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Abstract

Herein we investigate the feasibility of detecting photo-induced surface stress changes using the deflection response of cantilevers. For this purpose, silicon microcantilevers have been functionalised with spiropyran photochromic molecules, using both a monolayer and a polymeric brushes approach. Upon ultraviolet light irradiation, the spiropyran unit is converted to the merocyanine form due to the photo-induced cleavage of the Cspiro-O bond. The two forms of the molecule have dramatically different charge, polarity and molecular conformations. This makes spiropyrans an ideal system to study the correlation between photo-induced molecular changes and corresponding changes in surface stress. Our investigations include monitoring the changes in static cantilever deflection, and consequently, surface stress of the spiropyran functionalised cantilevers on exposure to ultraviolet light. Cantilever deflection data reveals that ultraviolet induced conformational changes in the spiropyran moiety cause a change in compressive surface stress and this varies with the type of functionalisation method implemented. The change in surface stress response from the spiropyran polymer brushes functionalised cantilevers gives an average surface stress change of 98 Nm−1 (n = 24) while the spiropyran monolayer coated cantilevers have an average surface stress change of about 446 Nm−1 (n = 8) upon irradiation with UV light.

Keywords

Microcantilever sensorsSurface stressNanomechanicsMolecular switchSpiropyran Photochromism

1 Introduction

Cantilevers are nanomechanical transducers which produce mechanical motion arising typically from molecular interactions and over the past two decades microcantilevers have been proposed as highly versatile sensors for a wide variety of applications [1,2]. These cantilevers are generally operated in static deflection mode, by rendering one surface sensitive to a specific external stimulus. Subsequent binding of target molecules to one side of the cantilever causes a static cantilever deflection that can be correlated to a specific surface binding reaction or molecular reorganisation process. So far, microcantilever based sensors have been successfully used to monitor a variety of

different physical [3,4], chemical [5,6] and biological interactions [7,8]. Early work presented the silicon cantilevers for temperature sensing [4]. Further advances in nanomechanics allowed the use of microcantilevers for the detection of biomarkers and the transduction of DNA hybridisation into a nanomechanical response [9–11], along with the use of silicon cantilevers for the detection of volatile organic compounds [5]. Silicon cantilever technology also uses microcantilevers for the detection of malignant melanoma [12,13]. Recent developments in cantilever sensor technology have demonstrated the chemo response of cantilever sensors in the detection of methane using thermally sensitive microcantilevers [14]. Other work has concentrated on improving the sensitivity of cantilever sensors by optimising the cantilever surface profile and cross-section [15]. Investigations into the performance of cantilever based sensors has reiterated the importance of the functionalisation method by comparing cantilever sensors with membrane-type surface stress sensors [16]. Cantilever sensor technology has also recently been applied in the detection of a veterinary drug kanamycin using aptamer-based cantilever array sensors [17]. Most recently cantilevers have been used in the unique detection of organic vapours below their auto-ignition temperature using heat transfer and joule heating of the cantilevers [18].

One of the most studied photochromic systems is the inter-conversion of spiropyran (SP) to merocyanine (MC) [19–21]. Spiropyrans are a class of organic molecular switches that undergo a reversible transition between a closed, non-polar and colourless SP form to a highly polar, open and coloured MC form upon irradiation with ultraviolet (UV) (365 nm) light (Fig. 1). Irradiation with white light (450–550 nm) converts the MC unit back to its closed SP form [19]. The photo-conversion between these two thermodynamically stable isomeric states induces a large change in dipole moment and also surface free energy [22], making spiropyrans particularly interesting targets for the development of microcantilever photo-induced surface stress sensors.
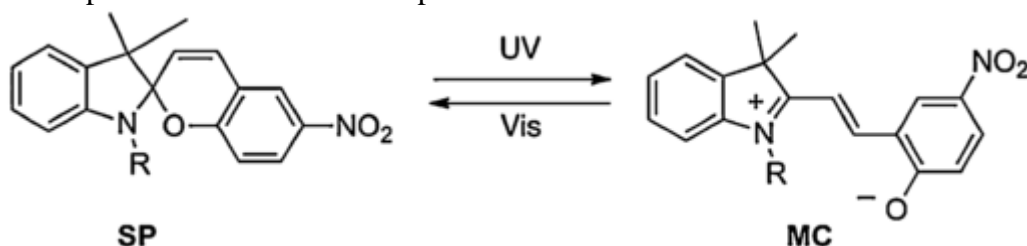

Fig. 1 Photochromic behaviour of spiropyran derivatives.

Previous work on spiropyran photochromic systems include their use for photo-induced optical sensing of metal ions, continuous flow optical sensing of solvents of different polarity [23,24], reversible photo-actuators for microfluidic applications [25–27], photo-chemopropulsion of microdroplets [28], and self-assembly [29,30], among others. More recently it was demonstrated that the conversion between the SP and MC forms can also be achieved mechanically under tensile loading, showing the capability to create mechanochromic materials using SP containing polymers [31]. Spiropyran coated thin films have also been demonstrated by Athanassiou et al. as photo-actuators under UV laser irradiation due to the UV-induced conversion of SP to MC form that causes a bending in the spiropyran doped polymer film [32].

This work presents a spiropyran functionalised cantilever array implemented as a chemical sensor to detect the conformation change of the spiropyran photosensitive molecule. In this study, the dimensions of our sensor surface, in the micrometer range, are dramatically smaller than those of the system previously reported by Athanassiou et al. [32] permitting the use of spiropyran coated silicon microcantilevers to gain additional quantitative information on the levels of stress induced in the spiropyran film

during its conformation change from the SP to the MC form (Fig. 1). The merging of microcantilever technology and spiropyran photochromic molecules offers a good route for the pairing of a highly sensitive transducer with an optically controlled sensing surface.

2 Materials and Methods

2.1 Materials

[3-(2-Aminoethylamino)propyl]trimethoxysilanetechnical grade ≥ 80 (Sigma-Aldrich), 1-ethyl-3-(3dimethylamino propyl) carbodiimide hydrochloride (EDC hydrochloride) (Sigma-Aldrich), 7-Octenyltrichlorosilane (Gelest), 5-norbornene-2-carboxylic acid, exo- (Sigma-Aldrich), 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (SP1) (TCI Europe), N,N'-Dicyclohexylcarbodiimide (DCC) (Sigma-Aldrich), 4-(dimethylamino)pyridine (DMAP) (Sigma-Aldrich) and Grubbs Generation-II catalyst (Sigma-Aldrich) were used as received.1′-(3-carboxypropyl)-3,3′-dimethyl-6-nitrospiro-1-benzopyran-2,2′-indoline (SP-COOH), was synthesised as described elsewhere [33]. The monomer (SP-norbornene) was prepared from the reaction of exo-5-norbornyl carboxylic acid with SP1 in the presence of N,N′-Dicyclohexylcarbodiimide (DCC) and 4-(Dimethylamino) pyridine (DMAP) as described elsewhere [34,35]. For the SP-norbornene and poly (SP-norbornene) synthesis, dry tetrahydrofuran and dry dichloromethane solvents were purchased from Sigma-Aldrich and used as received. The solvents for cleaning and solutions preparation − toluene, dichloromethane, acetone, isopropanol, ethanol and methanol were reagent grade (Sigma-Aldrich), and used without further purification.

2.2 Methods

2.2.1 Cantilever Deflection Measurements

Microcantilever arrays of rectangular silicon beams with a thin layer of gold on the top side were used. Each array consists of sixteen cantilevers and four reference fixed mirrors divided in four separate wells. Cantilever arrays were fabricated from single crystal silicon and are 300 μm long, 150 μm wide, and 1 μm thick (Micromotive GmbH, Germany). The optical detection system, the Veriscan3000 by Protiveris Inc., was already described in detail by Zhang et al. [36]. The "optical lever" or "beam bounce" technique was implemented using a monolithic array of laser sources with an array of focusing micro-lenses and a single position sensitive optical detector (PSD). The "optical lever" technique optically records changes in the deflection of each cantilever on the array with sub-nanometer resolution. The possibility exists of using all sixteen cantilevers (four cantilevers per well) on the cantilever array simultaneously in the Veriscan set-up. Fig. 2 shows a schematic of one well, containing four cantilevers and one reference rigid surface, with the laser beams reflected by the free end of each cantilever as well as the reference surface. A cantilever deflection measurement was used from each individual cantilever when the optical alignment of the laser on the back of the cantilever was optimal. If the reflected laser intensity was deemed to have not reached the minimum for accurate deflection measurements then the cantilever deflection from that cantilever was ignored. The temperature in the cell was kept constant at 23 °C.
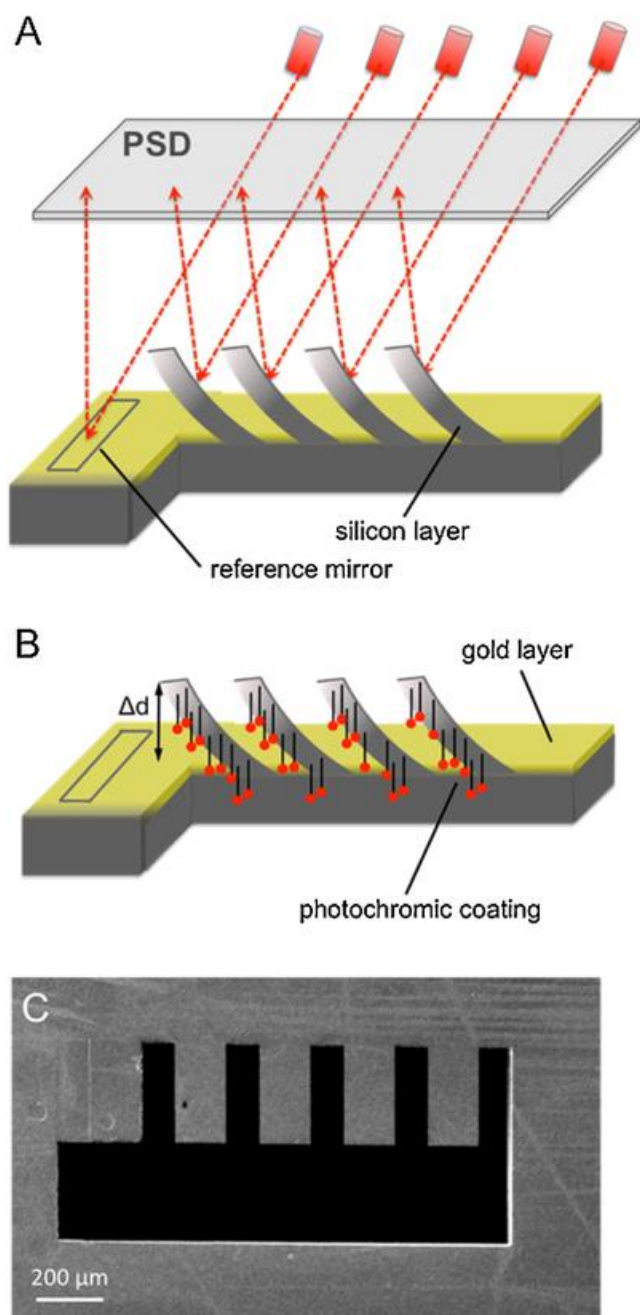
Fig. 2 (a) Schematic representation of the optical deflection detection method for one of the four wells containing a cantilever array (b) cantilever bending caused by the conformation change of the photochromic layer upon exposure to UV light (c) optical image of the cantilever array and the reference rigid surface.

Two different functionalisation methods were implemented: a monolayer and a polymer brushes layer approach. Functionalised SP cantilevers were exposed to a white light LED before being placed in the system in order to ensure the full conversion of the photochromic units to the SP form. A baseline cantilever deflection was recorded before exposing the cantilevers to a UV LED. The change in the cantilever deflection response during UV exposure was monitored. The change in cantilever deflection response was recorded during exposure to UV light over a set period of time (300 s).

2.2.2 Methods of SP functionalisation

a. Functionalisation of silicon microcantilevers with spiropyran monolayers

The protocol used to coat the cantilevers with spiropyran monolayers, is described in Fig. 3, steps 1–2. Prior to functionalisation, the cantilever array was washed with acetone, isopropanol, methanol and DI water, dried under a mild nitrogen stream and then treated with oxygen plasma for 2 minutes, to ensure the formation of hydroxyl groups on the silicon surface. Next, the cantilevers were coated with the spiropyran molecules using self-assembled monolayers (SAMs). The SAMs were generated by immersing the cantilever array into a 10^{-3} M solution of the silanisation agent ([3-(2-Aminoethylamino)propyl]trimethoxysilane) in toluene for 3 h at room temperature, while keeping an inert atmosphere using a glove box (Fig. 3a–step 1). The amino-coated cantilevers were then cleaned with toluene to remove any unbound silanising agent, rinsed with ethanol and dichloromethane, and dried under mild nitrogen stream. The amine functionalised cantilevers were then immersed in a mixed solution of 10^{-3} M SP-COOH in ethanol, and 2×10^{-3} M EDC in water (at 1:3 proportion in volume), and left for at least 48 h at room temperature in a dark place. After that, the cantilevers were rinsed with a 1:1 methanol–water solution for 30 min to remove unbound SP-COOH molecules. Finally, they were washed with copious amounts of deionised water and dried under a mild nitrogen stream. Prior to deflection testing, all cantilevers were stored in the dark, at room temperature. A scheme of the functionalised cantilever is shown in Fig. 3b.
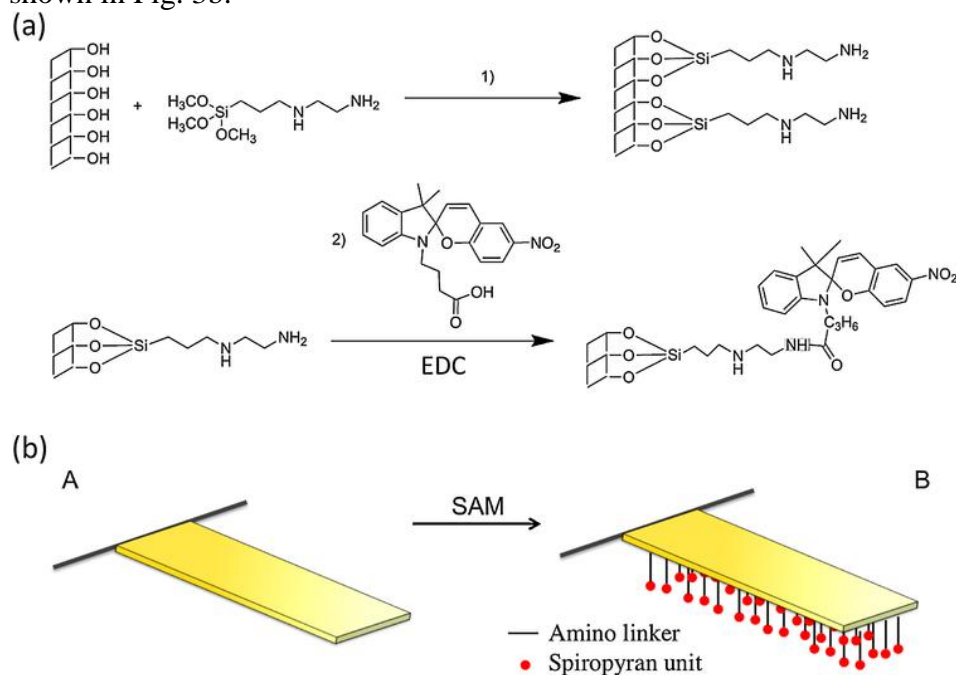

Fig. 3 (a) Scheme describing the functionalisation of the cantilevers with spiropyran self-assembled monolayers; (b) Schematic representation of the cantilever before (A) and after functionalisation with spiropyran self-assembled monolayers (B).

b. Functionalisation of silicon microcantilevers with spiropyran polymeric brushes

The functionalisation of the cantilevers with spiropyran polymeric brushes was achieved using surface-initiated ring-opening metathesis polymerisation (Si-ROMP) as schematically described in Fig. 4a, steps 1-4.
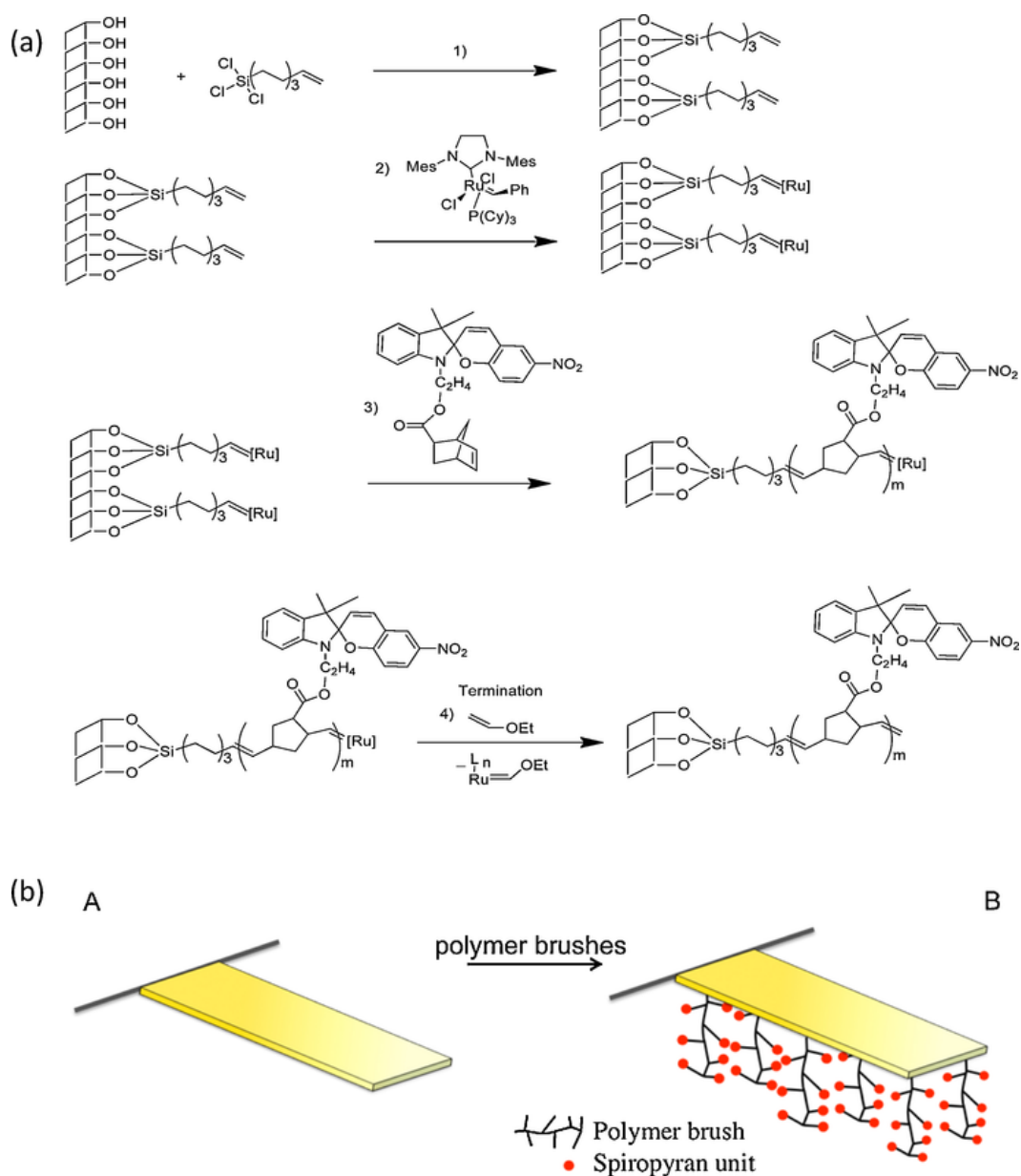
Fig. 4 (a) Scheme describing the functionalisation of the cantilevers with spiropyran polymeric brushes using surface-initiated ring opening metathesis polymerisation. (b) representation of the cantilever before (A) and after functionalisation with spiropyran polymeric brushes using surface-initiated ring opening metathesis polymerisation (B).

Prior to functionalisation, the cantilevers were washed with acetone, water and dried under mild nitrogen stream, then treated with oxygen plasma for 2 minutes, to ensure the formation of hydroxyl groups on the silicon surface. Next, the cantilevers were immersed in a solution of the silanisation agent (7-octenyl trichlorosilane) 0.1 M in dry toluene for 90 minutes (Fig. 4–step 1). They were then washed with acetone, dried under mild nitrogen stream, and left at room temperature for 24 h. Later, they were exposed to a solution of Grubbs Catalyst Second Generation 0.02 M in degassed dichloromethane for 2 h at room temperature (Fig. 4–step 2). After, the catalyst-attached cantilever was washed several times with degassed dichloromethane. Finally, the cantilever was exposed to a solution of spiropyran functionalised monomer, 0.2 M in degassed dichloromethane, for 8 h at room temperature and inert atmosphere (Fig. 4a–step 3). Steps 2 and 3 were conducted in an inert atmosphere using a glove box. The

polymerisation was quenched by adding excess of ethyl vinyl ether (Fig. 4a–step 4). Finally the array was washed with acetone to remove any physisorbed materials and left to dry. A scheme of a functionalised cantilever is shown in Fig. 4b.

2.2.3 SP Functionalised silicon substrate characterisation by Atomic Force Microscopy

Atomic Force Microscopy (AFM) characterisation was carried out using a commercial system (MFP-3D™ AFM, Asylum Research). AFM contact mode topography imaging and scratch thickness measurements of the dry SP functionalised cantilever substrates were implemented to produce surface topography scans and to determine the SP film thickness on the cantilever substrates, respectively. Scratches were produced using a scalpel for thickness measurements on the functionalised layers.

2.2.4 Calculation of surface stress

Differential stress was calculated using Eq. (1) [6]

$$\Delta\sigma = \frac{Et3_s}{6t_f(t_s+t_f)L}\Delta d \qquad (1)$$

Where $\Delta\sigma$ is the differential stress, t_f is the SP film thickness, t_s is the substrate thickness, L is the length of the cantilever, E is the Young's modulus of the cantilever, and Δd is the measured deflection. Once the geometry and material properties of the cantilever are determined, then the cantilever displacement, Δd, is directly proportional to the change in surface stress, $\Delta\sigma$. The consequent change of the cantilever surface stress can be measured by detecting the cantilever deflection and so the chemical process occurring on the cantilever surface can be detected and investigated. The cantilever dimensions provided by the supplier were used, assuming a Young's modulus of 180 GPa. The average cantilever deflection was calculated as the difference between the deflection of the functionalised cantilevers and the uncoated cantilever. Subtracting the spiropyran cantilever deflection from the uncoated deflection enables the response contribution due to the thermal and Schottky effects to be removed.

3 Results and Discussion
3.1 Cantilever Characterisation

Atomic Force Microscope characterisation of the spiropyran monolayer and the spiropyran polymer brushes samples was performed before UV exposure in the dry state. AFM topography scans of both coatings showed that a dense coating was produced using the ROMP polymer brushes grafting technique, and that this result is similar to the topography scans of SP polymer brushes shown by Samanta et al. [37] when a similar surface functionalisation technique was employed. Topography scans of the spiropyran monolayer coatings showed a less dense coating than that of the spiropyran polymeric brushes, see Fig. 5(a) and (b). AFM topography scans revealed the same reproducible morphology over different cantilever substrates.
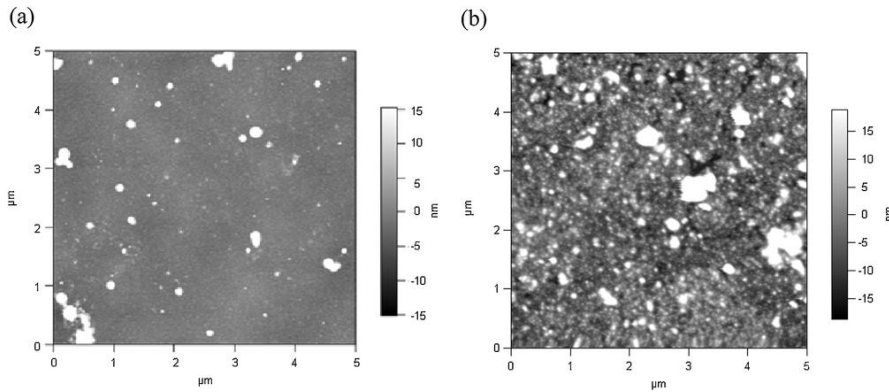
Fig. 5 AFM topography of SP monolayer (a) and SP polymer brushes (b) functionalised silicon substrate of cantilever array.

The monolayer spiropyran and the polymer brushes spiropyran film thickness was measured to be on average 8 nm $+/-$ 3.5 nm (n = 3) and 21 nm $+/-$ 10 nm (n = 3), respectively, using contact mode AFM scratch thickness tests mentioned earlier. The thickness of the monolayer (8 nm $+/-$ 3.5 nm (n = 3)) was much greater than expected, $\sim$2.5 nm as revealed using Molecular Orbital PACkage (MOPAC). This could be explained from the AFM topography of SP monolayer (Fig. 5a), that shows a thin homogenous coverage bellow 5 nm tickness with dispersed large agglomerates ($>$ 15 nm). A thicker spiropyran layer was produced, as expected, with the polymer brushes approach similar to those produced by Samanta et al. under similar experimental conditions [37].

3.2 Photo-induced Cantilever Deflection and Surface Stress Measurements

Fig. 6 presents the typical cantilever deflection response before and during UV exposure from (a) a monolayer reference cantilever, (b) a SP monolayer functionalised cantilever, (c) an uncoated polymer brush reference cantilever and (d) a SP polymer brushes cantilever. The reference cantilever is a cantilever with an amino-terminated silanising agent monolayer but without the spiropyran molecule. Although there is significant drift on some of the deflection data, the results show a clear difference between the cantilever deflection response from the test SP functionalised cantilevers and the reference cantilevers indicating the detection of the change of conformation of the SP molecule.
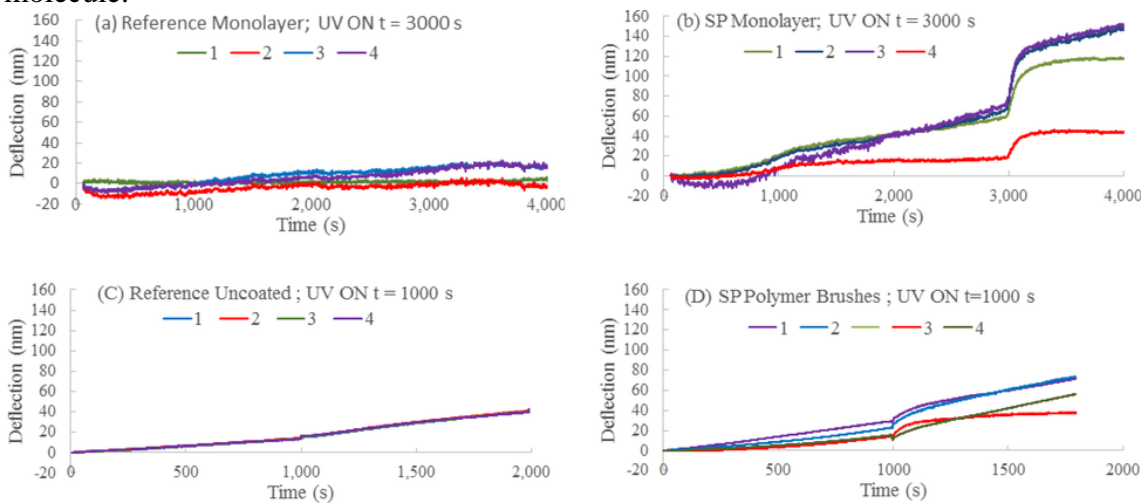
Fig. 6 Example cantilever deflection responses of Reference and Test SP cantilever sensors; (a) Reference Monolayer, (b) SP Monolayer (c) Reference Uncoated and (d) SP Polymer Brushes functionalised cantilevers pre and during UV exposure.

As can be seen in Table 1, the cantilever deflection response from the polymer brushes SP is less varied and smaller than the deflection response obtained from the monolayer SP functionalisation approach. The reference monolayer cantilever and the uncoated reference cantilevers all show a significantly smaller deflection response during exposure to UV light compared to the functionalised SP cantilevers. The results clearly showed that the test cantilever deflection response, due to the change in conformation of the spiropyran, is larger than the reference cantilever response. This conformational change between the SP and MC form is expected since it was previously confirmed by UV–vis spectroscopy when similar functionalisation procedures were used by us and others for other type of substrates such as silica microbeads [38], glass slides and glass micro-capillaries [33] (monolayer), and for glass slides [37] and glass micro-capillaries (SP brushes) [23,24].

Table 1
Cantilever deflection response on exposure to UV light.
Table 1

Substrate functionalisation type	Cantilever Deflection		Number of samples (n)
	Mean (nm)	Standard Deviation (nm)	
Reference Uncoated	14	5	28
Reference Monolayer	6	0.5	6
SP Monolayer	50	26	8
SP Polymer Brushes	35	13	24

Cantilever bending is induced as a result of light irradiation by two different processes. The first and fastest bending is due to photo-induced stresses caused by charge carriers being created as a result of photons of sufficient energy promoting electrons across the Schottky barrier. The second process is due to the slow bending of the cantilever due to thermal expansion, as a result of the absorption of photons whose energy is transformed into heat and has been studied by other groups [39,40].

As the cantilevers in these tests were exposed to light, the thermal and Schottky effect on cantilever deflection was measured. The cantilever deflection response, on exposure to UV light, for the reference uncoated cantilevers (thermal and Schottky effect) was found to be on average ca. 14 nm, see Table 1 above;, this is within the same range as results obtained by Helm et al. [41] who measured the deflection due to the Schottky effect on exposure to UV light (350 nm) to be on average ca. 5 nm. A comparison of the thermal and Shottky effect values obtained by Helm et al. and this work are reasonable considering the dependence on the type of cantilever deflection systems and the used set-up. The deflection response of spiropyran functionalised cantilevers is believed to be due to a combination of the thermal effect, the Schottky effect and the spiropyran conformation change, whereas the deflection response of reference uncoated cantilevers is due to the thermal and Schottky effect solely. The cantilever deflection response for uncoated cantilevers to UV light shows the thermal and Schottky deflection response (14 nm) is well below the deflection response from the spiropyran functionalised cantilevers on exposure to UV light, which is on average 50 nm for the monolayer

spiropyran functionalised cantilevers and 35 nm for the polymer brushes spiropyran functionalised cantilevers. The dominant factor causing the increased deflection response of the SP functionalised cantilevers compared to the reference cantilevers is the conformation change of SP.

The type of SP functionalisation method implemented was seen to affect the level of the cantilever deflection response on exposure to UV. The deflection response from the SP polymer brushes functionalised cantilevers is smaller compared to the SP monolayer approach and the response time is longer, as seen in Fig. 6. The differences in speed of response can be attributed to the fact that the spiropyran has a greater degree of freedom required for conformation change in response to light in the monolayer approach compared to the polymeric brushes, where due to the high density of SP units in the polymeric chain, the steric hindrance can decrease the ring-opening kinetics of the spiropyran as shown previously in the case of similar SP polymer brush coatings [23]. This would also explain the time delay in deflection response of the cantilever. Moreover, the smaller deflection response of the polymeric brushes cantilevers could be explained considering that in the polymeric brushes the SP unit appears as a pendant group in the polymeric chain, meaning that the distance from the cantilever surface to the SP unit is much greater than in the case of the monolayer, which would cause a smaller stress change on the cantilever surface, and therefore a smaller cantilever deflection. This work is validated by Wu et al. [42] who found that the efficiency of stress transmission dramatically decreased by increasing the chain length of linker used between the receptor molecule and the microcantilever surface.

The change in surface stress of the different cantilevers on exposure to UV light was also calculated using the measured cantilever deflection and Eq. (2). The surface stress was calculated using the differential cantilever deflection which is test cantilever deflection minus reference cantilever deflection. Table 2 shows the variation in surface stress compared to the functionalisation process used.

Table 2 Differential deflection and surface stress for cantilevers SP coated with the two employed processes.

	Film Thickness (nm)	SP Cantilever deflectiona (nm)	Surface Stressb (N m−1)
SP Monolayer	8	36	446
SP Polymer Brushes	21	21	98

aSP Cantilever deflection minus reference cantilever deflection.
bSurface Stress due to SP conformation change.

Mathad et al. [40] lists the three main factors which affect surface stress: surface reconstruction, intermolecular forces, and interaction energies. When the SP changes to the MC form there is a change in polarity as well as a change in the overall charge [19]. This induces a repulsive force in the functionalised layer probably due to the strong repulsion produced by the anionic nitrophenolate group of MC thus inducing a change in surface stress [43].

In both the monolayer and polymer brushes approaches it is known that the free end of the MC dipole is negative and consequently results in repulsive forces between neighbouring MC molecules. Steric effects due to the different volumes occupied by the SP and MC form also contribute to the change in surface stress of the cantilever. The MC occupies a larger volume than the SP form and consequently contributes further to

the intermolecular repulsive forces arising. The change in volume in the monolayer approach is also much closer to the surface. The polymer brushes are more mobile and the change in volume of the attached MC is at a greater distance from the cantilever surface, thus contributing less to the intermolecular forces and the corresponding change in surface stress. This has been endorsed by the cantilever deflection and surface stress data that shows a smaller surface stress induced in the polymer brushes spiropyran cantilevers (ca. 98 N m−1, Table 2) compared to the spiropyran monolayer functionalised cantilevers on exposure to UV light (ca. 446 N m−1, Table 2). Similar surface stress values (~50 N m−1) were calculated from microcantilevers, to detect changes in solvent type and pH, with end-grafted stimulus responsive polymer brushes by Abu-Lail et al. [6].

4 Conclusions

This work presents systematic deflection measurements of silicon microcantilevers coated with spiropyran photo-active molecules. Arrays of sixteen rectangular silicon cantilevers coated with a thin layer of gold on one side and SP moieties on the opposite side were used and their deflection response was measured during photo-activation with UV light. Different immobilisation procedures were tested based either on a monolayer approach, or on the use of grafted polymer brushes, where each monomer contains a SP unit.

Cantilevers with immobilised SP moieties produced, on exposure to UV light, a larger deflection response compared to uncoated ones. This was attributed to UV induced conformational changes of spiropyran molecules to their MC form that induce a compressive stress onto the cantilever surface, not balanced by the opposite, gold coated side. It was found that SP polymer brushes functionalisation method produced a more consistent, but smaller, change in surface stress and consequent cantilever deflection than a monolayer functionalisation approach. To conclude, a microcantilever based device has been demonstrated which mechanically transduces conformational changes of photochromic molecules. The cantilever sensor presented here allows quantification of photo-induced molecular change occurring on the cantilever surface, demonstrating its applicability, among others, for measuring molecular changes. Future work will include investigating the reversibility of spiropyran-merocyanine isomerisation using functionalised cantilevers and the ability to detect the presence of different metal ions as the merocyanine form of spiropyran unit is well known for its binding capacity towards divalent metal ions among other charged species [44–46]. This would open the possibility of producing a chemical microsensor which can be optically turned ON/OFF.

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