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Citation: *Appl. Phys. Lett.* **100**, 091901 (2012); doi: 10.1063/1.3688031

View online: <http://dx.doi.org/10.1063/1.3688031>

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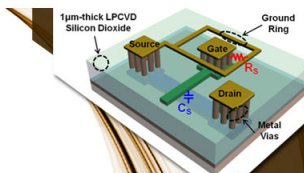
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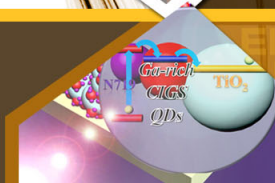
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Emissive properties of SiO₂ thin films through photonic windows

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(Received 20 December 2011; accepted 6 February 2012; published online 27 February 2012)

In this work, we study the selective emission properties of silicon-based three-dimensional photonic crystals coated with thin films of silicon dioxide presenting temperature emission measurements at 600 K of oxidized macroporous silicon structures. The photonic band gap of the structure is centered at 9 μm with 2.5 μm bandwidth. Through this photonic window defined by the gap, a narrow emission peak arises from the oxide layer. We propose the given structure as a selective thermal source for infrared spectroscopy applications in the fingerprint spectral region (6–12 μm wavelength). © 2012 American Institute of Physics. [doi:10.1063/1.3688031]

There has been a strong effort during the last years to develop appropriate thermal sources for infrared (IR) applications such as gas sensing and early detection of leakages,^{1,2} or personnel beacons for Infrared Identify Friend or Foe systems.^{3,4} In these applications, absorption measurements taken by infrared spectroscopy are the key technology which combine high selectivity and sensitivity, high reliability, and fast response time. IR-spectroscopy relies on the characteristic absorption of molecules to estimate the compound and its concentration, especially at wavelengths between 6 and 12 μm , the so-called fingerprint region, where measurements can be taken with the highest selectivity. An essential component of all spectroscopic systems is the radiation source. In general, high temperature thermal emitters are used as IR sources due to the high output power that can be obtained in a broadband spectral region, from the shorter to the larger IR wavelengths. This broadband radiation, however, can represent a main drawback when monitoring single species, as the source emission outside the molecule's absorption bands might be filtered and wasted. There is a need for narrowband (selective) thermal sources with high emissivity in the mentioned spectral region.

Thermal sources are typically metals heated by Joule effect, where emissivity is low and broadband. Ceramic- or silicon-based IR emitters and Globar lamps are also commonly used thermal sources, their emissivity at larger wavelengths is close to the blackbody radiation but still broadband. Therefore, an intermediate element is needed to tune this radiation, absorbing heat and selectively re-emitting IR light in the desired band with the highest emissivity. Photonic crystals (PC) are a suitable material for this purpose due to their ability for suppressing spontaneous emission and engineering thermal radiation in a controllable manner.⁵ Here, we present a macroporous silicon PC (Refs. 6 and 7) with a broadband photonic band gap (PBG) in the fingerprint spectral region. The selective emission behavior of the device is reached by the addition of a thin coating of

silicon dioxide (SiO₂) that presents natural emission peaks around 8.2 and 9.2 μm wavelength inside the forbidden spectral region of the PC. The working spectral region of the proposed selective emitter allows to work at a lower temperature than conventional thermal sources and save power consumption.

These subtle peaks are unique of the thin film configuration,^{8–10} and arise from transverse- and longitudinal-optical vibrational modes. Coating the macroporous silicon with such thin layer allows us to make use of these emission peaks in the device as a selective thermal source. The advantage of the given approach is double: first, the windowing effect allows to release the sharp emission of SiO₂; second, the huge area and the morphology of the oxide layer along the 3D structure greatly enhances the emission of the thin film that otherwise would be very low.

Macroporous silicon samples were prepared by electrochemical etching of silicon^{11,12} in 5 wt. % hydrofluoric acid (HF) solution with temperature stabilized at 10 °C. The starting material was n-type crystalline silicon with (100) orientation and a resistivity of 0.6 Ωcm . In order to define the pore distribution, a lithographic process with a 2- μm -periodicity square pattern was performed at the first stage of the fabrication.

During the etching process of silicon, the applied current and voltage are controlled to produce periodically modulated pores in depth. A sawtooth-like I-V profile was applied to obtain symmetric periods with strong variation of pore diameter from 0.6 to 1.7 μm . The periodicity in depth was chosen to be 2 μm in order to center the PBG of interest at 9 μm wavelength. Fig. 1 shows scanning electron microscope (SEM) images of the fabricated macroporous silicon structures. The formed PC has tetragonal symmetry with 13 periods in depth with a total area of the crystal of 25 mm². Higher aspect ratios and larger areas, up to wafer scale, have also been reported.¹³

Fabricated structures were oxidized in a furnace tube at 1050 °C under pure O₂ atmosphere. The oxidation temperature was chosen to exceed 1000 °C to obtain densified oxide

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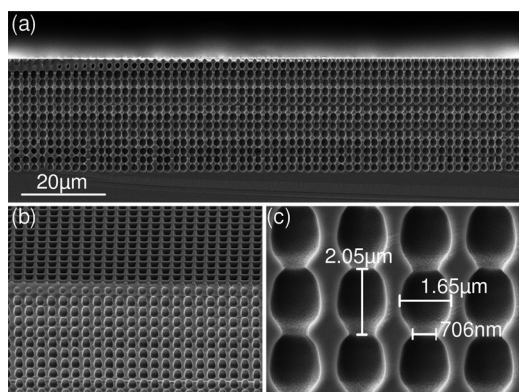


FIG. 1. (a) Cross-section image showing the uniformity of the fabricated structure. (b) Tilted-view showing the square arrangement of the pores. (c) Closer-view image showing the pore modulation in depth.

layers, avoiding porous oxides and residual silicon crystallites.¹¹ Several identical macroporous silicon PCs were oxidized during 5, 10, 17, and 35 minutes to obtain oxides with thickness ranging from 15 to 45 nm. Thinner oxidations were found not to present significant selective emission peaks. Thicker oxidations up to 100 nm showed optical responses similar to the 45 nm coating.

The optical response of the devices was measured using a Bruker Vertex 70 FT-IR spectrometer equipped with the emission adapter A540 that allows the study of the samples' emissivity as a function of temperature up to 673 K. Emissivity values were obtained after conducting a standard two-temperature calibration with a piece of polished silicon covered with a black organic film ($\epsilon = 0.95$) as reference.

In order to study the oxide's absorption in our particular case, oxide-covered macroporous silicon structures, we started by conducting a set of reflectance measurements. A summary is shown in Fig. 2. The spectral region with highest reflectivity around $9 \mu\text{m}$ shown in Fig. 2(a) corresponds to the PBG of the uncoated PC. A strong decay in reflectivity is

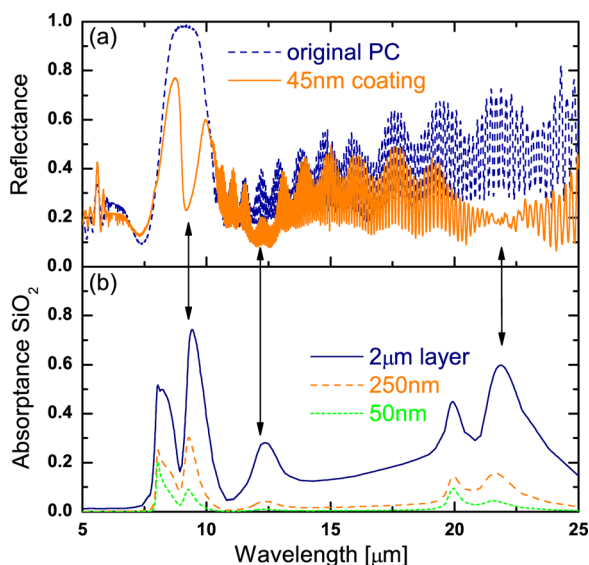


FIG. 2. (Color online) (a) Reflectance of macroporous silicon PC before and after the oxidation process. (b) Simulated absorbance of thin SiO_2 layers for various thicknesses. Arrows indicate the principal spectral regions of correlation between reflectance decay and oxide absorbance.

observed in the middle of the gap in the oxidized sample response (at $9.2 \mu\text{m}$ wavelength, specifically). Several decays are also observed around 12 and $22 \mu\text{m}$ in the mid-IR after the oxidation process. By comparing with the calculated absorbance of SiO_2 thin films¹⁴ in Fig. 2(b), we find a correlation between these decays and the absorption bands of the oxide (indicated by arrows in Fig. 2).

However, the effect of the oxide layer is much stronger than what is expected regarding the low absorbance of SiO_2 thin films. This is due to the morphology of macroporous silicon crystals, which are complex 3D structures with a big conformally coated surface area. The thin coating behaves as a thicker oxide layer when taking into account the whole pore surface. In addition, light experiences multiple diffraction phenomena in the gap region increasing the optical path of light through the oxide.

Fig. 3 shows a comparison of the results for the oxidized macroporous silicon samples with 15, 25, 35, and 45 nm oxide thickness. As expected, there is a dependency of reflectance decay strength in the middle of the gap with oxide thickness, since optical absorption depends on material thickness, while the spectral position of PBG remains unchanged. Furthermore, a small displacement of reflectance dip position in the $9.2 \mu\text{m}$ region is observed. For convenience, this is highlighted in the inset in Fig. 3. This result confirms that absorption peaks are dominated by the thin film phenomena, as reported by Philipp,⁸ stating a dependency of absorption peak position with film thickness. The inset figure also shows the minor influence of the $8.2 \mu\text{m}$ wavelength absorbance band (circled), due to its location at the edge of the structure's PBG.

Kirchhoffs' law of thermal radiation states an equity between absorption and emission in heated objects; therefore, the low reflectance region shown in Fig. 3 must appear as a narrow emissive peak in the middle of the optical gap. This is clearly observed in Fig. 4(a) between 9 and $10 \mu\text{m}$ wavelength by comparing non-oxidized PC response with 25- and 45-nm oxidized crystals. We found no trace of the oxide's emission peaks outside the gap due to the high emissive level of bulk silicon that masks the emission. A generalized increase in emissivity in the whole spectrum due

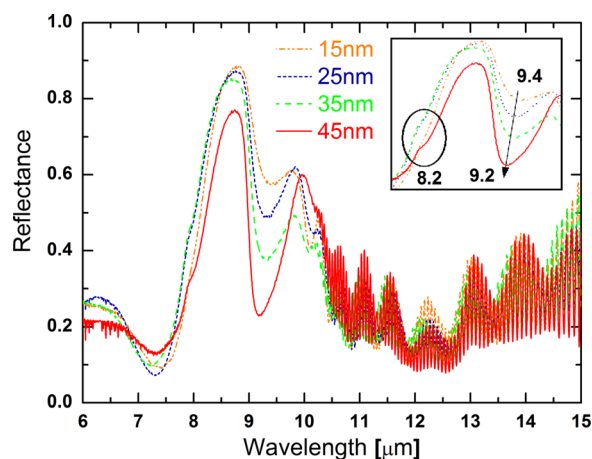


FIG. 3. (Color online) Reflectance of fabricated samples with various oxide thicknesses. Inset highlights the shift of the $9.2 \mu\text{m}$ peak as a function of oxide thickness and the minor influence of the $8.2 \mu\text{m}$ peak.

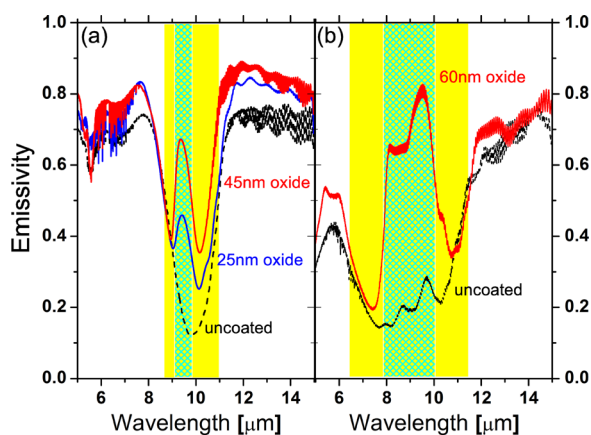


FIG. 4. (Color online) Selective emission measured at 600 K of narrowband (a) and broadband (b) PCs. Both results are compared with the emissivity of non-oxidized sample. Selective emission is highlighted (striped) inside the PBG region.

to the inclusion of the oxide layer is also noticeable. The presented measurements have been carried out at a temperature of 600 K.

To optimize the emitter in the fingerprint region, a photonic structure with wider PBG and wider emission band has been realized. The use of macroporous silicon allows the realization of quasiperiodic structures where periodicity can be progressively increased in depth.¹⁵ This gradual increment gives rise to a photonic structure with broadband PBG in the optical response. This PBG can be observed in Fig. 4(b) from 6.5 to 11.5 μm wavelength. Comparing with the previous periodic structure (Fig. 4(a)), the quasi-periodic crystal presents a gap enlargement from 2.5 to 5 μm.

After 60 nm oxidation, a high emission region is achieved in the middle of the PBG between 8 and 10 μm, thanks to SiO₂ absorption peaks placed at 8.2 and 9.2 μm. The measurements show an overlap between both peaks although this was not predicted by the simulations presented in Fig. 2(b). Calculations were done taking into account flat layers of SiO₂, while in the real experiments oxide is deposited on a 3D structure. We believe this difference between the predicted and the measured optical response comes from the dependence of oxide emission on the morphology of the thin film, as stated in Ref. 9.

In conclusion, a selective thermal emitter in the mid-infrared has been developed here by using the optical properties of thin films of silicon dioxide. We take profit of

the unique properties of photonic crystals to inhibit spontaneous emission in the precise region of interest. Coating the fabricated macroporous silicon structure with a thin oxide layer gives rise to a narrowband thermal source for mid-infrared spectroscopy applications capable to save power consumption. We have fabricated a broadband photonic crystal with 5 μm bandwidth photonic band gap in the fingerprint region in order to disclose the silicon dioxide emission between 8 and 10 μm wavelength. There are several advantages of the given approach: on one side, the amplification of the emissive properties of the thin film due to the increment of the optical path in the gap region and on the other side, selective emission peaks are intrinsic of the coating material and independent of the fabricated photonic structure, guaranteeing reproducibility of the emitter. This approach is extensible to other coatings with selective emission properties as the photonic gap of the crystal can be tuned to unmask the thin film emission at any desired wavelength.

This work has been partially funded by TEC2008-02520 and the Network of Excellence “Nanophotonics for Energy.”

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