ADVANCED MATERIALS

Polymer–Silicon Flexible Structures for Fast Chemical Vapor Detection**

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Although there are several aspects that contribute to an efficient chemical sensor system, the choice of responsive materials can help to optimize several key attributes critical for their ultimate performance, specifically high sensitivity, selectivity, fast response time, and wide dynamic range. Some common issues reported to date for sensors are limited detection range, slow response time, long recovery period, and fast saturation (limited dynamic range).[1] Most of these issues are directly related to the large volume of bulk porous material that is needed for measurable signal output, which leads to inherently slow sorption, diffusion, and desorption processes. One type of gas sensor that receives only limited attention despite being among the most frequently used sensors for measuring important environmental quantities is the humidity sensor.[2] Important applications of this type of sensor include for respiratory equipment, incubators, chemical gas purification, and surgical operations. The main requirements for humidity sensors are good sensitivity over a wide humidity range, low hysteresis, good reproducibility, and longevity.[2,3] Often sensors are required to be very small and suitable for integration into arrayed systems, such as odor-sensing arrays.

Humidity sensors currently tend to exploit the characteristics of bulk materials with the required resistive and capacitive response properties. This type of sensor comprises a moisture sensitive ceramic, metal, or polymer material that undergoes changes in resistance or capacitance with variations in ambient humidity.[3,4] Water vapor sensors that use polymeric materials commonly incorporate polyimides, polycarbonates, cellulose acetates, or conductive polymers.[5,6] The typical vapor sensitivity of such sensors is of the order of tens of parts per million (or ±0.05 % relative humidity, RH), which is sufficient for most routine measurements. However, this is not acceptable if a fast, real-time monitoring of vapor content variation is required. Increased sensitivity, to a low ppm level, can be achieved using a porous material to maximize the specific surface area available for water vapor adsorption.[7–9] For example, 0.4 ppm_v (parts per million by volume) water vapor detection was demonstrated by Salonen et al. using carbonized porous silicon.[9] Bruno et al. used a polymer-coated resonant device to obtain a sensitivity of 7 ppm_v.[10] In these cases, although the sensors reported showed good sensitivity they suffered sluggish response times, often requiring a few minutes to completely recover. Currently, modest sensitivity and slow response are the main obstacles to the design and development of microcantilever-based sensor technology.[11,12]

In this Communication, we present a bimaterial design for humidity sensing with a vapor-sensitive plasma-polymerized nanolayer coating on a silicon microcantilever with a low flexural rigidity (Fig. 1a,d). The coating acts as a sensitive mechanical actuator, which mediates high internal stresses, enabling fast response to the presence of vapor in the environment. In a bimaterial microcantilever, there is preferential swelling of the plasma-polymerized material when it is exposed to particular analytes. This causes a change in surface stress resulting in bending proportional to the external stimulus. For this bimaterial design, we observed unprecedented sensitivity to variations in the humidity, with resolution of ±10 ppb (±0.00005 % RH) with fast, millisecond-range response. These measurements are both several orders of magnitude better than the typical values reported in the literature. We suggest that the integration of a crosslinked polymer, high internal stresses, and firm adhesion to the silicon are critical factors that lead to desirable responsive behavior for a bimaterial structure.

The plasma-enhanced chemical vapor deposition exploited here offers the unique ability to polymerize a wide variety of precursors to obtain coatings that are sensitive to various analytes.[13–17] The most efficient vapor-responsive material, from a series of six polymers tested in this study, was plasma-polymerized methacrylonitrile (PP-MAN) (Fig. 1b and Supporting Information, SI). An atomic force microscopy (AFM) im-

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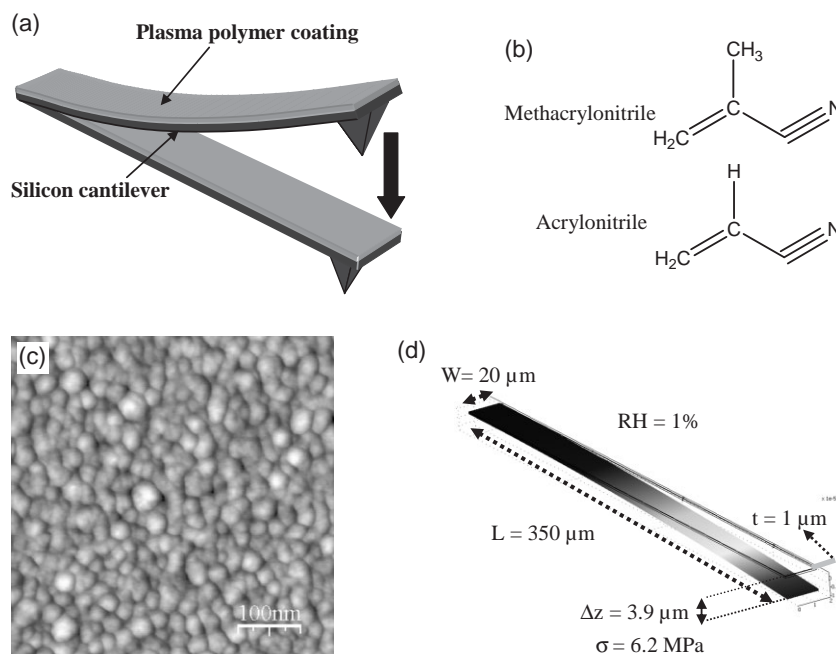Prescribed by ANSI Std Z39-18

Figure 1. a) Schematic of the polymer-coated microcantilever responding to water vapor. b) Chemical structure of methacrylonitrile and acrylonitrile. c) AFM topographical images of PP-MAN surface showing the nanodomain surface morphology (z range: 10 nm) d) FEA model of the deflected cantilever with parameters shown.

age of the PP-MAN coating with a thickness of 283 nm at 6 % RH showed a granular morphology with a surface microroughness of about 1.2 nm over a surface area of 1 μm × 1 μm (Fig. 1c, SI). Granular surface morphology, characteristic of plasma-polymeriyed films,[18] with an average nanodomain diameter of less than 30 nm facilitates a high specific surface area and is critical to the performance reported here. In fact, it has been demonstrated previously that enhanced surface area (due to well-defined grain boundaries) combined with locked-in residual stress in thin metal films deposited at slow rates provides significant enhancement in the sensitivity of the microcantilever-based sensors compared with smooth films.[19] Surface force measurements[20] showed the elastic modulus to be 1.6 GPa and indicated the presence of strong adhesive forces ((36±12) nN) (see SI). The contact angle of the PP-MAN of 75°±4° (surface energy of 43 N m^{-1}), compared with 56°±2° for the spin-coated sample characterizes the surface as modestly hydrophobic, possessing some polar groups.[21] Considering the higher contact angle of PP-MAN and the presence of C=N and C≡N stretch bands in the Fourier transform infrared (FTIR) spectra (see SI), we conclude that plasma polymerization results in crosslinked films with a modest surface concentration of the polar cyano groups. Surface analysis of the polymers with X-ray photoelectron spectroscopy (XPS) indicated that the chemical composition was close to that expected with, however, some oxygen

(12–14 %) present, possibly due to the free radicals within the sub-surface layer (see SI).[22]

Figure 2a shows the microcantilever at various RHs ranging from 6 to 66 %. The deflection of the PP-MAN cantilever under desiccation and humidification shows a modest <2 % hysteresis over 10 consecutive cycles (10 h timeframe) separated by several days and over a year of storage (Fig. 2b). It is remarkable that the response remained virtually unchanged (within ±5 %) after such long storage time under normal (variable temperature, humidity, and air quality) lab conditions. The deflection was virtually linear for a small RH range (<10 %) and the sensitivity (deflection/unit of humidity change) was calculated to be extremely high, 3.5 μm/1 % RH (Table 1). It is noteworthy that the presence of a human palm at a modest distance (about 30 cm) was clearly indicated by a 50 μm deflection. The response of identical cantilevers spin-coated with "conventional" PMAN (of thickness 470 nm) was remarkably lower. This cantilever showed a meager response, with a sensitivity of only 110 nm/1 % RH, close to that reported in the literature for a similar cantilever and nearly 30 times lower than the corresponding plasma-polymerized cantilever.[23] The plasma-polymerized acrylonitrile (PP-AN) cantilever also exhibited a high (although lower than PP-MAN) sensitivity, while the uncoated reference cantilever exhibited no visible deflections (Fig. 2b).

Here, in accordance with common understanding, we suggest that the adsorption (condensation) of water molecules on and rapid progressive swelling of the plasma-polymerized layer are the primary causes of differential stress across the bimaterial interface, which causes the bending of the entire structure. However, water condensation applies normal forces due to the vertical component of the surface energy of the liq-

Table 1. Summary of major parameters for various gas sensors.

	Sensitivity to H_2O [nm/20 ppm]	Detection precision [a] [ppb]	Response time [s]	Selectivity deflection ratio [b]	Shelf life [c] [years]
PP-MAN cantilever	3500	±10	$10^{-3} - 10^{-1}$	10^4	>1.5
Spin-coated PMAN cantilever	110	±300	NA	NA	NA
Typical bimaterial cantilever	10–100	±(100-500)	10-200	5-100	NA
Swollen PP coating from literature [40]	10	±10000	~100	NA	NA
Acoustic wave sensors [58,60]	NA	±6000	~10	8	<0.1
Silicon nanowires [61]	NA	±50	>300	0.2	NA

(a)

6%RH

50μm

66%RH

(b)

PP-MAN

PP-AN

Spin coated PMAN
Uncoated reference

Deflection (μm) / Relative Humidity (%)

(c)

— Finite element analysis
●— Experimental

ΔRH = 1%

PP-MAN

PP-MAN

Spin coated PMAN

Deflection (μm) / Thickness (nm)

(d)

PP-MAN

20°C
40°C
60°C

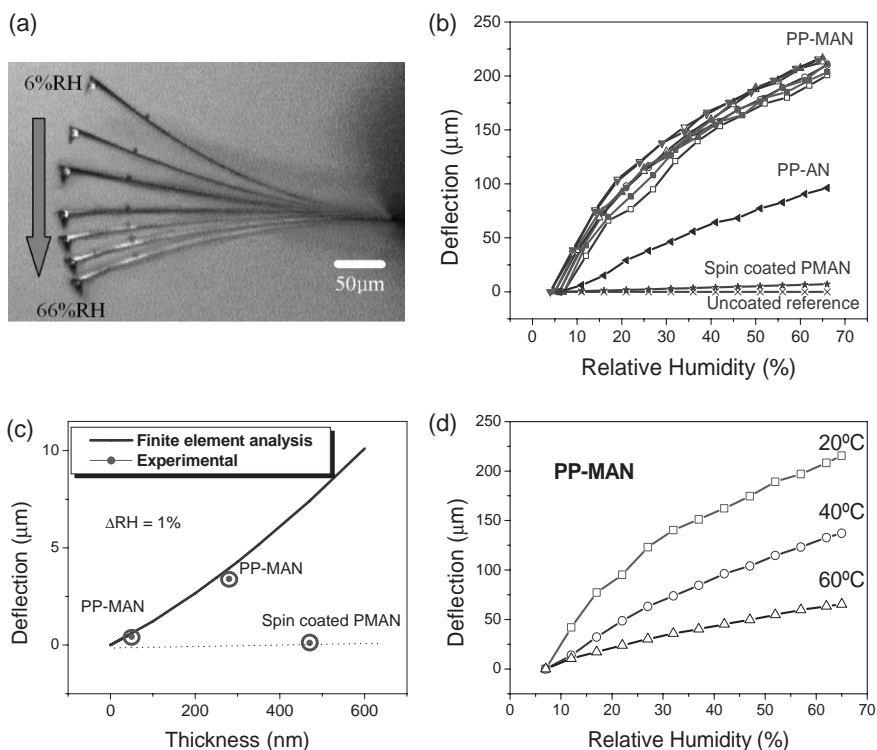Deflection (μm) / Relative Humidity (%)

Figure 2. a) Optical images showing the bending of the PP-MAN-coated cantilever for humidity changing from 6 to 66 % RH at an interval of 10 % RH, with deflection at 6 % taken as a reference point. b) The deflection vs. humidity (error bars are below the size of the symbols) of cantilevers coated with PP-MAN, PP-AN, spin-coated PMAN, and a bare silicon cantilever. Empty symbols indicate humidification and corresponding filled symbols indicate desiccation: triangles (5th consecutive cycle), inverted triangles (10th consecutive cycle), squares (four months after fabrication), circles (after 18 months), c) FEA theoretical deflection of the cantilever vs thickness of the PMAN coatings for 1 % change in RH (solid line) and experimentally observed deflections for 50 and 283 nm PP-MAN and 470 nm spin coated PMAN. Dotted line represents typical deflection for conventional cantilevers. d) Deflection vs humidity of PP-MAN cantilever at 20, 40, and 60 °C.

uid/vapor interface and normally results in a minor nanometer-scale deflection. This deflection is much smaller than any of those observed here.[24–26] Thus, although some enhancement may be due to capillary condensation inside the nanopores, micrometer-scale deflection leads us to believe that swelling is mostly responsible. Hence, the swelling of the PP-MAN layer was studied by measuring the coating thicknesses at three different RH levels (6, 30, and 66 %) (see SI). The thickness of the film increased by 12 % for a 60 % RH difference, a 0.2 % change per 1 % RH. Thus, the strain induced in the polymer film for a 1 % change in RH was calculated to be 4.3×10^{-4}. This level of strain generates a 5 MPa stress for the elastic modulus measured. The corresponding deflection can be roughly estimated using Stoney's equation[27,28]

$$\sigma = \frac{Et_s^2}{6R(1-\upsilon)t_f} \qquad (1)$$

where R is the radius of curvature, E is the elastic modulus, t_s is the thickness of the substrate, υ is the Poisson's ratio, and t_f is

the thickness of the polymer film. From Equation 1, the expected deflection due to the swelling-induced stress was calculated to be about 2 μm/1 % RH, which is lower to that obtained experimentally. Therefore, considering the limited accuracy of Stoney's equation for bimaterial structures with thicker coatings (25 % of the thickness of the cantilever in our case), we evaluated stresses for the polymer–silicon beam with finite element analysis (FEA) (Fig. 1d).[29] The estimated deflection due to the swelling-induced stresses with full stress transfer across the interface was estimated to be 3.9 μm/1 % RH, which is close to that obtained experimentally (3.5 μm/1 % RH) with some reduction probably caused by coating imperfections (Fig. 2c). The interfacial stress at the free end of the bimaterial structure was calculated to be 6.2 MPa (12 % higher than for a simple estimation from Stoney's equation) for a 1 % change in RH and reached nearly 370 MPa for a 60 % change in RH. The lower sensitivity of a 50 nm thick PP-MAN coating also agreed closely with the FEA evaluation (Fig. 2c). Thus, FEA simulation indicated that the swelling-related interfacial stresses were sufficient to cause the microcantilever bending behavior observed experimentally.

In the case of the spin-coated PMAN layers, the observed cantilever deflection was well below the theoretical estimation. This confirms that there is a failure to efficiently transfer the swelling-initiated stress (Fig. 2c). This result points to the importance of the strong adhesion of the coating, which results in maximal conversion of enthalpy-driven swelling into mechanical bending of the bimaterial cantilever. Indeed, the plasma-polymerized coatings introduced here displayed excellent adhesion to the cantilever surface. This was confirmed by the study of modified cantilevers after huge multiple deflections (up to 300 μm) and by a peel-off test. AFM imaging of the PP-MAN coating after multiple deflections showed no signs of rupture or delamination of the topmost plasma-polymerized layer (see SI). This is consistent with recent results for more mechanically stable plasma-polymerized coatings under repeated shearing.[30] Moreover, our peel-off test demonstrated that the PP-MAN coatings are extremely stable and cannot be removed with sticky tape.

Conventional bimaterial cantilevers are usually based on one-side modification with self-assembled monolayers (SAMs) that facilitate the adsorption of analytes leading to differential surface energy.[31-34] Although such a design has

been used successfully for chemical and biological detection, the sensitivity was inherently limited to the differential surface energy mediated by analyte adsorption.[35–39] If this difference reaches 20 mJ m^{-2} (a level that is likely between highly hydrophobic and hydrophilic surfaces), the bending force reaches several nanonewtons. This could lead to several hundred nanometers deflection for typical microcantilevers (stresses within 0.01–0.1 N m^{-1}). In contrast, in the case of plasma-polymerized nanocoatings, even modest swelling results in a bending force in the millinewton range (stress within 1–10 N m^{-1}), which facilitates micrometer-scale deflections.

Hence, unlike conventional bimaterial structures, which rely on small differences in the surface tension on the active and passive sides, the bimaterial design with plasma-polymerized coating utilizes a mechanism involving *large interfacial stresses* causing inherently higher bending forces. It is noteworthy that swelling of coatings has been employed previously as the mechanism to induce differential stress in a bimaterial cantilever for vapor sensing.[40] However, these coatings, amongst others (such as spin-coating, and inkjet printing), resulted in relatively modest deflections, typically of the order of several tens to a hundred nanometers.[41,42] The reported sensitivity of 10 nm/1 % RH for plasma-polymercoated cantilevers is more than two orders of magnitude lower than that measured here, indicating an insufficient transfer of swelling-induced stress to the polymer/inorganic interface.

The sensitivity achieved here is several orders of magnitude better than those known for microcantilever-based sensors and this system can be considered a miniature, fast, and inexpensive alternative.[43–46] Surface layers, such as SAMs, polymer brushes, hydrogels, thin metal films, and sol–gel layers have been employed as sensitive coatings.[47–50] Swelling of plasma-polymerized allylamine on cantilevers has been recently studied by Igarashi et al.[41] They concluded that less crosslinking of the polymers results in greater swelling, but these bimaterial structures showed only modest cantilever deflection, probably because of insufficient stress transfer ability. We suggest that the fine balance of local hydrophobic and hydrophilic interactions, important for fast intake and removal of water molecules, achieved for PP-MAN coatings by a randomized network of polar segments and hydrophobic methyl groups, is responsible for such swelling behavior (Fig. 1a). The coexistence of hydrophobic and hydrophilic groups in close proximity, as well as the internal stresses, promotes significant expansion and contraction. This suggestion is supported by the much less impressive performance of the PP-AN coating, which has no hydrophobic methyl groups (Figs 1b and 2b), and some other polymers with predominantly polar or hydrophobic segments (see below and SI). Finally, the response of the PP-MAN cantilever was tested at different temperatures. The greatest response was observed close to the room temperature (Fig. 2d).

Another important issue related to conventional sensors that relies on the swelling phenomenon is the relatively slow dynamics related to reaching the equilibrium state.[47] In con-

trast, our experiments clearly demonstrate an extraordinarily fast response for bimaterial cantilevers (see videos in SI). This fast response, which reaches a low millisecond range, is out of reach for conventional sensors, which have typical response times of the order of a few seconds to minutes as they are limited by the slow processes of molecular sorption and desorption within a bulk material.[51,52] In fact, considering that the analyte molecule propagation is controlled by molecular diffusion,[51] scaling down the thickness of the polymeric layer from the conventional 10 μm to 200+ nm should facilitate an equilibration time that is three orders of magnitude faster.

Two experiments were performed to quantify the response time of the sensor to varying humidity in large (ΔRH=16 % and 2 %) and small (ΔRH = 0.025 % and 0.002 %) ranges. Firstly, the PP-MAN cantilever was exposed to gentle dry nitrogen pulses (for 83 ms) followed by recovery (for 250 ms) to initial humidity (36 % RH) at a constant rate of 3 Hz (Fig. 3a, b). The corresponding periodic deflection of the PP-MAN cantilever and a reference uncoated cantilever were recorded for hundreds of cycles (see Fig. 3a and SI videos for representative segments) and the differential deflection was plotted in Figure 3b (the correction for the reference cantilever deflection was within 3 %). The responsive behavior was stable and reproducible with a characteristic asymmetric shape reflecting faster response and slower relaxation to the initial position. The response time was found to be (80±20) ms for a 16 % change in humidity (estimated from calibrated bending). This is a fast response to such a large range. Secondly, the cantilever was exposed to cyclic variations of humidity in a narrow range (±1 % RH) over a relatively long time (several minutes) and demonstrated a stable and repeatable response with no change in the base line (Fig. 3c).

On the other hand, for a nearly instantaneous change of humidity (by 0.01 %) the cantilever exhibited a response time (between 10 and 90 % of the total response) of 9.5 ms (Fig. 3d). Furthermore, linear ramps (1 % RH per second) of humidification and desiccation within 0.025 % RH or ±5 ppmv range (1 % RH corresponds to a vapor density of 0.23 g m^{-3} [3]) were monitored with a sampling frequency of 1 KHz (Fig. 3e). Under these conditions, we observed a linear response with a minimum distinguishable increment, limited by thermal vibrations, of 0.0005 % RH (or ±10 ppb), which exceeds that reported with cantilevers by two orders of magnitude (Table 1).[9] The extreme limits of the sensitivity were tested for the cantilever at a slow ramp rate of 0.02 % per second with a sampling frequency of 10 KHz (Fig. 3e). In such extreme conditions, an overall linear trend is observed beyond the thermal noise (thermal amplitude of 0.25 nm). This observation confirms that the smallest measurable change of water vapor content is ±10 ppb and the temporal resolution is below 2 ms. These deflection dynamics do not only show the excellent sensitivity of the bimaterial cantilever, but also extremely fast response times in variable environmental conditions. Remarkably, after fabrication the response was stable for repeated humidification and desiccation cycles over a period of more than a year.
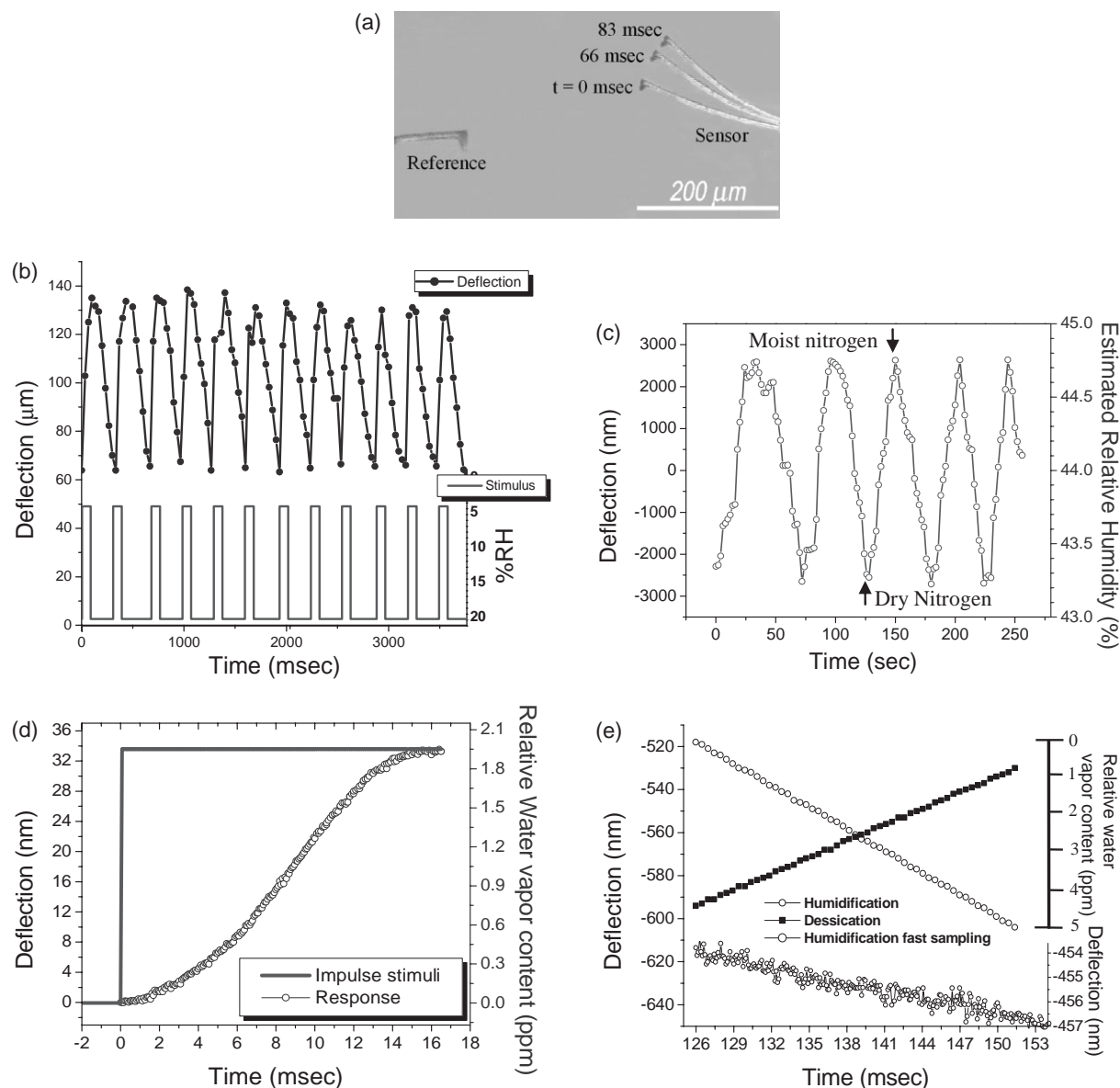
Figure 3. a) Overlaid snapshots of the PP-MAN coated cantilever and reference uncoated cantilever depicting the response to nitrogen pulse. b) Deflection of the cantilever under desiccating nitrogen pulses followed by relaxation to humid state. c) Response to cycles of small variations of humidity. d) Static deflection of cantilever in response to a sudden change in humidity (0.01 % step). e) Dynamic sampling for a linear humidification and desiccation for RH interval of 0.02 % (top) and 0.001 % (bottom).

While the results discussed so far have emphasized the high sensitivity and fast response time of the PP-MAN cantilevers to water vapor, this design can be extended to different gas or chemical analytes. This could potentially inspire a whole new class of real-time, fast, microscopic chemical sensing arrays of the kind required for environmental monitoring. [30,53] In fact, in our preliminary testing we demonstrated that a proper selection of plasma-polymerized coatings facilitates high sensitivity to organic compounds that can be used as components of plastic explosives (Fig. 4). For instance, PP-AN (thickness 240 nm) cantilevers showed a fast, reversible response to naphthalene vapor at 40 °C with a detection limit below 1 ppb, an exception-

ally low value (Fig. 4a).[54] Pentafluorostyrene (PP-FS) (thickness of 340 nm) cantilevers showed a huge, reversible, and robust response (a total bending of 300 μm) to saturated hydrazine, a potentially explosive and highly toxic chemical (Fig. 4b).[53] In this case, the detection limit was estimated to be close to 10 ppb, which far exceeds those reported using resistance of conductive polymers or fluorescence emission of conjugated polymers (100 ppb – 10 ppm).[55-57] It is interesting to note that a PP-FS coated cantilever that was initially bent by 180 °C still reacts to hydrazine vapor (Fig. 4b). We believe that the different plasma-polymerized coatings investigated here exhibit structural changes due to solvation forces in the pres-
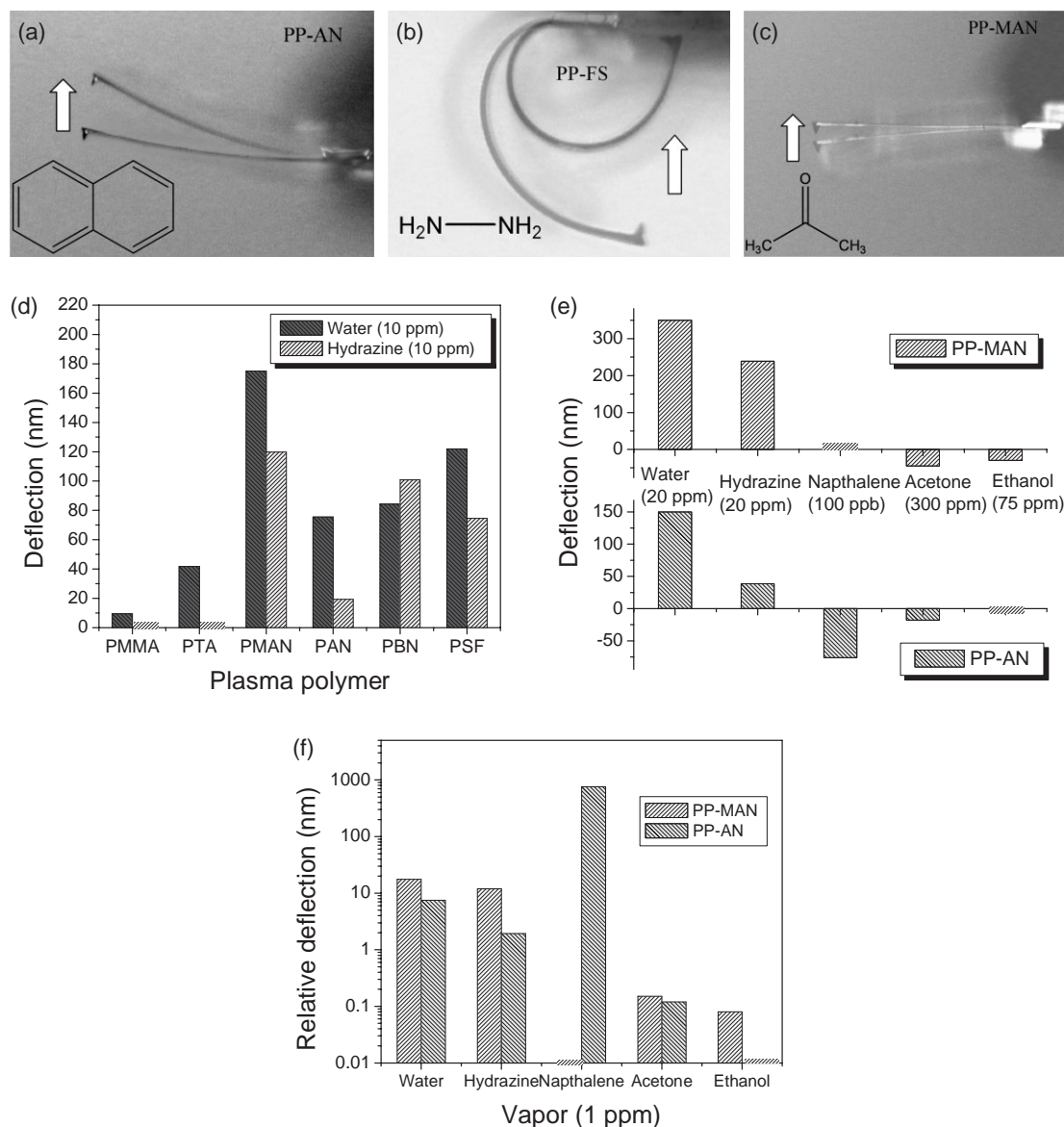
Figure 4. Optical images showing the deflection of the different cantilevers to different vapors: PP-AN cantilever to naphthalene (a), PP-SF cantilever to hydrazine (b), and PP-MAN cantilever to acetone (c). d) Response of different cantilevers to 10 ppm of water and hydrazine. e) The deflection of PP-MAN and PP-AN cantilevers to different vapors under saturated conditions. f) Logarithmic plot of the absolute deflection of PP-MAN and PP-AN cantilevers normalized to 1 ppm concentration of various analytes. For clarity, in (e) and (f) bars have been included in the plot even where there was no detectable deflection.

ence of the various organic vapors. The magnitude of the swelling of the polymers in the presence of various analytes will be the subject of further investigation.

To test selectivity, a critical consideration for the design of multifunctional sensor arrays, we monitored the response to a host of analytes of a series of cantilevers with different plasma-polymerized coatings (Fig. 4d). Cantilevers with plasma-polymerized methyl methacrylate (PP-MMA), trimethyl silyl acetonitrile (PP-TA), PP-MAN, PP-AN, benzonitrile (PP-BN), and PP-FS (with thickness within 250–310 nm) showed very different responses to 10 ppm of water and hydrazine vapor (Fig. 4d). The selectivity of some cantilevers to various analytes is illustrated by the response of PP-MAN and PP-AN cantilevers to water vapor (20 ppm), hydrazine (20 ppm), naphthalene (100 ppb), acetone (300 ppm), and ethanol (75 ppm) (Fig. 4c). This series of chemicals covers a wide range of relevant types of gases including several extreme cases that can be classified with existing solubility contribution schemes:[1] highly volatile (acetone and ethanol), hydrophilic with rich hydrogen-bonding network (water), highly hydrophobic (naphthalene), and highly reactive polar components of plastic explosives (hydrazine).

As we observed, for this series of chemicals, a PP-MAN cantilever exhibits a response of 350 nm for water, while it re-

mains insensitive to naphthalene and exhibits a *negative* deflection of 45 nm for acetone vapor, puzzling behavior at this stage. It is interesting to note that the PP-MAN cantilever also deflects in the negative directions in response to ethanol, while the PP-AN cantilever exhibits a negative deflection for naphthalene, to which PP-MAN remains insensitive. Figure 4f displays the absolute values of the cantilever deflections to various vapors normalized to 1 ppm. The plot clearly shows that the response of the cantilevers to different vapors spreads over four orders of magnitude, making the pattern of deflection distinguishable for an artificial neural network approach (the difference in response can be used as predefined parameters for recognition). This is important if the use of cantilevers in arrays is to be exploited.[22]

Comparison with the best sensitivity and response parameters for existing designs from other cantilevers with plasma-polymerized coatings, acoustic wave sensors, and recently reported silicon nanowires shows that the detection precision of our design is about one order of magnitude better, response time is at least two orders of magnitude faster, and selectivity is two orders of magnitude better than those reported in the literature (Tab. 1). We believe there are several factors that contribute to the outstanding response of our cantilevers, including the unique nanoporous morphology, minute thicknesses, crosslinked nature, and the strong interfacial adhesion of these nanocoatings. The sensitivity and response times achieved here are out of reach for current sensor designs, which usually employ bulky porous materials or weak differential bending forces. It is noteworthy that the plasma polymerization process employed here is a dry deposition technique, compatible with micromachine technology suitable for batch micro-electromechanical system (MEMS) fabrication and allowing seamless integration into arrayed structures. Each cantilever may be selectively coated with a different sensing layer, as the current resolution of spot-coated polymers is several hundred micrometers. Individual layers can have distinctive response patterns to different chemical vapors making it feasible to develop sensitive, fast, and microscopic odor-sensing structures that are capable of real-time sensing of toxic and explosive chemical vapors.[1,58,59]

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