

Detection of chemical species using ultraviolet microdisk lasers

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(Received 19 May 2004; accepted 19 August 2004)

We have utilized hybrid zinc oxide/silica microdisk lasers to sense volatile organic compounds, such as toluene and nitrobenzene. Nonspecific adsorption of these organic molecules onto the microdisk surface causes an increase in the disk refractive index, ultimately resulting in a redshift of the observed lasing wavelengths. The monitoring of these shifts provides the sensing modality. Microdisk lasers were found to respond rapidly and reversibly to the investigated chemicals demonstrating, in principal, the chemical and biological sensing capabilities of such devices.

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Over the past few years, several techniques have been developed for the construction of chemical sensors based upon photonic devices. Among them, sensors based on microdisk or microsphere resonators have demonstrated superior sensitivity due to very high quality factors of the resonances.^{1–8} This high refractive index sensitivity is essential when contemplating the detection of a single or a few molecules.^{4,6} Microdisks and microspheres sustain whispering gallery (WG) modes that are confined by total internal reflection at the boundary. The large quality factor of WG modes results in very high intracavity light intensity and extremely narrow resonant width.³ To this point, two mechanisms have been proposed and realized for microdisk/microsphere sensor applications. The first type of microdisk/microsphere sensor relies upon the buildup of pump light intensity inside the cavity to enhance the fluorescence of molecules near the cavity surface.^{2,7} The second variety measures the spectral shift of cavity modes or decrease of transmission, due to refractive index change of the cavity or an increase of optical absorption accompanying target localization.^{1,4,6} Owing to the extremely narrow linewidths displayed by WG modes, tiny spectral shifts, and thus a small number of molecules can be detected.⁵ However, in these demonstrations, the detection of spectral shift requires a laser source whose frequency can be continuously tuned. Moreover, the efficient evanescent coupling of light into and out of WG modes requires precise optical alignment, which is difficult to realize and maintain in a real-world sensing application. To overcome the above-mentioned limitations, we utilized microdisk lasers to sense the presence of volatile organic compounds. In particular, we detected the shift of lasing frequency when chemical molecules are adsorbed to the disk surface. As compared to passive cavities, the narrowing of WG modes by stimulated emission leads to a further improvement of sensitivity.

Recently, we fabricated ultraviolet microdisk lasers on silicon substrates.⁹ Silicon dioxide (SiO₂) microdisks were fabricated on a commercial silicon wafer by a combination of photolithographic, reactive ion etching and wet etching methods. Subsequently a thin layer of nanocrystalline zinc oxide (ZnO) was grown over the SiO₂ disks by metalorganic chemical vapor deposition. ZnO is a wide band gap semiconductor, and it served as a gain medium under optical pump-

ing. Scanning electron microscopy revealed that the SiO₂ disk surface was uniformly covered by ZnO nanoparticles with an average size of 30 nm. Lasing oscillation in the whispering gallery modes was realized at room temperature. Since adsorption of organic molecules onto metal oxide surfaces is largely due to nonspecific van der Waals interactions, we chose to examine the adsorption of toluene and nitrobenzene onto the microdisk surfaces. The observed sensitivity to these two molecules demonstrated the feasibility of ZnO/SiO₂ microdisk laser-based sensing scheme.

Beginning with toluene, we introduced the volatile phase analyte into a homemade sample cell permitting simultaneous optical interrogation. The cell, constructed from aluminum, had a TorrSeal adhered quartz window and two chromed luer lock ports to facilitate vapor delivery. Both of the analytes were initially prepared as saturated vapors in organic impermeable Tedlar bags (Pollution Measurement Corporation, Oak Park, IL). Subsequent vapor dilution, with N₂ gas, and delivery was performed using a Model 1010 Precision Gas Diluter (Custom Sensor Solutions, Naperville, IL). ZnO/SiO₂ microdisk lasers were optically pumped by a frequency tripled mode-locked Nd:YAG laser ($\lambda = 355$ nm 10Hz repetition rate, 20 ps pulse width). A microscope objective lens (10 $\times$) was used to focus the pump beam onto a single disk. A portion of the emission from the WG modes was scattered in the normal direction and collected by the same objective lens. Lasing spectra were then taken by a 0.5 m spectrometer with a liquid nitrogen cooled charge-coupled-device array detector.

Keeping the pump intensity above the lasing threshold, lasing spectra were measured upon exposure to toluene vapor. Figure 1 shows the spectra of laser emission from a 10- μ m-diam microdisk at the incident pump pulse energy of 15 nJ. The SiO₂ layer is 320 nm thick, and the ZnO layer is $\sim$ 55 nm thick. As shown in Fig. 1, lasing was observed in several WG modes. As the saturated toluene vapor, in N₂, flew into the sample cell, molecules were adsorbed onto the microdisk surface. The adsorption led to an increase of the effective index of refraction of the disk, thus the WG modes were shifted to longer wavelengths. After equilibrium was established between the vapor phase and surface-bound toluene molecules, the lasing wavelength did not shift further. Upon flushing with pure N₂ gas, the lasing modes returned to their initial wavelengths.

To test the detection range and linearity of the sensor, we then exposed the microdisk laser to varying concentrations

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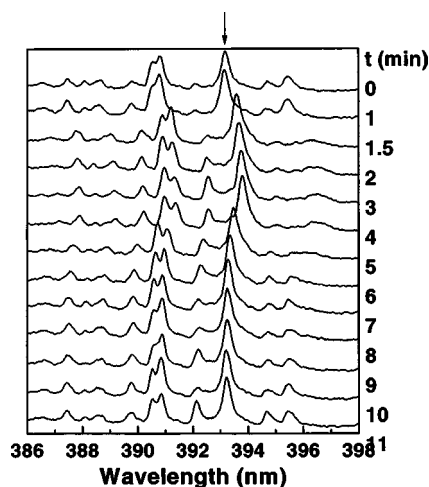


FIG. 1. Temporal evolution of emission spectra of a microdisk laser upon exposure to saturated toluene vapor in N_2 . The disk diameter is about $10\ \mu\text{m}$. The incident pump pulse energy is fixed at 15 nJ. At $t=1$ min, saturated vapor is introduced into the sample cell. At $t=4$ min, the vapor is switched to pure N_2 . The time interval is shown in units of minutes.

of toluene vapor. As the concentration was increased, in terms of percentage of saturated toluene vapor, the lasing wavelength shifts monotonically to longer wavelengths. Figure 2 demonstrated this by plotting the lasing wavelength shift as a function of the percentage of saturated toluene vapor exposed to the microdisk laser. Finally, we investigated the temporal response characteristics of the sensing scheme. Shown in Fig. 3 are the responses of a microdisk laser to both 50% and 100% saturated toluene vapor in N_2 . Both experiments validated the reversibility of the sensor response and showed a response time on the order of half a minute. While still very respectable, the relatively slow response is not a product of the sensing media or approach, but rather an artifact caused by the vapor delivery system employed. Specifically, the dilutor pump has a relatively large mixing chamber and the Bev-A-Line IV tubing used to deliver the vapor has a small, but significant affinity for these organic molecules. The result of this is that equilibrium must be reached not only at the disk surface, but also along the entirety of the tubing length causing the artificially slow response.

Figure 4 shows an extension of microdisk laser sensor to the detection of nitrobenzene vapor. The experimental expo-

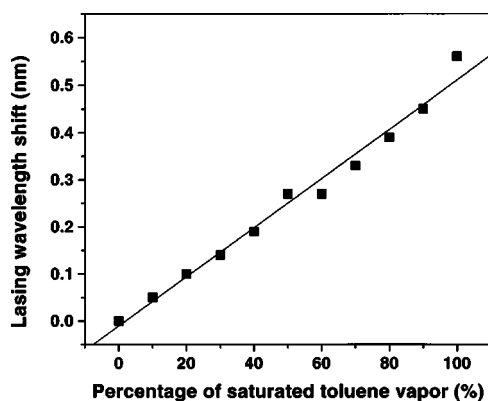


FIG. 2. Wavelength shift of the lasing mode (marked by the arrow in Fig. 1) as a function of increasing percentages of saturated toluene vapor. The straight line represents a linear fit.

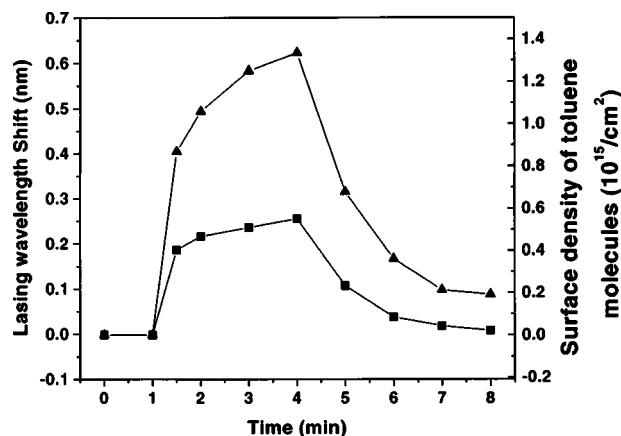


FIG. 3. Wavelength shift of the lasing mode (marked by the arrow in Fig. 1) vs time. The toluene concentrations are 50% saturated vapor in N_2 (squares) and 100% (triangles). The surface density of toluene molecules, calculated from the wavelength shift, is also presented on a second y axis.

sure procedure, identical to that for toluene, again results in an observed redshift of the WG lasing modes, with a maximum shift of 0.62 nm in response to 50% saturated nitrobenzene vapor. Notably, the ZnO/SiO_2 microdisk laser appears to be much more sensitive to nitrobenzene than toluene. In fact a concentration of nitrobenzene 300 times lower than that for toluene induces an equal shift in lasing frequency. We preliminarily attribute this to redox interactions between the n -type ZnO and the nitro group of the target molecule.¹⁰ Moreover, after the flow of nitrobenzene vapor is stopped, it takes much longer time for the lasing modes to shift back to their original spectral positions, probably due to tighter binding of the nitrobenzene molecules to the ZnO and/or the inner walls of the sample cell.

From the shift of lasing frequency, we can infer the amount of organic molecules adsorbed to the microdisk laser. The ZnO/SiO_2 disk layer supports three transverse electric modes (TE_0 , TE_1 , TE_2) and three transverse magnetic modes (TM_0 , TM_1 , TM_2). For the TE modes, the electric field is parallel to the disk plane; while for the TM modes, the electric field is perpendicular to the disk plane. From the guided mode profile normal to the disk plane, we calculate the effective index of refraction n_{eff} for the guided modes at the ZnO emission frequency. In the absence of any organic molecules, $n_{\text{eff}}=1.68$, 1.38, 1.09 for TE_0 , TE_1 , TE_2 modes, and $n_{\text{eff}}=1.47$, 1.28, 1.02 for TM_0 , TM_1 , TM_2 modes. From

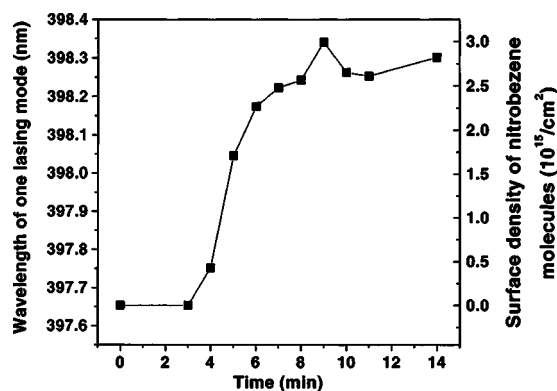


FIG. 4. Temporal change of the wavelength of a lasing mode and the corresponding surface density of nitrobenzene molecules upon exposure to 50% saturated nitrobenzene vapor in N_2 .

the effective index of refraction, we calculate the frequencies of WG modes in the microdisk. The radial variation of the electric field for a WG mode is given by the m th order Bessel function $J_m(2\pi n_{\text{eff}}r/\lambda)$, where r is the radial coordinate, and m is the azimuthal number. The boundary condition can be approximated by assuming that the field goes to zero at the disk edge: $J_m(2\pi n_{\text{eff}}R/\lambda)=0$, where R is the disk radius. By solving for the zero points of J_m , we obtain the wavelength $\lambda_{m,n}$ of the WG modes. n represents the order of the zero points of J_m , and it is called the radial number. Thus a WG mode is labeled as $\text{TEX}_{m,n}$ or $\text{TMX}_{m,n}$, where X is the order of the guided mode. For our disks, X can be 0, 1, or 2. In a 10 μm disk, there are many WG modes within the ZnO gain spectrum. The frequency spacing between some WG modes is so small that the modes cannot be resolved. Instead they appear to be one relatively broad peak. Although there are six guided modes, the observed lasing modes arise mostly from the fundamental transverse electric mode TE₀, because it has the largest spatial overlap with the ZnO layer (gain medium).

In the cylindrical coordinates, the electric field distribution of the $\text{TEX}_{m,n}$ mode can be expressed as

$$\mathbf{E}(r, \theta, z) = J_m\left(\frac{2\pi n_{\text{eff}}r}{\lambda}\right) e^{im\theta} f_X(z) \mathbf{e}_r, \quad (1)$$

where $\mathbf{e}_r$ is the unit vector along the radial (r) direction and $f_X(z)$ represents the TE mode profile in the vertical (z) direction. When organic molecules are absorbed onto the disk surface, they are polarized by the cavity electric field. The induced dipole moment of a single molecule is represented by $\mathbf{p}_m = \alpha \mathbf{E}$, where α is the molecular polarizability. The induced dipole causes a shift of the cavity photon energy $\hbar\delta\nu = -\mathbf{p}_m \cdot \mathbf{E}/2 = -\alpha|\mathbf{E}|^2/2$, according to Refs. 11 and 12. When many molecules are adsorbed randomly but uniformly onto the disk surface, we sum over their contributions to the frequency shift: $\hbar\delta\nu = -(1/2)\alpha\sigma\int|E(r, \theta, z=d)|^2 r dr d\theta$, where σ is the surface density of molecules. Thus, the fractional frequency shift is

$$\frac{\delta\nu}{\nu} = \frac{-\alpha\sigma\int|E(r, \theta, z=d)|^2 r dr d\theta}{2\int\epsilon_s(z)|E(r, \theta, z)|^2 r dr d\theta dz} = \frac{-\alpha\sigma|f_X(d)|^2}{2\int\epsilon_s(z)|f_X(z)|^2 dz}, \quad (2)$$

where $\epsilon_s(z)$ represents the material permittivity along the z direction. Using Eq. (2), we calculated the surface density of adsorbed molecules from the frequency shift of the WG

modes, plotted in Figs. 3 and 4 for toluene and nitrobenzene, respectively.

In conclusion, we have demonstrated that ZnO/SiO₂ microdisk lasers can be used as chemical sensors. When molecules from the vapor phase are adsorbed onto the disk surface, the lasing modes are redshifted due to an increase in the effective refractive index of the microdisk. From the shift, we calculate the spatial density of molecules on the microdisk. The drastically different sensitivity of the ZnO/SiO₂ microdisk laser to toluene and nitrobenzene demonstrates the potential of chemically selective sensing by utilizing differential adsorption or implementing an additional partition layer. Compared to the passive microdisk/microsphere sensors, it is advantageous that the microdisk laser-based sensors do not require tunable laser source, rather the pump laser frequency can remain fixed and detuned from any cavity resonance. Moreover, electrically pumped microdisk lasers have already been demonstrated,¹³ and their application to this sensor motif will further empower our approach by eliminating the need for optical pumping all together.

This work is supported by the MRSEC program of the National Science Foundation (DMR-00706097) at the Materials Science Center of Northwestern University. J.T.H. also acknowledges the Northwestern NSEC.

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