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Silicon Wafers with Facet-Dependent Electrical Conductivity Properties

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Abstract

By breaking intrinsic Si (100) and (111) wafers to expose sharp {111} and {112} facets, electrical conductivity measurements on single and different silicon crystal faces were performed through contacts with two tungsten probes. While Si {100} and {110} faces are barely conductive at low applied voltages, as expected, the Si {112} surface is highly conductive and Si {111} surface also shows good conductivity. Asymmetrical I - V curves have been recorded for the {111}/{112}, {111}/{110}, and {112}/{110} facet combinations because of different degrees of conduction band bending at these crystal surfaces presenting different barrier heights to current flow. In particular, the {111}/{110} and {112}/{110} facet combinations give I - V curves resembling those of p-n junctions, suggesting a novel field effect transistor design is possible capitalizing on the pronounced facet-dependent electrical conductivity properties of silicon.

By synthesizing polyhedral Cu_2O , TiO_2 , PbS , and Ag_2O crystals as cubes, octahedra, and rhombic dodecahedra exposing different facets and measuring their electrical properties, strongly facet-dependent electrical conductivity behaviors have been observed.¹⁻⁶ These interesting semiconductor properties can be explained in terms of the presence of an ultrathin surface layer having varying degrees of band bending for different surface planes. This effect controls the

relative obstacle of charge transport through a semiconductor crystal depending on the points of electrical contacts. Such a feature is highly useful for electronic component design. The observed large facet-dependent photocatalytic properties of polyhedral Cu_2O , TiO_2 , and other semiconductors can be similarly explained, as the efficiency of photoexcited charge migration to external surfaces or heterojunctions strongly depends on the contacting faces.⁷⁻¹³ Furthermore, this thin layer with dissimilar band structures for different surface planes also gives rise to the observed facet-dependent optical absorption and emission properties in semiconductor nanocrystals and quantum nanostructures that has been recognized recently.¹³⁻¹⁸ Since facet effects are observable in many semiconductor materials, it is highly interesting to examine possible existence of facet-dependent electrical properties of silicon. Silicon has largely been the material of choice for integrated circuit fabrication, and novel photonic devices also use Si nanostructures.^{19, 20} However, Si nanoparticles exposing different crystalline facets are not available. Use of commercially available intrinsic Si wafers without impurity doping seems the best material to explore facet effects of silicon, but there is concern that the large thickness of Si wafers (0.3–0.5 mm) can make all facets look similarly low in conductivity since micrometer-sized Cu_2O crystals have exhibited an appreciably lower electric current than smaller Cu_2O particles do.¹ Recently, density functional theory (DFT) calculations on tunable number of various Si planes have indicated that thin Si (111) and (112) planes possess metal-like density of states (DOS) structures.²¹ Encouraged by the simulation results, we have used 4-inch (10 cm) intrinsic, or non-doped, Si {100} and {111} wafers that can expose sharp {110} and {112} facets with simple breakage of these wafers along certain cut directions for two-probe electrical conductivity measurements. For complete electrical conductivity examination, the tungsten probes were brought to contact the same or adjacent different Si faces. Remarkably, large facet-dependent electrical conductivity behaviors have been recorded, and some facet combinations give diode-like responses. Band diagrams are constructed to explain these facet effects. Electrical resistance plots are presented to further illustrate how current flowing through silicon strongly depends on the contacting facets. Such exciting results suggest a completely different approach to field-effect transistor (FET) design. This work demonstrates semiconductor facet effects are widely observable and can be manifested over extremely large length scales from quantum nanostructures to wafer-sized crystals.

X-ray diffraction (XRD) patterns of the purchased 4" (10 cm) Si (100) and (111) wafers with respective thicknesses of 300 and 500 μm were collected to confirm their crystal orientations. Only Si (400) and (111) reflection peaks were recorded for the Si (100) and Si (111) wafers, respectively (Supporting Information, Figure S1), confirming they have correct crystal orientations. The measured electrical resistivity values of these wafers are close to the

manufacturer-provided resistivity ranges (Supporting Information, Figure S2). These circular wafers have a flat edge. After making a fine scratch parallel and perpendicular to the flat edge and applying a pressure to break the wafer, sharp edges exposing other crystal facets are obtained. For the Si (100) wafer, both scribe directions give {110} facets (Supporting Information, Figure S2). For the Si (111) wafer, parallel and perpendicular scribes expose {112} and {110} faces.^{22, 23} Scanning electron microscopy (SEM) images of the Si (100) and (111) wafers after exposing other crystal planes are shown in the Supporting Information, Figure S3. Clearly sharp faces have been created for subsequent electrical conductivity measurements.

Figure 1 shows I - V curves with applied voltages in the range of +6 V to -6 V (or +5 V to -5 V for the {111} face) and the corresponding SEM images of different Si surfaces. Additional I - V curves collected are available in the Supporting Information, Figure S4 to illustrate current consistency in the obtained I - V curves. The SEM images show tungsten probes are separated by just a few μm on the same surface near the cleaved substrate edge. Bulk Si band gap is 1.12 eV. All Si facets give I - V curves characteristic of a semiconductor with exception of the {112} facets. Both the {100} and {110} surfaces are barely conductive at low applied voltages, although the current rises sharply beyond 4-5 V for the {100} surface due to avalanche breakdown.²⁴ The somewhat asymmetrical I - V curves observed for the {110} case may be due to different probe contact areas, as one probe appears much sharper than the other. Clearly the {110} face is least conductive among the four silicon crystal facets. The {111} facet shows moderate but steady rise in current below 2 V and steeper increase in current beyond 4 V reaching 600 nA at 5 V. Current fluctuation comes from W probe vibration and is observable during I - V measurements. Surprisingly, the {112} surface is highly conductive with an I - V curve resembling that of a metal. At 6 V, the current can reach 175 μA . At 5 V, current for the most conductive {112} face is greater than 25 000 times than that for the least conductive {110} face.

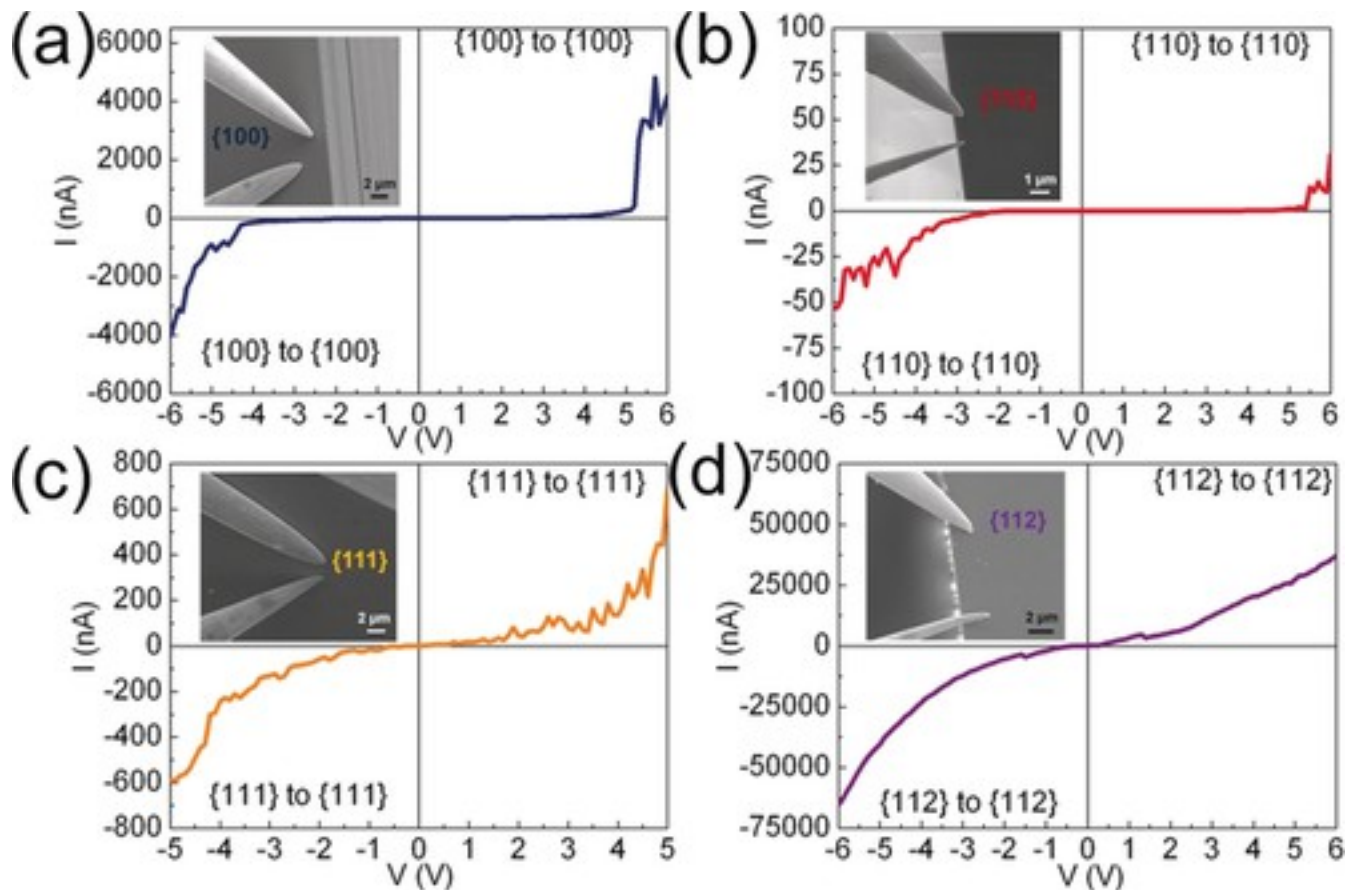


Figure 1

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I - V curves and SEM images of W probes making contacts to the a) $\{100\}$ facet of a Si (100) wafer, b) $\{110\}$ facet exposed by cutting a Si (100) wafer, c) $\{111\}$ facet of a Si (111) wafer, and d) $\{112\}$ facet exposed by cutting a Si (111) wafer.

These I - V curves, showing a voltage range of +5 V to -5 V for better comparison, are combined in Figure 2 a,b. There are obviously large electrical conductivity differences among these Si facets from highly conductive $\{112\}$ face to much less conductive $\{111\}$ and $\{100\}$ faces and nearly non-conductive $\{110\}$ face. These conductivity differences should not be due to possible formation of surface oxide as the freshly created surfaces are only exposed to air for less than 3 h. The relative conductivity order is $\{112\} > \{111\} > \{100\} > \{110\}$ faces. This order is similar to that observed for Cu_2O crystals with highly conductive $\{111\}$ facet, weakly conductive $\{100\}$ facet, and insulating $\{110\}$ facets.¹ Recently, DFT calculations on tunable number of Si lattice planes have shown that Si (100) and (110) planes should behave like a semiconductor having the same band gap size regardless of the number of planes used for the calculations, but certain numbers of Si (111) and (112) planes can display a metal-like band structure with continuous density of states (DOS) from valence band to conduction band.²¹ Remarkably, the electrical

conductivity measurements are generally consistent with these DFT calculation results. The emergence of metal-like band structures for the Si (111) and (112) planes has been suggested to relate to variation in Si–Si bond length and bond distortion for few Si plane layers within 2 nm, as well as 3s and 3p orbital electron contributions in the band structure.²¹ As a result, there are possibly physical and quantum mechanical origins to the presence of facet effects in semiconductor materials. It is puzzling why such large facet-dependent electrical properties of silicon were not recognized previously. One possibility is that the {112} facet is scarcely probed.

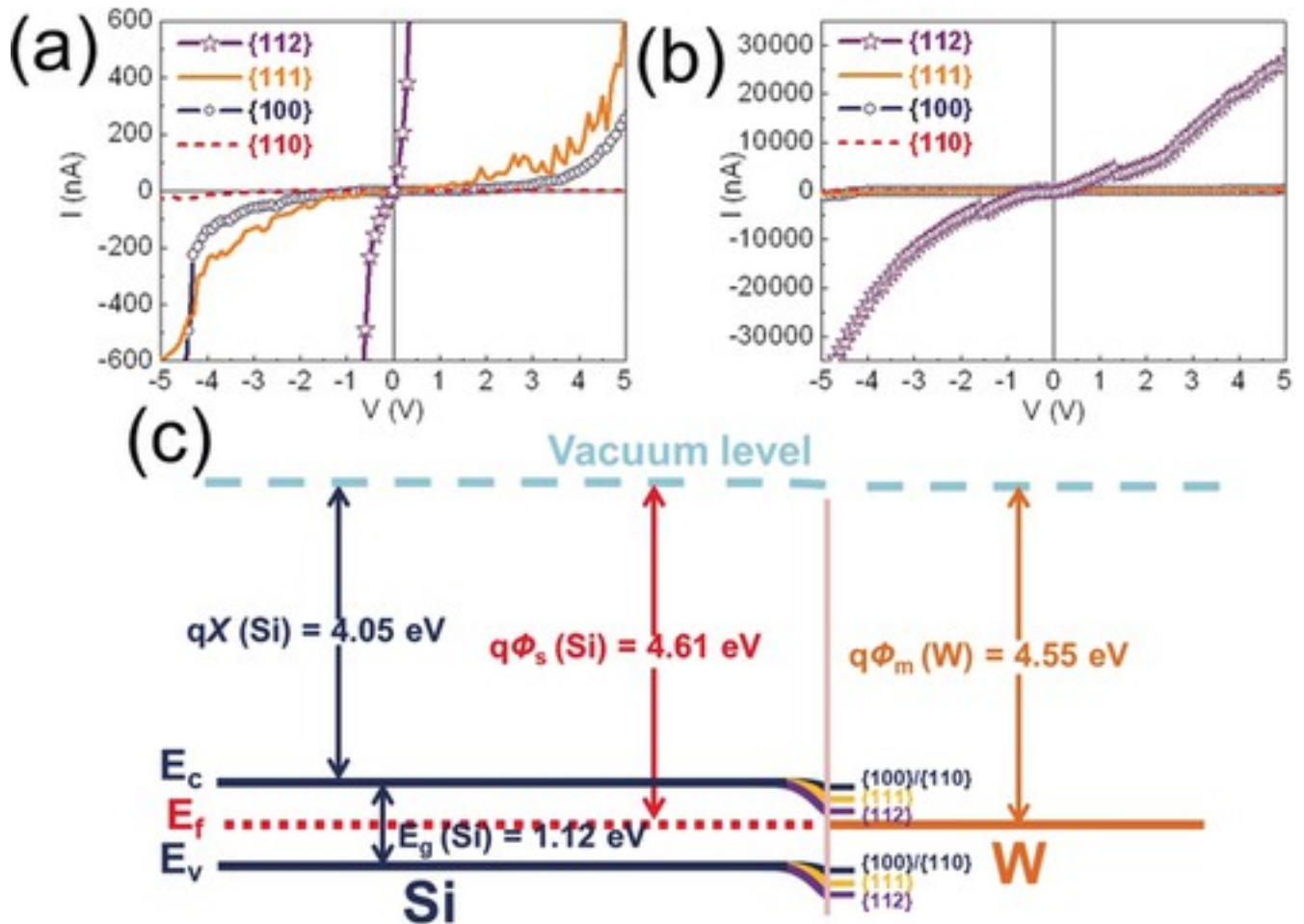


Figure 2

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a, b) I - V curves for the {100}, {110}, {111}, and {112} facets of a silicon wafer presented with different current magnitudes. c) Adjusted band diagram of Si with consideration of relative degrees of band bending for different crystal surfaces. The known tungsten band energy level is used to construct this band diagram. qX =semiconductor electron affinity, $q\Phi_s$ =semiconductor work function, $q\Phi_m$ =metal work function, E_c =conduction band energy, E_v =valence band energy, E_f =Fermi level.

A modified band diagram was constructed to explain the observed facet effects (Figure 2 c). The valence and conduction bands of silicon are drawn to bend downward with the consideration of better matched conduction band energy of Si {112} surface with the highest electron energy from tungsten to facilitate current flow. The {100} and {110} facets behave similarly both experimentally and in DFT calculations, so these surfaces should have a band diagram that is representative of bulk silicon with the least degree of conduction band energy bending or no bending. The {111} facet bends to a greater extent but should be less than that for the {112} surface. Such a modified band diagram is useful to understand the observed facet-dependent electrical conductivity properties of silicon.

From the I - V curves, electrical resistance diagrams can be constructed using the relationship $R=V/I$ (Supporting Information, Figure S5). The electrical resistance diagrams provide additional insights to the relative resistance of different facets of silicon to current flow. Clearly the Si {110} face presents significantly greater electrical resistance than the other Si faces. The {100} and {111} faces show some electrical resistance near 0 V, but resistance for the {111} face is quite small. The {112} face shows very low electrical resistance. Consistent with DFT calculation results, both the {111} and {112} faces have relatively low electrical resistance.

In the next set of experiments, tungsten probes were positioned to contact different Si facets (Figure 3). Again the two probes are close to each other within a few micrometers to reduce the current path length. Additional I - V curves for these four combinations of facets are available in the Supporting Information, Figure S6 to show the consistency of the measured current. The main purpose of such measurements is to see if asymmetrical I - V curves can be obtained as seen previously for Cu_2O , Ag_2O , TiO_2 , and PbS micro- and sub-microcrystals.^{1, 4-6} Remarkably, all facet combinations exhibit asymmetrical behaviors. Possibly because both Si {100} and {110} facets are barely conductive in the low-voltage region, connecting these poorly conducting facets still gives roughly symmetrical I - V curves with intermediate current magnitude. Another way to reveal additional insights from these I - V curves is to present their electrical resistance diagrams. The {100}/{110} case shows very large electrical resistance for both current directions in the +2 V to -2 V range than the other facet combinations (Figure 4 a). Connecting the highly conductive {112} facet and fairly conductive {111} facet produces asymmetrical I - V curves with appreciably larger current flowing in the direction of {112} face to {111} face than current flowing in the opposite direction (Figure 3 b). Because both Si faces are conductive, either current direction has very small electrical resistance values (Figure 4 b). Figure 5 a illustrates why current flow in the direction of {112} to {111} has a larger current. The Si {112} face has

conduction band energy closer to mobile electron energy level of W, so electrons flowing into the wafer from this facet sees a smaller barrier than entering the wafer from the {111} face.

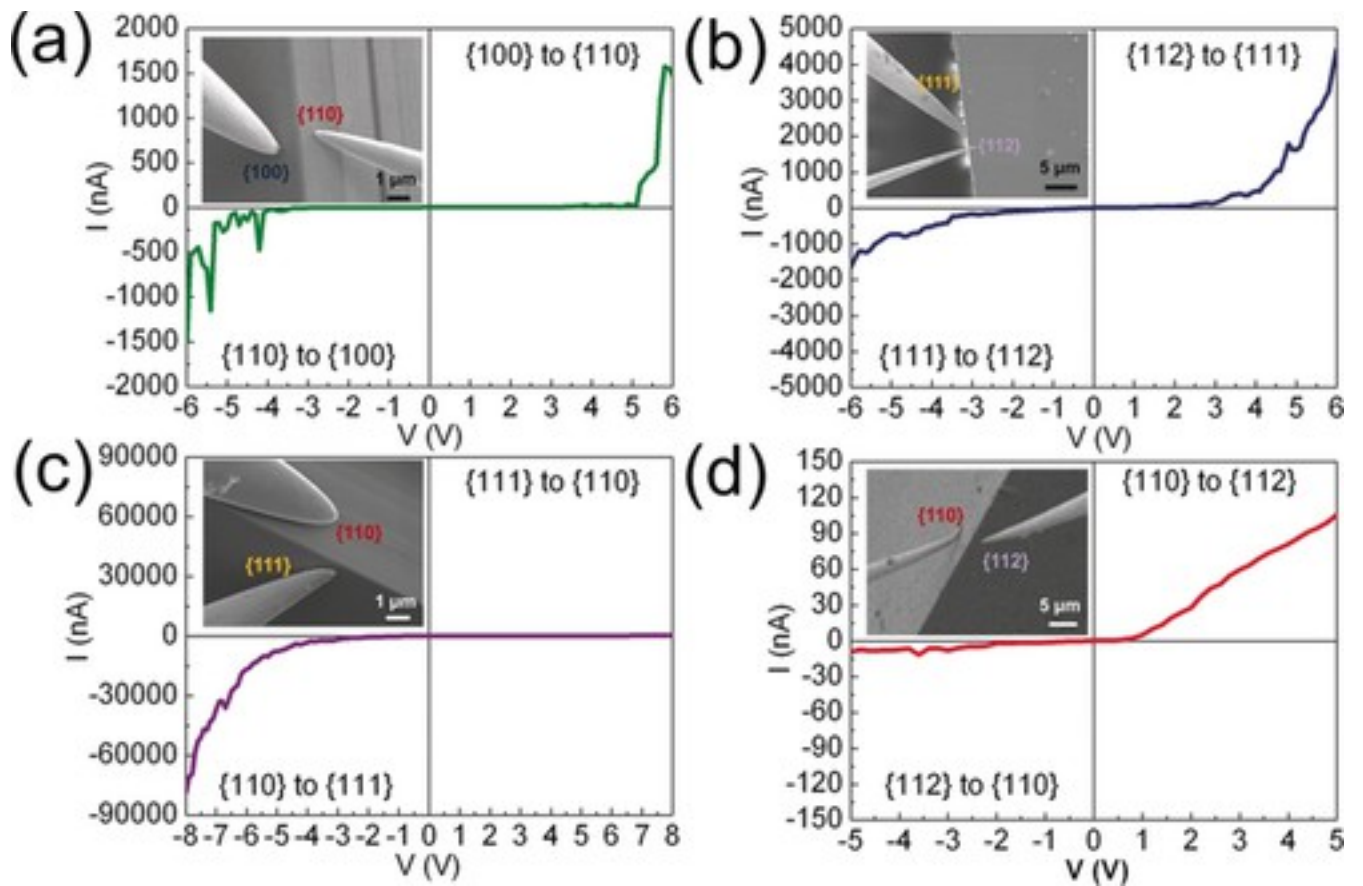


Figure 3

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I-V curves and SEM images of W probes making contacts to the a) {100} and {110}, b) {112} and {111}, c) {111} and {110}, and d) {110} and {112} facets of a Si wafer.

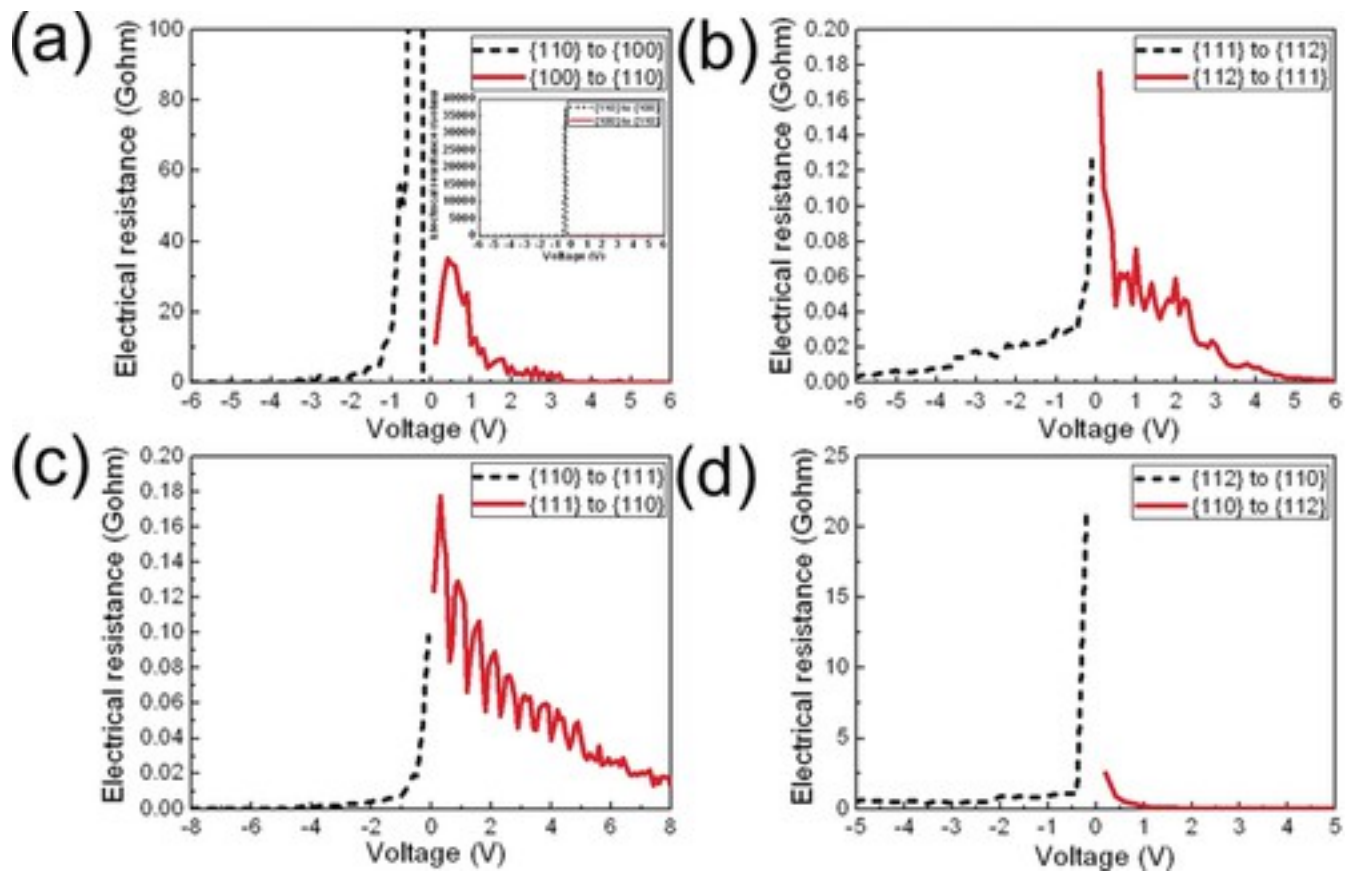


Figure 4

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Electrical resistance diagrams for electric current flowing from one Si facet to another to show varying resistance encountered for the a) Si {110} and {100}, b) Si {111} and {112}, c) Si {110} and {111}, and d) Si {112} and {110} facet combinations. Gohm stands for giga-ohm.

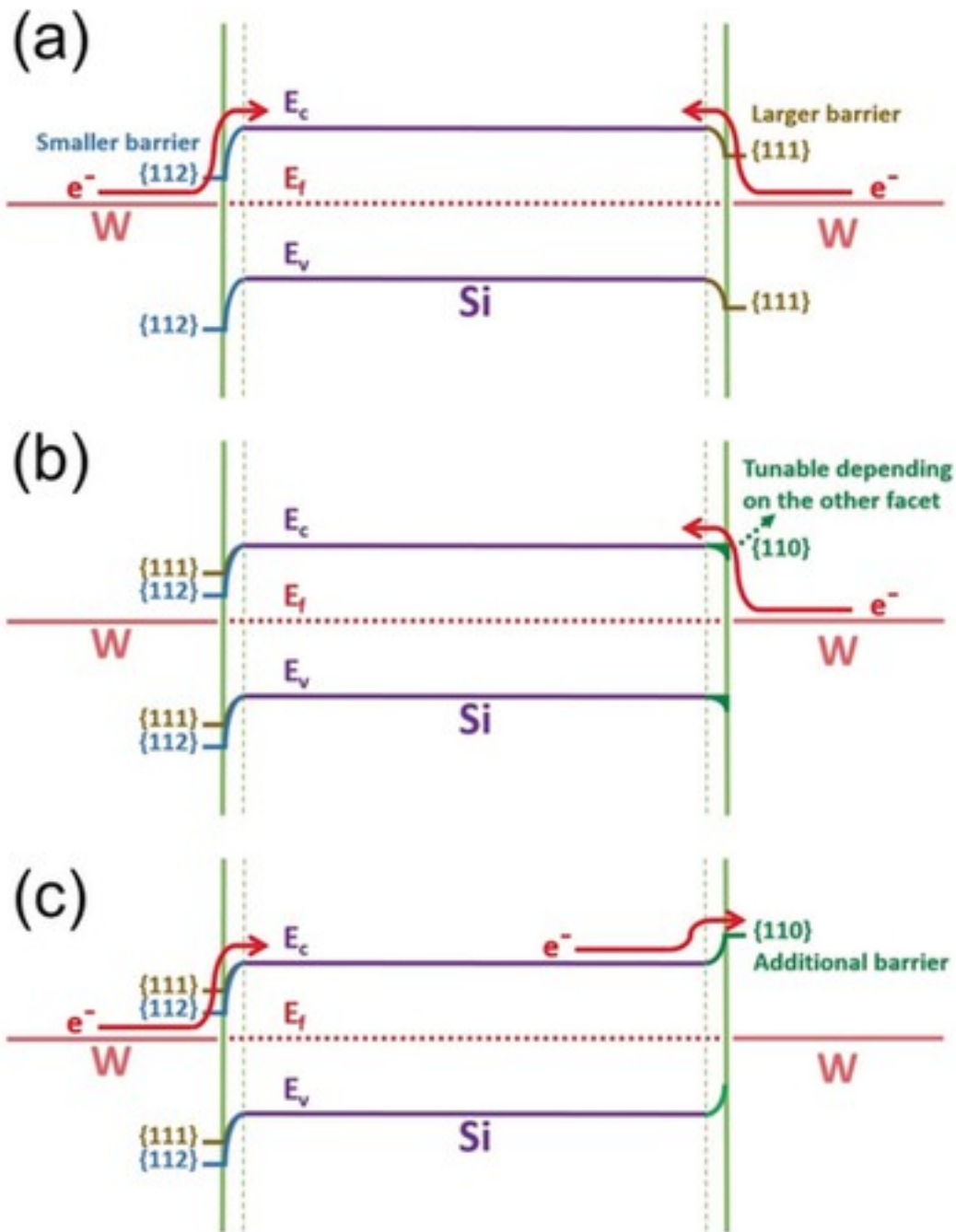


Figure 5

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Adjusted band diagrams for the situations of a) W probes contacting the {111} and {112} faces for current flow, b) current flow from the {110} face into Si wafer and exiting from the {111} or {112} face, and c) current flow from the {111} or {112} face into Si wafer and exiting from the {110} face. This depiction highlights the relative heights of energy barriers encountered when electric current flows through Si crystal. The vertical dash lines indicate the thin surface layer with tunable band bending to yield the observed facet effects.

I - V curves for the $\{111\}/\{110\}$ and $\{112\}/\{110\}$ combinations are more interesting because they give more desirable asymmetrical I - V responses. Current starts to rise beyond 0.5 V for both cases. At 8 V, the current reaches beyond 75 000 nA in the $\{110\}$ to $\{111\}$ direction, while the opposite current direction records only about 250 nA (Figure 3 c; Supporting Information, Figure S6). Although the current is much lower for the $\{110\}$ to $\{112\}$ direction, 115 nA at 5 V is still 11.5 times higher than that for the $\{112\}$ to $\{110\}$ direction (Figure 3 d). This kind of I - V curve suggests current rectifying effect can be achieved on a silicon wafer simply by switching the direction of current flow, especially if voltage is set at 4 V for maximum current difference in the $\{111\}/\{110\}$ combination. Electrical resistance plot shows small but still higher and persistent resistance with current flowing in the direction of $\{111\}$ to $\{110\}$ but rapidly decreased resistance to 0 in the $\{110\}$ to $\{111\}$ direction (Figure 4 c). The $\{112\}$ to $\{110\}$ direction gives much larger electrical resistance near 0 V than the opposite direction, and non-zero resistance persists to higher voltages.

In previous experiences on the I - V responses of Cu_2O , Ag_2O , and PbS crystals, large current has been obtained when electrons flow into the crystal through the more conductive facet. Once current flows into the crystal, a barrier present at the exiting facet is not a problem as accumulated electrons in the conduction band have sufficient energy to surpass the barrier. However, if electrons flow into a crystal through a poorly conductive facet, the barrier can be so high that current flow into the crystal is completely stopped. This is a dramatic manifestation of facet effects, as the poorly conductive facet acts like a gate preventing passage of current beyond this thin layer. According to the band diagram shown in Figure 2, a lower barrier would be expected with current flowing into the Si wafer from the much more conductive $\{111\}$ side and this direction of current flow should be larger, but in fact the opposite results were obtained. Clearly the band diagram needs to be revised when current flowing between different Si facets is considered. Figure 5 provides the proposed band diagram for current flow via Si $\{111\}/\{112\}$ and $\{110\}$ facets. Keeping the surface energies of $\{111\}$ and $\{112\}$ faces unchanged as that shown in Figure 2, but making energy of the $\{110\}$ face tunable, is useful to explain the observed I - V curves. Since the DFT calculations show the $\{110\}$ face has a typical band structure expected for semiconducting silicon, the $\{110\}$ face can be presented to have small or no band bending. With this range of zero to slight downward band bending, electrons entering a silicon wafer from the $\{110\}$ side encounter a barrier similar to that expected for bulk Si, so current rises only after 1 V. Mobile electrons exiting Si wafer from the $\{111\}$ or $\{112\}$ face see a much downward band bending or great pull of electrons toward the $\{111\}/\{112\}$ surface. It should be remembered that few (111) and (112) planes show DOS plots characteristic of a metal. This situation facilitates electron flow and generates a large current. The electron pull is much

larger for the {111} surface. The big downward energy difference between Si {111} face and W should also help current flow. Of course, relative degrees of band bending for the {111} and {112} faces can be adjusted to better fit the experimental results, but perhaps this simple band diagram is sufficient to illustrate current rectifying effects. Now we consider electrons flowing into Si wafer from the {111}/{112} surface and exiting through the {110} face. Electrons encounter the first barrier present at the {111}/{112} face. If downward electron flow from Si interior to W through the {111}/{112} surface is energetically favorable, current flow in the opposite direction should present considerable difficulty. Since the {110} surface is least conductive, electrons surmounting the first barrier into Si wafer meets another barrier at this end. Here the conduction band is drawn to bend upward to represent a barrier. Relative to bulk silicon, the Si {110} surface should pose as a barrier. In other words, upward or downward band bending can also depend on whether current is flowing into or out of a crystal, as essence of facet effects really involve charge carrier transfer across interface. The combined barrier height makes current flow from the {111}/{112} face to the {110} face unfavorable and small current results.

The current rectifying I - V curves demonstrated ushers novel thinking in FET fabrication. Starting with a Si (100) wafer, chemical etching to make trenches can expose {111} surfaces.²² Although not examined here, such a facet combination with large conductivity difference may yield asymmetrical I - V responses. Alternatively, use Si (111) wafers and create {110} or {112} side walls through mechanical or chemical method (or create {111}/{112} side walls from a Si (110) wafer if available). Electrical connection on the different Si facets may yield a working FET. The FET design is shown in the Supporting Information, Figure S7. A layer of SiO₂ on the Si wafer separates adjacent electronic components. With the width of the FET fin becoming ultrathin, it is possible that the operating voltage can be much lower than that recorded here. If such a transistor design can be realized, this 3D FET can more readily integrate with current semiconductor fabrication process than more laborious 2D materials do. The discovered semiconductor facet effects may be applied in a powerful way.

In conclusion, we have performed electrical conductivity measurements on the Si {100}, {110}, {111}, and {112} facets. The {112} facet is highly conductive, followed by the {111} facet. Both {100} and {110} facets are barely conductive at low applied voltages, but the {110} face is least conductive. Asymmetrical I - V curves were obtained by making electrical contacts simultaneously to {111}/{112}, {111}/{110}, and {112}/{110} facet combinations. Different degrees of band bending at the surface planes have been proposed to explain these electrical behaviors. From this work, one can envision a totally different approach to making FET that may

be simpler than the current design utilizing fundamental facet properties of semiconductor materials.

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Conflict of interest

The authors declare no conflict of interest.