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A Micro-Machined Optical Fiber Cantilever as a Miniaturized pH Sensor

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Abstract—A micro-cantilever fabricated using a combination of picosecond-laser machining and focused ion beam milling directly onto the end of a standard telecommunications optical fiber is demonstrated as a liquid pH sensor. Conventional pH meters typically require relatively large reaction volumes up to ~50 mL, which is not always convenient. The micro-scale nature of this sensor offers the potential for pH measurement on a smaller sample volume down to micro-liter. The fiber end-tip cantilever is coated with a pH sensitive layer, and the pH-induced deflection is monitored interfermetically. A detectable pH range from 4.0 to 10.0 is demonstrated for the cantilevers coated with 16-mercapto-hexadecanoic-1-acid as the functional layer, and a detectable pH range from 4.0 to 9.0 is demonstrated for the cantilevers coated with Al₂O₃ as the functional layer.

Index Terms—Focused ion beam, optical fiber cantilever, pH sensing, ps-laser machining.

I. INTRODUCTION

I N SOME applications, such as chemical analysis or the control of biological systems, it is important to monitor the pH of the aqueous media [1], [2]. Knowledge of pH is important to aid the understanding of processes as it can have a great influence on many biological and chemical reactions. Several techniques are commonly used in order to measure the pH of solutions. These include ion-sensitive field-effect transistors (ISFET) [3], magneto elastic sensors [4], conduction measurements [5] or optical techniques [6]. Electrical based techniques have many advantages: they are potentially low cost, can be easy to mass-manufacture, accurate, can have a large pH detection range, and are easy to interface. However, due to the typical sensor volume and the common use of

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a semi-permeable membrane in the device these techniques can be slow and require large sample volumes. Generally it is difficult to monitor pH in very small sample volumes in the $\sim \mu L$ regime. An alternative technique uses pH sensitive colorimetric or fluorescent indicators that can be monitored optically [7]–[11]. Here the optical absorbance or amplitude of a fluorescent signal is measured. These sensor schemes are simple and cost-effective but their reliance on an intensity measurement means they are susceptible to external factors such as excitation intensity fluctuations, temperature, concentration of the analyte or the indicator, or even bleaching or leaching of the indicator. There is also the potential risk that the indicator may interfere with the process that is being studied. Hence there is interest in developing miniaturized sensors that avoid the use of indicator species in the test solution.

The concept of using micro-cantilevers (MCLs) as highly sensitive chemical and physical sensors was first reported in [12]. The operation principle of MCLs can be divided into two classes: bending mode and dynamic mode. In the bending mode, differential surface stress can be calculated by monitoring the cantilever deflection using Stoney's equation [13]. However, in this analysis the clamping effect on the cantilever is ignored and this can lead to significant deviation between the modeled and experimental responses. Therefore, Tamayo et al. present an accurate and simple analytical expression to quantify the response of microcantilevers with different sizes and geometries suitable for biosensing [14]. Their results have shown excellent agreement with finite element simulations and DNA immobilization experiments. To date, physical sensors using MCLs have been demonstrated for a range of measurands including temperature, force, magnetic field, and infrared radiation [15]-[19]. Extremely sensitive chemical and biological sensors based on MCLs for analytes including DNA, alcohol, mercury, antigen-antibody binding, and bacteria have also been reported [20]–[23]. Unlike many other types of chemical sensor, MCLs are simple mechanical devices. They are small, typically $0.2-1\mu m$ thick, 20-100 μm wide, and 100-500 μ m long, which are connected to an appropriate support for convenient handling. Such devices have seen widespread use. For example, forming a sharp tip onto the end of a MCL makes it useful as a probe for mapping localized surface topology and is widely used for Atomic Force Microscopy (AFM) [24]. The recent advances in micro- and nanofabrication technologies enable the preparation of increasingly smaller mechanical transducers suitable for biomolecular interactions and fundamental biological processes. There have

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been significant developments in micro-cantilever biosensors recently as a result. Huber et al. [25] show that an assay based on micro-cantilever arrays can detect a specific gene mutation nanomechanically without amplification in total of RNA samples isolated from melanoma cells. Kosaka et al. [26] proposed an assay that combines mechanical and optoplasmonic transduction to detected cancer biomarkers in serum at a concentration of 10-16 g/ml. A more novel hybrid spin-cantilever structure that employs a high-Q single crystal diamond cantilever with a single nitrogen vacancy spin center embedded at the base was explored by Wu et al. as a sensor for potential quantum sensing applications [27]. In-situ measurement at room temperature has been carried out to detect an Angiopoietin-1 tumor angiogenesis marker with this hybrid microcantilever.

In the field of pH and chemical sensing, there has been significant progress on micro-cantilever based sensors in recent years. One approach is to use a surface-modified microcantilever to detect pH change. For example, Ji et al. [28] demonstrate a maximum pH sensitivity of 49 nm deflections per pH unit using a SiO₂/Au cantilever, with an operating range from pH 2 to 8. The relationship between pH and cantilever deflection is discussed, but the detailed explanation for cantilever deflection mechanism is unclear. A more widely used approach uses micro-patterned hydrogels which change in volume as a function of pH and therefore can act as a transducer. When hydrogels are utilized as sensing microstructures, the micro-patterning improves the mass transfer and chemomechanical response and leads to a reduced response time. For example, Bashir et al. [29] used swellable hydrogels as a transducer deposited on top of a micro cantilever and demonstrated the potential of this approach as an ultrasensitive pH sensor. In their work, silicon-on-insulator wafers were used to fabricate cantilevers on to which a polymer consisting of poly (methacrylic acid) (PMMA) with poly(ethylene glycol) dimethacrylate was patterned using free-radical UV polymerization. The mechanical amplification of polymer swelling as a function of pH change was $1 \text{nm}/5 \times 10^{-5} \text{ }\Delta\text{pH}$, however the effective measurement range is limited to between 5.9 pH and 6.5 pH. VanBlarcom et al. demonstrated a biodegradable pH-responsive hydrogel micro-cantilever sensor [30]. In this work they proposed a theoretical hydrogel swelling model to verify the testing result of the sensor in a protein-rich solution and $1 \text{ nm}/5.7 \times 10^{-5} \text{ }\Delta\text{pH}$ sensitivity is achieved for the resulting sensor with a detectable pH range from 5 to 6.5 based on modeling.

A common interrogation technique for micro-cantilever pH sensors is to use an electrical readout. A piezoresistive element can be employed to convert the bending of the microcantilever into an electrical signal based upon the resistivity change of the piezoresistive element as a function of surface stress changes [31]. The advantage of this approach is that the readout system can be integrated onto the sensor chip, however the readout current can be affected by the sensor temperature since any thermally induced changes in conductivity will lead to misinterpretation of surface stress. Another technique which is widely used for monitoring micro-cantilevers is the optical beam deflection method [32]. Here the cantilever deflection is determined by monitoring the position of a reflected laser beam from the cantilever using a position sensitive detector. This approach has high deflection sensitivity but requires precise mechanical alignment when setting-up the experiment. To address this issue, Martínez et al. [33] proposed dense optical cantilever array structures with minimal need for optical alignment to achieve high throughput biological application. Nordström et al. [34], meanwhile, present a waveguidemicrocantilever fabricated from SU-8 resin. The cantilever deflection is read out by monitoring changes in the optical intensity of light transmitted through the cantilever that also acts as a waveguide. Good results have been obtained in both air and liquid environments when the cantilever is deflected mechanically.

An alternative structure was proposed by Giorgio et al. [35]. In their work, a surface-acoustic-wave (SAW) based cantilever device for portable bio-chemical sensing is presented. Analytes on a functionalized surface of the cantilever shift the resonant frequency of a SAW-generating transducer due to the stressinduced variation of the speed of surface acoustic modes. The sensor can be exploited with passive wireless readout schemes which are suitable to form scalable devices for diagnostic purposes.

In all cases the ideal configuration would combine the sensing probe and interrogation scheme as a single element for portable plug-in sensing platform. A suitable structure was first demonstrated by Ianuzzi et al. [36], where the cantilever is directly fabricated at the end of an optical fiber. Here the cantilever is interrogated by light guided in the fiber, thereby offering a self-aligned miniaturised sensor with dimensions on the scale of an optical fiber. An alternative fabrication approach proposed by the same group uses 'top-down' lithography techniques to produce cantilevers onto the end of optical fibers [37]. This leads to the potential for mass production of optical fiber-top cantilevers.

In this paper, we use a laser micro-machining and Focussed Ion Beam milling (FIB) dual process to fabricate fiber-top cantilevers suitable for pH sensing. The fabricated structure forms an optical Fabry-Perot cavity; measurement of the cavity length allows us to infer the cantilever deflection that arises due to changes in pH. By forming the cantilever onto the end of an optical fiber allows inherent alignment to the readout system, via the fiber core during the fabrication stage, therefore no post fabrication mechanical alignment of the sensor is required. The interferometric approach to monitor cantilever deflection is significantly more robust than a simple intensitybased sensor set-up [38]. The use of optical fiber offers the potential for a miniaturized sensor with electromagnetic immunity, small physical size, and biocompatibility.

II. SENSOR FABRICATION

We have previously described a technique using a combination of ps-laser machining and FIB milling to fabricate cantilevers onto the end of single mode optical fibers [39], [40]. The combination of these techniques allows us to exploit the high material removal rate afforded by using ps-laser machining to form the basic sensing structure and then use FIB milling to refine the component dimensions.



Fig. 1. (a) A micromachined cantilever on the end of an optical fiber after initial laser machining, and (b) after FIB processing.

This allows sub-micron control over the cantilever thickness, and provides an optical quality surface in the regions that define the optical cavity. This dual process approach greatly reduces the total machining time in comparison with using FIB processing alone.

In summary, conventional single mode fibers (Corning, SMF28) are cleaved and then modified using a commercial picoseconds (ps) pulsed laser system (TrumpfTruMicro 5×50) to form the rough cantilever structure. The machining was performed at a laser wavelength of 343 nm using a 6 ps laser pulse with energy of 10 μ J per pulse and a focused spot of 6 μ m diameters. A detailed description of this machining process can be found in [40]. The resulting cantilever, shown in Fig.1 (a), is ~100 μ m long, 18 μ m wide and 8 μ m thick. It should be noted that due the resolution of the beam steering control system and fiber positioning accuracy, the minimum cantilever thickness machined by ps-laser is around 7-8 μ m.

After laser processing these cantilevers are brought to a FIB system to create a thinner cantilever with improved sensitivity. This finishing process has two main steps. First of all, a 30 kV voltage and 30 nA current is used to trim the cantilever thickness down to $\sim 3 \ \mu$ m. Then a lower current of 7 nA is used to polish the surface to provide a $\sim 1.5 \ \mu$ m thickness cantilever with an optical surface finish, a suitable thickness for pH measurement. This thickness can be controlled by FIB processing to better than ~ 100 nm therefore it is feasible to reproduce cantilever characteristics between several devices. The whole machining process takes approximately 20 minutes. A SEM image of such a cantilever is shown in Fig. 1(b).

III. EXPERIMENT AND ANALYSIS

A. Deflection Measurement Interrogation Set-Up

General speaking, cantilever sensors can be operated in two modes: vibration mode and static mode. Although vibration (or dynamic) mode is more sensitive in general, the sensitivity of the sensor is severely compromised in a liquid environment because of the fluid damping effect. Additionally, in this case the mass change related to pH variation is negligible, hence static mode of probing surface stress change rather than dynamic mode frequency shift is used in this paper.

We have previously described the interrogation of these fused silica cantilevers for a different application by using



Fig. 2. Schematic of pH measurement set-up.



Fig. 3. Reflection spectrum from the cavity formed between the fibre end face and the cantilever. Here a cavity length of 59.3μ m is observed.

static mode method [41]. We use reflections from the end of the fiber and the cantilever to define an optical cavity. Cantilever deflection is observed as a change in the reflected spectra from the cavity. The basic experimental set-up for monitoring the cantilever deflection due to changes in pH is illustrated in figure 2. In this system, a Micron Optics SM-125 optical sensing interrogator system directs tunable laser light along the fiber towards the sensing cantilever. This light is partially reflected by the fiber-to-air (a), airto-cantilever (b) and cantilever-to-air (c) interfaces, and the reflected intensity is recorded by the SM-125. The dominant reflection is from (c) which forms the main cavity between the fiber end face (a) and the outer cantilever surface (c). The laser wavelength is scanned and the resulting interferogram is recorded and analyzed by a bespoke LabView program using the process described below. This allows the cavity length, and hence the cantilever deflection, to be determined. A typical cavity interferogram is shown in figure 3, in which the interference fringes are clearly visible. It this case, the fringe visibility V~0.8 (defined as V = $(I_{max} - I_{min})/(I_{max} + I_{min})$), indicating that we have a near matched return signal from the reference and cantilever surfaces. In our experiments the overall signal/noise level is more than sufficient for our subsequent analysis routines.

The cavity length is determined by extracting the free spectral range of the cavity from the interferogram. Given the incident light source spectrum $I_0(\lambda)$, then in the case of a low finesse cavity as used here, the back reflected light intensity spectrum $I_R(\lambda)$, can be approximated by:

$$I_R(\lambda) = I_0(\lambda)[1 + V\cos(\frac{4\pi nL}{\lambda} + \varphi_0)$$
(1)

where V is the visibility of the interference spectrum and L is the real cavity length. Equation (1) tells us that the absolute cavity length information is encoded in both the optical phase of interfered signals and also in the free spectral range (FSR) of the cavity. Here, a Fast Fourier Transform (FFT) is applied to the interferogram, expressed in terms of optical frequency rather than wavelength, to recover the FP cavity length. Note that cavities of different lengths have significantly different FSR and hence are easily identified in the output of the FFT. Therefore we can be confident that we are recording the cavity formed between surface (a) and (c). This approach can be used to determine the cantilever deflection. Further details on this process can be found in [41].

B. Activation of Cantilever

To make the cantilever sensitive to pH one side of the cantilever must be 'activated', so that a change in pH results in a different surface strain on each face of the cantilever. It is this differential strain that causes the cantilever to deflect according to the Stoney equation [13], where the relation between the cantilever deflection z and the differential surface stress is obtained by the following equation:

$$z = \frac{3L^2(1-\mu)}{Et^2}\Delta\sigma \tag{2}$$

where *L* is the length of the cantilever, μ and *E* are Poisson's ratio and Young's modulus for the cantilever material respectively, *t* is the thickness of the cantilever, and $\Delta \sigma$ is the differential surface stress. Here, two different activation layers are investigated (i) Al₂O₃/Au and (ii) MHA (16-mercaptohexadecanoic-1-acid)/HDT (1, 6-hexanedithiol).

Before testing the pH sensitivity it was necessary to determine the background system noise level. This was achieved by immersing a passive (uncoated) cantilever into Potassium Buffer Solution (PBS) pH 7.0 solutions and monitoring the cantilever position. The experiment was temperature controlled (23 °C±0.2 °C) and insulated in order help maintain a stable environment. The relative cantilever deflection is acquired every 10 seconds over 200 minutes, with results shown in Fig. 4. Here the maximum cantilever deflection fluctuation is around ±12 nm, with an r.m.s. error of approximate ±6 nm. From this data we conclude that a temperature variation of the order of 0.4 °C does not significantly affect the cantilever deflection within the measured noise level.

In order to investigate the effect of flow turbulence upon the cantilever deflection the cavity length was monitored while injecting PBS 7.0 solution into the liquid chamber at a constant speed of 50μ L/min. The cantilever is initially immersed in PBS 7.0 solution and a thermocouple is also placed in the liquid cell to monitor the temperature change. The cavity length and temperature fluctuation during the onset of the flow



Fig. 4. Thermal stability of cantilever deflection over 200 minutes.



Fig. 5. Cantilever cavity fluctuation versus temperature change during onset of liquid flow over the sensor.

are plotted in Fig.5. After injection, the temperature dropped down rapidly by 0.3 °C then returned back to 23 °C after 40 seconds. The r.m.s. fluctuation in measured cavity size during this period was found to be 12.8 nm, comparable to the system noise level. For bio-sensing it is normal to stabilize the temperature to be compatible with the biological species being investigated, therefore only a limited temperature range has been considered in this work.

C. pH Sensing Results and Discussion

In order to measure pH, the cantilever is activated (or 'functionalised') with a pH sensitive coating layer. Two different coating layers are selected here. One of them is Al₂O₃/Au coating, which is easy to deposit and has shown high sensitivity on a Silicon Nitride cantilever [22]. Unfortunately, the measured pH range and coating lifetime can be limited for this material. Therefore, MHA/HDT coating was subsequently used because of its improved stability to pH [42]. Fig.6 shows the functionalised fiber cantilevers. Cantilever deflection towards the activate layer is defined as positive deflection.

 Al_2O_3/Au cantilevers were made by first evaporating 4 nm of Cr onto the SiO₂ surface and then depositing 20 nm



Fig. 6. Schematic configuration of optical fiber cantilever functionalised with different pH sensitive coatings.



Fig. 7. Cantilever deflection versus pH change.

Aluminum onto one side of the cantilever and storing it in air at room temperature overnight until the entire Al thin film oxidizes to Al_2O_3 . The backside of cantilever is coated with 4 nm of Cr and then 20 nm of gold, to form an inert surface.

The pH of the test liquid was controlled between 4.0 and 10.0 and verified using a commercial pH meter with a resolution of 0.1 pH unit at 23°C. The experiment took place at a temperature of $23^{\circ}C \pm 0.2^{\circ}C$.

Al₂O₃-coatings have been shown to be sensitive to pH e.g., they have been used to modify ISFET gate surfaces [43]. A coating of Al₂O₃ will change the influence of pH on cantilever surface stress, thus generating a bending signal. To reference the zero position of the cantilever, the freshly coated cantilever is first immersed in PBS 7.0 solution and the cavity length is recorded. After that PBS 9.0 solution is injected gently at a constant speed for several few minutes to ensure the cantilever has achieved a steady-state deflection, then the cantilever is washed with PBS 7.0 solution and injected PBS 8.5 solution. The same process is repeated from PBS 9.0 to PBS 4.0 decreasing by 0.5 pH each time. A subsequent cycle is taken from pH 4.0 to pH 9.0. The steady-state deflection of the cantilever is plotted as a function of pH in Fig.7. The response of the Al₂O₃/Au cantilever indicates that when pH>7.0 the surface stress increases as pH increases and deflection could reach ~180nm towards Al₂O₃ side at pH 9.0. The cantilever bends down towards the Au side when pH<7.0 and reach a maximum deflection around 100nm. It is clear that, from figure 6, the Al₂O₃/Au



Fig. 8. Cantilever deflection versus pH change.

functionalised cantilever is sensitive from pH 7.0 to pH 9.0, with \sim 100nm/pH sensitivity achieved. For the resolution of our system this equals to an r.m.s. pH resolution of \sim 0.1 pH.

Unfortunately the Al_2O_3 surface is not suitable for long term use in high or low pH solutions. In low pH solutions, reaction with the Cl ion results in production of $AlCl_3$, while in a high pH solution the surface will dissolve into solution due to chemical reactions that produce water soluble product.

To further investigate the life time of the micro-machined optical fiber cantilever sensor multiple cycles between pH 7.0 and 9.0 are performed. The measurement is taken every 10 seconds, and is shown in Fig. 8. It should be noted that when washing with PBS 7.0 solution, the injected volume was sufficient to wash away any reactant from the previous solution to ensure a constant solution concentration. From Fig.8, we can see that it takes ~100s for the sensor to reach steady-state for each pH change. The noise level when cantilever reaches equilibrium is ~10nm. When washing with PBS 7.0, the cantilever deflection is seen to return to the same position with a noise level around ~15nm.

The lifetime of the sensor is greatly influenced by the presence of chemical coatings on the surface of the cantilever; hence it is crucial to select a robust coating layer which could survive in both low and high pH environments. To further improve the life time of the cantilever pH sensor a MHA/Au functionalized cantilever is tested which is expected to extend the lifetime of sensor.

The 16-mercapto-hexadecanoic-1-acid (MHA)/HDT functionalised cantilever is by а Self-Assembled Monolayer (SAM) process [44]. A micro-machined optical fiber cantilever with the top surface coated with Au was immersed in 10 mM MHA solution overnight. A goldalkylthiolate monolayer was then produced in well-ordered, regularly oriented array. The functionalised cantilever is then washed with Ethanol and blown dry gently using nitrogen. After that, the reverse side of cantilever is coated with Au followed by the similar procedure above, in order to prevent cross-sensitivity to temperature. The HDT coated surface will protect the cantilever from any non-specific adsorption, which will affect the surface stress change.

The deflection of the cantilever is due to the sum of all interactions at the surface, these results in a gradual surface stress increase when pH increases from 4.0 to 10.0. It should also be noted that, while we have only demonstrated the



Fig. 9. (a) Steady-state cantilever deflection at pH 4.0 and pH 10.0 and (b) zoomed in image showing the single cycling between pH4.0 and pH10.0, t_r and t_f are the rising time and falling time respectively.



Fig. 10. MHA/HDT functionalised cantilever deflection versus pH change.

detection range from pH 4.0 to pH10.0 due to the PBS, we do not envisage any technical issues associated with the detection of pH beyond this range using different buffer solutions. The cantilever deflection change between pH4.0 and pH10.0 is shown in Fig. 9. A response time of 75 s is found from pH 4.0 to pH 10.0 and 30 s when pH is shift from 10.0 to 4.0.

The steady-state deflection is plotted as a function of pH in Fig. 10. The maximum cantilever deflection of \sim 90 nm is achieved at pH 10.0 whilst at pH 4.0 the cantilever is around zero deflection. Five cycles were used to investigate repeatability, and the maximum error was found to be 15 nm at around pH 4.0, the error elsewhere is around 10nm. It is clear



Fig. 11. Deflection response of optical fiber cantilever as a function of pH: Top: MHA/HDT cantilever; Below: Al_2O_3/Au cantilever.

from Fig.11 that the deflection depends on the pH changes of the buffer and the functionality of the –COOH monolayer on the Au coated surface. The deflection originates from the MHA liquid interface and also depends on the chemical environment of these interfaces. For MHA functionalised cantilever the acid dissociation constant (*pKa* is found to be ~5) in solution [42]. At pH<5 the majority of carboxy groups is protonated while at pH>5 most of them are likely to be deprotonated and become negatively charged, which is in the form of –COO[–]. Therefore increasing the pH will increase the population of –COO[–], this in turn increases the lateral forces in the MHA monolayer. The surface stress applied onto the cantilever surface will increase accordingly. Detailed analysis can be further explained in [46].

To compare the pH response of the two different functional coatings the cantilever steady-state deflection is plotted in Fig. 11 for cantilevers with the two different coatings as a function of pH. This shows that MHA functionalised cantilevers are capable of detecting pH over a range of pH 4.0 to 10.0, with an average sensitivity of ~15 nm/pH. Cantilever deflection has also been found in Al₂O₃ functionalised cantilever with a measurement range from pH 4.0 to 9.0 and the average sensitivity is ~60 nm/pH, which equals to ~0.1 pH resolution assuming ~6 nm deflection resolution. The pH sensitivity tends to increase in both large and small pH value. The same trend has also been reported in [28] for different function layers.

IV. CONCLUSION

In this paper, a micro-cantilever fabricated from the end of a standard telecommunication fiber with appropriate functional coatings is shown to be sensitive to pH. A combination of ps-laser and FIB machining techniques make it possible to form a cantilever with a dimension of 112 μ m long 15 μ m wide and ~1.5 μ m thick. Such a cantilever, functionalized using Al₂O₃/Au coatings, can be used to measure pH in the range of pH 4.0 to pH 9.0 with a maximum deflection of ~200 nm deflection at pH 9.0. A more robust sensor has been shown with a range of pH 4.0 to pH 10.0 with up to 90 nm deflection using a MHA/HDT functionalized cantilever. A pH detection time of approximate 2 minutes is observed using a small sample volume of ~50 μ L.

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REFERENCES

- I. Canals, J. A. Portal, E. Bosch, and M. Rosés, "Retention of ionizable compounds on HPLC. 4. Mobile-phase pH measurement in methanol/water," *Anal. Chem.*, vol. 72, no. 8, pp. 1802–1809, 2000.
- [2] W.-D. Huang, S. Deb, Y.-S. Seo, S. Rao, M. Chiao, and J. C. Chiao, "A passive radio-frequency pH-sensing tag for wireless food-quality monitoring," *IEEE Sensors J.*, vol. 12, no. 3, pp. 487–495, Mar. 2012.
- [3] L. H. Jiao and N. Barakat, "Ion-sensitive field effect transistor as a pH sensor," J. Nanosci. Nanotechnol., vol. 13, no. 2, pp. 1194–1198, 2013.
- [4] Q. Y. Cai and C. A. Grimes, "A remote query magnetoelastic pH sensor," Sens. Actuators B, Chem., vol. 71, nos. 1–2, pp. 112–117, 2000.
- [5] Y. Chen, S. C. Mun, and J. Kim, "A wide range conductometric pH sensor made with titanium dioxide/multiwall carbon nanotube/cellulose hybrid nanocomposite," *IEEE Sensors J.*, vol. 13, no. 11, pp. 4157–4162, Nov. 2013.
- [6] J. Goicoechea, C. R. Zamarreño, I. R. Matías, and F. J. Arregui, "Optical fiber pH sensors based on layer-by-layer electrostatic self-assembled neutral red," *Sens. Actuators B, Chem.*, vol. 132, no. 1, pp. 305–311, 2008.
- [7] V. Misra, H. Mishra, H. C. Joshi, and T. C. Pant, "An optical pH sensor based on excitation energy transfer in Nafion film," *Sens. Actuators B, Chem.*, vol. 82, nos. 2–3, pp. 133–141, 2002.
- [8] M. Tian, X. Peng, J. Fan, J. Wang, and S. Sun, "A fluorescent sensor for pH based on rhodamine fluorophore," *Dyes Pigments*, vol. 95, no. 1, pp. 112–115, 2012.
- [9] H. Lu et al., "Novel fluorescent pH sensors and a biological probe based on anthracene derivatives with aggregation-induced emission characteristics," *Langmuir*, vol. 26, no. 9, pp. 6838–6844, 2010.
- [10] B. Tang *et al.*, "A near-infrared neutral pH fluorescent probe for monitoring minor pH changes: Imaging in living HepG2 and HL-7702 cells," *J. Amer. Chem. Soc.*, vol. 131, no. 8, pp. 3016–3023, 2009.
- [11] S. Ogikubo et al., "Intracellular pH sensing using autofluorescence lifetime microscopy," J. Phys. Chem. B, vol. 115, no. 34, pp. 10385–10390, 2011.
- [12] T. Thundat, R. J. Warmack, G. Y. Chen, and D. P. Allison, "Thermal and ambient-induced deflections of scanning force microscope cantilevers," *Appl. Phys. Lett.*, vol. 64, no. 21, pp. 2894–2903, 1994.
- [13] G. G. Stoney, "The tension of metallic films deposited by electrolysis," *Proc. Roy. Soc. A*, vol. 82, no. 553, pp. 172–175, 1909.
- [14] J. Tamayo, J. J. Ruz, V. Pini, P. Kosaka, and M. Calleja, "Quantification of the surface stress in microcantilever biosensors: Revisiting Stoney's equation," *Nanotechnology*, vol. 23, no. 47, p. 475702, 2012.
- [15] H. J. Mamin and D. Rugar, "Sub-attonewton force detection at millikelvin temperatures," *Appl. Phys. Lett.*, vol. 79, no. 20, pp. 3358–3360, 2001.
- [16] P. G. Datskos, P. I. Oden, T. Thundat, E. A. Wachter, R. J. Warmack, and S. R. Hunter, "Remote infrared radiation detection using piezoresistive microcantilevers," *Appl. Phys. Lett.*, vol. 69, no. 20, pp. 2986–2988, 1996.
- [17] P. G. Datskos, P. I. Oden, T. Thundat, and R. J. Warmack, "Uncooled thermal imaging using a piezoresistive microcantilever," *Appl. Phys. Lett.*, vol. 69, no. 21, pp. 3277–3279, 1996.
- [18] R. Raiteri and H.-J. Butt, "Measuring electrochemically induced surface stress with an atomic force microscope," *J. Phys. Chem*, vol. 99, no. 43, pp. 15728–15732, 1996.
- [19] T. Thundat, P. I. Oden, and R. J. Warmack, "Microcantilever sensors," *Microscale Thermophys. Eng.*, vol. 1, no. 3, pp. 185–199, 1997.
- [20] S. Allen *et al.*, "Detection of antigen–antibody binding events with the atomic force microscope," *Biochemistry*, vol. 36, no. 24, pp. 7457–7463, 1997.
- [21] A. M. Moulin, S. J. O'Shea, and M. E. Welland, "Microcantilever-based biosensors," *Ultramicroscopy*, vol. 82, pp. 23–31, Feb. 2000.
- [22] R. Aiteri, M. Grattarola, H.-J. Butt, and P. Skládal, "Micromechanical cantilever-based biosensors," *Sens. Actuators B, Chem.*, vol. 79, pp. 115–126, Oct. 2001.
- [23] N. V. Lavrik, M. J. Sepaniak, and P. G. Datskos, "Cantilever transducers as a platform for chemical and biological sensors," *Rev. Sci. Instrum.*, vol. 75, no. 7, pp. 2229–2253, 2004.
- [24] B. Tiribilli, G. Margheri, P. Baschieri, C. Menozzi, D. Chavan, and D. Iannuzzi, "Fibre-top atomic force microscope probe with optical nearfield detection capabilities," *J. Microsc.*, vol. 242, no. 1, pp. 10–14, 2011.

- [25] F. Huber, H. P. Lang, N. Backmann, D. Rimoldi, and C. Gerber, "Direct detection of a *BRAF* mutation in total RNA from melanoma cells using cantilever arrays," *Nature Nanotechnol.*, vol. 8, pp. 125–129, Feb. 2013.
 [26] P. M. Kosaka *et al.*, "Detection of cancer biomarkers in serum
- [26] P. M. Kosaka *et al.*, "Detection of cancer biomarkers in serum using a hybrid mechanical and optoplasmonic nanosensor," *Nature Nanotechnol.*, vol. 9, pp. 1047–1052, Nov. 2014.
- [27] W.-H. Wu and K.-D. Zhu, "Hybrid spin-microcantilever sensor for environmental, chemical, and biological detection," *Nanotechnology*, vol. 26, no. 1, pp. 015501–015510, 2015.
- [28] H. Ji, K. M. Hansen, Z. Hu, and T. Thundat, "Detection of pH variation using modified microcantilever sensors," *Sens. Actuators B, Chem.*, vol. 72, no. 3, pp. 233–238, 2001.
- [29] R. Bashir, J. Z. Hilt, O. Elibol, and A. Gupta, "Micromechanical cantilever as an ultrasensitive pH microsensor," *Appl. Phys. Lett.*, vol. 81, no. 16, pp. 3091–3093, 2002.
- [30] D. S. VanBlarcom and N. A. Peppas, "Microcantilever sensing arrays from biodegradable, pH-responsive hydrogels," *Biomed. Microdevices*, vol. 13, no. 5, pp. 829–836, 2011.
- [31] C. Ziegler, "Cantilever-based biosensors," Anal. Bioanal. Chem., vol. 379, pp. 946–959, Aug. 2004.
- [32] G. Meyer and N. M. Amer, "Novel optical approach to atomic force microscopy," *Appl. Phys. Lett*, vol. 53, no. 12, pp. 1045–1047, 1988.
- [33] N. F. Martínez et al., "High throughput optical readout of dense arrays of nanomechanical systems for sensing applications," *Rev. Sci. Instrum.*, vol. 81, no. 12, p. 125109, 2010.
- [34] M. Nordström, D. A. Zauner, M. Calleja, J. Hübner, and A. Boisen, "Integrated optical readout for miniaturization of cantilever-based sensor system," *Appl. Phys. Lett.*, vol. 91, no. 10, p. 103512, 2007.
- [35] G. De Simoni, G. Signore, M. Agostini, F. Beltram, and V. Piazza, "A surface-acoustic-wave-based cantilever bio-sensor," *Biosensors Bioelectron.*, vol. 68, pp. 570–576, Jun. 2015.
- [36] D. Iannuzzi, S. Deladi, V. J. Gadgil, R. G. P. Sanders, H. Schreuders, and M. C. Elwenspoek, "Monolithic fiber-top sensor for critical environments and standard applications," *Appl. Phys. Lett.*, vol. 88, no. 5, p. 053501, 2006.
- [37] K. B. Gavan *et al.*, "Top-down approach to fiber-top cantilevers," *Opt. Lett.*, vol. 36, no. 15, pp. 2898–2900, 2011.
- [38] L. Su and S. R. Elliott, "All-fiber microcantilever sensor monitored by a low-cost fiber-to-tip structure with subnanometer resolution," *Opt. Lett.*, vol. 35, no. 8, pp. 1212–1214, 2011.
- [39] J. Li, F. Albri, R. R. J. Maier, W. N. MacPherson, and D. P. Hand, "Micro-machined optical fibre cantilever as sensor elements," *Proc. SPIE*, vol. 8428, p. 842816, Jun. 2012.
- [40] F. Albri, J. Li, R. R. J. Maier, W. N. MacPherson, and D. P. Hand, "Laser machining of sensing components on the end of optical fibres," *J. Micromech. Microeng.*, vol. 23, no. 4, p. 045021, 2013.
- [41] J. Li et al., "Fabricating optical fibre-top cantilevers for temperature sensing," Meas. Sci. Technol., vol. 25, no. 3, p. 035206, 2014.
- [42] J. Fritz *et al.*, "Stress at the solid-liquid interface of self-assembled monolayers on gold investigated with a nanomechanical sensor," *Langmuir*, vol. 16, no. 25, pp. 9694–9696, 2000.
- [43] C. D. Fung, P. W. Cheung, and W. H. Ko, "A generalized theory of an electrolyte-insulator-semiconductor field-effect transistor," *IEEE Trans. Electron Device*, vol. 33, no. 1, pp. 8–18, Jan. 1986.
- [44] R. G. Nuzzo and D. L. Allara, "Adsorption of bifunctional organic disulfides on gold surfaces," J. Amer. Chem. Soc., vol. 105, no. 13, pp. 4481–4483, 1983.
- [45] W. Shu et al., "DNA molecular motor driven micromechanical cantilever arrays," J. Amer. Chem. Soc., vol. 127, no. 48, pp. 17054–17060, 2005.
- [46] S. Kumar and J. H. Hoh, "Direct visualization of vesicle-bilayer complexes by atomic force microscopy," *Langmuir*, vol. 16, no. 25, pp. 9936–9940, 2000.

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