Investigations of titanium nanostructures on Si(111) 7×7 by means of scanning tunnelling microscopy and spectroscopy

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Abstract. The aim of this paper were investigations of the growth of Ti nanostructures created by means of an electron gun on Si(111)-(7×7) with the coverage below 0.1 ML. Titanium was deposited on the Si substrate at 673 K. The Ti nanostructures after deposition and subsequent annealing processes were imaged in situ by means of UHV STM. The current imaging tunnelling spectroscopy (CITS) showed a contrast between the semiconducting substrate and Ti nanostructures. Some of the I-V characteristics revealed the step-like character typical for the quantum size or Coulomb blockade effects. Annealing of the samples in the range of 673 K to 943 K led to appearing of the r19×r19 reconstruction. This reconstruction appeared at the cost of Ti nanostructures as a result of Ti atoms diffusion into Si sublayers.

1. Introduction
Investigations of the transition metals’ and their silicides’ nanostructures are interesting because of necessity of the electronic devices miniaturization and compatibility with the silicon technology [1]. Especially, nanowires and quantum dots are the focus of attention due to their specific electronic properties [2, 3]. The transition metals’ silicides are often used as contacts and interconnects due to the small lattice mismatch with the Si substrate [4]. This fact facilitates silicides application in nanoelectronics devices. The SPM characterization of silicides’ nanostructure led to some general conclusions that the number, shape and electronic properties depend not only on the annealing temperature but also on the initial amount of the deposited material [5,6,7]. It was also shown that the I-V curves measured above the nanoscale islands of TiSi₂ exhibit features attributed to single electron tunneling [8].
In this paper we were interested in the very early stage of Ti clusters growth and their evolution due to the post-deposition annealing procedure. Besides STM imaging, the CITS method was used to characterize the evolution of the local electronic properties.

2. Experimental details
The Si(111) substrates were degassed for several hours at approx. 970 K, and flashed for about 15 seconds at 1470 K by the direct heating method to obtain the (7x7) surface reconstruction. The flashing procedure was repeated few times in order to minimize surface defects. A number of atomic-scale STM/STS images were taken to test the resolution.

The base pressure in the preparation chamber was 5x10^{-10} mbar and the high-temperature flash augmented the pressure to 5x10^{-8} mbar. Titanium was deposited at 670K using an OMICRON EFM4 source. The evaporation parameters were maintained at constant levels (I_{emission}=1.6 mA, U = 800 V, I_{flux} =1 nA, time = 60s) and the obtained deposition speed was around 0.001ML/s. The number of deposited Ti monolayers was estimated by STM measurements. The pressure during evaporation did not exceed 2·10^{-9} mbar.

The samples with deposited material were investigated by means of STM/STS. Subsequently the samples were annealed for 10 minutes at different temperatures (873 K, 898 K, 923 K, 948 K) to induce a post-deposition growth. The temperature of the samples was monitored by a thermocouple. All the STM/STS measurements were performed in UHV system at room temperature with typical parameters: bias voltage ±2 V (2.5 V), tunneling current 0.07 ÷ 0.3 nA and scanning frequency 0.5 ÷ 2 Hz, with cut Pt/Ir tips.

3. Results and discussion
According to described above procedure, the 0.07 ML of Ti was deposited on the heated to 673 K Si substrate. Figure 1(a) shows the Ti clusters of 0.8 up to 1.7 nm in diameter with the height of about 0.2 nm what suggests that the clusters (or nano-islands) were of 1 ML height. Annealing procedure did not change the sample topography up to 873 K. At this temperature the first rings, 6-membered appeared. These rings, are marked in Fig. 1(b) with the white circles. Annealing at 898 K led to much higher density of those surface rings (Fig. 1(c)). Finally, at 923 K (Fig. 1(d)) the rings started to disappear, being covered by some species. We expected that these species were mostly composed of Si atoms, due to enhanced surface diffusion. The rings resembled the r19×r19 reconstruction induced on Si(111) surface by a presence of Ni or r7×r7 reconstruction induced by Co atoms [9, 10]. The presence of those rings was not reported at literature as regards Ti on Si(111), according to our best knowledge. The rings did not create a dense regular pattern on the surface as the amount of deposited Ti was too small. However, on the base of inter-ring distance which is close to 1.7 nm we expect the same type of reconstruction (r19×r19) as induced by the Ni presence on Si(111).

The presence of the rings changed the local electronic properties. The dI/dV curves (in Fig. 2b) show a comparison of the dI/dV curves measured above the rings, distorted 7×7 reconstruction and clean Si(111). Also the I-V and dI/dV characteristics measured above Ti clusters showed different shape comparing to the clean substrate. The most pronounced feature was found about 0.6 above the Fermi level. The maximum was more pronounced above small clusters but the I-V shape was very similar for both small and bigger clusters (Fig. 3a and 3b). This fact would suggest some common origin as the Schottky type barrier, for example. Similar explanation was used by Oh et al. [8] in their study of nanoscale TiSi2 islands on Si(111) substrate.

The most striking effect was found in some spots between the Ti clusters. The I-V curves showed a distinct step like structure, for example at the spot marked with “C” in Fig. 3c. The appropriate dI/dV curves show maxima at 1.19 eV below the Fermi level, 0.49 eV and 1.51 eV above it.
Fig. 1. STM images of: (a) Ti clusters after deposition onto Si(111) 7×7 at 673 K, (b) after annealing at 873 K, (c) 898 K, and (d) 923 K, respectively.

Fig. 2. (a) STM image of Si(111) substrate covered with Ti and annealed at 873 K, (b) dI/dV characteristics measured above rings (spots marked with “A”, continuous line), disordered 7×7 reconstruction (spots marked with B, in comparison to the clean Si(111) substrate (dashed line).
Fig. 3. (a) STM topography image of Ti clusters deposited onto Si(111) 7×7 substrate, (b) $dI/dV$ curves measured at spots “A” and “B” – above small and bigger Ti clusters, (c) I-V curve measured at the spot “C” and (d) $dI/dV$ curve from the same spot as in C.

This type of I-V curve is usually interpreted in the form of Coulomb Blockade effect or quantum size effect, sometimes as a combination of the both of them [11]. In the ideal case for the Coulomb Blockade effect the plateaus should have the same width. As it is not the case for our results the other explanation could be that clusters created lateral tunneling barrier between them creating a narrow quantum well for tunneling electrons with the specific states close to Fermi level. The theoretical simulation of this system electronic structure would be necessary to check the interpretation validity.

4. Summary
Ti nanoislands (clusters) were grown on Si(111) 7×7. Features along the $dI/dV$ curves measured above clusters may be explained by the presence of the Schottky barrier between the islands and Si substrate. This barrier is not dependent on size but shows distinct variation in barrier height.

The stepped I-V curves were found at the regions between Ti clusters, suggesting the presence of a quantum well. The resonant states with maxima at -1.19 eV (HOMO), +0.49 eV i +1.51 eV (LUMO) were found.
Annealing of the Si(111) 7×7 substrate covered with 0.07 ML of Ti at temperatures about 873 K led to appearance of rings characteristic for r19×r19 surface reconstruction. Creation of the rings modifies the local electronic properties as it was shown by means of CITS measurements.

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