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Transport limitations and Schottky barrier height in titanium silicide nanowires grown on the Si(111) surface

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The authors have performed electrical measurements at variable temperatures on self-assembled titanium silicide nanowires (NWs) grown on a Si(111) surface. The authors find a metallic $I(V)$ characteristic for the NWs at a temperature of 77 K, whereas scanning tunneling spectroscopic measurements obtained at temperatures below 25 K yield a rectifying behavior. This behavior indicates that the NWs are electronically decoupled from the Si surface on a voltage range of several hundreds of meV at low temperatures. From these measurements, the authors precisely determine the Schottky barrier height between the NWs and the Si surface. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2711378]

Titanium silicide is one of the refractory metal silicide widely used for applications in silicon technology, where interconnects with low resistivities are required.[1] But as the size of the semiconductor devices shrink below 0.25 μm, migration of Ti during the silicidation leads to bringing failure between the electrodes of the devices. Furthermore due to the reduced size of the interconnections, the transformation from the high resistivity C49-$TiSi_2$ phase to the low resistivity C54-$TiSi_2$ occurs at higher temperatures leading to more Si consumption and the formation of grain boundaries, with more stresses in the structures.[2] There is thus a need to develop alternatives approaches for the formation of titanium silicide wires at the nanometer scale.

Although the lattice mismatch between $TiSi_2$ and Si is quite significant and prevents the epitaxial growth of $TiSi_2$ on Si, recent studies have shown that titanium silicide nanowires (NWs) can be easily formed during the deposition of titanium with monolayer coverage on a Si(111) surface at temperatures around 850 °C.[3] These NWs extend over a few micrometers and due to their perfect crystal structure, they are expected to exhibit a low resistivity, as it was recently demonstrated for $CoSi_2$ NWs.[4] However, questions still arise about the transport properties at the interface between the NWs and Si.

In this letter, we report the growth of titanium silicide NWs and their subsequent electrical characterization by microscopic two-point probes and scanning tunneling spectroscopy (STS) at variable temperatures. While spectra obtained on the NWs yield a metallic behavior at higher temperatures than $T=77$ K, we observe the occurrence of a region with zero current below $T=25$ K in the tunneling spectra acquired on the NWs as well as on the Si surface. From this result, we show that the NW states are decoupled from the Si bulk states at low temperatures and due to the high doping level of the Si substrate, we are then able to precisely measure the Schottky barrier height of the NWs.

The experiments were carried out using n-type Si(111) substrates (0.005 Ω cm), which were prepared in ultrahigh vacuum (base pressure: 7×10^{-11} Torr) to obtain the reconstructed Si(111)-(7×7) surface. Titanium was deposited by sublimation from a Ti wire for 10 min. During the deposition, the Si sample was heated at 800 °C, the pressure in the preparation chamber being lower than 5×10^{-10} Torr. After the deposition, the sample temperature was quickly lowered to room temperature and the sample was transferred either to a two-tip prober equipped with a scanning electron microscope (Omicron nanoprobe) or to a low temperature scanning tunneling microscope (STM) (Omicron), where they were further cooled down to temperatures below 77 K. Polycrystalline W tips were chemically etched and annealed *in situ*. The tunneling spectroscopic measurements were acquired with fixed tip-sample distances, the differential conductance dI/dV being recorded with a lock-in amplifier (6 mV_{rms} at 1 kHz).

Figure 1(a) shows a typical STM image of islands observed on the Si(111) surface after the deposition of Ti, with the Si(111) surface heated to 800 °C. Two types of islands are generally seen: plateletlike structures and nanowires. While the platelets are found to grow on the terraces, the nanowires generally grow along the step edge of the Si terraces. Their length can reach a few micrometers and their height ranges between 2.5 and 7 nm. In contrast to the formation of $TiSi_2$ electrodes, which are obtained after the annealing of a Ti layer deposited on Si and where depleted areas of silicon or stripes of diffused Ti areas are observed around the electrodes,[5,6] the flatness of the Si terraces and the 7×7 superstructure are largely preserved after the growth of the NWs at 800 °C. More remarkably, the interface between the NWs and the Si terraces is quite abrupt, as shown by the inset of Fig. 1(a), where the two triangular subunits of the (7×7) unit cells are clearly seen along the edge of a NW.

Figure 1(b) shows the I-V curve measured with two STM tips contacting the end of a NW, as the one pointed by the arrow in Fig. 1. The voltage depends linearly on the current and the slope is 16 kΩ (a value much smaller than the 20 MΩ slope obtained when the probes are located on the Si surface). Although a higher resistivity (~800 $\mu\Omega$ cm) than the one usually found for a $TiSi_2$ film is

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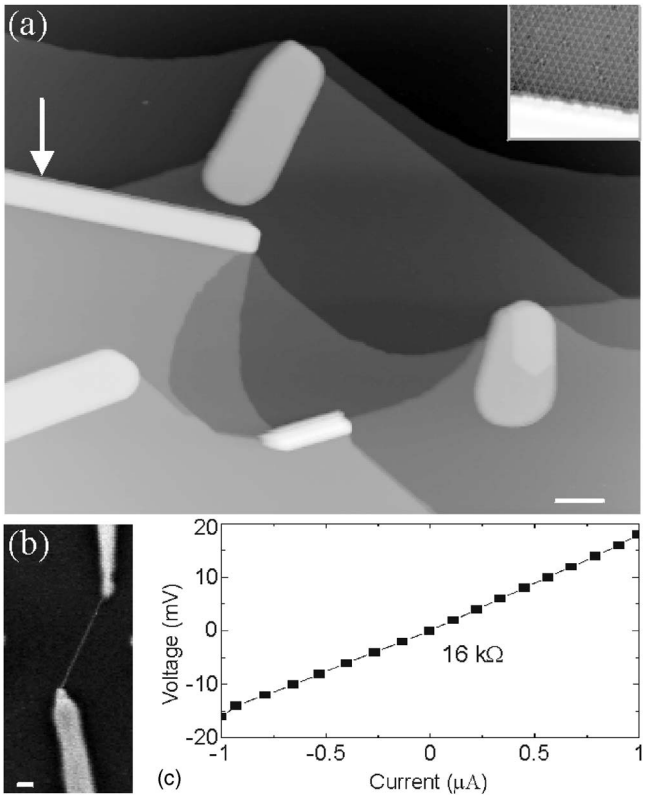

FIG. 1. (a) STM image of titanium silicide islands and NWs prepared on a Si(111) surface at 800 °C. Sample voltage V_s=−1.5 V, tunneling current I=100 pA, and temperature T=77 K. Inset: zoom onto the abrupt interface between the reconstructed Si(111)-(7×7) surface and the NW indicated by an arrow. Gray scale: 0 (black) to 5.5 nm (white). (b) Scanning electron microscopy image of a NW contacted by two STM tips and room temperature I-V curves obtained between the tips by passing current along the NW. The image has been filtered to enhance the NW contrast. The scale bars in (a) and (b) correspond to 100 nm.

obtained,[2] presumably due to the contact resistance, such a result indicates the metallic character of the NWs. This property is confirmed by tunneling spectroscopic measurements obtained on similar NWs. Indeed, at a temperature of T=77 K, the dI/dV curves shows a finite value at 0 V. In clear contrast, below T=25 K, the differential conductance becomes zero at a sample voltage V_s=0 V and a region of zero conductance appears at lower temperatures. This region extends over 0.92 eV at T=5 K and is asymmetric with respect to 0 V, being shifted towards positive energies. Since the NWs have a metallic character for $T \geqslant 77$ K and diffraction patterns performed on similar NWs have shown that the NWs consist of both C49-$TiSi_2$ and C54-$TiSi_2$ crystalline silicide phases,[3,7] which are known to be metallic even at 5 K,[8,9] the modification of the transport cannot be attributed to a temperature dependent variation of the NW conductivity.

In order to understand the origin of this zero conductance region, spectroscopic measurements were also acquired on the reconstructed Si(111) surface. At T=5 K, an asymmetric zero conductance region is clearly observed in Fig. 2(b), in agreement with recent STS results performed on this surface.[10] The apparent band gap was not observed at T=77 K,[10] and our temperature dependent measurements show that it still exists at T=25 K. The opening of the band gap thus looks similar for both the Si surface and the NWs below T=25 K.

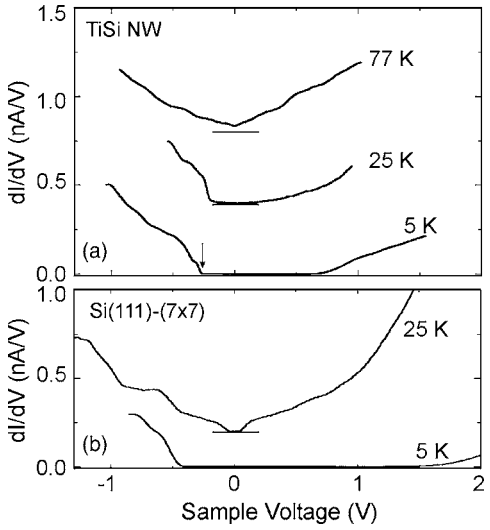

FIG. 2. Tunneling spectra acquired (a) on the titanium silicide NWs and (b) on the Si(111)-(7×7) surface at different temperatures. The curves are shifted for clarity and the zero of the conductivity is outlined by a segment. The vertical arrow indicates the onset, which corresponds to the Schottky barrier height between the NW and the Si surface.

Observation of a rectifying behavior in STS measurements performed on semiconductor surfaces has been attributed to a limited transport between the surface states and the bulk states.[11,12] In the case of a n-type Si(111) surface, a Schottky barrier (SB), with a height of 0.49 eV,[13] is formed between the empty surface states and the conduction band states, resulting in an upward band bending, as depicted in Fig. 3(a). When the temperature is lowered, the probability for the electrons to be transferred from the surface states to the bulk states is significantly reduced, causing the accumulation of nonequilibrium carriers at the surface, until the tunneling becomes effective at higher sample voltages.[10,14] Such a charging effect shifts the position of the Si surface states and gives rise to a zero conductance region in the dI/dV curves below T=25 K.

When the electrons tunnel from the tip into the NW states, they also have to escape into the Si bulk states, as shown in Fig. 3(b). They can either reach directly the Si bulk states by tunneling through the SB (thermionic emission is negligible in our temperature range) or travel first in the surface state layer before reaching the bulk states. Below T=25 K, even though the electrons can be transferred between the NWs and the Si surface states, our measurements

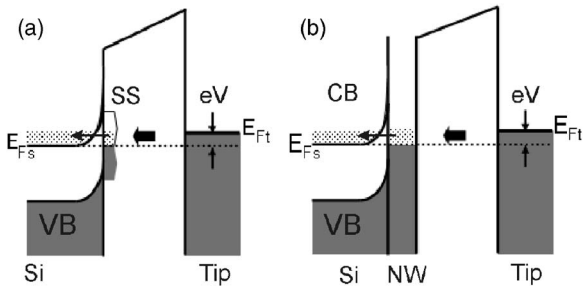

FIG. 3. Band diagrams showing the Schottky barrier between (a) the Si surface states and the Si bulk states and (b) the electronic states of a titanium silicide nanowire and the Si bulk states. In both systems, the two step transport process is indicated by thick and thin arrows, which correspond to the electronic transmission probability through the vacuum and Schottky barriers, respectively.

above have shown that they cannot easily reach the Si bulk states, making the second pathway inefficient. As the SB height between the NW states and the Si bulk states is expected to be of the same order of magnitude as the SB height between the Si surface and bulk states,[15] tunneling of electrons through the SB should be the dominant process and should already arise at small positive voltages due to the high doping level of the Si substrate. However an increase of the apparent band gap is observed in Fig. 3(a) below $T=25$ K. Such a result indicates that a transport limitation exists also between the NW states and the Si bulk states.

While the NWs are metallic, measurements of a band gap in the conductivity implies that the NWs are electronically decoupled from the Si surface at small biases and low temperatures. This decoupling implies that current will flow at negative sample voltages only when the flatband condition is achieved. Since the Fermi level in the Si bulk is aligned with the Si conduction band edge, from the flatband condition we can thus determine the height of the SB between the NWs and the Si surface at 5 K.

Analyzing the onset of the differential conductance at negative voltages for the NWs and plateletlike structures, we measure a reproducible SB height of 0.23 ± 0.02 eV for the NWs, whereas the distribution of the SB height extends from 0.21 to 0.6 eV for the plateletlike structure. Smaller barrier heights can therefore be built in comparison with those of 0.6 eV obtained from $TiSi_2$ films grown on the Si substrate,[15] probably due to a smoother interface. Finally, for the platelet structure it is worth noting that our results are consistent with those found for nanoscale sized $TiSi_2$ islands grown on Si (between 0.43 eV and 0.58 eV).[16]

In conclusion, we have performed tunneling spectroscopic measurements to study the transport properties between self-assembled NWs of titanium silicide and the Si surface. We observe a conduction which is temperature dependent and limited on a voltage range of several hundreds of meV at low temperatures. Such effect allows the NWs to become decouple electronically from the Si surface and, taking advantage of this effect, we are able to determine the SB height of the titanium silicide NWs. Since transport limitations have been observed for several semiconductor surfaces at low temperatures, our method is likely to be quite useful for the measurement of SB height of numerous nanostructures grown on semiconductor surfaces.

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