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Active waveguide effects from porous anodic alumina: An optical sensor proposition

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We present in this paper an active waveguide effect observed in porous anodic alumina (PA), which can be applied in optical sensors. The spectral position, shape, and polarization effect of the narrow waveguide modes is described. An analytical test with a commercial pesticide was performed. © 2010 American Institute of Physics. [doi:10.1063/1.3447375]

Synthesis and tailoring of nanostructured materials present alternative possibilities to build optical sensor devices. In this sense, nanopore materials have proved attractive for optoelectronic, photonic, and sensor applications.1–5 In particular, we have here described the porous anodic alumina (PA) films that comprise hexagonally packed pores with diameters at nanoscale range produced during aluminum anodization.6 The geometric shape and porosity of the PA matrix can be tailored by the appropriate control of the anodization parameters. In addition, the high transparency of anodic alumina in the direction along the pore channels, and the strong optical coupling of materials embedded inside them, results in strong optical response.1,3 PA can therefore be easily employed as an anchor to immobilize specific organic molecules and serves as an active matrix for optical devices. In this sense, nanopore materials have proved attractive for optoelectronic, photonic, and sensor applications.1–5

The PA exhibits a near-UV and visible luminescence at room temperature.9–11 The particular active waveguide effect from PA luminescence can be tuned with luminescent polymers deposited over the alumina layer or embedded in their pores. The PA preparation procedure can be found in the supplementary material.16

The photoluminescence (PL) was recorded from the edge of PA/Al films using a He–Cd LASER 325 nm line as excitation source. A charge coupled device spectrometer Ocean Optics (Ocean Optics) was used to record the PL emission. The in situ PL emission was collected by an optical fiber (200 μm cross section) directly from the near edge of the PA/Al films. The emission of the guided edge component was adjusted at maximum signal varying the angle of fiber in respect to the sample prior to data analysis in order to avoid the not guided component (frontal PL). Two types of luminescent polymers were deposited over PA/Al: poly(p-phenylene vinylene), PPV, and a polyfluorene copolymer (American Dye Source, Inc., ADS108GE), abbreviated here as PFO. It will be demonstrated that the PA emission interacts directly with the emission of polymeric species deposited over the porous layer. Both polymers were incorporated in the PA using a layer-by-layer technique. As a consequence, two sets of films were produced: those with PPV and those with PFO. In the case of PPV, a first layer of a sodium salt of dodecylsulfonic acid followed by a second layer of the polymer precursor, poly(xylilidene tetrahydrothiophenium chloride was deposited and thermically converted to PPV in an evacuated furnace at 120 °C for 30 min.12 For the films covered with PFO, incorporation inside the pores was achieved by immersion of the PA/Al substrates for 30 s inside a chloroform solution containing the dissolved copolymer.

The analytical tests were carried out using an optical fiber connected to the spectrometer and positioned at the edge of the PA/Al film orthogonal to the direction of the pores. A proper sample setup was assembled in order to ensure optical reproducibility during subsequent analytical measurements. A chloropyriphos pesticide solution was dropped over the PA/Al film and the PL was collected in situ. This was achieved by dropping 5 μl of pesticide solution previously dissolved in ethanolic solution in different concentrations: 10−6, 10−5, and 10−4 mol l−1. The PL was recorded immediately after all ethanol solvent had evaporated from the PA/Al surface. This was achieved by verifying the PL variation in situ. It was assumed that the ethanol was totally evaporated when the PL shape had stabilized prior to PL spectra collection.

Figure 1 illustrates the optical response of the Al/PA/air system.

FIG. 1. (Color online) (a) Specular reflectance, (b) edge PL emission, and (c) polarization component of a bare PA/Al film produced by one anodization step in galvanostatic mode under oxalic acid solution (0.3 mol l−1), 5 mA/cm2, 5 °C, and 1 h of anodization. Continuous black line in (b) represents the broad alumina emission.

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system and how it is strongly modified by the intrinsic photonic properties of the material. Figure 1(a) displays corresponding reflectivity spectrum and the well resolved fringe patterns result from Fabry–Pérot interference of the light reflected from various interfaces. The high reflectivity and amplitudes of the fringes demonstrate the optical quality and homogeneity of the Al/PA/air system. Figure 1(b) compares the room temperature emission spectra provided from the top and from the edge of the sample. An interesting feature of PA is its room temperature blue luminescence measured from the top of the sample. However, the planar waveguide formed by the reflecting aluminum substrate at the bottom, and the transparent layer of porous alumina over it, is enough to couple very narrow and the transparent layer of porous alumina over it, is enough formed by the reflecting aluminum substrate at the bottom, and the transparent layer of porous alumina over it, is enough polarized transverse electric (TE) and transverse magnetic (TM) propagating modes that originated from the broad PA host emission. These enhanced, self-selected waveguide modes are strongly polarized, as demonstrated in Fig. 1(c). The spectral position and shape of the narrow waveguide modes are highly sensitive to changes in the effective optical thickness and the enhanced luminescence properties of those species deposited over the substrate or embedded in the pores of the anodic alumina layer. At this time, it is not accurate to assume if the polymer is localized over the alumina substrate or embedded in their pores, or even in both (from inspection of SEM images from Figs. 2 and 3). However, the spectral displacement observed when we deposited the PFO or the PPV over the alumina layer indicates a change in the total refractive index of the optical waveguide. This is demonstrated in PA/Al films modified with PFO or PPV polymers (Figs. 2 and 3). The effect of optical thickness on PL emission is presented together with SEM images in these figures. For PA/Al film produced by the galvanostatic method, only the PL emission of PPV can be observed, which is much more intense than PA emission, and it is located at larger wavelengths than those from PA. The resultant PPV edge emission reveals a narrow spectrum with only two polarized modes. This represents the effect of the total oxide thickness on the waveguide propagation modes for this case. For PPV/PA/Al edge emission, it is possible to observe the spatial filter effect from PPV emission due to the strong narrowing of the emission lines for both polarization modes (TE/TMmax = 23, inset from Fig. 3 and Table SI). This result therefore demonstrates that the film morphology shows a homogeneous film with a high pore aspect ratio in respect to thickness of the oxide layer, 15 nm to 3.5 μm, respectively (Fig. 2). Although a thick oxide layer has been prepared, at the bottom of the pore we can observe, from inspection of SEM images, that the barrier oxide layer measures only 70 nm, which is small enough to allow Al plane approximation to the oxide layer. This characteristic is likely to produce the waveguide property in the PA/Al system.

The PFO/PA/Al edge emission resembles the emission of a bare PA/Al film but instead of a continuous broad emission, it shows multiple propagation modes. It is important to stress that in the spectral region depicted here, both emissions are seen for both PFO and PA. Figure 2 also shows the PFO emission when this polymer is deposited over a glass plate depicting a broad emission band and its normal phonon modes. It is important to point out that even with top porous morphology of lesser quality, the waveguide cavity still functions, interacting with species over the pores of the anodic alumina layer (Fig. 2). The PA/Al film produced by two anodization steps through the potentiostatic method depicts a porous film with well-arranged porous morphology and a thin oxide layer as shown in the inset of Fig. 3. In this figure only the PL emission of PPV can be observed, which is much more intense than PA emission, and it is located at larger wavelengths than those from PA. The resultant PPV edge emission reveals a narrow spectrum with only two polarized modes. This represents the effect of the total oxide thickness on the waveguide propagation modes for this case. For PPV/PA/Al edge emission, it is possible to observe the spatial filter effect from PPV emission due to the strong narrowing of the emission lines for both polarization modes (TE/TMmax = 23, inset from Fig. 3 and Table SI). This result therefore demonstrates that the film morphology

FIG. 2. (Color online) PL emission in different configurations of a PFO copolymer deposited over a PA/Al film produced by the galvanostatic method with only one anodization step. Experimental conditions: oxalic acid solution 0.3 mol l⁻¹, 5 mA cm⁻², 20 °C, and 1 h of anodization. To the right are SEM images showing the top and lateral view sections (inset).

FIG. 3. (Color online) PL emission in different configurations and polarization components (inset) of PPV deposited over a PA/Al film produced by two anodization steps in potentiostatic mode. Experimental conditions: oxalic acid solution 0.3 mol l⁻¹, 40 V, 5 °C, and 1 h of anodization during the first anodization step and 30 min during the second anodization step. To the right are SEM images showing the top and lateral view sections (inset).
interacts with luminescent polymers deposited over or embedded in the PA/Al layer. When PPV is over an aluminum layer, PL emission depicts the polymer phonon modes over a broad spectral region (black curve, Fig. 3). The edge emission for PPV over bare aluminum was not performed.

The application of the PA/Al waveguide for analytical devices is presented in Fig. 4. In this case, no polymer was deposited over the PA/Al layer. The pesticide used to test the device was chloropyriphos, a common pesticide used in seed production. As analytical response we choose the PL peak center variation from the narrow emission modes as a function of the pesticide concentration. However, as can be seen in both insets of Fig. 4, the particular shape of the PL spectrum gives us significant information about the sensitivity of the system, i.e., depending on the porous morphology and the reflectance efficiency of the bottom Al layer, we can produce several emission peaks resulting from the waveguide property, and, in this case, this offers us significant information about the sensitivity of the system for analytical purposes. For the PA/Al film shown in Fig. 4(a) (inset) we have at least 30 emission peaks that can be transduced as analytical signals. From Fig. 4(a) one can observe a displacement of adjacent PL emission modes as wavelength increases, becoming more evident in peaks located at larger wavelengths. This result demonstrates the sensitivity response efficiency inside the studied spectral window. On the other hand, if we choose to analyze just two sets of peaks from the Fig. 4 insets, we demonstrate that the logarithmic value of peak center variation is a linear function of the logarithmic pesticide concentration [Fig. 4(b)], which means that the pesticide can be quantitatively determined. At this point, it is important to state that the results reported here clearly demonstrate the feasibility of PA/Al films applied to pesticide determination, as well as extending the present preliminary results to a wider range of applications. However, further work is in progress to examine the effect of porous geometry and how nanostructure film modification will affect the selectivity of the optical sensor. These results will be reported in a future publication.

In conclusion, the results presented here demonstrate that the dominant oscillations shown in the laser-excited PL spectrum of the PA/Al films can be ascribed to the interference within a Fabry–Pérot optical cavity, where the separation of neighboring oscillations is highly sensitive to the film thickness and refractive index. Consequently, the sensor will respond to any change in the total refractive index of the PA layer caused by the collection of target molecules deposited over its layer or embedded in their pores. The main advantage of this is the ability to modify the porous surface, or the pore walls, by modifying the anodization parameters or using nanostructure-based techniques to enhance the selectivity control of the optical sensor.

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FIG. 4. (Color online) (a) Peak number as a function of its center for three different pesticide concentrations of a PA/Al film emission spectrum (inset) and (b) the logarithmic of peak center variation as a function of the logarithmic pesticide concentration for just two sets of peaks.