Enhanced photoconductivity and fine response tuning in nanostructured porous silicon microcavities

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Abstract. We used light confinement in optical microcavities to achieve a strong enhancement and a precise wavelength tunability of the electrical photoconductance of nanostructured porous silicon (PS). The devices consist of a periodic array of alternating PS layers, electrochemically etched to have high and low porosities - and therefore distinct dielectric functions. A central layer having a doubled thickness breaks up the symmetry of the one-dimensional photonic structure, producing a resonance in the photonic band gap that is clearly observed in the reflectance spectrum. The devices were transferred to a glass coated with a transparent SnO₂ electrode, while an Al contact was evaporated on its back side. The electrical conductance was measured as a function of the photon energy. A strong enhancement of the conductance is obtained in a narrow (17nm FWHM) band peaking at the resonance. We present experimental results of the angular dependence of this photoconductance peak energy, and propose an explanation of the conductivity behaviour supported by calculations of the internal electromagnetic field. These devices are promising candidates for finely tuned photoresistors with potential application as chemical sensors and biosensors.

1. Introduction

Photonic structures made of nanostructured semiconductors have generated great interest in the last ten years mainly due to the availability of simple preparation methods and potential applications in control of the emission, propagation, and detection of light. In particular, photonic structures made of porous materials, such as porous silicon (PS), allow the sensing of chemical or biological species through changes in the photonic response of the structure [1-4].

PS can be prepared by electrochemical anodization of crystalline silicon in a fluorine-containing electrolyte [1]. The porosity of PS (i.e. the ratio between the void space volume and the total volume of the material), depends on preparation conditions such as current density and electrolyte composition. Provided the size of the pore structure is smaller than the light wavelength, PS behaves as an effective medium with a dielectric constant averaged among silicon, air and other components eventually adsorbed on pore surfaces.

An important feature of the PS preparation process is that a porosity (and also a dielectric function) in-depth profile can be built by changing the current density in time. In particular, a periodic multilayer with specific photonic response, such as one-dimensional photonic crystals like Bragg mirrors, or optical microcavities, can be made by using periodic current patterns in time. Since all the layers of the device are porous, any analyte existent in the surrounding atmosphere penetrates to all the layers. This eventually leads to changes in the refractive index at the pore surfaces, leading to a change in the optical response that can be used for sensing purposes.[1,2]

In this work we show that the energy resolved photocurrent of PS devices may be managed using multilayers with an appropriate design. We show that the light confinement in that multilayers leads to finely tuned photocurrent spectra.
2. Experimental details

The complex refractive index and rate of increase of the layers thicknesses were determined in correlation with the current densities by preparing two series of single layers for two different current densities, (6.4 and 124 mA/cm$^2$), with different anodization times. A Teflon cell was employed, with a p-type (1-4 m$\Omega$cm) silicon wafer used as the anode in which the PS layer was etched, and a platinum wire as the cathode. The electrolyte was a 2:1 solution of ethyl alcohol and hydrofluoric acid (50%).

The reflectance spectra of the layers were acquired using a reflectance accessory at 15º and fitted using a two stages computer code based in the Looyenga-Landau effective medium model [5]. Initial estimations of the two parameters (porosity and thickness of the film) are obtained in a first stage by using a genetic algorithm. These estimations are then used as input for a second conventional algorithm in the final fit stage.

The resulting refractive indexes and extinction coefficients spectra for each current density were the same for all the layers prepared during different anodization times, within an error of 5-7%. Furthermore, the thicknesses were proportional to the etching times for both current densities. The resulting porosity values for the two layers were $p_1=52\%$ (for 6.4mA/cm$^2$) and $p_2=88\%$ (for 124mA/cm$^2$). The refractive indexes at 700nm were 2.24+0.0053i and 1.27+0.001i respectively.

Therefore, a rate of increase of the optical thickness was computed for each current density, and used to compute --as a function of the wavelength, and for each current density-- the etching time necessary to obtain a layer with an optical thickness of $(1/4)\lambda$.

A computer controlled current source was used to follow a current density time pattern that had been designed to create an optical microcavity centred at a wavelength of around 700 nm. The cavity was a layer with an optical thickness of $\lambda/2$, having a low porosity $p_1$ which was surrounded by two 4 period Bragg mirrors. The Bragg mirrors were made of alternating layers of low ($p_1$) and high ($p_2$) porosities, all of them with optical thickness of $(1/4)\lambda$. The total thickness of the sample is about 1.88µm. After the etching of the multilayer, a short pulse (4 sec) of 300-350 mA/cm$^2$ was applied in order to separate the porous multilayer from the monocrystalline substrate. This freestanding sample was transferred to a transparent, conducting SnO$_2$ film-coated glass slide. An aluminium layer was evaporated as a back contact.

The sample was illuminated through the transparent contact with a monochromatized light beam chopped at 17 Hz from a tungsten-halogen lamp. The linewidth of the resulted beam was lower than 1nm, which is negligible compared with the cavity bandwidth. A 60 mV DC bias was applied between both contacts and the photocurrent was measured as a function of the wavelength, by using a lock-in amplifier. The angular tuning was studied by acquiring the whole spectra for different incidence angles with the same experimental setup as described above, and also with an s-polarized He-Ne laser beam.

3. Results and Discussion

Figure 1 shows photocurrent raw data in the 550-900 nm range. A sharp photocurrent peak (FWHM of about 17 nm) can be observed. This feature can be attributed to the microcavity resonance, as demonstrated by the measured and computed reflectance spectrum shown in the insets. The spectral response of the conductance is a result of the intensification of the electromagnetic field within the cavity at the resonance energies. The field intensity in each layer can be computed using the transfer matrix formalism as follows: consider the light propagation through a single layer characterized by a complex dielectric function limited by media with refractive indexes $\eta_0$ on the input side and $\eta_e$ on the output side, respectively.
The fields $E_o$, $B_o$ and $E_i$, $B_i$ in the output and the input sides are related, for normal incidence, by the transfer matrix [6,7]:

$$\begin{bmatrix} E_i \\ B_i \end{bmatrix} = M \begin{bmatrix} E_o \\ B_o \end{bmatrix}$$  \hspace{1cm} (1)

where $M$ is the transfer matrix [6,7].

Equation (1) can be generalized for a multilayer of an arbitrary number of N layers. The relationship between the electric field in the layer $j$ of the stack $E_j$ and electric field in the input side can be obtained using the transfer matrix:

$$M_j = \begin{bmatrix} m_{11}^j & m_{12}^j \\ m_{21}^j & m_{22}^j \end{bmatrix} = \prod_{k<j} M_k$$  \hspace{1cm} (2)

Taking into account the boundary conditions, the enhancement factor that relates the field in the layer $j$ with the input intensity for the wavelength $\lambda$ can be calculated as [7],

$$\frac{E_j(\lambda)}{E_o(\lambda)} = (1 + r(\lambda)).m_{22}^j - \eta_0(\lambda).(1 - r(\lambda)).m_{12}^j$$  \hspace{1cm} (3)

where $r(\lambda)$ is the reflectance of the whole multilayer (which can be computed using the entire transfer matrix), $\eta_0(\lambda)$ is the complex refractive index of the input medium, and $E_o(\lambda)$, $E_j(\lambda)$ are the incident electric fields (in the input side) and the field in the layer $j$ respectively, all for the wavelength $\lambda$.

The field intensity enhancement in the layer $j$ is therefore:

$$I_j(\lambda) = \left( \frac{E_j(\lambda)}{E_o(\lambda)} \right)^2$$  \hspace{1cm} (4)

The field intensity in different points within each layer can be computed in the same way, substituting each layer by a number of thinner layers. Figure 2 shows, in a 3-D graph, the field intensity enhancement within the multilayer as a function of the depth and the photon energy. As can be observed, there is a large enhancement (about a factor of 14) for a narrow energy band in the cavity layer and in its neighbourhood.

We estimate the behaviour of the photoconductance of the microcavity by using a very simple model considering that the product $\mu \tau$ between carrier mobility and recombination time is independent on light intensity.
Figure 2: Intensity of the electromagnetic field inside the microcavity as a function of the position and wavelength.

Figure 3: Comparison of the measured and simulated (Eq. 2) photocurrent spectra for a microcavity centered at 700 nm. The value of the Rose factor was 0.75.

Within this simple model the photoconductance of each layer for a given light intensity can be considered proportional to the absorption coefficient $\alpha$. The dependence on the light intensity can be taken into account through the Rose parameter [8]. Hence, the conductance $G_j(\lambda)$ of the $j$ layer is

$$G_j(\lambda) \propto \frac{k_j(\lambda) \lambda}{t_j}, \quad (5)$$

where $k_j$ and $t_j$ are the extinction coefficient and the thickness of the $j$ layer for the wavelength $\lambda$.

The photocurrent $I_p$ is proportional to the conductance of the whole set of $N$ layers:

$$I_p \propto \left( \prod_{j=1}^{N} G_j(\lambda) \right)^{-1} \left( \sum_{j=1}^{N} \frac{t_j}{I_j(\lambda)} \right)^{-1}, \quad (6)$$

Figure 3 shows the $I_p$ values computed with this expression, using a Rose factor $\gamma = 0.75$ and the enhancement factors $I_f(\lambda)$ obtained by equation 4, for the present microcavity configuration. The experimental photocurrent spectrum (corrected for the light source spectrum and the monochromator spectral response) is also shown. The scales were adjusted to match the spectra. As it can be observed, the simple model reproduces quite well the general behaviour of the experimental photocurrent spectrum. A device having the same width, entirely made using a single porosity $p_1$ or $p_2$ will have a conductance lower by a factor of 16 or 3 respectively compared with the resonant device. Nevertheless, in case of a single layer the tunability is missed.

Since the light propagation characteristics through the multilayer depend on the incidence angle, a tuning of the mode wavelength can be performed by rotating the sample. The angular dependence of the photocurrent spectrum is shown in Figure 4, where the photocurrent spectra for different angles were plotted. The data for these spectra were also corrected to take into account the spectral response of the measurement system. As it can be observed, the tuning of the photocurrent peak can be performed finely, without major changes of the shape (the FWHM at 50º is about 20nm).

All the mentioned features can be used for sensing purposes. As an example, a microcavity can be tuned to obtain maximum photocurrent when a laser is used. The tunability of such a system is shown in Figure 5.
Figure 4: Photocurrent spectra of a microcavity for different incidence angles.

Figure 5: Changes in the photocurrent of a microcavity produced by change of the incidence angle of an He-Ne laser beam.

As the whole structure of the microcavity is porous all the component layers are connected to the surrounding atmosphere. Therefore any change of the refractive indexes of the layers, induced by the presence of analytes in the atmosphere, produces a change in the tuning of the microcavity. Since the spectral peak is very sharp, large changes are expected to be produced in the photocurrent due to these tuning changes, allowing the sensing of an analyte. The refractive index of PS changes when exposed to non specific flammable solvents like ethyl alcohol or isopropyl alcohol. A change of 2% in the refractive index produces a variation of up to 5% in the conductance of this device. The pore network surface has to be functionalized for specific analyte sensing.

4. Conclusions

Nanostructured porous silicon has been used to make an optical microcavity in order to enhance the photoconductance by photon confinement in the cavity. The device is a multilayer consisting in a half-wavelength optical thickness layer, limited by two periodic arrays alternating layers with high and low refractive indexes, all of them with a quarter-wavelength optical path. The reflectance spectrum and the internal field intensity were computed, showing a large field enhancement at the cavity for wavelengths corresponding to the resonance. The measured FWHM of the resonance of the reflectance spectrum was 17 nm with Q = 40. A finely tuned spectral photo-response has been experimentally obtained, with the same Q value, in accord with the results predicted using a simple model. These features result as a consequence of an enhancement of the electric field intensity by a factor up to 14 in the mode of the cavity.

5. References

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