Following recent advances in the control of the electronic properties of nanowires,[1–4] nonlithographic organization of nanowire arrays on surfaces remains a critical prerequisite for the large-scale fabrication of nanoscale circuitry.[5,6] Current strategies[7] include the application of physical means, such as electric fields,[4,8,9] gas[10] and liquid[11,12] flows, and slabs,[13] as well as chemical means including self-assembly[14,15] and biotemplated assembly.[16] Step decoration[15,17] is another attractive chemical approach that exploits the selective deposition of atoms, ions, or molecules at the atomic steps of the vicinal Al2O3(0001) surfaces. Here we demonstrate and characterize the longitudinally propagating decoration of atomic steps by a nanowire material. Single-wall carbon nanotubes that are catalytically produced on miscut C-plane sapphire wafers, grow along the 2-Å-high atomic steps of the vicinal α-Al2O3 (0001) surfaces to yield highly aligned, dense arrays of discrete, nanometer-wide, conducting or semiconducting wires on a dielectric material. The nanotubes reproduce the atomic features of the surface, such as steps, facets, and kinks. These findings open up the possibility of assembling nanotube architectures by atomic-scale surface engineering.

The phenomenon of atomic step decoration by single-wall carbon nanotubes (SWNTs) was first observed while investigating the effects of electric field and gas flow on the catalytic growth of SWNTs on different materials. Surprisingly, nanotubes grown on C-plane sapphire wafers, that is, α-Al2O3(0001) surfaces, showed the highest degree of alignment (Figures 1a, 2a, 3a–c, and 4a), but not in the directions of the field or the flow. When the same surface was precoated with a thin layer (20 nm) of amorphous SiO2, the nanotubes were aligned with the electric field (Figure 1b), as previously observed on SiO2-coated silicon.[8] This result indicated that the nanotubes grow in contact with the Al2O3 surface, which dictates their alignment. On the other hand, the nanotubes were not aligned along a particular crystallographic direction. Moreover, α-Al2O3 is a trigonal crystal of the R3c space group and an ideal α-Al2O3(0001) surface has C3 symmetric, from which one would expect alignment in at least three directions, not one. These facts ruled out the possibility of lattice-oriented SWNT growth.[21] However, commercial “C-plane” sapphire wafers are often cut and polished in a plane that slightly deviates from the actual C plane. The resulting vicinal α-Al2O3(0001) surfaces are terminated with parallel, regularly spaced atomic steps.[22] The atomic steps of most materials are generally more reactive than atomically flat areas.[21,22] We then hypothesized that SWNTs could have grown along such atomic steps. This is proven below for the case where no electric field was applied. Application of an electric field was shown to have no effect.

The morphology and dynamics of vicinal α-Al2O3(0001) surfaces have been investigated by several research groups.[22–24] The atomic steps, with a height equal to one
sixth of the hexagonal unit cell, that is, \( h = c/6 = 0.219 \text{ nm} \), follow a general direction perpendicular to the miscut direction (Figure 1c). Their average spacing is \( d = h \sin \theta \) where \( \theta \) is the miscut inclination. For convenience, we define a step vector \( \mathbf{s} = (\mathbf{c}/c) \times \mathbf{n} \), where \( \mathbf{c} \) is the principal lattice vector and \( \mathbf{n} \) is a unit vector normal to the surface. Then, \( \mathbf{s} \) points along the general step direction so that steps descend to the right, and its modulus equals the slope of the steps \( (s = h/d) \). We define the miscut azimuth \( \phi \) \((-60^\circ < \phi < +60^\circ)\) as the angle of \( \mathbf{s} \) relative to the [1120] direction, which is perpendicular to the (1120) c-glide plane, so that the sign of \( \phi \) expresses the handedness of chiral miscuts. The atomic step structure depends on the miscut azimuth \( \phi \). This is illustrated by Figure 1d, which represents different unreconstructed steps based on the bulk structure. The actual structure of the atomic steps is still unknown, although the high-temperature reconstruction of \( \alpha-\text{Al}_2\text{O}_3(0001) \) surfaces was recently characterized.

The characterization of a typical sample of aligned SWNTs on sapphire is shown in Figure 2. Figure 2a displays an AFM topographic image of the highly aligned SWNTs. The apparent diameter distribution of the SWNTs is \( 1.0 \pm 0.4 \text{ nm} \), which is 0.2 nm smaller than the value determined from Raman spectra \((1.2 \pm 0.5 \text{ nm})\). An asymmetric double-exposure back-reflection X-ray diffraction (XRD) method was used to determine the orientations of both the lattice and the miscut of the \( \alpha-\text{Al}_2\text{O}_3(0001) \) substrate (Figure 2b), in which a long and a short exposure were taken before and after \( 180^\circ \) rotation of the sample, respectively. The miscut inclination and azimuth are \( \theta = 2.1 \pm 0.2^\circ \) and \( \phi = 0 \pm 5^\circ \), respectively, and the general step direction, expressed by \( \mathbf{s} \), matches the direction of the nanotube alignment. In addition, a destructive characterization by thermal annealing at \( 1100^\circ \text{C} \) in air (Figure 2c) was performed. Then, the thermodynamically unstable \( c/6 \) atomic steps, which could not be resolved by AFM, bunch into visible macrosteps with heights of \( c-3c \) \([22, 23]\).

The step orientation and miscut inclination are independently determined from these images, thus yielding results \((\theta = 1.9 \pm 0.2^\circ)\) similar to those obtained from XRD studies. The angular distribution of the nanotubes and macrosteps with respect to reference marks are \( 108 \pm 4^\circ \) and \( 109 \pm 2^\circ \), respectively (see Supporting Information for histograms). This precise coincidence is a clear indication of step decoration. The apparent reduction in SWNT height is consistent with the size of \( c/6 \) atomic steps.

Similar experiments were performed on about twenty samples of SWNTs grown on either side of seven different C-plane sapphire wafers of random miscut inclinations (up to \( \theta = 4^\circ \)). Some representative results are displayed in Figure 3 (see Supporting Information for comprehensive data). In all cases, except for \( \theta < 0.5^\circ \), SWNTs grow parallel to the atomic steps and not to a particular lattice direction. The degree of alignment correlates with the miscut inclination. However, SWNTs grown on substrates having similar miscut inclinations show better alignment when the atomic steps run along low-index directions, such as [1120] (Figure 3c) or [1010] (Figure 3b), than along high-index directions (Figure 3d). This phenomenon may be attributed to the fact that straighter steps can have a closer interaction with the SWNTs. The density of the SWNT arrays also correlates with the value of \( \theta \). The samples with the lowest miscut inclination (Figure 3f) have visible atomic steps decorated by nanoparticles, but no nanotubes. The steps could play a role in stabilizing the catalyst nanoparticles, so that a higher density of steps leads to a higher yield of SWNTs.

Interestingly, certain samples show kinked nanotubes running in zigzags along two different low-index directions. In Figure 4a, alternating long and short segments of the same
SWNTs run along the [1120] and [1010] directions, respectively, in accordance with their proximity to the general step direction (a few segments along the [0110] and [21¯10] directions are occasionally seen too). This result can be attributed to SWNT growth along faceted atomic steps (Figure 4b). Since the sharp 30° kinks presumably occur during growth, they could involve pentagon–heptagon defects, which are an energetically favored alternative to bending or buckling. The energy associated with pentagon–heptagon defects was calculated to be about 7 eV,[26] whereas the minimum strain energy required to produce a 30° buckle in a 1-nm-diameter SWNT was estimated to be about 13 eV.[27] Single-nanotube Raman spectra from these samples exhibit a high intensity of D-band peaks, which indicates a significant loss of translational symmetry, that is consistent with this picture. Pentagon–heptagon defects are known to cause structural changes along the SWNTs,[28] thus producing interesting metal–semiconductor heterojunctions.[29] In addition, the right-handedness of the kinked nanotubes reveals the chirality of the miscut substrate, which could in principle distinguish between enantiomorphic SWNTs.

Figure 3. SWNTs on miscut sapphire. Comparative analysis of representative samples with different miscut inclination and azimuth angles (see Supporting Information for XRD and full data table): a) \( \theta = 3.4 \pm 0.3^\circ, \phi = 42 \pm 5^\circ \); b) \( \theta = 2.3 \pm 0.2^\circ, \phi = -33 \pm 5^\circ \); c) \( \theta = 2.1 \pm 0.2^\circ, \phi = 0 \pm 5^\circ \); d) \( \theta = 1.7 \pm 0.1^\circ, \phi = 18 \pm 5^\circ \); e) \( \theta = 0.4 \pm 0.2^\circ, \phi = -5 \pm 5^\circ \); and f) \( \theta = 0.3 \pm 0.2^\circ, \phi = -50 \pm 5^\circ \) (image sizes are 2.5 \( \mu \)m, except (e) and (f), where \( s \) is from AFM). Insets show AFM topographic images of the respective annealed samples (inset scale bars 100 nm) with macrosteps. In (f), the atomic steps are spaced enough to be observed, and are decorated with inactive catalyst nanoparticles.

Figure 4. SWNT growth along atomic steps. a) AFM amplitude image of kinked SWNTs growing along the [1120] direction (blue) with short segments along the [1010] direction (red), and occasionally [2110] (yellow) and [0110] (green; image size 5 \( \mu \)m). The short arrows in the respective color point to a few such segments. b) Illustration of a (10,0)-(6,6)-(10,0) kinked nanotube along [1120]-[1010]-[1120]. c) Model of a 1-nm-diameter SWNT along a [1120] atomic step. The color gradient represents an estimated SWNT–step electrostatic interaction energy per unit of nanotube length as a function of SWNT axis position, \( U(x,\gamma) \). This was calculated from the force exerted on a polarizable body by an inhomogeneous field, \( \mathbf{F} = (\alpha \mathbf{E} \cdot \mathbf{E}) \mathbf{E} \). Averaging the potential along the direction of the step and the SWNT \( \gamma \) gives \( U(x,\gamma) = -\frac{1}{2} \alpha \gamma E^2(x,\gamma) \), where \( \alpha \gamma \) is the transverse polarizability of the SWNT per length[31] and \( E(x,\gamma) \) is the local field. The latter was derived from the unreconstructed atomic step, by summation of Coulomb potentials from bulk Mulliken charges, averaged along the \( \gamma \) axis and corrected for slab edge effects by subtracting a similar potential without the step. (The blue-to-red scale is 0–750 eV nm\(^{-1}\)).
atomic steps has not yet been observed, because of their relatively low anisotropy energy below $\theta = 1^\circ$. The anisotropy is expected to increase at higher miscut inclinations as a result of step–step interactions, but could not be resolved by AFM. Here, the decoration by SWNTs reveals a faceting that would otherwise remain unobserved.

We propose a “wake-growth” mechanism to describe the atomic-step-templated formation of SWNTs, in which the catalyst nanoparticle slides along the atomic step and leaves the growing SWNT behind as a wake. This would involve three main factors: 1) higher nanotube-surface van der Waals (vdW) interactions near the step that result from increased contact area; 2) electrostatic interaction between the local electric fields created by uncompensated dipoles at the atomic steps and the induced dipoles across the SWNTs; and 3) better wetting of the atomic steps by the Fe metal catalyst nanoparticles, because of capillarity and higher coordination. The vdW contribution to the interaction energy per unit of nanotube length can be theoretically extrapolated from previous calculations on Si surfaces (2.2 eV nm$^{-1}$) by assuming proportionality with the substrate polarizability and a Clausius–Mossotti relation, which yields 1.4 eV nm$^{-1}$ on SiO$_2$ and 2.2 eV nm$^{-1}$ on Al$_2$O$_3$ surfaces. This small difference cannot account for the results in Figures 1a and b. Moreover, the lack of alignment by the approximately 1-nm-deep polishing scratches (Figure 2a) suggests that vdW interactions may not be the only aligning factor. On the other hand, electrostatic interactions may be especially high as a result of the ionic character of Al$_2$O$_3$. The electrostatic nanotube–step interaction was modeled, as a first approximation, by applying theoretical SWNT polarizabilities and a Coulomb potential near an unreconstructed step (Figure 4c). This electrostatic interaction is about 50 eV nm$^{-1}$ at a reasonable vdW distance (0.34 nm) from the step. Although this remarkable value should be diminished by surface relaxation and reconstruction, it may still significantly account, along with vdW forces, for the strong SWNT–Al$_2$O$_3$ interaction compared to that of SWNT–SiO$_2$ (Figure 1a,b), as well as for the high degree of nanotube alignment along the atomic steps.

The present study shows that atomic-scale surface features can direct the orientation and conformation, and possibly also the structure, of single-wall carbon nanotubes. The direction and morphology of the atomic steps can be macroscopically controlled in the crystal cutting process by the growing SWNT behind as a wake. Lastly, step-templated assembly may not be limited to carbon nanotubes and vicinal surfaces, but could be generally applicable to other axial-growth nanowires as well as to other controllable surface defects, such asetch pits, grain boundaries, and screw dislocations. This will enable new strategies for the large-scale fabrication of nanoscale devices from the bottom up.

**Keywords:** crystal engineering · nanostructures · nanotechnology · nanotubes · surface chemistry


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Atomic Step-Templated Formation of Single-Wall Carbon Nanotube Patterns

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Methods

C-plane sapphire wafers were purchased from Elan, St. Petersburg, Russia (roughness, Ra, ~1.5nm, 2 sides epi polished), with a maximum miscut angle of 4° specified by the manufacturer. The 5 cm wafers were cut in pieces of about 1 cm², and cleaned by sonication in acetone for 10 min, followed by rinsing in isopropanol and deionized water, spin dried and heated in a hot plate to 200°C for 10 min to evaporate the remaining water on the surface. C-plane sapphire with miscut angles <0.5° were purchased from Marketech International, inc. (Ra~0.5nm, 2 sides epi polished) and similarly treated. Platinum electrodes were patterned on the sapphire substrates by a standard photolithography (photoresist Microposit S1805, Shipley), followed by electron beam evaporation (Edwards Auto 306) of 30 nm titanium (99.99%, Holland Moran Ltd., Israel) and 60nm platinum (99.99%, Holland Moran Ltd. Israel), while cooled with liquid nitrogen. Amorphous SiO₂-coated sapphire substrates were prepared by electron beam evaporation of SiO₂ (99.99%,Kurt J.Lesker) prior to photolithography.

Single-wall carbon nanotubes (SWNTs) were grown by catalytic chemical vapor deposition (CVD), using ferritin protein as a precursor of monodisperse Fe catalyst nanoparticles, as previously reported[81]. Briefly, substrates were first oxidized by oxygen
plasma (March Plasmod GCM 200, 1-3 min, with 1 sccm of O$_2$), a ferritin solution of 1g/L (horse spleen ferritin, Sigma) was deposited on the samples for 10 min, washed with deionized water and blow dried, followed by a second plasma oxidation step, to eliminate all the organic matter. Finally, the CVD was carried out at 800ºC for 10 min with a mixture of 60% Ar (99.998%, Oxygen & Argon Industries, Israel), 40% H$_2$ (99.999%, Gordon Gas, Israel) and 0.2% ethylene (99.9%, Gordon Gas, Israel) at 1 atm and a flow rate of 1 L/min. SWNTs on SiO$_2$-coated sapphire were prepared precisely as previously described for oxidized Si wafers$^{[S1]}$. The lithographic electrodes used for electric field directed CVD were connected with a 4523AD Kulicke & Soffa wire bonder, to external electrodes. A 6517A Keithley source meter was used to apply an electric field of 2x10$^6$V/m between the patterned electrodes during the growth process, while monitoring possible leakage currents.

Atomic force microscopy (AFM) characterization of the SWNT and annealed sapphire was carried out in air tapping mode (Veeco, Multimode Nanoscope IV), using 70 kHz etched Si probes (FESP, Nanoprobes). Low-voltage field-emission scanning electron microscopy (FE-SEM) was done with a LEO Supra 55VP, in ultra high vacuum. Raman characterization was kindly performed by collaborators (see acknowledgments), by previously reported methods$^{[S2]}$.

The miscut inclination and azimuth angles were determined using an asymmetric double-exposure back-reflection XRD method. The X-rays were produced by an Elliot GX6 rotating anode generator operating at 1.2 KW and producing Cu radiation with a 200 µm focus. The radiation was partially monochromatized with wavelengths ~1.5-1.8 Å accounting for ~80% of the intensity. Diffraction patterns were recorded on imaging plates (Fuji) and scanned with a homemade reader. The sample, placed perpendicular to the X-ray beam, was first exposed for 2 hrs, and then rotated by 180° for a second exposure of 1 hr. The miscut angle $\theta$ was
measured in the following way: (i) The spots of the XRD patterns were aligned on an appropriate Greninger chart in order to read the angular relations on the back reflection pattern, and then the spots were plotted on a stereographic projection to measure the miscut inclination and azimuth\[^{[3]}\]; (ii) The distance between the centers of the first and second patterns was measured and defined as 2R. Then the miscut inclination is given by \( \theta = \tan^{-1}\left(\frac{R}{L}\right)/2 \), where \( L = 3 \text{ cm} \) is the distance between the sample and the X-ray imaging plate (7x7 cm) on which the diffraction patterns were recorded.

The miscut orientation and inclination were independently characterized by thermal annealing. A small piece of each sample, including a portion of lithographic electrodes for reference, was broken off and annealed at 1100ºC for 10 hrs, then analyzed by tapping-mode AFM.

![Supporting Figure 1](image)

**Supporting Figure 1.** Angular distributions of SWNTs (a) and macrosteps (b) referred to in Figure2.
Supporting Figure 2. Back-reflection XRD pattern from a high quality C-plane sapphire wafer with $\theta<0.15^\circ$ and a known lattice orientation. This pattern was used as reference to identify the lattice and miscut orientation in Figures 2-4, and S3 (vide infra).
Supporting Figure 3. Asymmetric double-exposure back-reflection XRD patterns, corresponding to Figure 3a-f respectively. The green and red patterns indicate the first (2 hrs.) and second (1 hr.) exposures respectively. The $s$ vectors (light blue) are perpendicular to the miscut direction (dark blue) and their length is proportional to the miscut inclination angle $\theta$. 
Supporting Table 1. Comprehensive results for representative samples.

<table>
<thead>
<tr>
<th>θ (deg)</th>
<th>θ (deg)</th>
<th>φ (deg)</th>
<th>SWNT orientation* (deg)</th>
<th>Step orientation* (deg)</th>
<th>Step orientation* (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>XRD</td>
<td>XRD</td>
<td>AFM</td>
<td>XRD</td>
<td>XRD</td>
</tr>
<tr>
<td>2.9 ± 0.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.4 ± 0.3</td>
<td>42 ± 5</td>
<td>84 ± 2</td>
<td>85 ± 5</td>
<td>78 ± 15</td>
</tr>
<tr>
<td>2.1 ± 0.3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.3 ± 0.2</td>
<td>-33 ± 5</td>
<td>0 ± 4</td>
<td>3 ± 4</td>
<td>0 ± 15</td>
</tr>
<tr>
<td>1.9 ± 0.2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.1 ± 0.2</td>
<td>0 ± 5</td>
<td>108 ± 4</td>
<td>109 ± 2</td>
<td>92 ± 15</td>
</tr>
<tr>
<td>1.9 ± 0.2&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.7 ± 0.1</td>
<td>18 ± 5</td>
<td>9 ± 29</td>
<td>32 ± 2</td>
<td>27 ± 15</td>
</tr>
<tr>
<td>0.32 ± 0.1&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.4 ± 0.2</td>
<td>-5 ± 5&lt;sup&gt;**&lt;/sup&gt;</td>
<td>25 ± 50</td>
<td>26 ± 10</td>
<td>11 ± 15</td>
</tr>
<tr>
<td>0.16 ± 0.05&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.3 ± 0.2</td>
<td>-50 ± 5&lt;sup&gt;**&lt;/sup&gt;</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

The signs, a-f, indicate the order in which each sample appears in Figures 2 and S3.

* SWNTs and steps angular distribution with respect to reference marks.

** The miscut azimuth for samples (e) and (f) was determined from the AFM images using the crystal orientation obtained from XRD photographs.

Supporting Information References

