pulses. The deposition temperature was 100°C, which is sufficient for the growth of Al<sub>2</sub>O<sub>3</sub> [9,19].

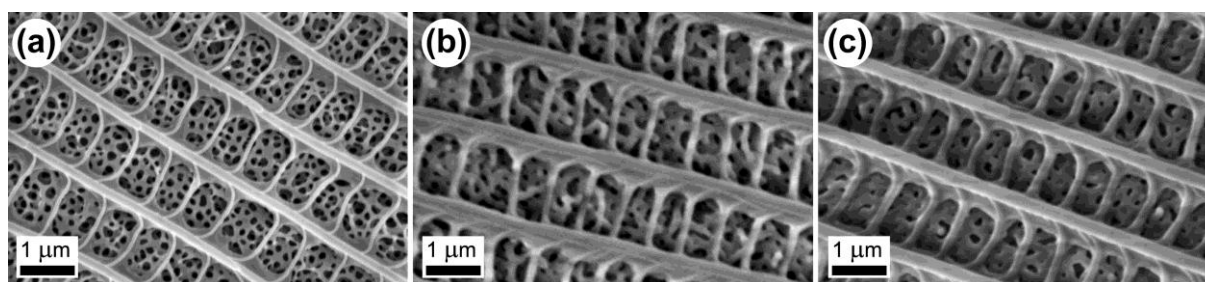
For the vapor sensing experiment the untreated and the coated samples were laid into an air-proof aluminum cell which had gas inlet and outlet and a quartz window to provide UV transmittance. The optical reflectance measurements were done through the quartz window using a modular fiber optic spectrophotometer (Avantes HS1024\*122 TEC). The samples were illuminated under normal incident light by a dual deuterium-halogen source (Avantes AvaLight-DH-S-BAL). The reflected light was collected with an optical fiber oriented at an angle yielding maximal reflectance signal from the butterfly wing. Taking into account the position of the wing scales respective to the wing membrane (there is about 15° between scales plane and wing membrane plane) and other

structural characteristics, the global reflectance will be different from the specular one, in our case the maximum was determined to be at 45° to the wing surface. Depending on the particular nanoarchitectures occurring in the wing scales the reflected light may have a complicated angular dependence [20]. One of the advantages of the pepper-pot type nanoarchitectures is the milder angular dependence of their reflectance as compared to the Morpho-type scales [21,22]. A further advantage of collecting the light at 45° from the normal is the decoupling of the illuminating light reflected from the outer surface of the quartz window from the light reflected from the wing surface [23]. The collected light was analyzed over a wavelength range from 200 to 800 nm.

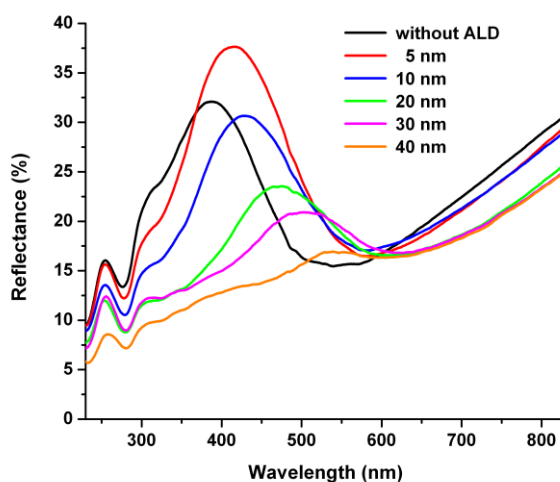
The gas mixing equipment was based on Aalborg digital flow controllers which set the vapor concentration by letting pass synthetic air (Messer: 80% N<sub>2</sub>, 20% O<sub>2</sub>, others <20ppm) and saturated volatile vapor (from gas bubblers containing the liquids) in the required ratio [13]. During the measurements the color of the wing in synthetic air was set as a reference, therefore in the vapor detection measurement the variations in the reflectance were followed. This means that the reflectance of the wing in air will be 100% for the full wavelength range while the vapor mixture results a change in the optical properties of the wing, which generates a deviation of the reflectance spectra from the reference. The deviation of the reflectance was recorded as a function of time while concentration of the vapors was controlled as follows. One complete cycle of measurement contains 20 s of vapor flow followed by 60 s of synthetic air flow to clean the cell, repeated 5 times. The vapor concentration was increased in 20% steps. The temporal evolution of the optical reflectance variation can be represented as a 3D surface plot [4].

## 3. Results and Discussion

The pore size of the photonic crystal structures in the investigated butterfly wing scales is 200 nm or smaller, in the pepper-pot type nanoarchitecture of *Polyommatus icarus* there are circular air voids, which in fact originate from spherical voids (Figure 1a, for cross sectional TEM images of pepper-pot type structures see Figure 1 in [12]), while in *Morpho aega* there are parallel lamellas on the sides of the ridges (see Figure 1 in [3]). Taking into account the highly conformal mode of cover layer deposited by ALD, the deeper and narrower parts will be also well coated. We performed experiments starting from thinner layers, in this way 5, 10, 20, 30, 40 nm of Al<sub>2</sub>O<sub>3</sub> was deposited by ALD. The SEM image on Figure 1 shows the differences in the *P. icarus* scale surface while no ALD layer is present (a), and after 20 nm (b) and 40 nm (c) of Al<sub>2</sub>O<sub>3</sub> deposition. The progression in the resulted micro



**Figure 1.** Scanning electron micrographs of *Polyommatus icarus* wing scales. (a.) original condition, without deposition, (b.) 20 nm, and (c.) 40 nm of deposited Al<sub>2</sub>O<sub>3</sub>.



**Figure 2.** Optical reflectance spectra of *Polyommatus icarus* wings in the original state (without ALD) and with increasing thickness of deposited  $\text{Al}_2\text{O}_3$

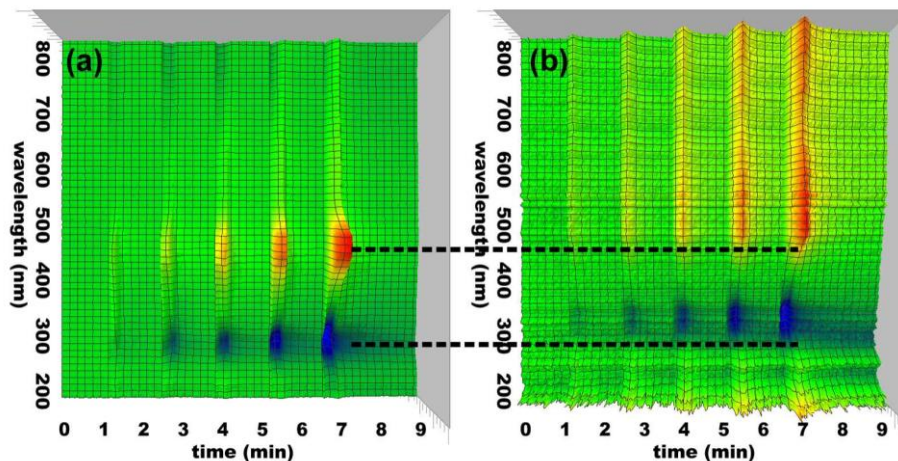
and nanostructure thickness shows that 40 nm coverage over the original structure makes the pores to shrink significantly, or completely close. On one hand this hinders the molecules of the ALD process to penetrate in the depth of the structure, the layer would grow only at the superior surface. On the other hand, the gas / vapor sensing is based on the filling of the structure with the vapor to be measured, therefore the complete closing of the voids is disadvantageous. The color change of butterfly wings as a result of ALD was reported earlier for Morpho type scales [19]. We also observed the photonic band gap shift for the pepper-pot type nanoarchitectures. On blue butterfly wings even with naked eye one can observe the change to a greenish hue, depending on the thickness. Figure 2 shows the changes of the reflectance with increasing ALD layer thickness. The spectra were measured on *P. icarus* wing with integrating sphere. The peak at 387 nm for the wing before ALD shifts towards the longer wavelengths. While the  $\text{Al}_2\text{O}_3$  layer occupies larger and larger amount from the volume of the air voids in the structure, the effective refractive index increases, and this implies the modification of the photonic band gap results in the redshift of the spectrum. The detailed calculation to compute in which way a thin layer of high refractive index material will modify the reflectance of a complex nanoarchitecture, like that found in pepper-pot type scales, which lack long range order, is a very demanding task, beyond the scope of the present paper. Such computations have been attempted before for simpler, regular structures and which are coated only in the exterior, but only qualitative agreement was obtained [9]. In our case, first an increase in the peak intensity is followed by a decrease of peak intensity with the increase of the thickness, which results a color desaturation – the color turns grayish at 40 nm  $\text{Al}_2\text{O}_3$  thickness. These two changes indicate that it is not useful to increase of the thickness more than 30 nm if optical applications are aimed at.

Earlier we investigated the temperature dependence of the relative spectral change when the wing scales are exposed to vapors of different volatiles [4] and showed that the lower temperatures increase the spectral shift and thus the magnitude of the gas sensing signal. The key of the spectral change mechanism is the capillary condensation of the different vapors inside the nanostructure. The size of the nanopores and their small curvatures in the nanostructure may support the formation of ink-bottle effect [24] which results in the

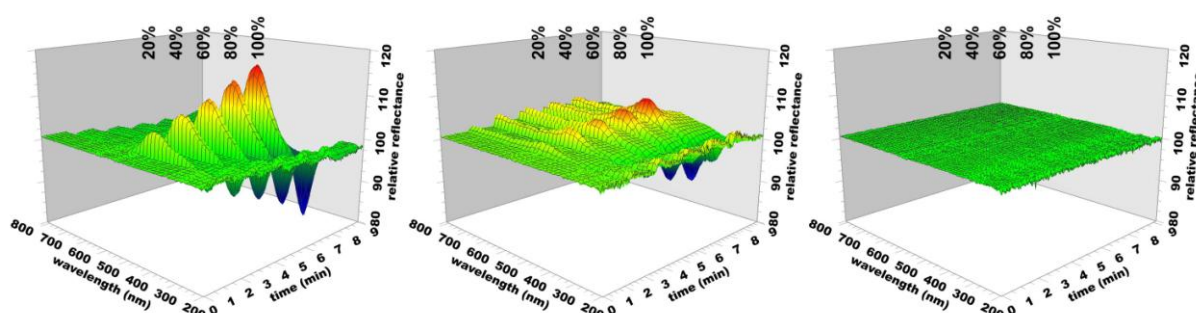
condensation of the vapors, while at lower temperatures the magnitude of the spectral changes is higher due to the decrease of the vapor pressure needed for condensation. This is important as the deposited atomic layer will change not only the pore size in the scales, but the chemical behavior of the surface, too. The changing surface tension will modify the development of the (temperature dependent) condensation, and in this way the gas detection signal.

We showed that the ALD coating changes the refractive index contrast of the photonic nanoarchitecture which yields the (red) shift of the spectral position (Figure 2). Therewith, the  $\text{Al}_2\text{O}_3$  layer also changes the characteristic size of nanopores which is expected to influence the gas / vapor sensing properties through the curvature-dependent ink-bottle effect. These two makes also the signal in gas measuring experiments to change. First, comparing the spectral position of the signal, *P. icarus* wing was measured in ethanol vapor (Figure 3) before and after a 5 nm  $\text{Al}_2\text{O}_3$  deposition. The 3D color graph is shown from the top, for the easier comparison of the wavelengths. The ethanol concentration values increase in steps of 20% from 0% to 100%. One can see in the case of the modified sample that the positive and negative peaks are shifted towards the longer wavelengths. The red shift is now expanded with the broadening of the positive peaks.

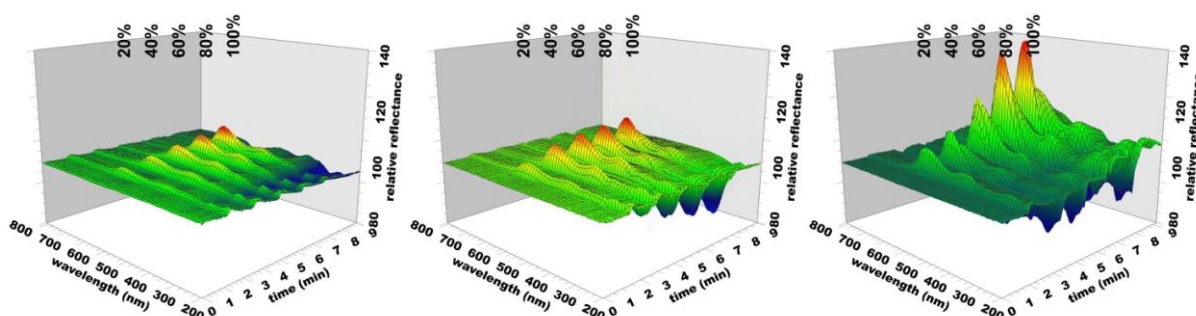
As we pointed out earlier, after the 5 nm thickness, the optical reflectance peak intensity diminishes while the ALD layer thickness increases (Figure 2). In gas sensing experiments a concentration dependent peak shift is observed, so in the modified samples a smaller signal is expected. To verify this presumption, we carried out identical experiments with *P. icarus* wings using water vapors, changing the samples with different  $\text{Al}_2\text{O}_3$  thicknesses. It is clearly visible on 3D color map examples (Figure 4) that even 10 nm of deposited layer makes the signal to drop to almost zero. This very clearly shows that indeed the thickness of the deposited layer has to be controlled with nanometer precision, fortunately ALD is a procedure that allows this precision. When comparing Figure 2 and Figure 4, one may conclude that, despite the fact that after the deposition of the 10 nm  $\text{Al}_2\text{O}_3$  nm the reflectance in artificial air has comparable magnitude with the uncoated wing, the response is almost completely lost in the wing with 10 nm ALD coating. This may be the consequence of the narrowing of the smallest pores, which hinder the penetration



**Figure 3.** Signals on *Polyommatus icarus* wing in ethanol vapor. The comparison of the uncoated (a) and 5 nm thick (b)  $\text{Al}_2\text{O}_3$  layer. Top view of the 3D color graph. Green corresponds the reflectance unchanged from that in ambient air, blue shades correspond to negative change, while yellow-red, to positive peaks. The ethanol concentration values increase in steps of 20% from 0% to 100%.



**Figure 4.** The effect of the increasing deposited thickness. Uncoated, 5 and 10 nm of  $\text{Al}_2\text{O}_3$  on the wings of *Polyommatus icarus* in water vapors. The vapor concentration is shown on the top of the graphs.



**Figure 5.** *Morpho aega* wings coated with 5 nm  $\text{Al}_2\text{O}_3$ , in ethanol, acetone and water vapors. The vapor concentration is shown on the top of the graphs.

of the vapors inside the nanoarchitecture. On the other hand ALD proved to be a handy tool to manipulate the optical properties of photonic crystals and their surface chemistry, however, in sensor applications one has to consider the free penetration in the structure for the desired optical change to occur.

For real sensor applications a factor of crucial importance is the existence of a characteristic signal corresponding to the analytes, and an easy and accurate way for their discrimination. On pristine uncoated wings selectivity was demonstrated [2,3]. In the present paper we tested under the same experimental conditions with different vapors for ALD coated samples if the selectivity is preserved. Figure 5 shows the results for *M. aega* wings with 5 nm  $\text{Al}_2\text{O}_3$  layer thickness for ethanol, acetone and water vapors of different

concentrations. Looking at the graphs one can see the characteristic differences in the relative peak intensity of the positive and negative peaks. One can clearly observe that specific signals are obtained for each of the three test vapors. This underscores that selectivity is not associated with surface chemistry, but with the nanostructure itself. Moreover, such a 3D surface as shown in Figure 4, contains a large amount of information, not only the static spectral distribution of the signal is important, but also the evolution in time when gas / vapor concentration changes from 0% to a given value or reversely. This could contain representative features and the correlation of the changes occurring in certain spectral ranges is also bearing important information. If applying real time signal processing and more sophisticated data handling algorithms, like Principal Component Analysis [1] it could

make possible the instant determination of vapors, possibly even of mixtures.

All the presented experiments were carried out on aluminum oxide coated samples. Taking into account the surface chemistry influence on the interaction with vapor molecules, it is worth to try other materials to be deposited, too.

#### 4. Conclusions

ALD is very convenient tool for the low temperature, conformal coating of even intricate nanoarchitectures, like those occurring in the photonic crystal type nanostructures of butterflies possessing structural color. The main reflectance peak of such nanoarchitectures can be shifted continuously with the precise control of the thickness of the deposited ALD layer. However after a certain thickness value, the photonic properties and as a consequence the sensibility as a detector are deteriorated as the filling fraction of the high refractive index material becomes dominant. Simultaneously with this, the nanoarchitecture becomes less suitable for allowing fast exchanges with the surrounding atmosphere. Therefore the thickness of the deposited layer has to be controlled with nanometer precision. Fortunately, ALD is very well suited for this purpose.

The selectivity, i.e. the characteristic responses for different vapors given by a certain photonic nanoarchitecture is preserved after the ALD modification of its surface.

Careful modification of the naturally occurring nanoarchitectures may be useful under several aspects: (i) within certain limits the reflectance maximum can be tuned to the desired position; (ii) the surface chemistry of the natural nanoarchitecture may be modified; (iii) may provide the means to improve the reflectivity by optimizing the filling fraction ratio (see Figure 2, 5 nm ALD layer thickness).

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