Ultralow-voltage field-ionization discharge on whiskered silicon nanowires for gas-sensing applications

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Several hundred million volts per centimetre of electric-field strength are required to field-ionize gas species. Such fields are produced on sharp metallic tips under a bias of a few kilovolts. Here, we show that field ionization is possible at dramatically lower fields on semiconductor nanomaterials containing surface states, particularly with metal-catalysed whiskers grown on silicon nanowires. The low-voltage field-ionization phenomena observed here cannot be explained solely on the basis of the large field-amplification effect of suspended gold nanoparticles present on the whisker tips. We postulate that field penetration causes upward band-bending at the surface of exposed silicon containing surface states in the vicinity of the catalyst. Band-bending enables the valence electron to tunnel into the surface states at reduced fields. This work provides a basis for development of low-voltage ionization sensors. Although demonstrated on silicon, low-voltage field ionization can be detected on any sharp semiconductor tip containing proper surface states.

Development of devices that can field-ionize gas molecules at low bias voltages may be essential for many applications such as ion mobility spectrometry and highly selective portable gas sensing. Recent developments in synthesis of dense nanostructures with ultrasharp tips offered promise to ionize gas molecules for their accurate fingerprinting, but their high operating voltages are not favourable for ubiquitous applications.

Field ionization (FI) consists of a valence electron of a gas atom or molecule (henceforth referred to as a particle) tunnelling through a potential barrier, commonly into a vacant energy state of the conduction band of a metal at the anode. Classic FI action on metallic specimens requires extremely high positive electric fields, of the order of a few hundred million volts per centimetre. Such fields are only achievable in the vicinity of very sharp electrodes under a large bias. For instance, to produce FI of nitrogen on metal tips with end radii of 10–20 nm, it is necessary to apply a bias of 1–2 kV (ref. 6). Figure 1a shows the potential diagram of an imaging particle near a metal surface subject to a positive field. There is a critical distance \( d_c \) between the particle and the metal surface below which FI cannot occur. \( d_c \) is about 4–5 Å for metals and is given by

\[
d_c \cong \frac{(U_i - \Phi)}{eF_{\text{vac}}}
\]

where \( U_i \) is the ionization potential of the particle, \( \Phi \) is the metal work function, \( e \) is the elemental electron charge and \( F_{\text{vac}} \) stands for the electric field in vacuum at the particle surface. Figure 1b shows a three-dimensional schematic view of a single nanowire bearing whiskers branching from the trunk. Each whisker can act as an individual FI source, because at the apex it carries the highest electric field among other prominent features. Figure 1c shows a magnified view of a generic FI tip that can be the apex of one of the whiskers. A comprehensive illustration of various particle–tip interactions is presented in this figure at the atomic scale. Particles can be supplied from the surroundings or crawl up along the specimen shank to the ionization zone. The former process dominates at low fields and the latter at low temperatures or at high fields where the current is limited by gas supply. Considerably higher field strengths are necessary to ionize a particle adsorbed on a prominent surface atom than one in the gas phase several ångströms away from it. Ionization of an adsorbed particle is referred to as field desorption, or field evaporation if the particle originates from the specimen lattice itself.

Here we show that FI can take place at dramatically lower field strengths, at the surface of sharp semiconductor–metal interfaces containing surface states. Occurrence of exotic ionization discharge on gold-catalysed whiskered silicon nanowires was demonstrated. In particular, measurable FI currents were recorded at below 10 V, that is, three orders of magnitude smaller than the voltages recorded using sharp metallic specimens. In addition to the lowering of threshold FI voltages, we showed that whiskering at the nanoscale provides an ample number of FI sites, so that, even though each whisker has an extremely small contribution, the total field-ion current can be detectable.

Detection of anomalous FI

Silicon nanowires covered with dense whiskers were grown using a two-step vapour–liquid–solid (VLS) technique (see Methods). Measurements were carried out on as-grown whiskered nanowires, whiskered nanowires after removal of gold tips, and regular whiskerless nanowires. The effect of doping on the FI current was studied as well. Scanning electron microscopy (SEM) micrographs of the smooth and whiskered silicon(111) nanowires are shown in Fig. 2a and b–d respectively. The nanowires were incorporated at the anode of identical ionization cells with an electrode separation of 100 μm (Fig. 2e). Thus, a bias of \( V = 10 \text{ V} \) would produce an applied field of 10⁶ V cm⁻¹. Such a field must be amplified by a factor of \( \sim 1.7 \times 10^2 \) to generate \( 1.7 \times 10^4 \text{ V cm}^{-1} \) (this is the best-image field of \( \text{N}_2 \); the threshold field strength might be slightly smaller), required to field-ionize nitrogen on metallic tips. Various models have been proposed to explain...
the field-enhancement effect on sharp tips

Figure 1 | Field ionization dynamics. a. Energy-band diagram for FI of a gas particle under a positive applied field in the vicinity of a metal surface. $E_f$ is the Fermi level, $\Phi$ is the metal work function, $U_i$ is the ionization potential, $F_{vac}$ is the electric-field strength in vacuum and $d_c$ is the distance at which $E_f$ and the ground state of the atom coincide, referred to as the critical distance. b. Schematic illustration of a VLS-grown nanowire containing whiskers on the trunk. c. Atomic-scale view of a sharp tip that can be the apex of one of the nanoscale whiskers, showing field ionization and field adsorption of an alien particle (double lobe dark, or blue in the coloured version), and field evaporation of a lattice atom (double lobe light, or orange in the coloured version). The lattice atoms (spheres) are drawn without taking into account any specific crystal orientation. FI can happen after the impinging particle loses its kinetic energy during several rebounds, or, at higher fields, the particle crawls from the specimen trunk up to the ionization zone. The latter process is referred to as field desorption. The critical distance, $d_c$, is depicted as a ‘critical surface’ (disc) in the three-dimensional illustration.

Figure 2 | Nanowires used to measure anomalous semiconductor-assisted gas ionization. a. A close-up SEM image of smooth silicon nanowires after annealing in HCl. b, c. SEM micrographs of a forest of, and a single, whiskered silicon nanowire that showed low-voltage FI; d, that of whiskered nanowires after removal of gold catalyst for the tips. e. A three-dimensional schematic illustration of the device used to measure gas ionization on both types of nanowire. Note that the nanowires were planted at the anode. $d_{gap} = 100 \mu$m is the spacing between anode and cathode. f. The anode discharge current in $N_2$, and the $N_2$ pressure, versus time at $V = 6 \, V$. The curves were obtained using the device with undoped whiskered silicon nanowires. As the field-enhancement effect on sharp tips, but owing to the vast variety of shape and size of the whiskers, ranging from well-protruded branches to small buds, it is impossible to define a single enhancement factor for the apparatus (see Supplementary Information). Nevertheless, even the sharpest whiskers formed on our silicon nanowires are not capable of producing such high field-amplification factors. The upper limit of the field strength at the apex of a hemisphere-on-shank is given by $F_{max} \approx V / 5r_t$ (ref. 5). As a result, to achieve $1 \, V \, \AA^{-1}$ ($10^8 \, V \, \text{cm}^{-1}$), at $V = 10 \, V$, the protrusion tip curvature needs to be about $r_t \approx 2 \, \AA$ (0.2 nm), obviously far sharper than the whisker tips grown in this work. Figure 2f shows the evolution of discharge current with time, measured while nitrogen was slowly injected into the test chamber. The curve was obtained using the device containing undoped whiskered nanowires with their gold catalyst intact. Interestingly, the linear dependence of current on pressure is consistent with FI action. The other two nanowire variants did not show FI within the voltage range studied. Figure 3a shows the $I$–$V$ curves of undoped whiskered nanowires obtained in a wide pressure range of nitrogen in full logarithmic coordinates. The inset shows the pressure...
dependence of current at three bias voltages. In contrast to the case of discharge in parallel plates, where the conduction is ohmic at low voltages, conduction begins with FI at $V \lesssim 6$ V. Note the slightly greater-than-unity slopes in this region, particularly at low pressure. At low fields, the FI current is expected to rigorously depend on the field strength (field-limited regime) and to be a strong function of $U_1$ (refs 5, 7). Such dependence can be employed to fingerprint the unknown gas particle, as $U_1$ is a unique quantity. However, no tangible difference was observed between the $I$–$V$ curves of nitrogen, helium, argon and ammonia, particularly at $V \lesssim 6$ V. We therefore conclude that $V \lesssim 6$ V corresponds to the supply-limited regime, where the ionization rate is already high enough that all of the imoping particles are ionized and the current mildly increases with field strength. The supply-limited FI current does not depend on $U_1$, whereas it is proportional to the gas pressure close to the tip. The steep current rise observed at $V \approx 6$ V can be associated with desorption of field-adsorbed particles along the nanowires, which owing to polarization forces crawl up to the apex of whiskers, where the field strength is maximum. At high voltages the curves converge, for the conduction becomes space charge limited. In this regime, the space-charge-limited insulator injected plasma cube law holds because the curves have a slope of $\sim 3$, that is, $I \propto V^3$ (ref. 13). The $I$–$V$ curves obtained from the p-type doped whiskered nanowires are shown in Fig. 3b. At low voltages, where we believe FI begins, the amplitudes of the probed currents are comparable to that of the undoped sample. This is suggestive that FI is not a strong function of the Fermi level in the bulk of protrusions. However, the doped sample exhibits larger current at higher voltages, consistent with its lower resistivity. Anomalous FI ceased on whiskered nanowires after removal of the gold catalyst from their tips. Figure 3c shows the resultant $I$–$V$ curves, which resemble that of discharge in parallel plates where the conduction is ohmic at low voltages and tends to saturate before the Townsend discharge mechanism takes effect.

**Selectivity in the field-desorption regime**

Figure 3d–f shows the $I$–$V$ curves corresponding to field desorption of nitrogen, helium and argon, measured using undoped whiskered nanowires at three different pressures ($P = 0.1, 2$ and 10 torr respectively). In comparison to the low-pressure scenario, the rate of FI of the desorbing particle decreases owing to formation of a multi-adlayer of gas molecules on the emitter surface. As a result, in contrast to the low-pressure case, where all the species in the gap are ionized ($P = 10^{-7}$–$10^{-4}$ torr in Fig. 3a and the inset), the discharge current becomes related to $U_1$. The phenomenon is discernible in the $I$–$V$ curves plotted in Fig. 3d–f, as, in general, the species with higher $U_1$ have exhibited lower currents. Apparently, this can enable selective gas discrimination on the basis of the field-ion $I$–$V$ behaviour of different gas types. It is clearly seen that helium has generated a smaller field-ion current than nitrogen. In addition, activation and deactivation of adsorption sites with different bonding energies has produced kinks that are readily repeated among different gas types. The peaks correspond to the voltages at which these sites start to lose the adsorbed particles owing to field desorption; therefore, the current ceases to rise until a site with a higher bonding energy is activated (valleys). Because of its higher $U_1$, the kinks corresponding to the field-ion current of helium lag in voltage as compared with those of nitrogen in Fig. 3d,e, and with those of argon in Fig. 3f. The fact that currents are pressure independent confirms that the ion current is initiated from adsorbed molecules rather than free molecules in the gap.

**Semiconductors versus metals**

It is well known that, under certain conditions, FI requires lower applied fields on semiconductors than on metals. Field penetration into the semiconductor may cause significant upward band bending and make the near-surface region become p-type degenerate. As shown in the energy-band diagram of Fig. 4a, the electron may then
Figure 4 | Energy-band diagrams for FI on a semiconductor surface. The semiconductor work function at the surface, $\Phi$, increases by the amount of band bending, $\Phi_b$, due to field penetration. $F_{vac}$ and $F_s$ are the electric-field strengths in vacuum and semiconductor respectively, $\lambda$, is the field penetration depth and $\epsilon_r$ is the semiconductor relative permittivity. a. This model predicts reduction of $d_s$ on the semiconductor at the same imaging field owing to a larger effective surface work function. A shorter $d_s$ implies a higher tunnelling probability and, therefore, a higher field-ion current. b. The solid and dotted lines represent the potential energies of the imaging-gas electron near a metal and a semiconductor surface, respectively. $d_s$ is assumed to be nearly the same for both materials. The potential barriers change from triangular to trapezoidal, and becomes larger in the semiconductor ($\Delta U_{semicond} > \Delta U_{metal}$). As a result, it is expected that the imaging field and the field-ion current decrease at the same time. The effect of surface states is not considered in this model. c. The effect of surface states. The tunnelling electron can enter the surface states, even without surface inversion. The tunnelling probability is higher for tunnelling into the states closer to the valence band ($d_{c1} < d_{c2}$). In the low-field case ($F_{vac2}$), there is normally no empty state available for the ground-state electron to tunnel unless the semiconductor is heavily p-type degenerate. In addition, the penetration probability is very small as $d_{c3}$ is the degenerate Fermi level. The types of surface state that could be involved in the FI process are discussed in detail in Supplementary Information. This last model is more effective in explaining the low-field FI behaviour we observed herein. c is not drawn to scale with a and b.

The ion currents obtained in this work, however, are not in agreement with (3) for $d_{c-semicond} < d_{c-metal}$ as their amplitudes are much smaller than if the ion emission were from metallic tips with the same geometry. The total number of FI sites in the sample with whiskered nanowires is estimated to be of the order of $10^{11}$ from our SEM observations (see Supplementary Information). These are gold-terminated whiskers of silicon with an average tip curvature of roughly $\approx 6.7$ nm. On the occasion of FI at $V = 6$ V, $t = 100$ s, where $F_{vac} = 7 \times 10^{-11}$ A at $P = 2.5 \times 10^{-6}$ torr, as shown in Fig. 2f, each whisker is expected to emit a continuous field-ion current of about $7 \times 10^{-11}$ A/3 = $7 \times 10^{-12}$ A, where the upper limit of field strength on the tips would be $1.8 \times 10^{6}$ V cm$^{-1}$ at this voltage (using $F_{max} = V/Sr$). In fact, this is a rough overestimate: as the whiskers have a certain diameter/length distribution, the local fields could be weaker (see Supplementary Information). Compared with FI action on metallic tips, requiring 100 times stronger fields ($10^{8}$ V cm$^{-1}$), and producing currents of the order of pico- to microamperes, it is clear that both the required field and the measured currents turned out to be dramatically lower here. As a result, the first assumption of FI occurring at a smaller critical distances on semiconductors is ruled out. This is in contrast with the earlier work, where enhanced FI was explained on the basis of $d_{c-semicond}$ being less than $d_{c-metal}$ (ref. 15). Table 1 summarizes the results of some earlier field-ion I–V measurements, mainly during field-ion microscopy. Data were extracted from the I–V curves in the field-limited regime. The last row contains the result of this work, showing a reduction of about two orders of magnitude in the field. Note that the sub-10 V helium FI of Singh et al. on $\beta$-W nanorods was due to the large field enhancement of atomically sharp nanorod tip apexes, in the rage of 0.1–0.2 nm, capable of generating 0.5–1.0 V Å$^{-1}$ (ref. 16).
Table 1 | FI on different tip materials compared with our whiskered silicon nanowires.

<table>
<thead>
<tr>
<th>Tip material</th>
<th>( t_s ) (nm)</th>
<th>Tip voltage</th>
<th>Field strength* ((x10^8 \text{ V cm}^{-1}))</th>
<th>Current (A)</th>
<th>Gas</th>
<th>Pressure (torr)</th>
<th>Reference</th>
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<tr>
<td>Ir</td>
<td>100</td>
<td>12 kV</td>
<td>2.4</td>
<td>4.0 \times 10^{-10}</td>
<td>H₂</td>
<td>10^{-3}</td>
<td>Fig. 4 of ref. 7</td>
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<tr>
<td>Ir</td>
<td>80-150</td>
<td>15 kV</td>
<td>2.4</td>
<td>10^{-10}</td>
<td>H₂</td>
<td>10^{-2}</td>
<td>Fig. 5 of ref. 20</td>
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<tr>
<td>Ge</td>
<td>250</td>
<td>17.8 kV</td>
<td>1.4</td>
<td>6.3 \times 10^{-14}</td>
<td>Ar</td>
<td>2 \times 10^{-6}</td>
<td>Fig. 3 of ref. 21</td>
</tr>
<tr>
<td>W</td>
<td>100</td>
<td>-</td>
<td>1.3</td>
<td>10^{-10}</td>
<td>Ar</td>
<td>~10^{-6}</td>
<td>Fig. 3 of ref. 22</td>
</tr>
<tr>
<td>Wβ-W</td>
<td>Single atom</td>
<td>1.6 kV</td>
<td>-</td>
<td>-</td>
<td>Ar</td>
<td>8.4 \times 10^{-6}</td>
<td>Ref. 23</td>
</tr>
<tr>
<td>Si/Au nanowhiskers</td>
<td>~10</td>
<td>6 V</td>
<td>0.018 (maximum)</td>
<td>7 \times 10^{-22}</td>
<td>N₂</td>
<td>2.5 \times 10^{-6}</td>
<td>This work</td>
</tr>
</tbody>
</table>

*Values of the field magnitude are shown here if available in the references, or the maximum value was suggested on the basis of \( F_{\text{max}} = V/t_s \).
are very close, and the polarizabilities are not very different either ($U_2(N_2) = 15.6$ eV, $U_2(\text{Ar}) = 15.75$ eV, $\alpha(N_2) = 1.74$ Å$^2$ and $\alpha(\text{Ar}) = 1.64$ Å$^2$; ref. 19). We believe this is due to the higher sensitivity of the device to argon than to nitrogen, as it can be clearly seen in Fig. 5a that argon has produced a higher current than nitrogen at comparable partial pressures. A similar effect was observed when argon was used as the host gas (see Supplementary Information).

Conclusion
We have demonstrated occurrence of anomalously strong FI on gold-catalysed whiskered silicon nanowires and explained our observations on the basis of combination effects of geometrical field enhancement and silicon surface states close to the gold–silicon interface at the whisker tips. Although unintentional incorporation of impurities in nanowires from the catalysts adversely affects the electrical properties and impedes the development of high-performance electronic and photonic devices, the application of nanowires grown by VLS processes offers a unique advantage for FI applications by offering nanostructures with unmatched dimensions that readily come with high density of surface states associated with the impurities and dangling bonds. To precisely quantify and predict the magnitude of semiconductor-assisted field-ionization, field-desorption and field-evaporation processes, systematic measurements are required to find the position and density of gold-induced surface states. In addition, because the anomalous enhancement of field-ion currents measured in this work was correlated with geometrical amplification of the field on whisker tips, it is difficult to quantify these two effects separately. Future work can focus on engineering confined surface levels with known density and location at sharp semiconductor surfaces. In this case, low-voltage FI can offer implications for accurate fingerprinting of gases, for instance in bio-chemical, environmental and disease-sensing applications.

Methods
Synthesis of smooth and whiskered Si nanowires. Whiskered silicon nanowires were synthesized by a two-step VLS technique using SiH₄ as the precursor. A 3-nm-thick layer of Au was first evaporated on ultraclean oxide-free p-type Si(111) substrates, with a volume resistivity of $\rho < 0.005$ Ω cm. The substrates were then heated at 610 °C for 20 min in 10 torr H₂ to form Au–Si alloy and then dewet the film, creating alloy droplets. Primary nanowires (nanowire trunks) were grown at 680 °C for 1 h under 15 s.c.c.m. flow of SiH₄. Next, the samples were annealed for 5 min by introducing 15 s.c.c.m. HCl into the chamber, while the temperature was ramped down from 680 to 580 °C. HCl was used to inhibit upward growth of primary nanowires and cause downstream migration of the Au–Si eutectic. SiH₄ was then reintroduced into the chamber at the same rate for 5 min to form the whiskers from the alloy that was spread during the intermediate annealing step. For smooth nanowires, the last step was not carried out. Whiskered nanowires were boron doped by flowing 3.0 s.c.c.m. B₂H₆ (100 ppm in H₂) during the growth. Gold nanoparticles were removed from the tips by immersion into a solution of 9:1 (parts by volume) commercial triiodide etchant (Transene;36% HCl) for 20 s.

Current–voltage–pressure measurements. Cylindrical ionization cells were fabricated on both smooth and whiskered Si nanowires. A secondary circular flat electrode (aluminium) was mounted on the samples using a 100-μm-thick polypropylene film. The film contained patterned channels to facilitate flow of gas (see Fig. 2e). Ohmic connections were made to both electrodes. The devices were installed in a custom-made vacuum chamber with electrical feedthroughs and mass flow controllers capable of regulating the output flow rate down to 1 s.c.c.m. Frequent purging with dry nitrogen ensured total removal of water vapour. The pressure was kept precisely constant by a proportional–integral–derivative controller during the course of each voltage sweep. Two source measure units connected separately to each electrode were used to carry out a staircase sweep, one in the positive direction and the other in the negative direction. To ensure that the charging current due to the cell capacitance was negligible, the sweep parameters were chosen as $\Delta V < 1$ V and $\Delta t = 50$ ms.

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References

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Author contributions
R.B.S. designed and carried out experiments, analysed data and wrote the manuscript. M.S.I. supervised the project, analysed data and edited the manuscript. Both authors discussed the results, and commented on the manuscript.

Additional information
The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturematerials. Reprints and permissions information is available online at http://npg.nature.com/permissions. Correspondence and requests for materials should be addressed to R.B.S.