

Nanomechanical mass sensing and stiffness spectrometry based on two-dimensional vibrations of resonant nanowires

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One-dimensional nanomechanical resonators based on nanowires and nanotubes have emerged as promising candidates for mass sensors^{1–6}. When the resonator is clamped at one end and the atoms or molecules being measured land on the other end (which is free to vibrate), the resonance frequency of the device decreases by an amount that is proportional to the mass of the atoms or molecules. However, atoms and molecules can land at any position along the resonator, and many biomolecules have sizes that are comparable to the size of the resonator, so the relationship between the added mass and the frequency shift breaks down^{7–10}. Moreover, whereas resonators fabricated by top-down methods tend to vibrate in just one dimension because they are usually shaped like diving boards, perfectly axisymmetric one-dimensional nanoresonators can support flexural vibrations with the same amplitude and frequency in two dimensions¹¹. Here, we propose a new approach to mass sensing and stiffness spectroscopy based on the fact that the nanoresonator will enter a superposition state of two orthogonal vibrations with different frequencies when this symmetry is broken. Measuring these frequencies allows the mass, stiffness and azimuthal arrival direction of the adsorbate to be determined.

The development of ultrasensitive mass spectrometers capable of characterizing the proteome at the single cell level with high accuracy will speed up the identification of disease biomarkers and the discovery of new drugs for treatment^{12,13}. Although resonators fabricated by top-down approaches have achieved mass sensitivities in the zeptogram range (10^{-21} g)^{8,14–16}, devices based on nanowires and nanotubes have approached the yoctogram scale (10^{-24} g)^{1–6} and the ultimate detection limit corresponding to the mass of one single atom (1 Da = 1.66 yoctogram). Despite their small size, nanowires and nanotubes can be detected by optical methods, leading to a wide range of applications in which the resonators can be operated in different environments without coming into contact with the displacement sensors and readout circuitry^{5,6,17–19}.

In this work, we have investigated horizontal silicon nanowires epitaxially clamped at the sidewalls of pre-patterned microtrenches on silicon substrates by using a vapour–liquid–solid growth mechanism²⁰. The stochastic Brownian displacement of the nanowires at room temperature was measured using a home-made optical interferometer (Fig. 1a)^{5,6}. We selected nanowires protruding at 90° with respect to the sidewall to which they were anchored (Fig. 1b). The length and diameter of the selected nanowires were in the range of 5–10 μm and 100–300 nm, respectively. The thermal displacement fluctuations of the nanowires exhibited two resonance

peaks and, based on measurements of 60 different nanowires, we found the mean frequency difference to be 0.7% of the average frequency (Fig. 1c).

To gain insight into the origin of the thermomechanical fluctuations and predict the changes in the resonant properties upon molecular adsorption, we adopted the Ritz formulation on the basis of linear, two-dimensional small deformation elasticity theory^{21,22} (see Supplementary Information). Silicon nanowires were axially oriented along the $\langle 111 \rangle$ direction, and exhibited a hexagonal cross-section formed by the $\{112\}$ planes. Theoretically, these nanowires vibrate in all planes of flexural vibration with the same frequency¹¹. However, a small imperfection in the cross-section breaks the symmetry of the nanowire and the single vibrational resonance peak is split into two closely spaced peaks of similar amplitude, with the peaks corresponding to vibrations in orthogonal planes. For an unloaded nanowire, it can be shown that the two orthogonal vibration modes are determined by the directions in which the cross-section area moments are at a maximum (I_{max}) and minimum (I_{min}).

If we assume, for the sake of understanding, that the nanowires have elliptical cross-sections (with major radius R_{max} and minor radius R_{min}), the asymmetry factor $\Omega \equiv (R_{\text{max}} - R_{\text{min}})/R_{\text{min}}$ can be obtained from the expression $\Omega = (\omega_f - \omega_s)/\omega_f$, where ω_f and ω_s are the fast and slow vibration frequencies. Based on Fig. 1c, this suggests a difference of only 0.7% between R_{max} and R_{min} . The observation of the frequency splitting critically depends on the mechanical energy loss. In air, the large hydrodynamic force leads to a very low quality factor ($Q \approx 5$), which means that the splitting of the resonant peaks cannot be resolved (Fig. 1c, inset). However, Q is much higher ($\sim 2,000$) in vacuum, because the suspended nanowires exhibit almost defect-free structural quality, high surface smoothness and large clamp robustness. Hence, a small asymmetry in the nanowire cross-section results in an observable frequency difference (Fig. 1c). In general we can observe the frequency difference when $\Omega > 1/Q$; this means that the effect can be observed in vacuum when the asymmetry in the cross-section is as small as 0.1% (that is, 0.1 nm for a nanowire with a diameter of 100 nm).

Let us now study the effect of a molecular adsorbate on the nanowire at a longitudinal position z_0 with length $\Delta z \ll L$, and oriented with an azimuth angle β with respect to the fast vibration axis (Fig. 2a). We anticipate that, in addition to the shift of the resonance frequencies, the deposition will cause the planes of vibration to rotate. Applying the Ritz formalism it is useful to define the following three parameters: the sum of the relative shift of the frequencies (equation (1) below); the difference in the relative shift of the

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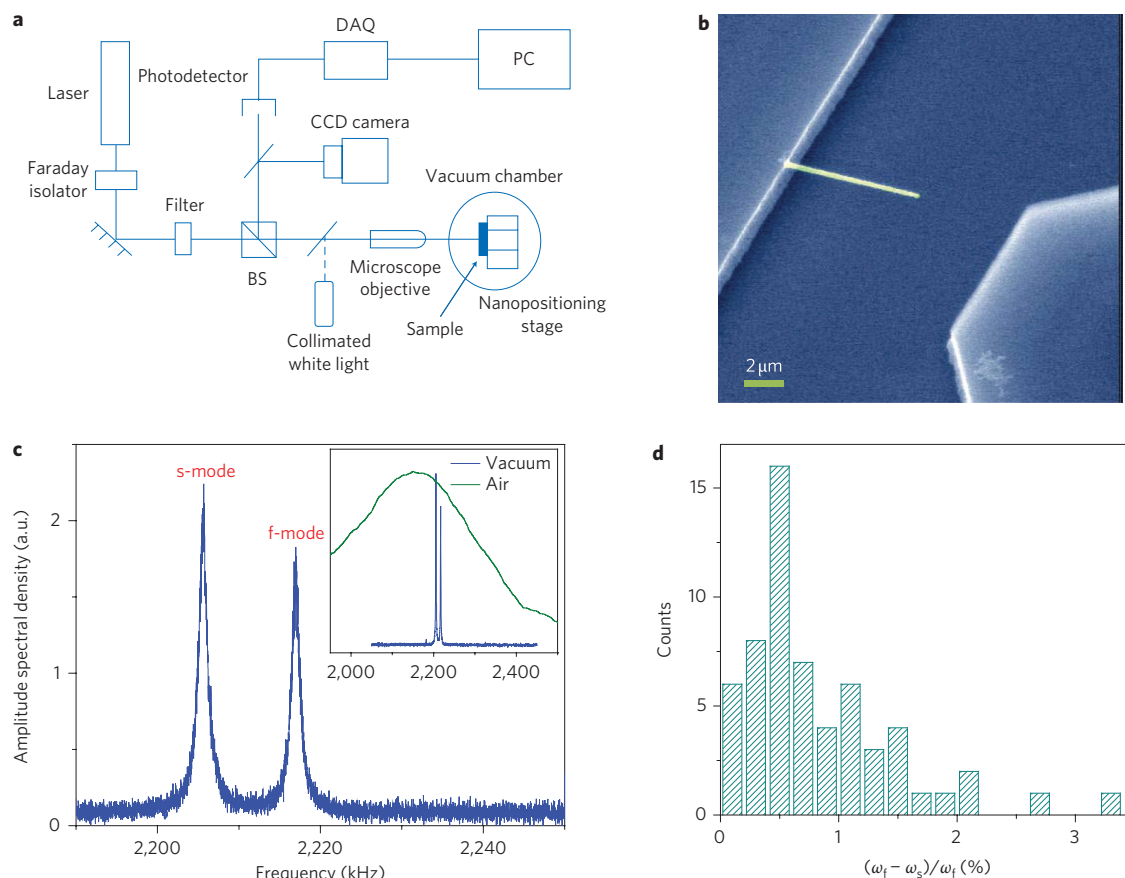


Figure 1 | Thermal displacement fluctuations of silicon nanowires. **a**, Schematic of the optical interferometer used to detect the out-of-plane nanowire vibrations. The nanowire longitudinal axis and incident laser beam are orthogonal. The nanowire sample was placed in a vacuum chamber at approximately 1×10^{-6} torr and room temperature. The spot size was $\sim 0.7 \mu\text{m}$ and the incident power 0.5 mW. Picometre-scale modulation of the height of the nanowire above the substrate results in a measurable intensity modulation due to the interference between the light reflected from the nanowires and from the substrate. DAQ, data acquisition card; BS, beamsplitter; CCD, charge-coupled device. **b**, Scanning electron micrograph (SEM) of a typical nanowire used in this work. Nanowires anchored normal to the trench wall were selected, with lengths and diameters of 5–10 μm and 100–300 nm, respectively. **c**, A fast Fourier transform of the signal from the photodetector is dominated by the displacement thermal fluctuation of the nanowires. Only a single resonant peak can be seen in air (green line in inset), but two resonant peaks can be clearly seen in vacuum (blue lines). Depending on the nanowire dimensions, the resonance frequencies range from 2 to 6 MHz. s-mode and f-mode refers to the splitting of the resonance frequency into slower and faster vibration modes vibrating at orthogonal directions. **d**, Histogram of the relative frequency separation between the two close resonance peaks observed in vacuum. Sixty devices were studied.

frequencies (equation (2)); and the rotation angle of the vibration planes (equation (3)). In the case that the cross-section and thickness of the adsorbate are much smaller than those of the nanowire and the asymmetry factor is small, these parameters can respectively be written as

$$\frac{\Delta\omega_s}{\omega_s} + \frac{\Delta\omega_f}{\omega_f} \cong \left\{ -\psi(z_0)^2 \frac{\rho_D}{\rho_{NW}} + \phi(z_0)^2 \frac{E_D}{E_{NW}} \right\} \frac{V_D}{V_{NW}} \quad (1)$$

$$\frac{\Delta\omega_f}{\omega_f} - \frac{\Delta\omega_s}{\omega_s} \cong \phi(z_0)^2 \frac{E_D}{E_{NW}} \frac{V_D}{V_{NW}} \cos(2\beta) \quad (2)$$

$$\Delta\alpha \cong \frac{\phi(z_0)^2}{2\Omega_0} \frac{E_D}{E_{NW}} \frac{V_D}{V_{NW}} \sin(2\beta) \quad (3)$$

where ψ and ϕ indicate the non-dimensionalized eigenmode amplitude and curvature, E is Young's modulus, ρ is mass density, V is volume, Ω_0 is the initial asymmetry factor, and the subscripts D and NW refer to the deposited material and the nanowire. The eigenmode shape and curvature are well-known functions for

beams with length-to-width ratios greater than 5, as in the present case (see Supplementary Information)⁷.

The sum of the relative frequency shifts (equation (1)) is proportional to the volume of adsorbed material and independent of the azimuth deposition angle β . However, two opposing mechanisms are at work regarding the volume of adsorbed material: the added mass causes the sum of the relative frequency shifts to decrease, while increasing the adsorbate stiffness causes the sum to increase^{7,10}. The added-mass effect dominates as the adsorption approaches the free end. Conversely, the adsorbate stiffness effect is amplified by the vibration curvature, so it is negligible near the free end of the nanowire and maximal at the fixed end.

The difference between the relative frequency shifts (equation (2)) only depends on the adsorbate stiffness and is not affected by changes in the resonator mass. Changes in the difference are therefore more pronounced when the adsorption occurs near the clamped end of the resonator and the deposition is along one of the vibration planes. Conversely, adsorption near the free end or at an angle close to 45° with respect to one of the planes of vibration has a negligible effect on the difference between the relative frequency shifts.

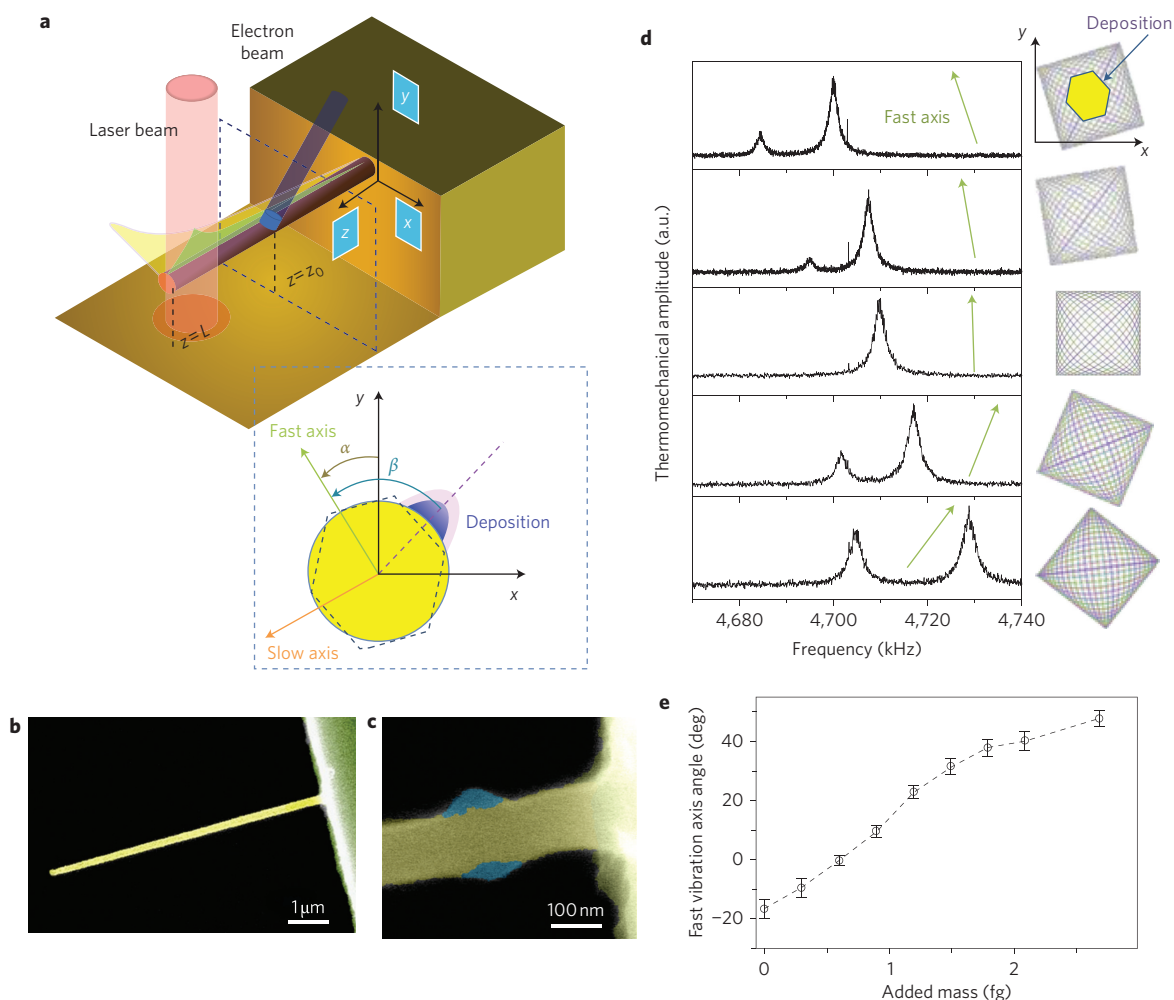


Figure 2 | Rotation of the fundamental vibration planes of silicon nanowires. **a**, Schematic of electron-beam-induced deposition of carbon on nanowires. In the chosen coordinate system, the y and z axes are set along the optical and nanowire longitudinal axes, respectively. The nanowire fundamental flexural vibration mode splits into two close resonance peaks of similar amplitude. The vibration axes in which the nanowire vibrates at the lower and higher frequencies are referred to as slow and fast axes, respectively. The azimuth angle (x - y plane) between the deposition axis and the fast axis is referred to as β . **b,c**, SEM images of a 100-nm-thick nanowire before (**b**) and after (**c**) electron-beam-induced carbon deposition near the clamped end. The electron beam causes slow deposition of an amorphous carbon layer through dissociation of organic species present in the SEM chamber. In nanowires with diameters less than 150 nm, we observed that the electron beam efficiently transmits through the nanowire to produce an almost symmetric carbon deposition on the opposite side (bottom of image). **d**, Evolution of the frequency spectra (top to bottom) of the nanowire thermal displacement after four depositions of ~ 0.6 fg near the nanowire clamped end. Deposition was performed at an angle of $\sim 45^\circ$ to the optical axis, as indicated by the blue arrow. Each deposition rotates the fast vibration plane through 7 – 12° towards the deposition direction, as indicated by the green arrows. Note that the middle panel only shows the peak corresponding to the fast eigenmode in which the nanowire vibrates along the optical axis. In this case, the slow eigenmode peak vanishes as the nanowire vibrates parallel to the silicon substrate, and the optical interferometric signal in our configuration is only sensitive to the out-of-plane displacement. On the right, orbits of the nanowire tip in the x - y plane are plotted. **e**, Angle between the fast vibration axis and the optical axis (α) versus mass added to the clamped end of the nanowire. The first five data points are taken from **d**.

The high axisymmetry of the silicon nanowires means that adsorption of a minuscule mass can easily rotate the vibration planes (equation (3)). The optical interferometry technique is sensitive to the out-of-plane component of the nanowire displacement. Because the split eigenmodes vibrate in orthogonal directions with nearly the same amplitude, measurement of the out-of-plane amplitude readily allows us to determine the vibration direction of the eigenmodes with respect to the optical axis. Such a measurement therefore provides a new sensing parameter in highly symmetric one-dimensional nanomechanical resonators. This method is in line with a growing trend in nanomechanical sensing towards the use of amplitude variations in eigenmodes instead of, or in addition to, frequency shifts^{23,24}. The amount of rotation is inversely proportional to the asymmetry factor (Ω_0) and depends on the

deposition angle. In the limit of small depositions, the rotation is zero for depositions along one of the vibration planes, and reaches a maximum value when the deposition angle is 45° with respect to the vibration planes. The sign of the rotation angle is defined such that the fast vibration axis approaches the deposition axis. Because the rotation arises from the mechanical stiffness of the adsorbate, it is enhanced as the deposition approaches the fixed nanowire end.

The imperfection-induced splitting of the resonance frequency allows the mass and mechanical properties of the adsorbate to be measured. In addition, for set-ups where adsorption arises from multiple sources, the source can be discriminated on the basis of the deposition angle. The method requires knowledge of the longitudinal position of the adsorbate on the nanowire, which can be derived by measuring the frequency split in several eigenmodes^{7,9,10}.

To experimentally validate the proposed sensing paradigm, discrete masses were deposited on the nanowire by focusing the electron beam of a scanning electron microscope (SEM) on a specific region of the nanowire²³. The electron beam causes the slow deposition of an amorphous carbon layer through the dissociation of organic species present in the SEM chamber (Fig. 2b,c).

Figure 2d,e shows the effect of successive carbon depositions of ~ 0.6 fg near the nanowire fixed end on the orientation of the fundamental vibration axes. The deposition was performed at an angle of 45° to the optical axis (Fig. 2a). Initially, the angle between the plane of the fast vibration and the optical axis was $\alpha = -17 \pm 2^\circ$ (green arrow in Fig. 2d). Each deposition rotated the fast vibration plane by $7\text{--}12^\circ$ towards the deposition direction. When the fast vibration axis was at 45° to the deposition axis, the vibration angle therefore had a maximum mass sensitivity of ~ 50 ag per degree. Once the fast vibration direction reached the deposition direction, further deposition did not induce a rotation of the vibration planes. In the present set-up, the position sensitivity was ~ 10 pm $\text{Hz}^{-1/2}$. By externally driving the nanowires to obtain resonant amplitudes of ~ 100 nm, the angle uncertainty could be reduced to 0.01° , which implies mass sensitivities of the order of 100 zg. Note that the adsorption-induced rotation of the vibration planes is a mechanical effect, so mass sensitivity depends on Young's modulus of the adsorbate (equation (3)).

To further take advantage of the sensitivity and spectroscopic capability of the proposed technique, we studied what happens when adsorption occurs along the fast vibration axis. In this case, the vibration axes do not rotate and the difference between frequency shifts exhibits the maximum responsivity to adsorption (equation (2)). Using this geometry, the mass and mechanical properties of the adsorbate can be determined by measuring the sum and difference of the relative frequency shift (equations (1) and (2)). Figure 3 shows the sum and difference of the relative frequency shifts as a function of the longitudinal deposition position for a mass of ~ 3 fg. The sum of the frequency shifts changes from a maximal and positive value when the deposition is near the clamped end of the resonator towards a minimal and negative value when the deposition is near the free end. The difference between the frequency shifts resembles the curvature of the fundamental eigenmode (that is, the maximum value occurs near the clamped end, with a negligible value near the free end). Fitting the experimental values (symbols) to the theoretical expressions (dashed lines in Fig. 3), and considering a density of $1,950 \text{ kg m}^{-3}$ for the deposited carbon, we determine that the Young's modulus of the deposited material is ~ 55 GPa.

Assuming that frequency sensitivity is limited by thermomechanical noise²⁵, and using silicon nanowires like those used here, the technique is capable of measuring mass with zeptogram sensitivity, discriminating variations in the Young's modulus of ~ 0.1 kPa per femtogram of sample. Dry proteins have a Young's modulus in the range 0.1–10 GPa. Therefore the proposed technique could detect variations of 100 ppm in the Young's modulus of a single protein. This capability of resonant nanowires for measuring mechanical properties in addition to mass with ultrahigh sensitivity opens the door to relevant biomedical applications. The important role of mechanical properties in biological processes and pathogenic disorders is becoming increasingly clear^{26–28}. For example, a single point mutation in the capsid protein of some viruses can significantly change the elasticity of the virus particle²⁹. In the case of the human immunodeficiency virus, its stiffness largely decreases during the maturation process, acting as mechanical switch in the infection process³⁰. We envisage the application of resonant nanowires in the detection of subtle protein changes at the level of single mutations that are manifested as biologically relevant mechanical changes.

To conclude, nanowire-based nanomechanical resonators meet many of the key requirements for developing an ultrasensitive

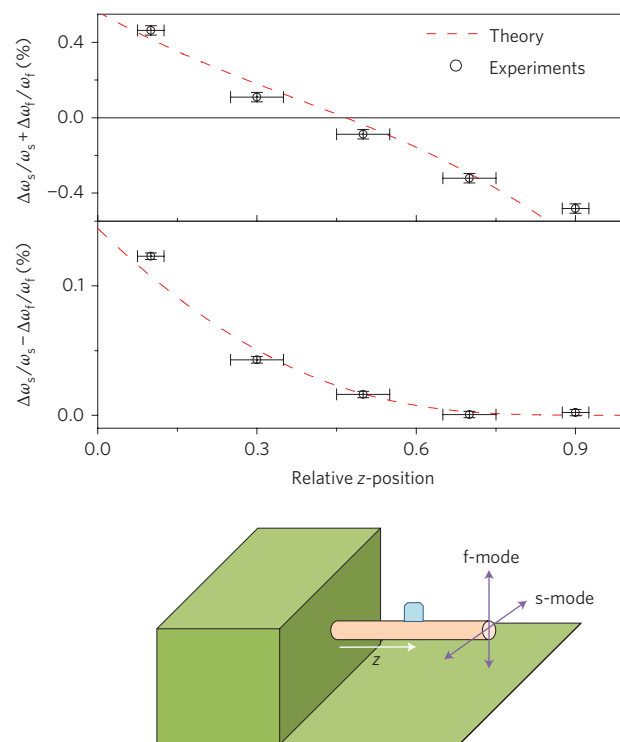


Figure 3 | Effect of mass deposition position on frequency splitting. Plots showing the sum (top) and difference (bottom) of the relative frequency shifts of a one-dimensional nanowire resonator as a function of the position z at which a mass of 3 fg is deposited on the nanowire along the fast-mode vibration axis (see schematic). The symbols are experimental data and the dashed red line is a theoretical prediction based on the Ritz method applied to the beam equation in two dimensions (see text and Supplementary Information). The mass and mechanical properties of the adsorbate can be determined by measuring the sum and difference of the relative frequency shifts.

biological spectrometer, including high sensitivity, high mechanical selectivity, small size (and hence small sample consumption) and the capability for multiplexed detection. One of the remaining challenges—to transport intact biomolecules in vacuum to the nanomechanical resonator—has recently been circumvented through the use of an electrospray injection system¹³.

Methods

Device fabrication. Silicon on insulator (SOI) substrates with a $\langle 110 \rangle$ orientation of the 2- μm -thick device layer were patterned by photolithography and reactive ion etching to define the simple supporting microstructures with $\langle 111 \rangle$ oriented sidewalls on which the nanowires were intended to grow. Before nanowire growth, the substrates were coated with 80- or 150-nm-diameter gold nanoparticles (British Biocell). Silicon nanowires were grown in an atmospheric-pressure chemical vapour deposition (CVD) reactor at 800°C with 10% H_2/Ar as both diluent and carrier gas. Flow rates of 270 and 45 s.c.c.m. were used, respectively. The carrier gas was passed through a liquid SiCl_4 bubbler maintained at 0°C to maintain a constant vapour pressure.

Optical interferometry. The silicon die was mounted on a three-axis piezoelectric translation stage for positioning and scanning under the probe beam. The sample on the piezoelectric translation stage was placed into a small vacuum chamber pumped down to the $\sim 1 \times 10^{-6}$ torr. A 5-mW He-Ne gas laser beam ($\lambda = 633$ nm) was directed to the sample through an intensity filter, beamsplitter and a $\times 50$ objective with a numerical aperture of 0.55. The spot size was $0.6\text{--}0.8 \mu\text{m}$. The optical power of the beam incident on the nanowires was ~ 0.5 mW. Interferometric contrast arose between the laser beam reflected from the nanowires and that reflected from the substrate underneath. The reflected light was collected by the objective and detected by a photovoltaic silicon pin diode followed by a low-noise current-to-voltage preamplifier and high-speed digitizer connected to a PC. The lengths and diameters of the investigated nanowires were 5–10 μm and 100–300 nm, respectively.

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Author contributions

J.T. and M.C. wrote this manuscript with input from all authors. All authors analysed and interpreted the data. A.S. and M.F.-R. built the CVD reactor and fabricated the devices. E.G. and D.R. performed the detection and mass adsorption experiments and collected the data. J.T., E.G. and D.R. developed the theoretical model. E.G., D.R. and J.T. designed the experiments. J.M. and R.G. designed the set-up for SEM carbon deposition.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper at www.nature.com/naturenanotechnology. Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>. Correspondence and requests for materials should be addressed to J.T.