OPTICALLY DEFINED CHEMICAL FUNCTIONALIZATION OF SILICON NANOMECHANICAL RESONATORS FOR MASS SENSING

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Nanomechanical resonators with their extremely small mass and high surface/volume ratio present a unique opportunity for mass sensing[1-4]. However, functionalization with selective vapor adsorptive functional groups has been an impediment to the realization of nanomechanical systems for mass sensing. Functional groups that adsorb analytes of interest should be patterned only on the nanoresonator itself, and should not be located on structural elements or micro-channel walls, which would greatly limit the minimum detectible limit of the overall device. Also, traditional spin cast polymer films present the problem of being many times thicker than the nanomechanical resonator, essentially burying the resonator in the adsorptive polymer and completely damping the resonator. To address this, we are using a generic monolayer functionalization scheme based on a UV-mediated reaction between terminal alkenes and a hydrogen terminated silicon surface[5]. Specifically, we report the selective surface functionalization with a vapor adsorptive monolayer of hexafluoro-dimethylcarbinol on polycrystalline silicon nanomechanical resonators.

I. INTRODUCTION

The ability to selectively functionalize individual nanomechanical resonators with functional groups that absorb a specific class of molecules is an enabling technology for realizing nanomechanical systems for mass sensing applications. Functional groups physically located on structural borders or non-moving elements can greatly limit the mass sensitivity of nanomechanical systems since those polymers still absorb analytes of interest without a means of detecting them. Using a UV patternable functionalization scheme allows one to functionalize only the resonators and not the surrounding supporting structures. Such a technique can be extended to selectively functionalize designated areas of the resonators for increased resonator sensitivity and to functionalize different resonators with different polymers by using a series of UV masks. Using polycrystalline silicon as a substrate provides the opportunity to take full advantage of existing technologies in microelectronics processing. On the negative side, chemical functionalization of silicon is complicated by the fact that silicon readily oxidizes in air to produce an amorphous oxide.

In recent years, new attachment methods for the organic functionalization of silicon surfaces through formation of direct silicon-carbon bonds have been reported [5-9]. Here we report the successful application of these reactions as a route for the attachment of hexafluorodimethylcarbinol to polycrystalline silicon substrates. Thick films incorporating the hexafluorodimethylcarbinol group have already been shown in SAW devices[10] to be an effective sorbent polymer for dimethyl methylphosphonate (DMMP), a surrogate of the nerve agent Sarin. In this work we seek to functionalize thin silicon films with a monolayer of a sorbent polymer in order to realize ultra-sensitive mass detectors.

As we report here, the resultant modified silicon surfaces we have achieved are reproducibly prepared, stable under ambient conditions (limiting silicon oxide growth), and show no detectable nonspecific binding. The high fidelity of these surfaces promises substantial benefit to the emerging technology of NEMS ultra-sensitive mass sensors.

II. EXPERIMENTAL

A. *Resonator Fabrication and Characterization*

A dome-shaped resonator geometry was chosen for this study because of the high surface area available for functionalization which maximizes the ability for analyte detection by adsorption to the resonator's functionalized area. Further, the dome's high rigidity facilitates both functionalization and post-processing.

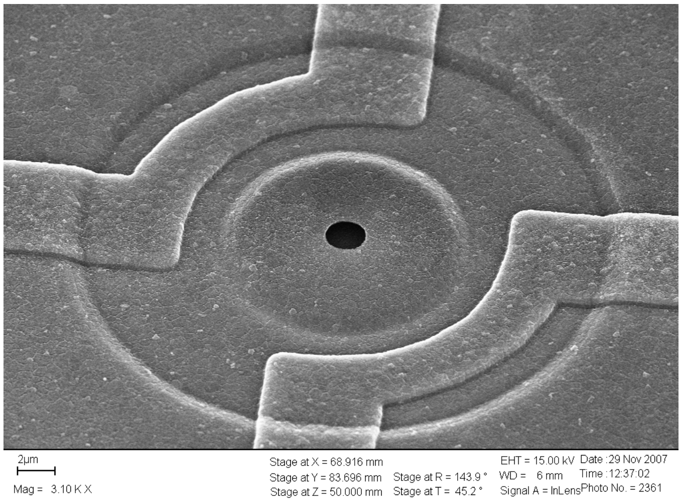

Fig. 1. SEM micrograph of released polysilicon nanomechanical dome resonator with heavily doped polysilicon thermoelastic actuator.

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Nanomechanical dome resonators were fabricated from a 320 nm thick gate polysilicon layer of a standard CMOS fabrication process (1.5 μm AMI available through MOSIS). Post-processing release of the dome resonator (Fig. 1) was performed at the Naval Research Laboratory Nanofabrication Facility using a timed etch in BOE (50 min.). Optical transduction was used to study the vibratory response of the resonators from vacuum (~10^{-6} Pa) to atmospheric pressure (Fig. 2). A point-type excitation is provided by modulation of the intensity of a blue diode laser (wavelength 412 nm) focused on the attachment of the resonator to the substrate. The resulting motion was detected interferometrically by focusing another laser (red CW HeNe, 633 nm) at a different point on the resonator and measuring the modulation of the intensity of the reflected light [11].

B. Mass sensitivity and Quality Factor

The Quality factor (Q) of a nanomechanical resonator is an important parameter for vibrational-based sensors since their sensitivity is typically directly proportional to Q. The Quality Factor is a measure of the damping in the resonator due to both internal losses (clamping losses, internal friction such as thermoelastic dissipation, and surface effects) and external fluidic energy loss to the surrounding fluid, either through free-molecular momentum transfer or viscous effects [3,12]. Because external losses can be quite high when the resonator is operated in ambient air, it is important to quantify these losses. Plotting these losses as a function of pressure indicates if the viscous losses should be computed by free-molecular or viscous methods. The quality factor as a function of pressure is shown as figure (2).

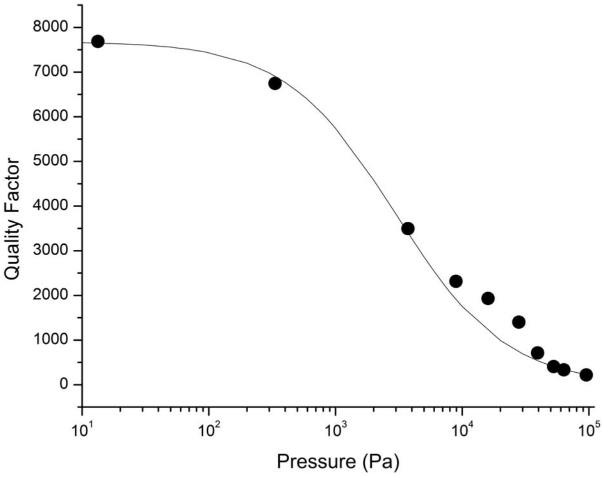

Fig. 2. Measured pressure dependence (points) of first vibratory mode (47 MHz) from vacuum to atmospheric pressure with a theoretical estimate computed and plotted (trace).

Because the quality factor is found to be roughly inversely proportional to pressure, we conclude that the damping is in the free-molecular flow regime, even at ambient pressure. For systems at low pressures, or nano-systems with extremely small characteristic lengths, the fluid losses can be determined using free-molecular flow models. If the system is operating in a free-molecular flow regime, the quality factor will be inversely proportional to the pressure. The experimental results confirm this, showing that the damping is free-molecular, even at atmospheric pressure. This is consistent with previous experience with nano-scale resonators [13,14].

The fluidic quality factor for nano-scale resonators as a function of pressure can be estimated using free-molecular flow theory [15,16] and is given by:

$$Q_f = \rho_s d\omega / C \tag{1}$$

where d is the thickness of the membrane, ρ_s is the density of the polysilicon resonator material, and C is the drag per unit area of a cross-section of the dome divided by its velocity. C can be estimated using the linear free-molecular flow theory:

$$C = 3.90 \frac{P}{\sqrt{2kT/m_g}} \tag{2}$$

where P is the pressure, T the temperature, k the Boltzmann constant, and m_g the mass of the gas molecules in the system [12]. The fluidic quality factor is then equal to

$$Q_f = 0.256 \frac{\rho_s d\omega}{P} \sqrt{\frac{m_g}{2kT}} \ . \tag{3}$$

The total quality factor of the resonator is then found by combining the fluidic quality factor with the intrinsic quality factor, Q_{int}, measured at ultra-high vacuum:

$$Q = \frac{1}{\frac{1}{Q_f} + \frac{1}{Q_{\text{int}}}} \tag{4}$$

The measured Q_{int} was 7,800. A theoretical estimate of the quality factor is shown in Fig. 2 (trace) as a function of pressure computed using equations (3) and (4), an estimated density for polysilicon of 2331 kg/m^3 [17], and a mass per air molecule of 4.81 x 10^{-26} kg. [18].

The pressure dependence of the quality factor shown in Fig. 2 indicates that the polysilicon film has low internal loss (as inferred for pressures < 1000 Pa) and becomes dominated by viscous losses when operated in air. The dome geometry, while not the best shape for use in air, is a good compromise since in air it resonates in its fundamental mode with a quality factor of 300 and in higher order modes with Q's ~ two times higher[19].

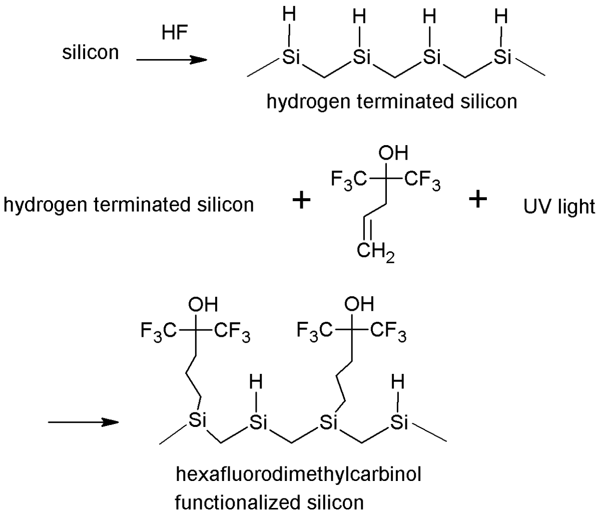

Fig. 3. Reaction scheme for H-terminated silicon selective functionalization with 2-allyl hexafluoroisopropanol using a deep UV mask.

C. Resonator Functionalization

The functionalization technique is outlined in Fig. 3. The starting point for the silicon functionalization scheme is to hydrogen terminate the surface using a quick dip in 50% HF(aq). In order to control the re-oxidation of the silicon surface, it is immediately coated with a drop of 2-allyl hexafluoroisopropanol (SynQuest Laboratories) and covered by a quartz mask. The sample is then exposed using a UV Xe lamp for ~15 hours. Only the open areas in the quartz mask are exposed to the deep-UV radiation, and thus only those areas are functionalized.

III. RESULTS

The XPS spectra of the functionalized silicon are shown in Fig. 4. XPS spectra were also taken before functionalization to get a measure of adventitious carbon and oxide formation using the same pre-functionalization techniques (50% HF(aq) for silicon), and to give credence to the fact that this functionalization can be performed in air. Before the XPS data were collected, the quartz mask was removed from the sample. The samples were rinsed in IPA and MEOH and dried at 100 °C on a hotplate for 1 minute.

XPS measurements were performed using a commercial system (Thermo VG Scientific Escalab 220i-XL) equipped with a monochromatic Al Kα source, a hemispherical electron energy analyzer (58° angle between monochromator and analyzer), and a magnetic electron lens. The nominal XPS spot size and analyzer field of view were < 1 mm^2. The binding energies (BEs) are reported with 0.15 eV precision. For the thin organic monolayers in this study, charge compensation was not necessary and was not applied. We present data acquired in normal-emission angle-integrated scans of the C1s, Si 2p, F 1s, and O 1s regions (15-25 eV windows with 0.15 eV spacing, 30 eV pass energy, 0.36 eV analyzer resolution). Spectra of the various regions were accumulated for 20 scans with a dwell time of 100 msec, to obtain a signal-to-noise ratio adequate for resolving the multiple components. Typically, spectra were acquired from three separate spots on each sample, primarily to test the monolayer uniformity. The corresponding calculated coverage values varied by no more than 10% for each of the samples. The peaks in the elemental core-level spectra were fit using commercial XPS analysis software[20]. Multiple-component fitting in the C 1s region always started from the lowest BE component and its full-core-fwhm's for the higher-BE components. In each case, the minimum number of components that produced unstructured fit residuals was chosen.

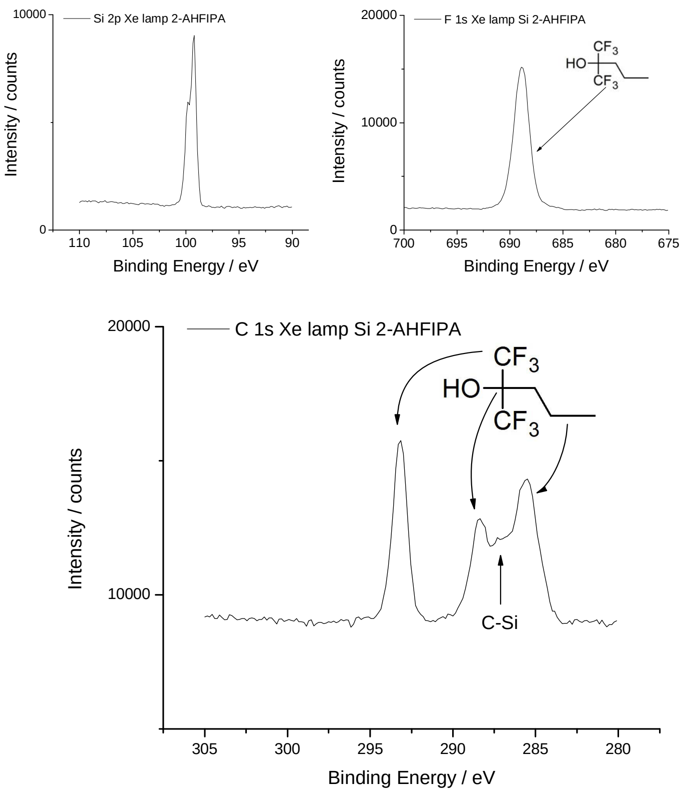

Fig. 4. XPS spectra (Si-2p, F-1s, and C-1s) for functionalized silicon surface.

The atomic fluorine to carbon ratio was 61% and atomic fluorine to silicon ratio was 45%. XPS being a very surface sensitive technique, these ratios essentially demonstrate that for every silicon atom, there is a carbon atom and fluorine atom present on the surface, which infers that we have greater than 50% of a monolayer coverage on the silicon surface. The C 1s portion of the data also shows chemical shift information which gives concrete evidence for the attachment of hexafluoroisopropanol to the silicon surface. Electronegativity of nearby atoms such as oxygen and fluorine can shift the carbon 1s peak such that the more electronegative the neighboring atom, the further the shift to higher binding energy. The C 1s region was fit using 4 individual peaks for the CF_3 group (293.2 eV), C-OH group (286.8 eV), the C-Si group (288.3 eV), and the CH_2 groups (285.4 eV). The relative area of each group came to be (2.2: 1.7: 1: 2.7) which matches well to the stoichiometry of the molecule (2: 1: 1: 3).

Spectra were also taken after one day and one week to determine how long the monolayer is stable in air. The results of the in-air study show some growth of adventitious carbon on the silicon, but no growth of silicon oxide, suggesting that the substrate is passivated against oxide growth. Long term studies are underway that examine degradation of the monolayer over time.

IV. Conclusions

The purpose of this work is to demonstrate the ability to functionalize very thin films of vapor sorbent molecules onto lithographically defined mechanical resonators. Using a photo-induced functionalization scheme allows us to functionalize only the resonator, and not the surrounding area, which would severely decrease sensitivity. The advantages of monolayer functionalization are: the molecule is chemically bonded to the resonator, thereby opening the potential for better cycling of the device, and the film is thin in comparison to the thickness of the resonator. Thin films (320 nm) of polysilicon have been fabricated using standard CMOS techniques and are shown to be operable in air. The measured pressure dependence determines the mass sensitivity and fits well to computational results. This work demonstrates the ability to create low-cost CMOS MEMS resonators using relatively inexpensive cost-sharing services that make use of multi-project wafers, such as MOSIS, that significantly decrease the cost of each design. Studies of analyte adsorption to functionalized resonators are underway.

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References

[1] K. L. Ekinci, H.X. Huang, M. L. Roukes, M. L. *Appl. Phys. Lett*. vol. 84, , pp. 4469-4471, 2004.

[2] Y. T. Yang, C. Callegari, X. L. Feng, K. L. Ekinci, and M. L. Roukes *Nano Lett*, vol. 6, pp. 583-586, 2006.

[3] J. F. Vignola, J. A. Judge, J. Jarzynski, M. Zalalutdinov, B. H. Houston, J. W. Baldwin *Appl. Phys. Lett*., vol. 88, 041921, 2006.

[4] Y. K. Yong, J. R. Vig *IEEE Trans. Ultrason., Ferroelectr. Freq. Control*, vol. 36, pp. 452-458, 1989.

[5] M.R. Linford, P. Fenter, P.M. Eisenberger, C.E.D. Chidsey *J. Am. Chem. Soc.*, vol. 117, pp. 3145-3155, 1995. T. Strother, W. Cai, X. Zhao, R. J. Hamers, and L.M. Smith *J. Am. Chem. Soc.*, vol. 122, pp. 1205-1209, 2000.

[6] Wagner, P.; Nock, S.; Spudich, J. A.; Volkmuth, W. D.; Chu, S.; Cicero, R. L.; Wade, C. P.; Linford, M. R.; Chidsey, C. E. D. *J. Struct. Biol.*, vol. 119, pp. 189-201, 1997.

[7] Sieval, A. B.; Demirel, A. L.; Nissink, J. W. M.; Linford, M. R.;van der Mass, J. H.; de Jeu, W. H.; Zuilhof, H.; Sudholter, E. J. R. *Langmuir*, vol. 14, pp. 1759-1768, 1998.

[8] Terry, J.; Linford, M. R.; Wigren, C.; Cao, R.; Pianetta, P.; Chidsey C. E. D. *J. Appl. Phys.*, vol. 85, pp. 213-221, 1999.

[9] Hamers, R. J.; Hovis, J. S.; Seung, L.; Liu, H.; Shan, J. *J. Phys. Chem. B*, vol. 101, pp. 1489-1492, 1997.

[10] A.W. Snow, L.G. Sprague, R.L. Soulen, J.W. Grate, and H. Wohltjen J. *Appl. Poly. Sci.*, vol. 43, pp. 1659-1671, 1991.

[11] M.K. Zalalutdinov, J.W. Baldwin, M.H. Marcus, R.B. Reichenback, J.M. Parpia, and B.H. Houston *Appl. Phys. Lett.* vol. 88, 143504, 2006.

[12] M.J. Martin, B.H. Houston, J.W. Baldwin, M.K. Zalalutdinov *J. Microelectromech. Syst*. vol 17, pp. 503-511, April 2008.

[13] M. J. Martin and B. H. Houston, *Appl. Phys. Lett.*, Vol. 91(10), 103116, 2007.

[14] V. Sazonova, Y. Yalsh, I. Ustunel, D. Roundy, T. A. Arias, and P. L. McEuen Nature, vol. 431, pp. 284-287, 2004.

[15] F. R. Blom, S. Bouwstra, M. Elwenspoek, and J. H. J. Fluitman, *J. Vac. Sci. Tech. B*, vol. 10, pp. 19-26, 1992.

[16] R. B. Bhiladvala and Z. J. Wang, *Phys. Rev. E*, vol. 69, 036307, 2004.

[17] S. D. Senturia, *Microsystem Design*. Boston, MA: Kluwer Academic Publishing, 2001.

[18] G. A. Bird, *Molecular Gas Dynamics and the Simulation of Gas Flows*. Oxford, UK: Clarendon Press, 1994.

[19] M.K. Ghatkesar, et al. Nanotechnology, vol. 18, 445502, 2007.

[20] R. Hesse, T. Chasse, R. Szargan,. J. Fresenius *Anal. Chem.*, vol. 365, pp. 48-54, 1999.