JOURNAL OF APPLIED PHYSICS **99**, 046103 (2006)

Optical study of ΓL high energy photonic pseudogaps in ZnO inverted opals

P. D. García and C. López[a)]
Instituto de Ciencia de Materiales de Madrid (CSIC), Calle Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain

(Received 7 July 2005; accepted 9 January 2006; published online 17 February 2006)

We provide experimental evidence of the opening of two new pseudogaps in the high energy region of the ΓL direction in ZnO inverted opals. The appearance of these new pseudogaps is brought about by the increase of refractive index contrast. The calculated band diagram in the ΓL direction, which corresponds to propagation along the (111) crystallographic direction, accounts for the spectral width and position dependence of the pseudogaps on the ZnO fraction present in the opal. To prove this we have performed an optical study by means of reflection and transmission spectroscopy of ZnO inverted opals with different degrees of infiltration. We also study the pseudogap appearing in the highest energy spectral position as a function of sample thickness. In addition, the band engineering developed here allows us to isolate a nondispersive band from the others. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2172721]

Dispersion relation of light propagating through photonic crystals[1] (PCs) organizes in bands and can be viewed as a result of multiple scattering due to the modulation of the dielectric function. Such dispersion relation presents, eventually, frequency intervals called photonic band gaps (PBG) in which light is not allowed to propagate in any direction inside the crystal. When these frequency intervals forbid propagation of light just for certain directions, they are called pseudogaps. This remarkable property of PCs gives rise to several optical phenomena, which do not appear in homogeneous media and have been the subject of study for the last two decades.[2] Among such structures, synthetic opals[3] represent a perfect playground due to its versatility and high quality. The methods used to grow such structures profit from the natural capability that some microspheres have to self-assemble crystallizing, eventually, in face-centerd-cubic (fcc) structures. Vertical deposition[4] is commonly used since it provides extremely high quality samples which is capital to resolve optical features in the high energy regime[5,6] ($a/\lambda > 1$, where a is the lattice parameter and λ is the wavelength of light in vacuum) that, to date, have not been rivaled by any other fabrication technique. This is necessary to study and understand the high energy response of PCs which present, in this region, many of the most remarkable phenomena relating to its photonic nature as anomalous refraction,[7] small group velocity,[8] and, for certain structures, the opening of a complete PBG.[9] Even though as-grown synthetic opals do not present PBG and their symmetry and topology are fixed by the growth process, they can behave as templates in which different materials can be filled allowing band engineering.[10] This may allow modifying the band diagram for such systems varying the refractive index contrast of the structure. Careful progressive infiltration with ZnO has revealed peculiar in that many new features develop that were unexpected from previous experience with silica or other oxides.[11] Besides, ZnO is of such current interest that its infiltration and characterization in PBG environments are crucial.

In this work we present an optical study of the high energy response of ZnO inverted opals. Such systems present, in this frequency interval and for ΓL direction in reciprocal space, the opening of two extra pseudogaps in addition to the lower energy pseudogap present in bare opals. The width of these extra pseudogaps depends on the ZnO fraction present in the opal, which can be controlled in the infiltration process. We provide experimental evidence of this fact by means of optical reflection and transmission measurements for different filling fractions in good agreement with the calculated bands. In addition, we perform an optical study of the pseudogap appearing in the highest energy interval as a function of sample thickness. Our samples exceed the required high quality necessary to resolve their high energy spectral features.

ZnO inverted opals were fabricated with a modified CVD method[12] using monodisperse spheres of poliestyrene (PS) sinthesized by emulsion polymerization.[13] The refractive index of ZnO was measured in a wide spectral range (from 0.4 μm to 1.6 μm) by variable angle spectroscopic ellipsometry, resulting in good agreement with previously reported data.[14]

Bands calculated[15] for different ZnO filling fractions in the opals (Fig. 1, left) show how, as a consequence of the increased refractive index contrast, two new pseudogaps are opened in the high energy region of the ΓL direction in addition to the lower energy pseudogap opened in bare opals (which we shall call A). For a ZnO pore filling fraction over 40% a second pseudogap (B) appears between the 16th and 17th bands with a spectral position centerd around $a/\lambda = 1.6$. This spectral position redshifts with increasing infiltration. The calculated width of this second pseudogap is maximum for 60% ZnO filling fraction (top panel of Fig. 1) and decreasing for further infiltration. In addition to this

---

[a)] Electronic mail: cefe@icmm.csic.es

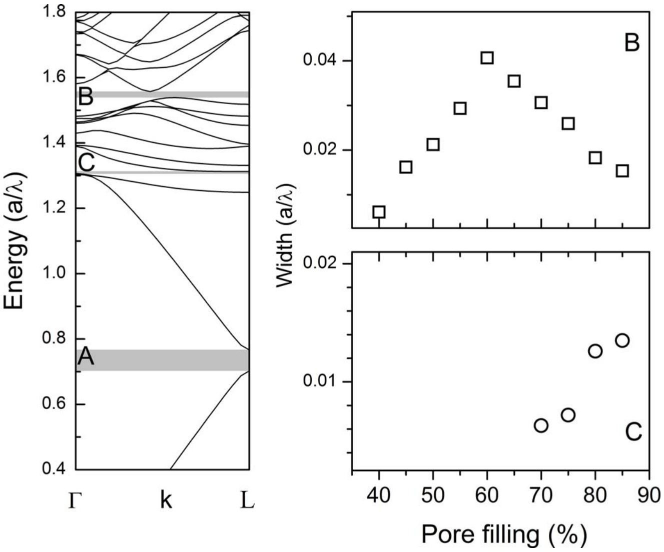

FIG. 1. Left panel: photonic bands with the three pseudogaps opened for 85% ZnO pore unfilling. Top right: spectral width of the second pseudogap (B) centered around $a/\lambda = 1.6$. Bottom right: spectral width of the third pseudogap (C) opened in the high energy region ($a/\lambda = 1.3$) for greater pore filling fraction.

pseudogap, a third pseudogap (C) opens between the fifth and sixth bands when the ZnO pore filling fraction reaches 70%. The spectral position of the C pseudogap is centerd around $a/\lambda = 1.3$ and varies likewise with the infiltration rate. Its spectral width grows monotonically (lower panel of Fig. 1) with the filling fraction until a complete infiltration (considered for the method used in the process to be 86% of the pore) is reached.

In order to verify the calculated positions and widths of the B and C pseudogaps appearing in the high energy region, we have unfilled samples with ZnO varying the degree of infiltrate. We have performed an optical study of the three pseudogaps as a function of ZnO filling fraction (Fig. 2) for a fixed opal thickness (14 layers) by means of reflection and transmission spectroscopy. As it is known, a pseudogap in the photonic band diagram for a certain direction gives a peak in the reflectance spectra whose intensity grows with the spectral width of the gap. The intensity and the spectral position of the reflectance peak centerd around $a/\lambda = 1.6$ evolve in agreement with the calculations. It grows with the ZnO pore filling fraction ($>40\%$) having a maximum for 60% of ZnO inside the pore and decreasing for greater pore filling fraction. For a 75% ZnO infiltration, the C pseudogap opens around $a/\lambda = 1.3$ in agreement with numerical calculations. The spectral width of the C pseudogap is lower than those of B and A, which accounts for the intensities of reflectance peaks from each pseudogap. Transmission spectra give complementary information to reflectance ones. In addition to the dip corresponding to the C gap, neighboring dips can be accounted for by diffraction process.[16] We have also performed an optical study of the B pseudogap as a function of sample thickness (number of layers) for a fixed filling fraction (60% for which the width presents a maximum and so does the reflectance intensity). In the evolution of the peak as a function of thickness (Fig. 3), we observe a blueshift which is in agreement with finite size effects for bare opals previously reported.[17] The study of finite size effects shows that, for 14-layer-thick samples, these peaks reach a stationary line shape and spectral position, in agreement with the assumption of an infinite-crystal behavior.

For a 60% ZnO pore filling fraction (for which the B pseudogap has maximum width), we have compared reflectance and transmittance spectra with the calculated band diagram in the ΓL direction. It can be observed (Fig. 4) that the second-order peaks, both in reflection and transmission, agree in spectral position ($\lambda = 0.43\ \mu$m) with the B pseudogap opened as a result of increased refractive index contrast. A spectral region corresponding to diffraction bands ($1.35a/\lambda < 1.58$) can be observed in reflectance spectrum which does not present peaks or Fabry-Perot oscillations. In the same frequency interval, transmittance falls and presents some remarkable features. The existence of a lower transmission can be explained attending to the different nature of bands which populate this energy region. Bands can be di-

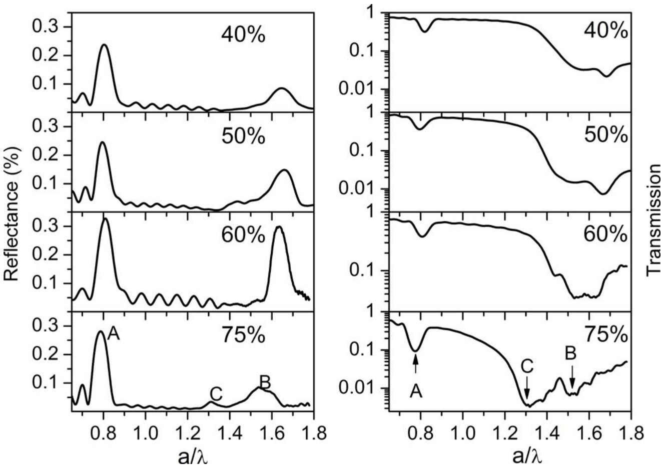

FIG. 2. Evolution of the three pseudogaps as a function of the pore filling fraction for a fixed thickness (14 layers) as observed in the reflectance and transmittance spectra.

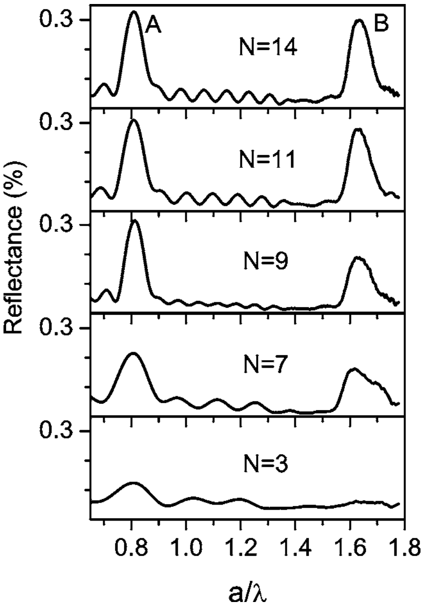

FIG. 3. Evolution of the A and B pseudogaps as a function of sample thickness for fixed pore filling fraction (60%).

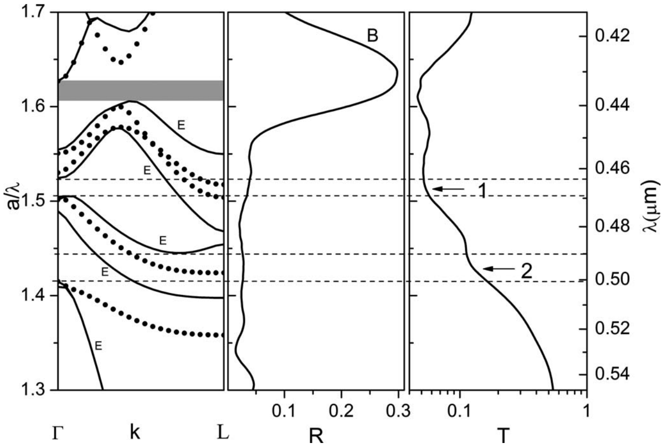

FIG. 4. Left panel: calculated band diagram for 60% pore filling fraction for which the B pseudogap is completely opened. Reflectance and transmittance spectra are shown for this pore filling fraction. Dashed lines show the spectral ranges where just one mode can be excited.

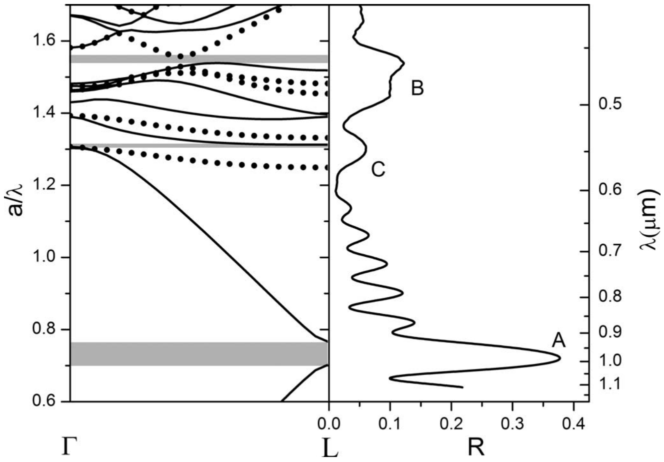

FIG. 5. Left panel: calculated band diagram for an 85% pore filling fraction where three pseudogaps are opened. Right panel: reflectance spectrum for this pore filling fraction where three peaks are observed.

vided into two groups:[5] bands associated with a homogeneous medium with an effective refractive index (linear bands) and those associated with diffraction by different sets of planes (diffraction bands). The latter ones represent eigenmodes with non-null components in crystallographic directions other than the incident (ΓL in our case). This means that light which couples with these modes will have a moment in other directions of the crystal besides the incident one. Even tough many of these bands are uncoupled due to symmetry reasons,[18] allowed modes still exist. We find interesting information about the coupling of these modes with light in reflectance and transmittance spectra (Fig. 4). Different approaches explaining the features which appear in the spectra can be found in the literature.[5,6] In the figure we can observe two dips (1, 2) in transmission which do not correspond to peaks in reflection. This dips appear in spectral regions where just one mode or diffraction band is allowed (E-labeled states). The absence of features in reflection among the existence of dips in transmission can be understood calculating the structure of the mode exited by the light.[19]

Increasing the ZnO filling fraction over 70%, a third pseudogap (C) can be opened between the A and B ones whose width increases monotonically with the filling fraction. For 85% filling fraction, the width of the C pseudogap is enough to observe a peak in the reflectance spectrum (Fig. 5). It can also be observed that, with a degree of infiltration over 70%, the first allowed diffraction band (sixth band) becomes isolated from the others. The group velocity associated with flat bands becomes small,[8] increasing the interaction between electromagnetic radiation and the materials forming the crystal. Such low group velocity modes could be useful to enhance ZnO emission which could eventually open up routes to fabricate efficient light emitting devices in the UV part of the spectrum.

To summarize, we provide theoretical and experimental evidences of the opening of two extra pseudogaps occurring in the high energy range of ZnO inverted opals. The high quality of our samples allows us to perform an optical study of the three pseudogaps by means of reflection and transmission as a function of the pore filling fraction which is accounted for by the calculations. We also present the optical response of the widest high energy pseudogap as a function of the sample thickness. Finally, this process allows us to isolate a nondispersive band which might provide a perfect playground to study low group velocity propagation in three dimensional photonic crystals.

This work has been partially financed by the EU network of excellence FP6-511616 PHOREMOST and by the Spanish MEC through MAT-2003-01237. The authors gratefully acknowledge R. Serna for ellipsometric measurements on ZnO films and J. F. Galisteo-López, B. H. Juárez, and A. Blanco for fruitful discussions.

[1] E. Yablonovitch, Phys. Rev. Lett. **58**, 2059 (1987); S. John, *ibid.* **58**, 2486 (1987).
[2] For a recent review, see C. López, Adv. Mater. (Weinheim, Ger.) **15**, 1679 (2003).
[3] V. N. Astratov, Nuovo Cimento D **17D**, 1349 (1995).
[4] P. Jiang, J. F. Bertone, K. S. Hwang, and V. L. Colvin, Chem. Mater. **11**, 2131 (1999).
[5] J. F. Galisteo-López and C. López, Phys. Rev. B **70**, 035108 (2004).
[6] H. Miguez, V. Kitaev, and G. A. Ozin, Appl. Phys. Lett. **84**, 1239 (2004).
[7] M. Notomi, Phys. Rev. B **62**, 10696 (2000).
[8] K. Sakoda, *Optical Properties of Photonic Crystals* (Springer, Berlin, 2001).
[9] A. Blanco *et al.*, Nature (London) **405**, 437 (2000).
[10] F. García-Santamaría, M. Ibisate, I. Rodríguez, F. Meseguer, and C. López, Adv. Mater. (Weinheim, Ger.) **15**, 788 (2003).
[11] P. D. García, J. F. Galisteo-López, and C. López, Appl. Phys. Lett. **87**, 201109 (2005).
[12] J. W. Goodwin, J. Hearn, C. C. Ho, and R. H. Ottewill, Colloid Polym. Sci. **252**, 464 (1974).
[13] B. H. Juárez, P. D. García, D. Golmayo, A. Blanco, and C. López, Adv. Mater. (Weinheim, Ger.) **17**, 2761 (2005).
[14] H. Yoshikawa and S. Adachi, Jpn. J. Appl. Phys., Part 1 **36**, 6237 (1997).
[15] S. G. Johnson and J. D. Joannopoulos, Opt. Express **8**, 173 (2001).
[16] F. García-Santamaría, J. F. Galisteo-López, P. V. Braun, and C. López, Phys. Rev. B **71**, 195112 (2005).
[17] J. F. Galisteo-López, E. Palacios-Lidón, E. Castillo-Martínez, and C. López, Phys. Rev. B **68**, 115109 (2003).
[18] F. López-Tejeria, T. Ochiai, K. Sakoda, and J. Sánchez-Dehesa, Phys. Rev. B **65**, 195110 (2002).
[19] The specific calculation of the amplitude for these modes of the components in the different crystallographic directions is out of the scope of this work.