

Surface-sensitive diamond photonic crystals for high-performance gas detection

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Diamond slotted photonic crystal (PhC) cavities were fabricated and used for gas detection. They exhibit wavelength sensitivity reaching a 350 nm per unit change of the refractive index of the gaseous environment of the PhC. With a simple oxidized surface termination, diamond PhCs display an ultrahigh sensitivity to the surface adsorption of polar molecules. Gaseous concentrations as low as 80 parts per million (ppm) of hexanol vapor in nitrogen are probed, and a detection limit in the ppm range is inferred, demonstrating a high interest of such devices for trace sensing. © 2016 Optical Society of America

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Slotted photonic crystals (PhCs) have recently gained considerable interest for sensing applications due to the tight confinement of the optical mode in the low refractive index region that is provided by the slot in the photonic crystal. Since the PhC transmission is significantly altered by any subtle refractive index change in the slot [1–4], this property can be used to sense refractive index changes due to the modification of the surrounding environment of the PhC caused by, for example, a slight concentration evolution in a mixture of two gases with different refractive indices. Silicon and III-V semiconductors has successfully been used to demonstrate the fabrication of PhC [2,5–7] or ring resonator [8,9] gas sensors. However, it is often challenging to prepare stable and highly selective functionalizations on semiconductors [3]. In contrast, diamond has been widely documented for its high chemical stability and versatility [10,11], as well as its outstanding optical and mechanical properties. Stable functionalizations of the diamond surface for the detection of specific chemical species have already been successfully used in the case of MEMS [12] or electronic devices [13]. However, these sensor sensitivities remain low, and an enhancement of their performances is desired. A competing approach consists of combining the sensitivity of 2D slotted PhCs with the versatile diamond interface for the development of diamond-based sensors, which are able to detect and identify

volatile organic compounds with applications in environmental monitoring, safety, or medicine.

In this Letter, we fabricated diamond PhCs exhibiting specific surface affinities, thanks to two diamond surface terminations, namely a hydrogenated one that can be reliably prepared using a plasma hydrogenation of the sample and an oxidized one that can be prepared using, for example, exposure of a diamond surface to UV under pure oxygen or air [14]. In the first case, the surface has no particular affinity to polar molecules, i.e., molecules that have a natural electric dipole or multipole moment such as water or alcohols [15]. In the second case, the oxidized surface termination allows a dipole–dipole interaction with polar molecules and has an increased affinity to them. As a demonstration, pentane (C_5H_{12} , an apolar molecule) and hexanol ($C_6H_{13}OH$, a polar molecule) vapors were detected successfully with different sensitivity and dynamics. Similar results are expected for other polar and apolar molecules. We observed a cavity resonance wavelength shift of 7.5 pm/parts per million (ppm) when an oxidized diamond PhC is exposed to hexanol vapors. We unambiguously attribute this high sensitivity to the cumulative effect of (1) the sensitivity to refractive index changes of the volume surrounding the photonic crystal, and (2) the refractive index change induced by the surface adsorption of polar molecules on the oxidized diamond surface.

The investigated structures consist of a slotted PhC cavity made in a width-modulated waveguide with a design similar to the one used in silicon [16]. The scanning electron microscope image of the structure is provided in Fig. 1(a) with its access waveguides. The photonic crystal has a period of $a = 640$ nm and a hole radius of 200 nm; it is fabricated in a 360 nm thick slab of polycrystalline diamond grown on a silicon wafer as described in [17,18]. The slot is 130 nm wide, and the PhC waveguide has a width equal to $1.15a\sqrt{3}$. The 30 holes near the waveguide center are shifted in a perpendicular direction with respect to the waveguide, to create a localized defect state that has been thoroughly analyzed in [18] with 3D-finite difference in time domain (FDTD) simulations. Suspended access waveguides allow injecting light into the PhC and collecting it from the outside. The fabricated PhCs are characterized in a gas cell that can be filled using various gases or pumped down to a

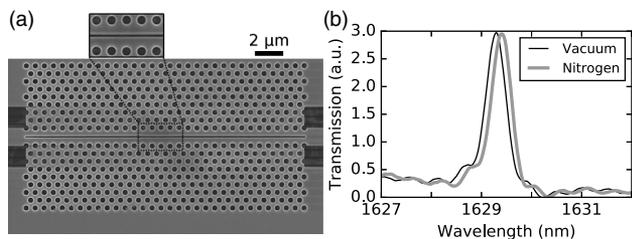


Fig. 1. (a) Scanning electron microscope view of the structure with its access waveguides. The PhC period, the hole radius, and the slot width are equal to 640, 200, and 130 nm, respectively. (b) Transmission spectrum of the cavity near the resonance ($Q = 5400$) when the refractive index of the surrounding medium is changed from 1 (vacuum) to 1.00028 (nitrogen).

one-millibar pressure. Care was taken for all gases to be kept at the same temperature as the cell to avoid temperature gradients during the exposure tests. A tunable laser in the wavelength range of 1560–1680 nm with 30 μ W output power is used as a light source. Its wavelength can be continuously swept, and successive transmission measurements can be recorded every 5 s. Light is injected and collected through the cell windows using two microscope objectives with a working distance of 5 mm and a numerical aperture of 0.65. The transmitted power is recorded by a photodiode and the resonance wavelength extracted using a Lorentzian fit. The fabricated cavity exhibits a resonant frequency at $\lambda = 1629$ nm, in agreement with the simulations, and a quality factor of 5400 as seen in Fig. 1(b). The experimental Q -factor is much smaller than the simulated one that is equal to 8×10^5 . This discrepancy is mainly attributed to light scattering at grain boundaries in polycrystalline diamond [18].

Conventionally, one often characterizes the refractive index change due to the modification of the PhC surrounding medium by the frequency shift observed, as expressed in nanometers per a unitary refractive index change. To characterize the diamond photonic crystal as a gas sensor, at room temperature, we compared the resonance frequency of the cavity when it is filled with nitrogen and when it is under a partial vacuum of 100 Pa. As can be seen in Fig. 1(b), a frequency shift of 100 pm is observed for a diamond in oxidized state. Since there is no chemisorption reaction expected between N_2 and diamond, the frequency shift can be attributed to a change of the refractive index of the surrounding medium of the PhC. From the value of the refractive index of nitrogen at ambient temperature, namely $n_{\text{nitrogen}} = 1.00028$, we estimate a sensitivity $S = \Delta\lambda/\Delta n \approx 0.1/2.8 \times 10^{-4} = 360$ nm/RIU (refractive index unit), a value similar to that obtained with silicon photonic crystals [2,19,20]. We also calculated the slotted PhC sensitivity with 3D-FDTD simulations. The measured sensitivity is in good agreement with the simulated one that is equal to 500 nm/RIU. It should also be emphasized that the sensitivity of this diamond PhC structure to unwanted temperature changes is one order of magnitude smaller than the one of a similar structure in silicon since the thermo-optical coefficient of diamond, $\frac{1}{n} \frac{\partial n}{\partial T}$, is equal to 4×10^{-6} [21], 10 times less than the one of silicon [22]. The resonance wavelength shift due to temperature fluctuation is expected to be less than ± 3 pm, much smaller than the measured shifts. To further reduce the sensitivity to unwanted temperature changes, a Peltier stabilizer or specific athermal designs may be necessary.

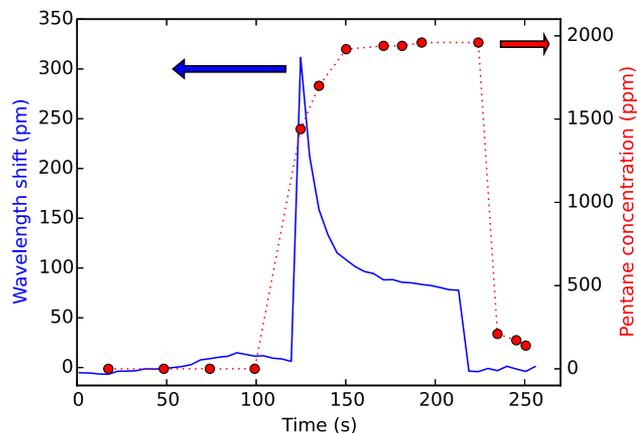


Fig. 2. Time response of an oxidized diamond PhC to pentane vapors (blue solid curve, left scale) and pentane vapor concentration measured with a PID (red dotted curve, right scale).

To test the surface sensitivity of the PhC, a simple gas generator system was used to generate gas vapors. A line providing a controlled nitrogen flow regulated at 2 l/min is connected to the gas cell and is used as a dilution background. A deviated line equipped with two valves allows us to incorporate the analyte while keeping the total flow rate constant. A photo ionization detector (PID) is used to check the analyte concentration in a steady state. To illustrate the diamond surface sensitivity, pentane and the hexanol molecules are used. These molecules, with similar masses, are, respectively, apolar and polar and, thus, are expected to behave differently with the diamond surface. The same behavior is expected with other apolar molecules such as methane, or polar molecules such as water vapor.

Figure 2 shows the evolution of the resonance shifts of a diamond PhC cavity when exposed to diluted pentane vapors. The diamond surface has been oxidized by the oxidation process as described in [18], namely using a 2 h UV exposure at 250 hPa under air, leading to the formation of polar functions on the diamond surface. No further surface treatment was necessary to assess the reactivity of the PhC to the pentane vapors. The PhC was exposed to a pure nitrogen flux during the first 120 s and then to a nitrogen flux with pentane vapor during the following 100 s before being again re-exposed to pure N_2 . A transmission spectrum is recorded every 5 s, and a Lorentzian fit of the resonance allows us to precisely determine the frequency shift (blue solid curve). Simultaneously, the pentane concentration measured with the PID is recorded (red dotted curve). As the temperature is kept constant during exposure and as pentane displays a refractive index that is larger than that of nitrogen, the redshift observed during gas exposure is clearly associated with the increase of the refractive index of the PhC environment. Since no reaction is expected between the pentane and the oxidized diamond surface, the PhC is only sensitive to a refractive index change in its vicinity. The initial transient spike at the onset of the pentane gas flow is due to the overpressure when the valve is switched on to inject the analyte, prior pressure, and flux stabilization. The measured frequency shift reaches 80 pm. After exposure, the frequency of the resonance returns to its initial position in less than 5 s. The measured concentration with the PID also returns to zero, but after more than 1 min and is not represented in the figure. The fact

that the dynamics of the PhC gas sensors is faster than the one of the PID is due to the small volume probed by the PhC sensors, as compared to the PID that measures the pentane concentration in a much larger volume of 200 ml and, as a consequence, smoothes out the rapid variation of pentane concentration. The readout from the PID gives a concentration of 2000 ppm after equilibrium. We can deduce from the previous measurement that the sensitivity, s , of the PhC sensor, here expressed as the wavelength shift over the analyte concentration $s = \Delta\lambda/C_{\text{analyte}}$, reaches 0.04 pm/ppm of pentane. Since the fluctuation in the cavity resonance wavelength measurement is ± 10 pm, we can estimate that the sensor is able to detect pentane concentrations as low as 250 ppm. Thanks to the very small volume probed by the PhC cavity that is only 5×10^{-14} cm³, if we consider the pentane as an ideal gas, the limit of detection corresponds to 300 molecules of pentane in the volume probed by the PhC.

Since pentane is an apolar molecule, there is no adsorption between pentane and the diamond surface. Moreover, because the diamond film is not porous, no swelling of the cavity is expected as it can be the case with polymers [23]. This explains the relatively low sensitivity of the PhC to pentane or to similar apolar molecules since, in this case, the PhC behaves as a sensor sensitive to the refractive index change of the volume probed by the optical mode. The PhC response to a polar molecule such as hexanol is expected to be very different, since a reversible binding of a polar molecule with the oxidized diamond surface is possible through a dipole–dipole interaction. As a consequence, an increase of the refractive index due to molecular adsorption at the diamond surface only is expected.

To confirm this hypothesis, the PhC cavity has been exposed to a nitrogen flux with hexanol vapor, a polar molecule. The hexanol concentration has been measured using the PID and tuned at 80 ppm, i.e., 25 times lower than that used for the pentane vapor. Because of the lower volatility of hexanol than pentane and because of the lower hexanol concentration, the pressure was kept constant during the experiment. The PhC is exposed to pure nitrogen during 120 s, followed by nitrogen mixed with hexanol vapor during 380 s before being again exposed to pure N₂. As seen in Fig. 3, the wavelength shift induced by the hexanol vapor reaches values of 600 pm. This value is much higher than that induced by pentane, and the time response of the PhC is much slower for hexanol than it is for pentane. In the case of hexanol, we consider that two processes coexist for the wavelength shift: a global refractive index change that corresponds to the replacement of the gas in the cell, and a surface refractive index change caused by the hexanol adsorption and desorption from the diamond surface. To be more quantitative, the part of the curve corresponding to hexanol desorption under nitrogen has been fitted using a two-phase exponential model. This gives time constants of 19.1 and 144 s for the fast and slow decays, respectively. The fast decay time is associated with the time necessary to drain the hexanol vapors from the pipes and the gas cell, while the slow decay time is associated with the binding time constants of the hexanol molecules on the diamond surface.

To confirm that the observed response is due to the reactivity of the diamond surface to the hexanol adsorption and not to some adsorption on the gas cell itself, the surface of the same sample has been hydrogenated using the process described in [18] with a shorter duration to avoid a full hydrogenation of the

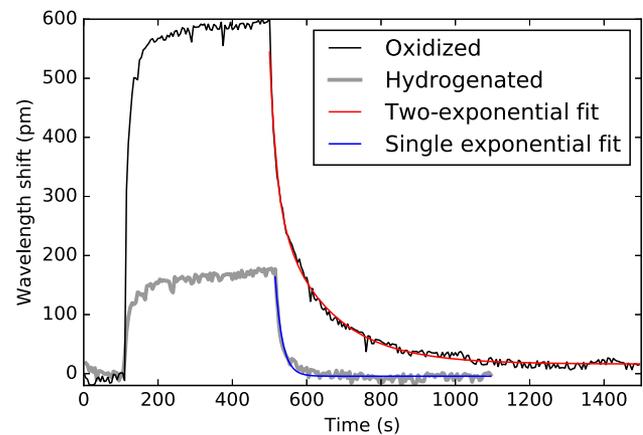


Fig. 3. Time response of a diamond PhC exposed to a N₂ flux containing 80 ppm of hexanol during 380 s for two different diamond surface states: oxidized diamond PhC (thin black line) and a partially hydrogenated diamond surface (thick gray line). The two-exponential fit equation of the wavelength shift as a function of time is $\Delta\lambda = 276 \exp(-t/144) + 252 \exp(-t/19.1) + 16.2$. The single exponential fit equation is $\Delta\lambda = 168 \exp(-t/19.2) - 4.33$.

surface that has been shown to strongly decrease the Q -factor [18]. Here, after hydrogenation, the quality factor is reduced from 5400 to 3500. The hydrogenated sample has been exposed to hexanol vapors in the same conditions as the oxidized one. In this case, the wavelength shift is only 180 pm, a value three times smaller than in the case of an oxidized surface. Moreover, the time response of the PhC is much faster than in the case of the oxidized one. A single exponential curve fitting gives a time constant of 19.2 s. As expected, this value is associated with the time required to drain the experimental setup from hexanol; it is very similar to the fast decay time measured in the case of an oxidized diamond.

For an oxidized diamond PhC, in the case of hexanol vapors, we can deduce a sensitivity of 7.5 pm/ppm and estimate a detection limit of 1.3 ppm, i.e., a value 150 times below that probed with pentane. This detection limit is about 10 times better than that of other photonic crystal gas sensors capable of sensing methane [6,20] or isopropanol vapors [23]. This detection limit still compares favorably with more complex photonic structures covered with a porous material such as a ZnO film [9] or aluminosilicate film [24] that, respectively, achieve estimated detection limits of 25 ppm for ethanol vapor and 5 ppm for ammonia. Using a silicon photonic crystal covered by a polymer, Chen *et al.* reported a sensitivity almost 10 times above that reported here [7]. However, this high sensitivity is related to that of the polymer matrix that captures target molecules in a volume that spreads throughout 70 nm around the photonic crystal surface. This may reflect a high sensitivity, but the diffusion process through the large polymer matrix is terribly slow with respect to a simple surface reaction as observed with diamond. Indeed, sensitivity down to 2 parts per billion with a response time of more than 1 h has been reported for a 2 μ m thick coating over a silicon nitride ring resonator [25]. In fact, here the reaction observed on the oxidized diamond photonic crystal is a surface reaction, rather than a molecule diffusion and accumulation through an absorptive layer. As a result, it exhibits a much shorter response time, good reversibility, and repeatability. It also offers the perspective

Table 1. Long-Term Evolution of the Sensitivity and Resonance Wavelength of the Diamond Photonic Crystal

Measurement	Initial	7 Days	80 Days	Regenerated
Wavelength shift (pm) under hexanol vapors	600	500	180	610
Resonance wavelength (nm)	1626.4	1626.7	1629.5	1626.8

of the detection of a very small number of molecules, as the sensitivity in the ppm range is of the same order as the one encountered in more mature diamond sensors such as surface acoustic wave-based sensors [26].

Finally, the long-term evolution of the sensitivity of the oxidized diamond PhC has been evaluated. A sample with oxidized surface PhCs was stored without particular care during 80 days. As seen in Table 1, the PhC response to hexanol vapors has slightly decreased after seven days. After 80 days, a third measurement with hexanol vapors has been done, and this decrease is clearly apparent. At the same time, a shift of the cavity resonance wavelength of more than 3 nm to longer wavelengths, while the quality factor of the resonance remains stable near 5300, indicates a substantial increase of the refractive index at the diamond surface. This increase can be attributed to a fouling phenomenon. The nature of the adsorbed molecules is not precisely known, but they do not absorb light significantly at 1.55 μm since the quality factor remains unchanged. The adsorption of molecules on the diamond surface is coherent with the decrease of the PhC response to hexanol vapor since adsorbed molecules prevent hexanol from reaching the diamond surface. The initial state of the diamond surface can be recovered by using again the oxidation process initially used to prepare the sample. Indeed, after re-oxidation, the organic contaminants have been transformed into volatile species, and a clean oxidized diamond surface is restored for sensing. As seen in Table 1, the resonant wavelength is blueshifted after the regenerative oxidation, but the diamond is not etched by the process since the resonant wavelength is slightly longer than the initial one. The PhC response to hexanol vapors is also restored to its initial value. These results show that some molecules are adsorbed on the oxidized diamond surface. Such an adsorption can be avoided if the samples are stored under neutral atmosphere or vacuum. This phenomenon might put some constraints for the future realization and use of ultrahigh quality factor cavities on diamond. In the case of a diamond sensor application, the accumulation of contaminants at the diamond surface is not an issue since the simple UV exposure previously described allows the regeneration of the sensors.

In conclusion, we have demonstrated the fabrication of a diamond PhC cavity with a high sensitivity to surface adsorption of a specific class of molecules. Detection limits to hexanol vapors down to 1.3 ppm have been observed on an oxidized diamond surface. This value appears to be mainly limited by the accurate measurement of the resonance shift that can be improved using higher Q -factor cavities and minimizing the influence of external parameters such as small temperature changes. Better cavity designs with a larger surface-to-volume ratio as reported in [27] can also strongly increase the sensitivity measured in nm/RIU. Finally, we have shown that fouling occurs on oxidized diamond photonic crystals when the PhCs are stored in air. These results represent a first step toward the functionalization of diamond

PhCs for sensors targeting the detection of specific gas traces at high sensitivity. For example, such a functionalization could target explosive gases and could be done by grafting odorant binding proteins using the chemical processes described in [12].

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