PHOTOLUMINESCENCE ENHANCEMENT OF FLUORESCEIN BY ITS INFILTRATION IN PHOTOLUMINESCENT POROUS SILICON BRAGG MIRRORS

E. GÓMEZ-BAROJAS[1], G. SANTAMARÍA-JUÁREZ[1], E. QUIROGA-GONZÁLEZ[2], J. A. LUNA-LÓPEZ[1], R. SILVA-GONZÁLEZ[2] AND E. SÁNCHEZ-MORA[2]

[1]*CIDS-IC, Benemérita Universidad Autónoma de Puebla. Apdo. Postal 196, Puebla, Pue. 72000. México*
E-mail: egomez@ifuap.buap.mx

[2]*Institute of Physics, Benemérita Universidad Autónoma de Puebla. Apdo. Postal J-48, Puebla, Pue. 72570 México*

SUMMARY

We report on the study of the optical properties of porous silicon dielectric Bragg reflectors (DBM) infiltrated with Fluorescein-5-maleimide (FM) molecules. The DBMs were obtained by an electrochemical anodizing process of Si in a two electrodes Teflon cell. The objective is to enhance the photoluminescence (PL) intensity of FM by introducing it in a DBR with resonance frequency at the maximum of the PL, and taking advantage of the non-linear amplification dependence with the intensity. It is desired that the DBM shows intrinsic PL with maximum in the range of FM. It was seen that PL spectra of PSi layers with thermally grown SiO_2 on its pore walls (SiO_2/PSi) shows that SiO_2 diminishes drastically the PL intensity of PSi. On the other hand, the PL was not affected when as-anodized DBMs were silanized with 3-mercaptopropyltrimethoxysilane (MPTS) solution. These were infiltrated with FM solutions in the range of concentrations from 0 to 2.4 mM with 0.4 increments, presenting PL intensity that increases as the FM concentration increases.

1. INTRODUCTION

A common use of Bragg reflectors (DBMs) is the optical amplification of photoluminescence (PL), designing them to resonate at the frequency of the PL. When the DBMs are constructed by porous Si (PSi) layers, the luminescent materials can be infiltrated. Additionally, as micro- and meso-porous Si usually presents PL, this is added to the one of the guest material. This could be positive, as the DBMs could present an exponential amplification depending on the intensity [1]. If the maximum of the PL spectrum of PSi is in the range of the maximum of the PL spectrum of the guest, the signal to noise ratio could be enhanced by orders of magnitude.

It is widely recommended in the literature to perform pre-oxidation and oxidation processes in a wide range of temperature and time conditions, in order to stabilize or passivate the non-radiative PSi surface defects [2] and also as a requirement for chemical functionalization to enhance the infiltration with dye composites [3]. Other researchers have reported that the oxidation of PSi is the primary cause of luminescence degradation of PSi [4]. In order to clarify this subject, in this work we report an experimental study about the effect of oxidizing PSi and infiltrating PSi DBMs with fluorescein molecules on their photoluminescence intensity.

2. EXPERIMENTAL RESULTS AND DISCUSSIONS

Previously, PSi layers were synthesized by electrochemical etching of single side polished silicon p-type (1,0,0) wafers with resistivity of 0.01- 0.02 Ω·cm. The etchant contained Ethanol:HF:Glycerol (60:30:10). The porosity of the PSi layers was determined by the gravimetric technique [5]. The thicknesses of the PSi layers were calculated using the formula given by Vinegoni et al. [5] and the etching rate was determined. The refraction indices of the PSi layers were determined using the equation given by Pap et al. [6]. Two sets of PSi layers were thermally oxidized. One set at 300°C, with 10 ml/min O_2 gas flux for 3, 30 and 60 min. The PSi layers of the 2nd set were oxidized at 800°C, with 10 ml/min O_2 gas flux for 5 and 15 min. The PL spectra of the first set are shown in Fig. 1(a) and a PL spectrum of an as prepared PSi layer is included for comparison which is an intense and broad spectrum in the range from 550 to 925 nm. It is seen, that as the oxidation time increases from 3 to 60 min the PL intensity of the SiO_2/PSi layers diminishes drastically. The PL spectra of the 2nd set are shown in (b). A similar effect is observed as the oxidation time is increased the PL of the SiO_2/PSi layer is drastically reduced. We infer that SiO_2 passivate surface states of PSi that produce photoluminescence.

We decided to synthesize DBMs with no oxidation process to keep full PL intensity. DBMs are narrow–band dielectric mirrors obtained by stacking periodically two layers of high refractive index (layer H) and low refractive index (layer L) whose thickness is $\lambda/4$. The FM fluorescence wavelength λ= 520 nm was chosen. Then, DBMs with 31 periods were fabricated with parameters: for layer-H: n_H=1.93, P=57% and thickness 0.083 μm and for layer-L: n_L=1.36, P=78% and thickness 0.119 μm. Care was taken to form reflecting interfaces of H-layers with the adjoining media so that the reflecting beams interfere constructively. A computer program was used control the current source. The as anodized DBRs were silanized with a 2.5 v/v of 3-MPTS and 2-Propanol solution for 15

min. Then, they were infiltrated by dipping them into FM solutions with concentrations in the range from 0 to 2.4 with 0.4 mM increment.

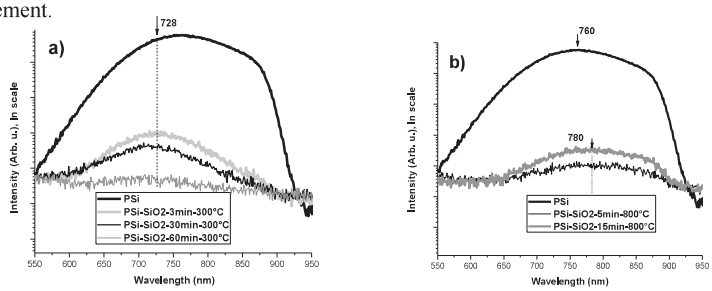

Figure 1. PL spectra of SiO_2/PSi layers; where the SiO_2 was grown: (a) at 300°C and (b) at 800°C for different oxidation times.

Figure 2 shows room temperature PL spectra of the DBMs with 31 periods excited with the 278 nm line of a Xe lamp. All DBMs present a wide PL emission band (400-780 nm) whose peaks are located at about 556 nm. It is seen that the amplitude of the spectra increases as the FM concentration is increased. The Fluorescence band peak of FM molecule lies in this range therefore it is possible that a constructive interference between the emission beams of FM molecules and the PL emission of PSi-DBMs takes place.

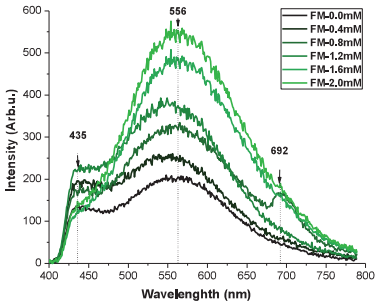

Figure 2. Room temperature PL spectra of 31 periods DBMs silanized with 3-MPTS and infiltrated with different FM concentrations.

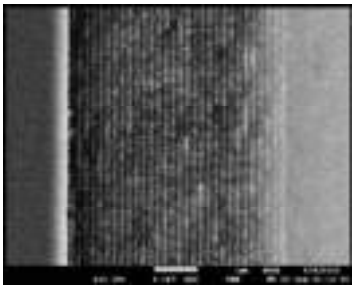

Figure 3. Cross section SEM micrograph at 15000X of a 31 period DBM. This image is the evidence that the DBR was well fabricated.

5. CONCLUSIONS

PL spectra of SiO_2/PSi layers show that SiO_2 quenches the PL emission of PSi in the visible range. The PL spectra of the DBMs infiltrated with FM molecules show that the amplitude of PL spectra is increased as the FM concentration is increased. The PL enhancement suggests that the fluorescein molecules indeed infiltrate the PSi matrix.

REFERENCES

1. F. A. I. Chaqmaqchee, N. Balkan, and J. M. Ulloa Herrero., J. Nanoscale Research Lett. 7 (2102) 525-
2. A. Chouket, H. Elhouichet, R. Boukherroub, and M. Oueslati. J. Phys. stat. sol. (a) **204,** 5 (2007) 1518-1522.
3. A. Chouket, H. Elhouichet, H. Koyama, B. Gelloz, M. Oueslati, and N. J. Koshida. Thin Solid Films. **518** (2010) S212-S216.
4. M. A. Tischler, R.T. Collins, J.H. Stathis, and J.C. Tsang. J. Appl. Phys. Lett. **60,** 5 (1992) 639-641.
5. L. Pavesi. *Revista del Nuovo Cimento*. **20**, 10 (1997) 1-76.
6. A. E. Pap, K. Kordás, J. Vähäkangas, A. Uusimäki, S. Leppävuori, L. Pilon, S. Szatmári. *J. Optical Materials.* **28** (2006) 506-513.
7. L. Wang *, A. Roitberg 1, C. Meuse, A.K. Gaigalas. Spectrochimica Acta Part A **57** (2001) 1781–1791.