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Functionalization layer effect on the mechanical properties of silicon based micro-cantilever mass sensors: A theoretical study

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ABSTRACT

In this paper we calculate the surface stress and surface elastic constants of a model functionalized Si(1 1 1) surface by means of *ab initio* Density Functional Theory calculations. Subsequently these values are used in Finite Element Method simulations to predict the resonance frequency shift induced in a silicon cantilever by surface functionalization; this "multiscale" approach considers both changes in mass and elasticity of the microstructure induced by molecular adsorption. Interestingly our results show that the change in surface elastic constants, often ignored in experimental analysis, may account for 50% of the frequency shift and thus lead to a large overestimation of the attached mass.

In the last decades, microcantilever based sensors have gained large attention since they can be employed to detect specific molecules with a very high sensitivity. Moreover, it has been shown that by coating the surface of the beam with a chemical functionalization layer able to selectively bind to a target analyte, detection gains high chemical/biochemical selectivity [1–3]. When a cantilever comes in contact with the target substance, it responds with a mechanical transduction signal that can be related to the concentration of the molecule in the environment. The working principle of this kind of sensors is well known in surface physics [4,5] and it is based on the following effects: upon attachment of the analyte to the modified microcantilever surface, the surface stress varies and, as a consequence, the cantilever bends, at the same time the resonance frequency of the beam changes. Both the amount of bending (static detection mode) and the resonance frequency shift (dynamical detection mode) can be measured with high accuracy and can be exploited to accurately determine the amount of the adsorbed mass [6]. Although many cantilever sensors take advantage of adsorption induced bending as the transduction method, an approach based on resonance frequency shifts can potentially provide ultimate sensitivity for detection of a single molecule [6]. The resonance frequency of a beam can be expressed as: $f = 1/(2\pi)\sqrt{K/m^*}$, where K is the effective spring constant and m^* is the effective mass of the cantilever. For a given measured frequency shift, Δf, accurate quantitative analysis would require to know which amount of the shift can be ascribed to the adsorbed mass (change in m^*) and which to changes in surface elastic constants (change in K). Unfortunately, this estimate is not easily achieved and, during experimental analysis, the frequency shift is usually fully ascribed to the absorbed mass leading to an overestimation of the detected amount of analyte. In this letter for a model Si(1 1 1) surface we show that the change in surface stiffness induced by surface functionalization accounts for 50% of the frequency shift of a silicon micro-cantilever with typical experimental dimensions (see *e.g.* Ref. [7]). This means that assigning all the effect to change in effective mass of the beam would lead to a large error in the quantitative estimate of the attached mass. We also show that considering only the strain-independent part of the surface stress a negligible contribution to Δf is obtained.

Among the possible functionalization layers employed for silicon surface modification, we focussed on a self-assembled monolayer (SAM) containing molecules (propyl-urea) able to form bidimensional H-bonded networks. The study of this test case is extremely important because the stiffness and the surface stress can be tailored by changing the lateral intermolecular interactions by engineering the molecular structure. H-bonds, being stronger than van der Waals interactions, are expected to enhance detection performances in term of chemical specificity, stability and sensitivity. Moreover the propyl-urea molecule presents an amine

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group (—NH_2) as terminal ending moiety and, as such, it could be employed in the same way 3-aminopropyltriethoxysilane is often used as interface layer between silicon microcantilever and an antibody (*e.g.* [8]). Besides being employed as biosensing devices, propyl-urea functionalized cantilevers may be used to measure the PH of a solution, since the H-bond network of the SAM and its amine groups would respond to changes in the H^+ and OH^- concentration.

Our theoretical predictions are based on a “multiscale” approach that combines *ab initio* atomistic calculations and Finite Elements Method (FEM) simulations: *ab initio* simulations are used to predict the structure of the functionalized surfaces [26] and to accurately evaluate the changes in surface stress and surface elastic constants with respect to the unmodified silicon surface. Surface mechanical properties are quite difficult to evaluate or measure, yet first principle simulations represent an accurate and unique approach used to access them (see *e.g.* Refs. [9–11]). Surface stress and surface elastic constant are then employed in FEM simulations to calculate the resonance frequency of cantilevers with modified surfaces.

First principle calculations, carried out with the Quantum ESPRESSO code [12], are based on the Density Functional Theory (DFT) within the Generalized Gradient Approximation (GGA) employing the PBE (Pendew, Burke and Ernzerhof) [13] functional. The PBE form is essential to predict correct hydrogen bonding energy (see *e.g.* Ref. [14] for the case of water) and thus SAM cohesive energies. In our investigations, electronic wave functions are expanded in plane waves, and electron-ion interactions are treated by employing ultra-soft pseudopotentials. For all the calculations we adopted a plane wave cutoff of 30 Ry (300 Ry) for the description of the wave functions (charge densities). The Brillouin Zone sampling was done by employing an 10 × 10 × 10 Monkhorst-Pack [15] mesh for the bulk calculations and an 10 × 10 × 1 or equivalent grids for the surface calculations.[1]

Surface calculations were performed in orthorombic supercells containing symmetric Si(1 1 1) slabs composed of a variable number of layers (from 8 to 16). To avoid spurious interaction between periodic images, a vacuum space of about 10 Å was included in the supercells. Structures were considered converged when the variation of the total energy and the forces acting on the atoms were of the order of 10^{-5} Ry and 10^{-4} Ry/Bohr respectively. Surface stresses,[2] σ_i^{surf}, are obtained by calculating the stress tensor of the simulation supercell, σ_i^{bulk}, by applying the Nielson-Martin stress theorem [18], which represents the stress as a functional of the ground-state density.[3] σ_i^{surf} and σ_i^{bulk} are related by the equation: $\sigma_i^{surf} = 1/2\sigma_i^{bulk}c$, where *c* is the length of the supercell along the surface normal and the factor ½ accounts for the two equivalent surfaces in our slab calculations [9]. The calculated values were corrected because of a fictitious stress arising from a finite basis-set effect [19]. Surface elastic constants are calculated by relating the effect of strain on the Si(1 1 1) slab to the second order derivative of the energy with respect to strain, ε_i:

$$\left.\frac{\partial^2 E^{tot}}{\partial\varepsilon_i \partial\varepsilon_j}\right|_{\varepsilon=0} = V_0 D_{ij} \quad (1)$$

V_0 is the slab equilibrium volume and D_{ij} represents the plate elastic response to an axial strain applied in the directions (*x*, *y*) parallel to the surface (see Fig. 1). The response of the system can be divided in two parts [20]: the bulk contribution arising from the inner atomic layers and the contribution associated with the two identical surfaces corresponding to the outer atomic layers. As such, the second term of Eq. (1) can be rewritten as:(2)$V_0D_{ij} = 2S_{ij}A_0 + V_0C'_{ij}$ being A_0 the equilibrium surface area, S_{ij} the surface elastic constants and C'_{ij} the bulk elastic constants. The last-named takes into account that the plate in free to contract in the surface normal direction while strained along the surface [21,22]. When S_{ij} (with *i* = *j*) is positive surface creation causes a stiffening on the top layer, whereas a negative sign indicates surface softening associated with local bond weakening. Negative S_{ij} (with $i \neq j$) values correspond instead to a softening of the surface and imply that the surface stress in the *i* direction is opposite with respect to the *j* surface stress component, similarly to a negative Poisson's ratio in the case of a bulk system; positive S_{ij} can be thought as a positive Poission's ratio.

Table 1
Surface stress and surface elastic constants for the clean Si(1 1 1), hydrogenated Si(1 1 1)–H and functionalized (SAM-Si(1 1 1)) silicon surfaces. σ_i^{surf} corresponds to the surface stress along the principal axis of the stress tensor and $\bar{\sigma}^{surf}$ to the trace of the same tensor. In the cases of the clean and hydrogenated Si(1 1 1) the principal axis coincide with the cartesian directions of the supercell surface (*i* = *x*, *y*, see arrows of Fig. 1), whereas in the functionalized surface the principal axis are indicated by the vectors v_1 and v_2 reported as green arrows in panel C of Fig. 1. The last two lines report the FEM results for the first frequency mode of a model functionalized cantilever and the relative frequency shift calculated with respect to the hydrogenated case. SAM-Si(1 1 1)[a] reports the values obtained without considering the effect of propyl-urea added mass and SAM-Si(1 1 1)[b] reports the values obtained removing also the effect of the strain dependent surface stress.

	Clean-Si(1 1 1)	H-Si(1 1 1)	SAM-Si(1 1 1)
σ_1^{surf} J/m^2	−0.41	−0.10	0.89
σ_1^{surf} J/m^2	−0.41	−0.10	−0.04
$\bar{\sigma}^{surf}$ J/m^2	−0.41	−0.10	0.42
S_{11} eV/Å^2	0.151	0.258	0.305
S_{22} eV/Å^2	0.151	0.258	0.306
S_{12} eV/Å^2	−0.138	−0.104	2.441
f – 1st Hz		126,211.85	126,135.05 126,176.20^a 126,212.52^b
$\Delta f/f_0$		–	-6.08×10^{-4} -2.82×10^{-4a} -5.31×10^{-6b}

As our reference systems, we first computed the stress and the elastic constants for the clean and hydrogenated Si(1 1 1) surfaces (see Table 1). Both these surfaces experience compressive stresses of −0.41 and −0.10 J/m^2 respectively, in agreement with the value reported by Vanderbilt for the clean surface [9]. The origin of such compressive stress can be related to the spilling off of the electronic charge pertaining to each Si dangling bond at surface: this generates surface dipoles perpendicular to the surface that repel each other. Dangling bond saturation by means of hydrogen atoms strongly reduces such effect as indicated by the decrease of the surface stress value in the hydrogenated Si(1 1 1). In both cases the Si—Si bond lengths at the surface are smaller than that found in silicon bulk (about −1.7% and −0.4% for clean and hydrogenated surfaces); as such, surface bonds appear to be stronger and, for this reason, the surface elastic constants are positive, indicating a local mechanical stiffening. In the case of the propyl-urea functionalized Si(1 1 1) surface the most stable structure was discussed in a previous work [21] and it corresponds to a half monolayer coverage in which H bonded molecular chains oriented roughly along the surface supercell diagonal (about 41° off the *x* axis) form as reported in Fig. 1. To optimize the H-bonds along the chains, the molecules are folded with respect to the surface normal and the molecular dipoles (indicated approximately by the red arrow of Fig. 1) are all

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[1] Within the computational scheme presented above, we have obtained equilibrium lattice parameters for Si in the fcc structure of *a* = 5.475 Å. This value is in good agreement with the experimental lattice parameter (*a* = 5.43 Å) [16] and with other PBE values [17].

[2] By convention, if the surface tends to shrink the surface stress has a positive sign (tensile stress), while if the surface tends to expand, the corresponding stress has a negative sign and it is compressive.

[3] The Voigt notation is here used. In the case of strain, it implies $\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}, 2\varepsilon_{yz}, 2\varepsilon_{xz}, 2\varepsilon_{xy} = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6)$.