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Vertical-cavity surface-emitting laser vapor sensor using swelling polymer reflection modulation

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Vapor detection using a low-refractive index polymer for reflection modulation of the top mirror in a vertical-cavity surface-emitting laser (VCSEL) is demonstrated. The VCSEL sensor concept presents a simple method to detect the response of a sensor polymer in the presence of volatile organic compounds. We model the physics as a change in the top mirror loss caused by swelling of the polymer upon absorbing the target volatile organic compound. Further we show how acetone vapors at 82 000 ppm concentration can change the polymer coated VCSEL output power by 20 μW. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4754291]

Vapor sensing is important in environmental and health monitoring where it is used to trace the concentration of a volatile organic compound (VOC), e.g., acetone, in time.1 Different transduction mechanisms for detection of VOCs has been proposed over the years such as polymer coated cantilevers, thin-film resistors, and optical fibers.2–4 Sensors using polymer coatings have the advantage that a unique fingerprint response for each VOC can be obtained by using an array of different polymers.5,6 Vertical-cavity surface-emitting lasers (VCSELs) are easily made into arrays and are thus a good candidate for the optical detection of such polymeric vapors at 82 000 ppm concentration can change the polymer coated VCSEL output power by 20 μW.© 2012 American Institute of Physics.

In order to model the sensor we use the standard laser equations.11 The laser power output can be written as

\[ P(I) = \eta_d(I) \frac{h \nu}{q} [I - I_{th}(I)], \]

where \( h \) is Planck’s constant, \( \nu \) the lasing frequency, \( q \) the electron charge, \( \eta_d \) the differential quantum efficiency of light output from the top mirror, \( I \) the drive current, and \( I_{th} \) the threshold current. In Eq. (1) it is indicated that the power depends on the optical propagation phase \( \phi = \frac{2\pi}{\lambda_n} \) of the sensing polymer of thickness \( t \) and refractive index \( n_p \). From transfer matrix theory the mirror loss for a DBR stack with a swelling polymer coating can be found to be

\[ \alpha_m(\phi) = \frac{1}{L} \ln \left\{ \frac{n_A + n_B(\phi) - n_A\sin^2(\phi)}{n_C + n_D(\phi) - n_C\sin^2(\phi)} \right\}, \]

where

\[ n_A = \left( \frac{n_A n_L}{n_A n_H} - n_0 \right)^2 \]

\[ n_C = \left( \frac{n_A n_L}{n_A n_H} + n_0 \right)^2 \]

\[ n_B = \left( \frac{n_B n_H}{n_B n_L} - n_p \right)^2 \]

\[ n_D = \left( \frac{n_B n_H}{n_B n_L} + n_p \right)^2 \]

where \( n_s \) is the refractive index of the substrate, \( n_L \) and \( n_H \) are the low and high refractive index of the DBR, \( n_0 \) the

![Figure 1](http://apl.aip.org/abs/images/143505-1/101143505-1-1024x683.png)
refractive index of air, and \( n_p \) the refractive index of the polymer. For a zero thickness \( \phi = 0 \) the mirror loss as defined in Eq. (2) is simplified to the expected result for a DBR mirror. The change in mirror loss changes the differential quantum efficiency according to

\[
\eta_{dl}(\phi) = \eta_d F_d(\phi) \frac{\alpha_m(\phi)}{\langle x_i \rangle + \alpha_m(\phi)},
\]

where \( \eta_d \) is the internal quantum efficiency, \( F_d \) the fractional output of the top mirror, and \( \langle x_i \rangle \) the total cavity loss. Assuming a logarithmic gain-current relation the threshold carrier density depends exponentially on the mirror loss as

\[
N_{th}(\phi) = N_e \exp \left\{ \frac{\langle x_i \rangle + \alpha_m(\phi)}{N_w \Gamma_1 \gamma_0} \right\},
\]

where \( N_e \) is the transparency carrier density, \( N_w \) the number of quantum wells, \( \Gamma_1 \) the single-well confinement factor, and \( \gamma_0 \) the gain coefficient. Thus the threshold current also depends exponentially on the mirror loss as

\[
I_{th}(\phi) = \frac{q N_w V_1}{n_i^2} \left[ B N_{th}(\phi)^2 + C N_{th}(\phi)^3 \right],
\]

where \( V_1 \) is the single-well volume. Equations (1)–(7) describe the response of the VCSEL to a change in the polymer optical thickness or phase \( \phi \). From taking the derivative of Eq. (1) with respect to the phase \( \phi \) it is found that the term containing \( \partial \eta_{dl} / \partial \phi \) is of opposite sign to that containing \( \partial \eta_0 / \partial \phi \). Hence in order to operate at maximum responsivity the laser drive current is set close to \( I_{th} \), such that the contribution of the change in \( \eta_{dl} \) becomes negligible. Equation (2) shows that the mirror loss depends on the sine to the phase, and therefore the optical film thickness should be different from that of an anti-reflection coating, \( N_{tr} = \frac{2}{\pi} \langle x_i \rangle \), as there the sensitivity of the sensor is zero. To model the change in \( \phi \) we assume a swelling type behavior. It has been shown that the optical thickness, \( N_{tr} \), of the polymer can be related to the acetone partial pressure through the theory of Flory-Huggins sorption. The degree of swelling, \( \alpha \), as function of the acetone partial pressure, \( P \), normalized to the saturation pressure, \( P_{svp} \), is given by

\[
P = P_{svp} \left( 1 - \frac{1}{\alpha} \right) \exp \left\{ \frac{1}{\alpha + \zeta / \alpha^2} \right\},
\]

where \( \zeta \) is the Flory-Huggins interaction parameter. We use the estimate \( \zeta = 0.8 \) from the analysis carried out by Mönch et al. on the transmittance of a polystyrene/polymethylmethacrylate optical Bragg filter. The thickness \( t \) of the swollen polymer

\[
t(p) = \alpha(p) t_0,
\]

depends on \( \alpha \) and the initial thickness \( t_0 \). The refractive index of the polymer, \( n_p \), depends on \( \alpha \) as given by Lorentz-Lorenz theory

\[
\frac{n_p^2 - 1}{n_p^2 + 2} = \frac{\alpha}{\langle x_i \rangle} \frac{1}{n_p^2 + 2} + \frac{1}{n_p^2 + 2} \frac{1}{\alpha n_p^2 + 2},
\]

where \( n_s \) is the solvent refractive index and \( n_{p,0} \) is the polymer refractive index. The refractive index decreases as the thickness increases, which is due to the lower refractive index of the absorbed vapor. The output power of the VCSEL was simulated using Eqs. (1)–(10) together with the parameters in Table I. We have chosen parameters representative for a GaAs quantum well VCSEL to model the response. For the parameters \( C \) and \( \langle x_i \rangle \) to be reasonable, they have been fitted to the laser diode used in the experiment. In the model the thickness has been set to a value slightly above \( \phi = \pi/2 \). In Fig. 2 the computed laser diode power (dashed line) is shown as a function of time. The output power is seen to increase for an increasing acetone concentration. Not shown in the graph, the model predicts decreasing \( I_{th} \) and \( \eta_{dl} \), which causes the output power to increase at constant current.

Two single-mode 850 nm VCSEL diodes (Finisar® HFE4093-332) were used for the experiment: (1) one reference, (2) another coated with 80 nm polystyrene by plasma polymerization. The thickness was measured on a silicon wafer.

![Figure 2](image-url)
wafer coated concurrently with the VCSEL. The response measurement was performed by flowing diluted acetone vapors through a measurement chamber at a constant pressure of 600 Torr. The measurement chamber had a volume of 1800 cm$^3$ with a filling time constant of 36 min at a flow of 50 sccm. During response measurements the VCSEL forward bias current was swept from 2 to 0.5 mA at a sampling frequency of 33 mHz. The VCSEL output power was measured using Si photodiodes (Thorlabs$^\text{®}$ FDS100). The acetone response of the coated VCSEL for a single cycle (90 min acetone flow, 90 min nitrogen flow) is seen in Fig. 2 together with the acetone concentration calculated based on the input flows and the chamber volume.\textsuperscript{10} The response of the coated VCSEL is seen to follow the acetone concentration both during filling the chamber with acetone and on purging the chamber with nitrogen. The response is 21 $\mu$W for an acetone concentration of 82 000 ppm. The polymer thickness was not optimized for responsivity, and the VCSEL could not be operated at high powers due to power roll-off at increasing currents. To estimate the sensitivity that could be achieved with this technique we consider the following ideal case. For a laser diode operated at $I_{th}$ with a $t = 80$ nm thick sensing polymer we get a responsivity of 2 nW/ppm at $P_{1,0} = 2$ dBm in the ppm acetone concentration range by using Eqs. (1)–(10) together with Table I. The ratio of the responsivity to the detected optical power is around $-120$ dB in the electrical domain. The sensitivity will depend on the noise floor as determined by the VCSEL in the case of the photodetection being shot noise limited. Typical values for the VCSEL relative intensity noise (RIN) are $-120$ to $-130$ dB/Hz, and thus ppm sensitivity should in theory be achievable. The sensitivity then comes down to the responsivity of the polymer. From Eqs. (8)–(10) and Table I we calculate that the optical thickness changes less than 0.5 nm from 10 ppm to 10 000 ppm. This is in the order of the surface roughness of the polymer, and thus it can be expected that only the change in refractive index will contribute to the responsivity. Removing Eq. (9) from the model the responsivity becomes $1$ nW/ppm which should still enable detection with ppm sensitivity. Detection of VOCs at ppm is demonstrated by mass sensing using polymer coated cantilevers.\textsuperscript{17}

![FIG. 3](image-url)\textsuperscript{3}

**FIG. 3.** Plot of the coated VCSELs differential quantum efficiency, $\eta_{dl}$ (solid line, left axis) and threshold current $I_{th}$ (dashed line, right axis) versus time.

In summary we have shown that coating a VCSEL with a swelling polymer enables the transduction of VOCs. Specifically, detection of acetone has been demonstrated. The sensor can be made using standard VCSEL processing technology and the photodetector integrated epitaxially to make a compact, mass-producible sensor. Integrating the photodiode at the opposite side of the swelling polymer further has the advantage that a larger sensitivity can be achieved.\textsuperscript{12}

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\begin{thebibliography}{99}
\bibitem{3} J. Li, Y. Lu, Q. Ye, M. Cinke, J. Han, and M. Meyyappan, *Nano Lett.* 3, 929 (2003).
\end{thebibliography}