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Theory of bending of Si nanocantilevers induced by molecular adsorption: a modified Stoney formula for the calibration of nanomechanochemical sensors

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Abstract
We investigate the bending of nanometer thick Si cantilevers induced by chemisorption of H atoms and acetylene molecules, using atomistic simulations and continuum theories. We show that the bending curvature of Si nanocantilevers does not follow the classical Stoney formula, but agrees well with a modified Stoney formula that we have derived. Our studies reveal the dominant role of atomic structure and surface stress in governing the bending behavior of nanofilms, and demonstrate that the modified Stoney formula has to be used for the calibration of nanomechanochemical sensors in detecting trace amounts of molecules.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Mechanochemical sensors are widely used for detecting molecules [1–4]. The working principle of mechanochemical sensors is based on bending of a cantilever, typically made of crystalline Si, induced by molecular adsorption. As molecules are adsorbed on one side of a Si cantilever, they apply effectively an external surface stress load, bending the cantilever. The bending curvature is generally related to the surface stress and hence to the molecular coverage by the well-known Stoney formula [5], which has been used ubiquitously for the calibration of mechanochemical sensors [1–4]. One simply calculates the amount of molecular coverage through the measured bending curvature using the Stoney formula.

For a given amount of molecular adsorption, the thinner the cantilever, the larger the bending curvature. Thus, it is desirable to make the cantilever as thin as possible to increase the sensitivity of a mechanochemical sensor, so that even a small trace amount of molecules can be detected. The thickness of Si cantilevers used in current sensors [1–4] is in the range of micrometers. One could increase the sensor's sensitivity by orders of magnitude if the Si cantilevers could be thinned down to the range of a few or tens of nanometers. Recent progress in epitaxial growth and nanopatterning techniques [6, 7] has indeed shown promise for making this a reality. On the other hand, however, the mechanical response of nanoscale structures, such as bending of nanofilms [6–8], can be drastically different from that of macroscopic or microscopic structures [9–12]. Therefore, a natural question is how the bending of a Si nanocantilever induced by molecular adsorption will be different from that of a Si microcantilever. The answer to this question is critically important for the accurate calibration of mechanochemical sensors made of Si nanocantilevers.

Here, we present a systematic study of the bending of nanometer thick Si cantilevers induced by chemisorption of H atoms and acetylene molecules as a function of molecular coverage and cantilever thickness, using atomistic simulations and continuum theoretical analysis. We show that when the thickness of the Si cantilever is reduced to a few nanometers,

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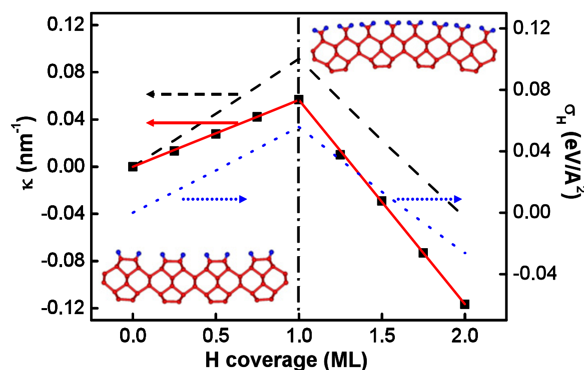

Figure 1. The calculated H induced surface stress (the dotted line labeled on the right y-axis) and the simulated bending curvature (square dots labeled on the left y-axis) of a six-layer Si cantilever as a function of the H coverage on its top surface. The dashed line is calibration using the Stoney formula (labeled on the left y-axis). The insets indicate the atomic surface structure for two different regimes of H coverage with a 'phase transition' at 1 ML, where the top layer are H atoms (blue online) and the rest are Si (red online). The left and right insets are respectively at 1 and 2 ML H coverage.

its curvature of bending induced by molecular adsorption can no longer be described by the classical Stoney formula. We have derived a modified Stoney formula, by taking into account a finite layer thickness of molecules (adsorbates) in addition to the cantilever thickness, which shows very good agreement with the simulated bending curvatures. Our studies reveal the dominant role of atomic structure and surface stress in governing the bending behavior of nanofilms, and suggest that the modified Stoney formula has to be used for the calibration of nanomechanochemical sensors in detecting trace amounts of molecules.

2. Simulation details

Our atomistic simulations are carried out using Tersoff's many-body potentials [13] for Si, C, and H elements. To simulate the bending of 'one-dimensional (1D)' Si cantilevers (beams), we take the beam with free ends along the [110] direction terminated with (001) top and bottom surfaces, which are (2×1) reconstructed, consisting of rows of dimers [8, 14]. A periodic boundary condition was used along the $[1\bar{1}0]$ direction (i.e., an infinite beam width) to save computational time. For the given thickness of Si cantilever and molecule coverage, the final ground state 'bent' structure was determined from the initial 'flat' structure by atomic static relaxation, until the forces on all the atoms converged to less than 10^{-5} eV Å^{-1}. The bending curvature of the final bent structure was then calculated by averaging over the circumferential curvatures of one or two atomic planes in the middle of the bent cantilever of odd- or even-layer thicknesses, respectively.

3. Results and discussion

Figure 1 shows the calculated results for the H induced surface stress (dotted line) and bending curvature (κ) (square dots) of a Si cantilever six atomic layers thick ($\sim$0.7 nm) as a function of the H coverage adsorbed on its top surface (see the insets), ranging from zero to two monolayers (MLs). We note that the (2×1) reconstruction induces an anisotropic intrinsic surface stress in the Si(001) surface [8, 14], but in an even-layer Si cantilever the intrinsic surface stresses in the top and bottom cantilever surfaces cancel each other out [8], so the cantilever stays flat without molecular adsorption. When H atoms adsorb on its top surface, they induce either a tensile or a compressive surface stress compared with that of the bottom surface depending on the H coverage. Below 1 ML, H adsorption induces a tensile stress in the top surface increasing with increasing H coverage, while beyond 1 ML the induced stress decreases towards compression with increasing coverage and becomes compressive after $\sim$1.6 ML H coverage (the dotted line labeled on the right y-axis in figure 1). The cantilever initially bends in a concave up manner (positive curvature) under the H induced tensile stress with a curvature increasing linearly with increasing H coverage up to 1 ML (left panel of figure 1). Beyond 1 ML, the bending curvature decreases with increasing H coverage from 1 to 2 ML (right panel of figure 1); it becomes negative (bending concave down) beyond $\sim$1.33 ML H coverage.

The dependence of the surface stress and bending curvature on the H coverage changes suddenly to a different trend at 1 ML of H coverage, because there is a surface structural 'phase transition'. Below 1 ML, there is one H atom adsorbed on one surface Si atom, retaining the surface Si dimer bond (the inset in the left panel of figure 1). This H–Si atomic configuration induces a local tensile stress. Above 1 ML, there are two H atoms adsorbed on one surface Si atom, breaking the surface Si dimer bond (the inset in the right panel of figure 1). This configuration induces a local compressive stress. Consequently, there are two different characteristic regimes of surface structure and hence bending behavior.

Using the calculated H induced surface stress in the top surface (σ_H) and the known elastic constants of Si [8], we have attempted to predict the bending curvature using the Stoney formula (plotted as a dashed line in figure 1) as $\kappa = 6\sigma_H/C_{Si}t_{Si}^2$, where $C_{Si} = E/(1-\nu^2)$ is the elastic constant related to Young's modulus (E) and the Poisson ratio (ν), and t_{Si} is the cantilever thickness. However, this prediction gives a very poor description of the simulated bending curvatures. Comparing to the simulation data, we see that the Stoney formula overestimates the slope of κ versus coverage below 1 ML H coverage and underestimates the slope above 1 ML. This means that if the Stoney formula were used for calibrating the H coverage from the measured bending curvatures using a sensor made of this Si nanocantilever, we would substantially underestimate the H coverage by as much as $\sim$37% when the H coverage is below 1 ML, and overestimate by as much as $\sim$27% when the H coverage is above 1 ML.

One important question is at what thickness the calibration with the classical Stoney formula becomes inaccurate. To answer this question we have simulated the bending curvatures as a function of the even-layer Si cantilever thickness at the fixed H coverage. Figure 2 shows typical results at two coverages, 1 ML (square dots, referenced to 0 ML coverage) and 2 ML (circle dots, referenced to 1 ML coverage), for the thickness range of 0.5–4 nm. We again compared them with the Stoney formula, shown as the dashed lines (the top and bottom ones are respectively for 1 and 2 ML coverage) in

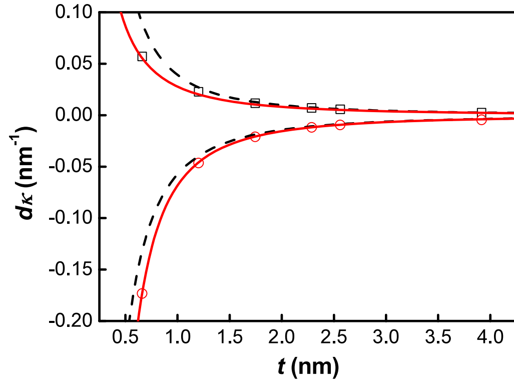

Figure 2. Simulated bending curvature of 1 ML (square dots) and 2 ML (circle dots) H covered even-layer Si cantilevers as a function of the cantilever thickness. Dashed and solid lines are calibrations using the classical and modified Stoney formulas, respectively.

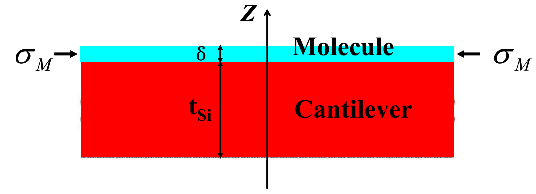

Figure 3. Schematics showing the physical and geometric parameters used for the derivation of the modified Stoney formula.

figure 2. Apparently, the two disagree with each other when the cantilever thickness is smaller than ∼2 nm.

To resolve the above discrepancy, we derive below a modified Stoney formula for calculating the bending curvature of an ultrathin nanometer thick cantilever induced by molecular adsorption. The classical Stoney formula is in fact only applicable for relatively thick cantilevers, or when the cantilever thickness is much larger than the thickness of the adsorbed molecular layer so that the thickness of the latter can be neglected. The derivation of the Stoney formula assumes that the molecule induced surface stress σ_H is constant during and after bending. This is approximately true for a thick cantilever of very small bending curvature. But it is no longer valid when the cantilever becomes very thin, down to a few or tens of nanometers (i.e., tens of atomic layers), because the bending curvature increases considerably with decreasing cantilever thickness. For example, if a cantilever thickness is reduced from 1 μm to 1 nm, its bending curvature will increase by six orders of magnitude. The very large bending curvature of a nanocantilever means a very large bending strain in the molecular layer, which will in turn change the molecule induced surface stress upon bending. Therefore, we derive a modified Stoney formula by taking into account a finite thickness of molecules, as schematically shown in figure 3. The surface stress in the molecular layer upon bending can be calculated as

$$\sigma_M = \sigma_H + C_M\delta\varepsilon_M = \sigma_H + C_M\delta\kappa(t_{Si}/2 + \delta/2 - z_0) \quad (1)$$

by adding the bending strain induced additional 'surface' stress, $C_M\delta\varepsilon_M$, to the original molecule induced intrinsic stress, σ_H, in the flat surface. C_M is the elastic constant of the molecule layer with a thickness of δ, and ε_M is the bending induced strain in the molecule layer, which depends on κ, t_{Si}, and z_0 (the position of the neutral plane). Here we consider the average strain in the molecule layer, neglecting its thickness variation. The total strain energy (E) is the sum of the molecule layer strain energy (E_M) and the Si beam strain energy (E_b),

$$E = E_M + E_b = \int \sigma_M \,d\varepsilon_M + (C_{Si}/2)\int_{-t_{Si}/2}^{t_{Si}/2} [\kappa(z - z_0)]^2 \,dz. \quad (2)$$

Minimization of E with respect to κ and z_0 leads to the following *modified* Stoney formula:

$$\kappa = \frac{6\sigma_H}{C_{Si}t^2 + 4C_M\delta t} = \frac{6\sigma_H}{C_{Si}t^2 + 4C_{s-M}t}. \quad (3)$$

In equation (3), we introduce an effective in-plane elastic constant of the molecule layer $C_{s-M} = C_M\delta$ as a fitting parameter since both C_M and δ are arbitrary unknowns. Figure 2 shows that equation (3) gives an excellent fit (solid lines) to the simulated data with the parameter $C_{s-M} = 0.858$ and -0.343 eV Å^{-2} for 1 and 2 ML H coverages, respectively. The reason that we have a negative C_{s-M} for 2 ML coverage is that we are still using the C_{Si} of bulk Si in the fitting, but it should be effectively smaller due to broken dimer bonds in the top surface after 1 ML coverage.

The fitting indicates that the modified Stoney formula correctly predicts the scaling relation between molecule adsorption induced bending curvature and cantilever thickness for nanoscale ultrathin cantilevers. For large t, equation (3) reduces to the classical Stoney formula. For small t, however, the modified Stoney formula predicts a different scaling relation, changing from the classical behavior of $\kappa \sim t^{-2}$ to the nanoscale behavior of $\kappa \sim (at^2 + bt)^{-1}$. The above analysis shows that when the thickness is reduced to the nanometer scale, the discreteness (atomic nature) of the cantilever structure and the effect of the molecule induced surface stress become increasingly significant. This makes the bending behavior of a nanofilm not only quantitatively but also qualitatively different from that of a macroscopic thick film [8]. For molecule adsorption induced bending of Si cantilevers, the critical cantilever thickness may be roughly estimated when the $4C_{s-M}t$ term in the modified Stoney formula becomes negligible with respect to the $C_{Si}t^2$ term. We found that for t larger than 8 nm, the difference of the classical Stoney formula and modified Stoney formula is less than 5%. In general, we may expect the critical thickness to be ∼5 nm for molecule deposited Si cantilevers when the surface stress makes the bending of nanoscale cantilevers appreciably different from those of microscopic and macroscopic cantilevers. Below this limit, it is mandatory to use the modified Stoney formula.

We also carried out atomistic simulations to determine the bending curvature of a five-layer Si nanocantilever with different coverages of C_2H_2 molecule adsorption on its top surface. In an odd-layer cantilever, there exists a surface stress imbalance between its top and bottom surfaces [8], which provides a unique self-driving force bending the cantilever. Such spontaneous self-bending of Si nanofilms has been confirmed as well as quantified by direct MD atomistic simulations. A five-layer pure Si cantilever without deposition

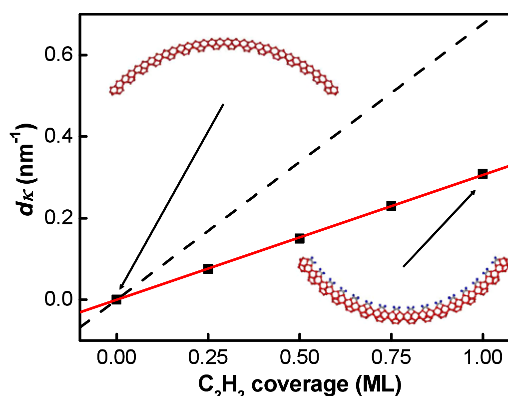

Figure 4. The simulated change of bending curvature of a five-layer Si cantilever after C_2H_2 molecules were adsorbed on the top surface, bridging adjacent Si dimers in the same row (square dots). Dashed and solid lines are calibrations using the classical and modified Stoney formulas, respectively. The insets show the atomic structures of Si cantilevers at 0 ML (left) and 1 ML (right) C_2H_2 coverage.

of molecules will self-bend in a concave downward manner with a radius of curvature 74 Å, shown as the left inset in figure 4, due to the imbalance of the intrinsic top compressive and bottom tensile surface stress [8]. The deposition of C_2H_2 on the Si(100) surface has two configurations [15]: one having the C–C bond sited on top of and parallel to the Si dimer, and the other having the C–C bond in between bridging two adjacent Si dimers in the same dimer row where C_2H_2 bonds to one atom of each dimer. The bridge structure is more accessible kinetically to incoming molecules and stable at room temperature [15], as is adopted in our simulations. C_2H_2 was deposited on the top compressive surface. The equilibrium configuration for 1 ML C_2H_2 coverage is shown in the right inset of figure 4. The C_2H_2 deposition induces a local tensile surface stress. The top surface stress changes from -83.85 to -29.03, 29.45, 96.55 and 167.1 meV Å^{-2} (not only quantitatively, but also qualitatively with regard to sign) for 0 to 0.25, 0.5, 0.75 and 1 ML. The resulting bending curvature increases linearly with increasing C_2H_2 coverage (square dots in figure 4). With increasing C_2H_2 coverage, the Si cantilever gradually bends less and then bends in the other direction (the bending curvature changes from -0.135 to -0.060, 0.015, 0.095 and 0.173 nm^{-1} (here a minus sign means bending in a concave down manner) compared with the bending of the Si cantilever without molecule adsorption. Although the initial bending curvature is nonzero, still the modified Stoney formula (the solid line in figure 4) can be fitted to the simulation results very well while the classical Stoney formula (the dashed line in figure 4) cannot.

4. Conclusion

In summary, our studies of molecule deposition on Si cantilevers can be generalized to other semiconductor nanofilms. The atomic level molecule deposition induced surface stress effects make the bending of nanoscale thin cantilevers different from those of microscopic and macroscopic thick cantilevers. Quantitatively, the modified Stoney formula has to be used in calibrating the molecular coverage from the measured bending curvatures of the molecule adsorbed nanocantilevers. These findings have broad implications for nanomechanochemical sensors [1–4] made of nanometer thick cantilevers and for nanomechanical architectures [16] made of nanoscale thin films.

Acknowledgment

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