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Electronic and structural properties of titanium silicide nanostructures formed on Si (111) 7×7 reconstructed surface

R. STIUFIUC*, T. SOUBIRON, B. GRANDIDIER, D. DERESMES
Institut d'Electronique, Microélectronique et Nanotechnologie, IEMN, (CNRS, UMR 8520) Av. Poincaré, B.P.69, 59652 Villeneuve d'Ascq, France

The formation of self-assembled titanium silicide nanostructures by reactive deposition of titanium on Si(111) 7×7 reconstructed surface at 800 °C, in ultrahigh vacuum (UHV) conditions, has been investigated by scanning tunneling microscopy (STM). The electronic properties of the same nanostructures have been studied using the scanning tunneling spectroscopy technique (STS) at 77 K in UHV conditions. In order to better understand the electronic properties of the nanostructures we have performed scanning tunneling spectroscopy (STS) measurements on both systems: the Si (111) 7x7 reconstructed surface and the TiSi nanostructures. From the topographic images we observed the formation of several types of titanium silicide nanostructures having different shapes and dimensions. We report here the successful formation of long and narrow structures which can be considered to be TiSi nanowires (NW) together with some island structures having a flat top region. Concerning the electronic transport properties, using our specific experimental set up, we evidenced the existence of an ohmic contact between all types of nanostructures and the silicon substrate in the 300 – 77 K temperature range. We explain this behavior using a model which takes into account the presence of silicon surface states bands at 77 K.

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1. Introduction

The silicide nanowires self-formation on silicon surface was quite recently discovered for $DySi_2$ [1] and the method was successfully applied for other rare earths and transitional metals. Titanium silicide is one of the refractory metal silicide the most studied since it is widely used for applications in silicon technology as Ohmic contacts, low-resistivity interconnects or Schottky barriers. It can be formed by a solid-state reaction between a thin film of Ti and the Si substrate followed by annealing at high temperature. The thin film reaction often results in the formation of $TiSi_2$ which exhibits two phases: a metastable base-centred orthorhombic structure (C49) and a face-centred orthorhombic structure (C54). The transitions between these two phases as well as their electronic properties have been extensively studied [2,3]. Diminishing Ti film thickness down to few monolayers does not lead to epitaxial growth of $TiSi_2$ film since the lattice mismatch between $TiSi_2$ and Si is too important. However, it leads to epitaxial growth of titanium silicide islands and nanowires which can be of great interest for future electronic devices. Due to their self-organization on the silicon substrate the electronic properties of the nanowires are strongly influenced by substrate electronic properties. Previous works using near field microscopy have been done in order to study the growth mechanism and orientation of such nanostructures [4]. In this article we report scanning tunnelling microscopy observations of self organized titanium silicide nanostructures and a study of their electronic transport properties by scanning tunnelling spectroscopy (STS) at 77 K.

2. Experimental details

The TiSi nanostructures have been obtained using a one step preparation method consisting of titanium evaporation onto the Si (111) surface heated at a temperature of 800 °C, in ultra high vacuum conditions (UHV). The n-type Si (111) samples (P doped with a resistivity of 5 mOhm cm) were prepared by degassing overnight at 600 °C and flashing at 1250 °C while maintaining the pressure of the preparation chamber in the 10^{-10} Torr range. Titanium was deposited by sublimation from a pure titanium wire. The titanium silicide nanostructures have been studied using a low temperature, ultra high vacuum Omicron Scanning Tunneling Microscope (Omicron UHV LT STM) having a base pressure of 2×10^{-10} Torr. The 7×7 reconstruction of the Si(111) surface was confirmed by STM prior to Ti deposition. The topographic images have been achieved using a voltage bias between -2V and +2V and a feedback current of 100pA while the spectroscopic measurements have been taken for bias voltages in the range -2V, + 2V and feedback currents between 100 and 400 pA. In order to reduce the influence of the transmission coefficient and to diminish the background noise we have taken a large number of spectra (more than 100 for each spectroscopic measurement) and averaged them. The spectra displayed in this paper amount to the differential conductivity

(dI/dV) or normalized differential conductivity $(dI/dV)(I/V)^{-1}$ vs. Bias Voltage for different regions of the silicon surface and titanium silicide nanostructures.

3. Results and discussion

After titanium deposition on the Si (111) 7×7 reconstructed surface the samples were cooled down to 77 K and analyzed by STM and scanning tunneling spectroscopy (STS). Using our topographic images we have identified the presence of two main types of $TiSi_2$ nanostructures on the Si(111) surface: platelet like nanostructures (NS) and long narrow nanowires (NW) as it can be seen in Fig. 1. The platelet like structures, which can be associated with 2D islands, have typical dimensions of a few hundred nanometers long (100-500 nm), ~ 150 nm wide and a height between 0.8 – 3 nm whereas the nanowires have a length that can reach a few micrometers, a width of ~50 nm and a height between 3 and 7 nm. We observed a tendency of the nanowires to grow on the Si step edges while the 2D islands form mainly on the terraces. For the nanostructures with the lowest height (0.8 nm high) we observed a well defined reconstruction on the top region (Fig. 2b) which could indicate the formation of well ordered crystalline $TiSi_2$. The reconstruction observed in Fig. 2b does not correspond to any reconstructions reported so far for TiSi nanostructures. As far as we can see, there is a good correlation between the lattice parameters of the TiSi and the silicon 7x7 ones. We explain the formation of such unexpected reconstruction by the very low height of the nanostructure which implies a big influence of the silicon substrate on the titanium silicide formation. For nanostructures having a bigger height this atomic reconstruction was no longer observed on their flat top regions. The quality of the silicon surface was examined on different regions of the surface in order to observe if the Si atoms, used for titanium silicide formation, damaged the surface reconstruction. In all the cases the 7×7 reconstruction of the Si(111) surface was clearly visible, proving the efficiency of the one step preparation method, as it can be seen in Fig. 2c.

Fig. 1. 1.2μm × 1.2 μm STM image of the titanium silicide nanostructures formed on the Si(111) surface. The image was acquired at a bias voltage of +2V, a 100 pA feedback current and a temperature of 77 K.

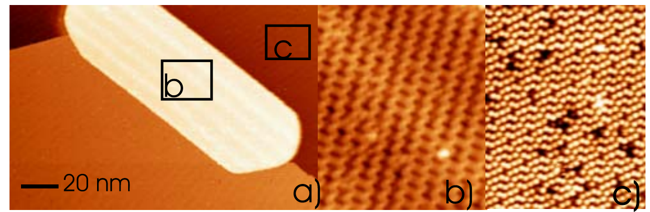

Fig. 2. STM image of a titanium silicide nanostructure where we were able to observe an atomic reconstruction on the top surface (b). The image was taken with a bias voltage of +2V and a tunneling current of 0.1 nA. The typical dimensions of the nanostructure are $145\times50\times0.8$ nm^3. The observed reconstruction together with the 7×7 reconstruction of the silicon substrates are shown in figures b and c.

As our main interest in this article is the understanding of electronic transport through titanium silicide nanostructures we performed scanning tunneling spectroscopy (STS) measurements at 77 K for the observed nanostructures. The spectroscopic measurements performed on the nanowires and 2D platelet islands at 77 K are presented in Fig. 3. We have plotted the conductivity spectra taken on a nanowire (NW) and on two different regions of a nanostructure (nanostructure #1 and nanostructure #2). A topographic image of the measured nanostructures, with the tunneling conditions U = +2V and I = 100pA, is also presented. All conductivity spectra (dI/dV) taken on the nanostructures show a finite value at 0V, indicating a metallic behavior. This implies the existence of an ohmic contact at the interface between the nanostructures and the silicon semiconducting surface. Previous studies on C49 and C54 crystalline silicide phases showed these phases are metallic even at 5 K [3,5] suggesting a Schottky barrier formation at the nanostructure/substrate interface.

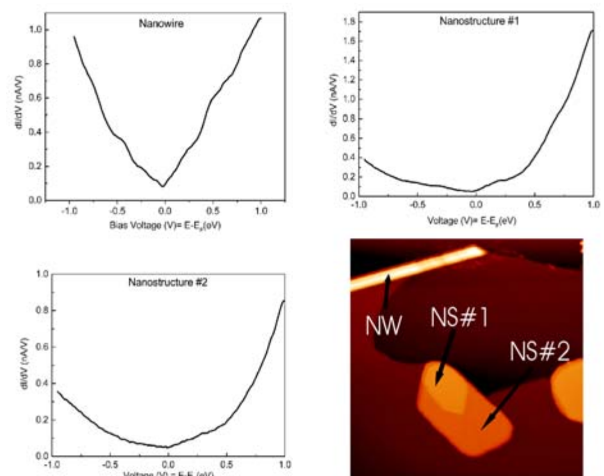

Fig. 3. Conductivity spectra vs. bias voltage obtained for nanowires (upper left) and two different positions on the nanostructures (upper right and lower left). In the lower right corner we present a 730×730 nm^2 topographical image of the measured nanostructures (U=+2V, I=100 pA). All the conductivity spectra were acquired at voltages between +1V and -1V with a tunneling current of 100 pA for the nanostructures and 200 pA for the nanowires.

In order to understand this behavior we have performed STS measurements at the same temperature on the bare silicon surface. In Fig. 4 we represented the normalized conductivity (dI/dV)/(I/V) vs. bias voltage (which is proportional to the local density of states (LDOS) [6]. The LDOS presents a strong peak in the intrinsic band gap at ~0.4 eV due to the dopants contribution (we use highly n-type doped Si substrate). Close to the valence band a few interesting peaks can be clearly observed in the gap. We attribute these peaks to the surface state bands of the silicon substrate (SS). This picture is very consistent with other studies performed on the Si(111) 7×7 surface having a dimer-adatom-stacking-fault (DAS) structure[7].

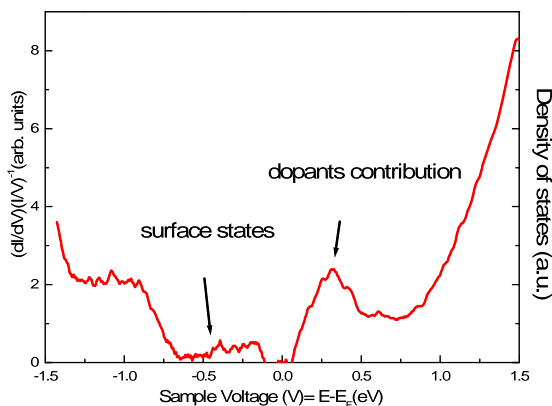

Fig. 4. The normalized conductivity spectra taken on the Si(111) 7x7 surface (U=+1.5V and I=200pA).

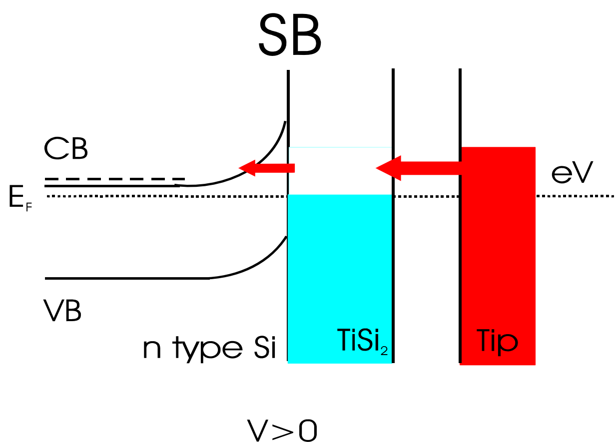

Fig. 5. Schematic representation of the tunneling mechanism for a positive bias voltage of the substrate with respect to the tip. The transmission probabilities through the two barriers are indicated with a big arrow (for the tip - nanostructure vacuum barrier) and a smaller one (for the depletion region).

The surface states originate from the surface reconstruction, are localized in the outermost atomic layers and can be considered as a quasi 2D metallic system. Energetically they are located inside of the bulk gap and have the capability to pin the Fermi level around the mid gap. Their crucial importance in the electronic transport properties reside in the fact they are always in contact with the bulk Si substrate. Consequently a Shottky barrier will always arise between the surface states and the silicon bulk states. All the electrons passing through the system has to overcome this Shottky. In the absence of the $TiSi_2$ nanostructures the electronic tunneling from the tip to the Si will take place in a two step process: first the electrons will "jump" from the tip to the empty surface states via a tunneling mechanism than they will tunnel the Schottky barrier via thermoionic emission.

When the titanium silicide nanostructures are formed on the silicon surface, the reconstruction is destroyed and the Shottky barrier will form between the nanostructures (having a metallic behavior) and the bulk silicon, causing an upward band bending of the semiconductor energy bands. In Fig. 5 we depicted the band diagram in the case of a positive bias of the semiconductor with respect to the tip, which corresponds to the reverse bias of the Schottky barrier. Again, in this case, the electrons will pass from the tip to the semiconductor in a two step process. First they have to tunnel through the vacuum barrier between the tip and the nanowire and than they have to tunnel the depleted region induced by the Schottky barrier formation via thermoionic emission. The thermoionic emission is strongly influenced by the semiconductor depletion layer width and consequently by the temperature. By using highly n-type doped semiconductors we reduced the depletion region and the Schottky barrier became quite "transparent" for the electrons. In the case of negative bias of the substrate (with respect to the tip) the Schottky barrier will be forward biased. In this case the semiconductor band bending is reduced with increasing bias voltage and the electrons will pass almost unperturbed from the semiconductor to the $TiSi_2$. The conductivity spectra at 77 K presented in Fig. 3 point out that in our case the Schottky barrier can be easily tunneled by the electrons for the forward bias as well as for reversed bias giving rise to a metallic behavior of the electrical conductance, a very important issue for technological applications.

4. Conclusions

In this paper we report a new preparation method for the $TiSi_2$ nanostructures. The successful formation of the nanowires (NW) has been observed in all our topographic images. We also detected the presence on the surface of other types of nanostructures which we called 2D nanoisland, due to their specific dimensions. For the nanostructures with the lowest height (~0.8 nm) we observed an unusual reconstruction on the top surface attributed to the strong influence of the silicon substrate. For nanostructures with bigger heights the reconstruction was no longer observed. Using scanning tunneling spectroscopy measurements taken at 77 K we determined the electronic transport properties of the system formed by the nanostructures and the silicon substrate. For all studied nanostructures we observed a metallic behavior of the nanostructures indicating the existence of an ohmic contact between the $TiSi_2$ nanostructures and the Si(111)

surface. We explained it using a simple tunneling model which takes into account the surface state bands of the Si(111) surface and the Shottky barrier which forms between nanostructures and the silicon bulk states.

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*Corresponding author: Rares.Stiufiuc@isen.fr