Chemical sensing in Fourier space

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Chemical sensing using optical diffraction from an array of microcantilevers is demonstrated. Properly fashioned arrays of micromachined silicon-nitride cantilevers containing embedded deformable diffraction gratings are functionalized with chemically selective coatings. Adsorption of specific molecules on the cantilever leads to bending, which changes the diffraction pattern of a laser beam reflecting off the array. Quantitative chemical information can be obtained by monitoring the displacement of diffraction peaks as a function of analyte exposure. © *2000 American Institute of Physics.* [S0003-6951(00)00251-5]

Efforts to achieve chemical sensing using arrays are playing an increasingly important role in scientific and technological endeavors. Examples include detection of analytes that are central to chemical and biomedical applications. At present, almost all chemical sensing is carried out using single-sensor elements.[1,2] Hence, most chemical and biological sensors are not compatible for array arrangement that involves hundreds of sensor elements. In addition, most chemical and biological sensors rely on an electrical signal as a means for readout, since most signal transduction mechanisms are electrical in character. If, on the other hand, the arrayed sensors are optically compatible, the readout from the arrays could be directly interfaced with the human eye, eliminating the need for converting an electrical signal to an optical one. One approach could rely on the elegant and proven technique of Fourier optics using arrays of diffraction gratings for display, interpretation, pattern recognition, and data analysis.[3] The currently used optical sensors such as fiber-optics-based sensors cannot be arrayed to obtain diffraction patterns. Therefore, at present those sensors are not suitable for signal manipulation using Fourier techniques.

Our work has been stimulated in part by the need for alternate readout and display techniques for chemical sensing using microcantilevers that can be made into arrays consisting of hundreds of elements.[4–6] Optical techniques for measuring cantilever deflection, such as optical beam deflection, have been routinely used in atomic-force microscopy. For measuring deflections of a large number of cantilevers simultaneously, optical beam deflection is not easy to implement. Fourier optics, on the other hand, can be used to capture the collective effect of a large number of events and, therefore, is ideally suited for arrays of cantilevers. We are motivated by the possibility of using the tremendous opportunities provided by Fourier transform techniques for signal manipulation and control.

There are several reasons why chemical sensing using diffraction techniques offers many advantages. First, conventional chemical sensing using a microcantilever array involves coating each cantilever in the array with a chemically specific coating.[7] Because there is a growing need towards using smaller cantilevers due to their higher sensitivity, the approach of chemically coating each cantilever element for chemical speciation may be impractical. It is easier to functionalize a group of cantilevers than a single element. Second, in a micromachined array it is difficult to make all the individual cantilevers identical. Contaminants, poor adhesion, and partial coating can produce a wide variation in the chemical response. Therefore, techniques based on statistical averages where a group of identically modified cantilever elements collectively responds to an analyte by diffraction offer excellent ways of avoiding these problems.

The use of interdigital diffraction grating cantilevers for optically detecting cantilever deflection has been demonstrated for atomic-force microscopy[8,9] and infrared sensing.[10–12] Figure 1 shows a scanning electron micrograph (SEM) of an array containing cantilever beams made of SiN_x. The details of the design and fabrication of the array can be found in Refs. 11 and 12. The array consists of approximately 200 microcantilevers with dimensions of 300 μm length, 12 μm width, and 1 μm thickness. Each cantilever is in a two-dimensional frame (size 315 μm × 120 μm) formed by scaffolding. A system of secondary smaller can-
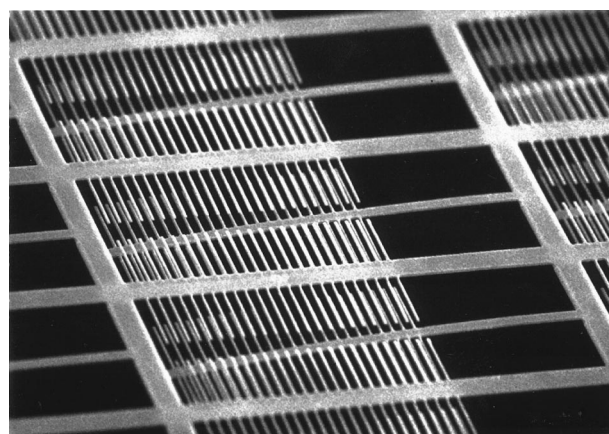

FIG. 1. SEM micrograph of an interdigital cantilever array after exposure to Hg vapor. Scale bar is 38 μm. Bending of the cantilever elements with respect to nonmovable elements due to Hg adsorption can be clearly seen.

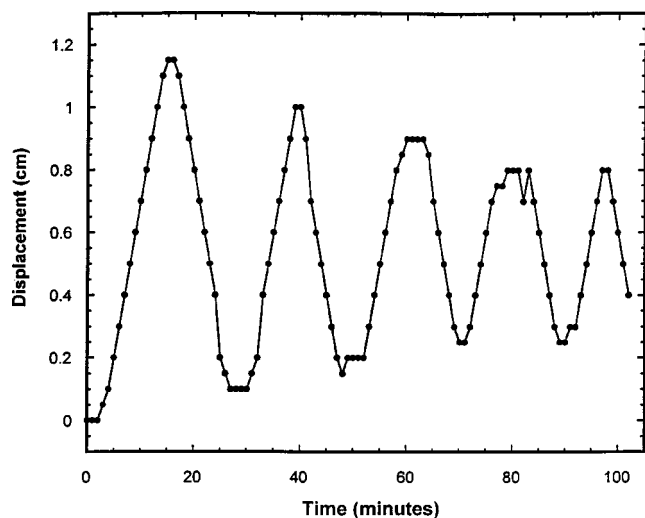[a]Electronic mail: thundattg@ornl.gov

FIG. 2. Typical response of a first-order peak as a function of mercury-vapor exposure time. A steady flow of dry nitrogen with 125 ppb mercury-vapor concentration was maintained during the entire experiment.

tilevers (fingers) protrudes from each cantilever and the scaffolding forming an interdigitated array. The secondary cantilevers have a dimension of 50 μm length, 2.5 μm width, and 1 μm thickness. Therefore, there exist two sets of cantilevers that are orthogonal to each other. However, the secondary cantilevers are much smaller in length and, therefore, have higher spring constants. The cantilevers are arranged in such a way that the fingers at the free end of the cantilever enmesh with the fingers protruding from the scaffolding. When the cantilever deflects, the vertical separation between these sets of gratings increases.

For chemical-vapor sensing, the cantilever array was placed in a container with an optical window, through which a steady flow of nitrogen gas with different chemical vapors was maintained. Adsorption of analyte on each cantilever beam changes its differential surface stress, resulting in proportional deflection.[13] When the array was illuminated with a He–Ne laser beam, the incident light was diffracted by the grating at a series-specific angle corresponding to the particular order of the diffraction. The experiments were carried out on first-and second-order diffraction peaks. In some of the experiments, the diffraction spots were projected on to a wall with a calibrated screen. The distance between the laser and the array was about 10 cm, while the distance between the array and the screen was around 5 m. The motion of the diffraction spots was measured along the screen. In some other experiments, individual peaks were followed using a photodetector.

To illustrate the concept of chemical sensing in Fourier space, we have demonstrated detection of mercury vapor in nitrogen using gold-coated cantilever arrays.[14] When the cantilever array was exposed to Hg vapor, the projected diffraction peaks were found to move in a cyclic pattern on the screen. Figure 2 shows the movements of diffraction spots as a function of time of mercury-vapor exposure. The concentration of Hg vapor in the stream was 125 parts per billion (1 mg/m^3), as calibrated by a commercial Hg vapor analyzer (Arizona Instruments, Phoenix, AZ).

Because of the molecular adsorption, every other cantilever is displaced by an amount equivalent to its position on the plane inclined at an angle θ_i (in radians) with respect to the plane of the reference cantilever array. Assuming the diffracted intensity can be adequately described by the Fraunhofer model, for an observation angle θ relative to the upward normal to the diffraction grating, the intensity of the diffraction peak as a function of angle can be expressed as

$$I(\theta) \propto \left| \frac{\sin(ka/2)}{(ka/2)} \frac{\{1 - \exp[-ikb(N+1)]\}}{\{1 - \exp(-ikb)\}} \right.$$

$$+ \exp(-ikb/2) \frac{\sin(k'a/2)}{(k'a/2)}$$

$$\left. \times \frac{\{1 - \exp[-ik'b(N+1)]\}}{\{1 - \exp(-ik'b)\}} \right|^2, \tag{1}$$

where λ is the wavelength, δ is the displacement between the fingers, N is the number of interdigitated cantilever units, $k = 2\pi \sin\theta/\lambda$, and $k' = 2\pi(\sin\theta + \sin\theta_i)/\lambda$. The parameters a and b are the width and pitch of the fingers, respectively. Here, for simplicity, we have neglected the parabolic behavior of the cantilever bending and shadowing effects. It is also assumed that the incident photon field is coherent and effectively at infinite distance from the cantilever array. The details of the theory will be published elsewhere.[15] The displacement of the peak on a screen is proportional to the displacement parameter δ. The first peak position corresponds to a displacement of approximately $\lambda/4$ between the fixed and movable fingers of the interdigitated array. From Fig. 2 it is clear that during mercury-vapor exposure the cantilevers moved approximately 1.28 μm.

Finally, to demonstrate that these cantilever arrays can also be used to detect physical parameters, we have carried out experiments to detect the thermal response of these cantilevers. Bi-material microcantilevers have excellent temperature sensitivity and can be used for remote temperature detection.[16–18] To demonstrate the temperature effect, we placed the cantilever array 10 cm away from the temperature source. The temperature of the source was measured using thermocouple wires in contact. The cantilever array and temperature sources were arranged in such a way as to avoid any effects due to convection currents. Figure 3 shows the spatial response of one of the first-order peaks as a function of temperature of the source.

In conclusion, we have demonstrated an optical signal transduction mechanism for chemical sensing based on Fourier optics of microcantilever deformable diffraction gratings. There will undoubtedly be further developments in this field as more complex cantilever array structures are designed in future research. For example, one could make cantilever arrays in such a way that they mimic the Fourier transform of a desired display and thereby achieve pattern recognition. When diffraction is obtained from such an array, the resultant spectrum will be a real image. Conversely, cantilevers can be modified with selective chemical agents in such a way that inverse Fourier transforming using a lens can form the real pattern on the cantilever array. For example, cantilevers can be coated in such a way that alphabets or a pattern could be displayed on a screen identifying the chemical agents. Or, when arrays are illuminated with white light they could produce interference colors depending on the relative displacement between the movable and fixed canti-
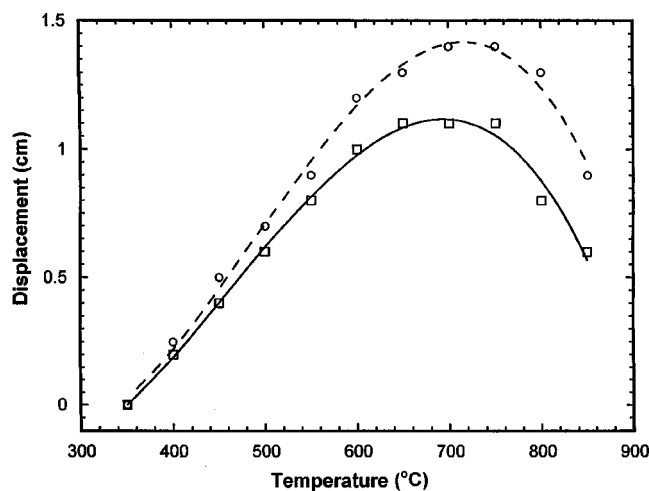
FIG. 3. Displacement response of a spatially filtered first-order diffraction peak as a function of object temperature. The object, a soldering iron, was 10 cm away from the cantilever array. The upper (circle) and lower (square) curves represent the response when interrogated by green and red lasers, respectively. The peaks are shifted due to the difference in wavelengths.

levers. This can lead to micromachined chips that change colors, as in the case of litmus papers. This technique can also be used under solution for detecting biochemical reactions.[19] In addition, interesting electrochemical experiments can be conducted in such a way that these cantilevers act as working electrodes. Cantilevers coated with metals of different electrochemical potential can be used to display and investigate electrodeposition, corrosion, as well as solid–liquid interfaces.

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