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SCANNING TUNNELING MICROSCOPY INVESTIGATION OF THE Si(001)-c(8 × 8) NANOSTRUCTURED SURFACE

PACS 68.55.-a, 81.15.Aa, 68.37.Ef

The rarely observed Si(001)-c(8 × 8) reconstruction is a unique nanostructured state of the Si(001) surface. It was obtained through the sample contamination with trace amounts of Cu below the electron spectroscopy detection limit. As our detailed STM investigation shows, the surface is not atomically flat in the c(8 × 8) state. Instead, the principal elements of this reconstruction belong to two subsequent atomic layers. They are the epitaxial Si ad-dimers in the first atomic layer and the double dimer vacancies in the second atomic layer.

K e y w o r d s: silicon, surface, reconstruction, scanning tunneling microscopy.

1. Introduction

Long period reconstructions of semiconductor surfaces are fascinating examples of the spontaneous nanostructuring, driven thermodynamically to reach a minimum of the surface free energy. A larger supercell of the reconstruction usually means its more intricate atomic structure, which is also harder to decipher. A scanning tunneling microscopy (STM) technique is an indispensable tool for understanding the complicated surface reconstructions due to its unique atomic resolution capability [1]. If the lateral periodicity of a surface exceeds 1 nm, then the reconstruction can be formally considered as a nanostructure. The famous examples observed by STM include the Si(111)-(7 × 7) [2] and the Au(111)-22 × $\sqrt{3}$ [3] reconstructions with characteristic periodicities of 2.7 nm and 6.3 nm, respectively. At the National Taras Shevchenko University of Kyiv, a home-made ultrahigh vacuum (UHV) STM [4] was built in the electron spectroscopy laboratory headed by Prof. M.G. Nakhodkin. One of its application areas became the research of silicon and germanium surface reconstructions, in particular a detailed investigation of the corner holes on the Si(111)-(7 × 7) reconstruction [5].

The Si(001) semiconductor surface is extremely important in the commercial microelectronics technology and was intensively investigated for several recent decades. Its basic ground state is a 2 × 1 dimer row reconstruction with a 0.768 nm × 0.384 nm rectangular unit cell, as was finally and decisively established by the STM technique [6]. The STM laboratory in Nakhodkin's scientific group was also involved in the Si(001) research, with a particular emphasis on its nanostructured states. In this area, a detailed STM characterization of the Si(001)-c(4 × 4) reconstruction was performed, and a refined mixed ad-dimer model of this surface was established [7]. Its lateral periodicity of 1.536 nm satisfies the definition of the nanostructured surface, while the driving force of nanostructuring is the attainment of a local free energy minimum (instead of the global one) by the previously roughened silicon surface. The researches of other authors had revealed a further "long range" Si(001)-c(8 × 8) reconstruction, but several suggested atomic models of this nanostructured surface (lateral periodicity of 3.072 nm) are in conflict with one another [8–11]. The atomic resolution capability of the STM technique seemed to be an ideal prerequisite for resolving this controversy. Therefore, a detailed STM investigation of the Si(001)-c(8 × 8) nanostructure was set as a primary goal of the present work, which was entirely performed in the laboratory guided by Prof. Nakhodkin.

2. Experimental

The Si(001) samples were cut from standard phosphor-doped (4.5 Ω · cm) microelectronics grade silicon wafers. The *ex-situ* preparation consisted of consecutive rinsing in acetone, distilled water, hydrofluoric acid, and distilled water immediately before the loading into the load-lock of a UHV chamber. The latter

had a base pressure of 3×10^{-10} mbar and hosted STM, Auger electron spectroscopy (AES), as well as sample preparation facilities. *In-situ*, the atomically clean Si(001)-(2 × 1) reconstructed surface was prepared by the outgassing at 900 K for several hours, annealing at 1500 K for 1 min, rapid quenching to 1200 K, and cooling down to 300 K over half of an hour. All STM images were obtained at room temperature in the constant current mode with a platinum-iridium (80% Pt, 20% Ir) probe tip.

3. Preparation of Si(001)-(2 × 1) and Si(001)-c(8 × 8) Reconstructions

In Figs. 1–2, we present the comparative large-scale views (65 nm × 65 nm) of the Si(001) surface with 2×1 and c(8×8) reconstructions. Figure 1 is the STM image of the Si(001)-(2×1) surface, as obtained after the standard sample preparation procedure described in the previous section. We observe atomically flat terraces "t" separated by single atomic steps "s". The regular structure on any terrace is the 2×1 dimer row reconstruction (in agreement with other authors [6]), which is the ground state (global free energy minimum) of the Si(001). The dimer rows, seen as continuous stripes in the given field of view, are perpendicular to each other if they belong to neighboring terraces. We also observe irregularities within the periodic pattern of stripes in the form of impurity clusters "i" above the dimer rows, as well as vacancies "v" (ranging from single atomic to large groups of absent dimers) within the rows.

Figure 2 is the STM image (65 nm × 65 nm) of the Si(001) surface, which finds itself predominantly in the c(8 × 8) reconstructed state. The preparation of this sample included all standard steps, as described in the previous section, but additionally a mechanical contact of the Si surface with a copper sample has accidentally taken place during the handling (ideally only the teflon tweezers can touch silicon before loading into the molybdenum sample holder). This was enough for the formation of extended c(8 × 8) domains on the Si(001), while the rest of the surface still exhibited the 2×1 dimer row reconstruction with the increased amount of vacancies. No Cu was detected on the surface by means of Auger electron spectroscopy (AES), suggesting the inadvertent copper contamination at some level below the AES detection limit. This observation fully confirms the initial

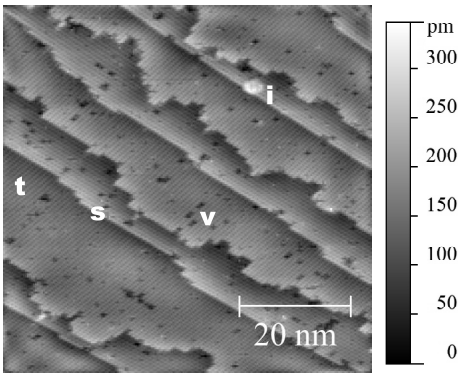


Fig. 1. STM image (65 nm × 65 nm field of view) of the Si(001)-(2 × 1) surface after the standard preparation procedure. Right to the image is the grey scale ruler for the conversion into real height. Sample bias voltage: –1.5 V, tunneling current: 0.3 nA. Designated within the image: t – terrace, s – step, i – impurity, v – vacancy. See the text for the discussion

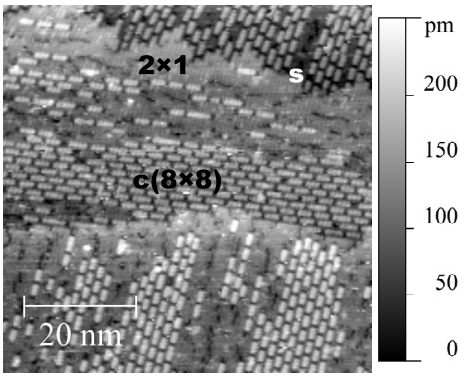


Fig. 2. STM image (65 nm × 65 nm field of view) of the Si(001) with a mixture of (2×1) and c(8×8) resulting from the contamination with trace amounts of Cu. Right to the image is the grey scale ruler for the conversion into real height. Sample bias voltage: +1.7 V, tunneling current: 0.3 nA. Designated within the image are (2 × 1) and c(8 × 8) domains and a single atomic step "s" between adjacent terraces. See the text for the discussion

STM work on Si(001)-c(8×8) [8]. The given preparation procedure is strongly reminiscent of another case where the nanostructuring of the Si(001) surface was achieved by the contamination with a trace amount of Ni [12]. For this, the single touching of the sample by stainless steel (Ni-containing) tweezers was enough for the so-called 2×n nm-scale vacancy superstructure with no long-range order to develop, while the preparation procedure was otherwise the standard one.

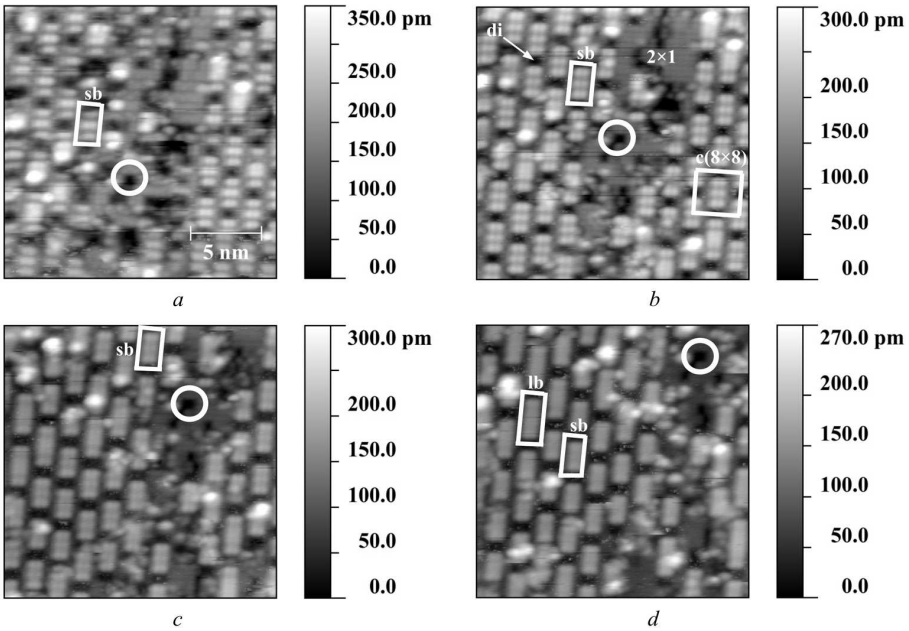


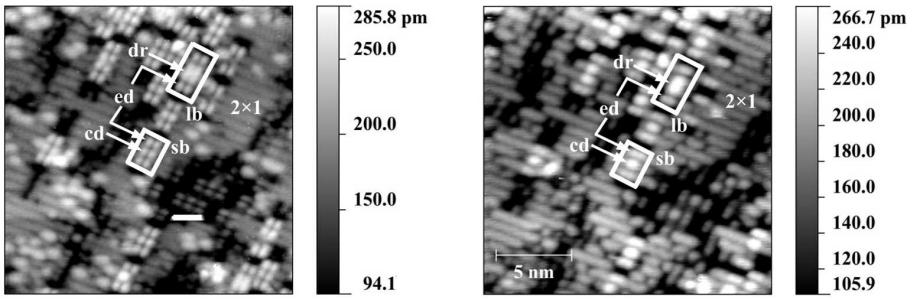
Fig. 3. STM images of the Si(001)-c(8 × 8) in empty states at various sample bias voltages: *a*) +0.8 V; *b*) +1.2 V; *c*) +1.8 V; *d*) +2.4 V. Tunneling current: 0.3 nA. All images are 18.7 nm × 18.7 nm in size and show the same area on the sample with certain shifts due to the thermal drift. As a guide for an eye, the same vacancy cluster is encircled in white on all four images. Right to every image is a grey scale ruler for the conversion into real height. Designated are: a standard topmost building block of the c(8 × 8) reconstruction "sb", a longer topmost building block "lb", deep interval between the topmost building blocks "di", and the c(8 × 8) unit cell

4. Voltage-Dependent STM of the Si(001)-c(8 × 8)

In what follows, we will investigate the influence of surface electronic states on the Si(001)-c(8 × 8) appearance in STM images. Figures 3, *a*–*d* are the STM images of empty states of the same surface area (excluding some shifts due to thermal drift) obtained at different positive sample bias voltages. The images show a part of the surface covered predominantly by the c(8 × 8) reconstruction, but also containing a highly defective (2×1) domain. As a guide for an eye, the same vacancy group inside the (2 × 1) domain is encircled in white on panels *a* through *d*.

As was already clear from Fig. 2, the Si(001)-c(8 × 8) superstructure consists of the topmost rectangular building blocks arranged in a brickwall pattern. The panels of Fig. 3 allow a detailed view of these reconstruction's elements, while a single rectangular block is outlined in every panel ("sb" designation means standard block). There is a strong bias voltage influence on the way, by which these elements are imaged in the STM. At a low enough positive sample bias voltage, as can be seen in Fig. 3, *a* at +0.8 V, one block consists of three short stripes. At +1.2 V, each stripe breaks up into two distinct atomic-size maxima (Fig. 3, *b*), presuming that each topmost building block of the reconstruction consists of six Si atoms. For higher positive bias voltages +1.8 V (Fig. 3, *c*) and especially +2.4 V (Fig. 3, *d*), these atomic maxima are not imaged distinctly, and the topmost building blocks of the c(8 × 8) look like uniformly filled rectangles. It is worth noting that not all building blocks are equal. Instead, some of them appear longer than others (the "lb" designation means a longer block). Their presence destroys the long-range order of the observed superstructure.

The STM images of Fig. 3 contain the (2 × 1) domain with numerous vacancies, which can serve as height reference points. These vacancies are of the same brightness (or height according to a grey scale ruler) as the deep intervals (marked as "di") between the topmost rectangular blocks within the c(8 × 8) superstructure. The blocks themselves are substantially brighter than the (2 × 1) area, suggesting that



a *b*

Fig. 4. STM images of the Si(001)-c(8 × 8) in empty states vs occupied states. Sample bias voltages: *a*) +1.2 V; *b*) –1.8 V. Tunneling current: 0.3 nA. All images are 18.7 nm × 18.7 nm in size and show the same area on the sample. Designated are: a standard topmost building block of the c(8 × 8) reconstruction "sb", a longer topmost building block "lb", edge dimer "ed", central dimer "cd", fragment of the dimer row "dr"

they consist of atoms of the next atomic layer relative to the (2 × 1) dimer rows. Thus, the c(8 × 8) reconstruction involves two atomic layers: the topmost layer (consisting of adatoms forming rectangular building blocks) and the surface layer (on which adatoms are adsorbed). The deep intervals are vacancy groups within the surface layer, their lateral size indicating that four surface atoms are missing in every interval.

Next, we compare the same "sb" and "lb" features obtained both in empty and occupied states. In Figs. 4, *a*–*b*, we observe the same surface area imaged at sample bias voltages of +1.2 V (*a*) and –1.8 V (*b*). This area was predominantly covered by the (2 × 1) dimer rows, but it also contained a certain amount of the c(8 × 8) building blocks. All six bright features of the standard block, which are clearly distinguished in Fig. 4, *a*, coalesce pairwise into three short stripes in Fig. 4, *b*, looking similar to the image of empty states at low bias voltages (Fig. 3, *a*). This observation strongly suggests that the standard building block "sb" consists of three Si dimers, while the central dimer "cd" is imaged brighter due to the effect of the local density of states. Both the height and the orientation of these dimers relative to the (2 × 1) dimer rows clearly indicate that they are the epitaxial ad-dimers of the next atomic layer. These dimers are not densely packed, since the distance between them is equal to two unreconstructed Si(001) in-plane units.

The epitaxial ad-dimers already form a short fragment (arrow marked as "dr") of the next layer dimer row in the central part of the "lb" feature, as is clearly seen in Figs. 4, *a*–*b*. According to its observed length, this fragment contains three densely packed dimers (the packing periodicity is equal to a single unreconstructed Si(001) in-plane unit length), as opposed to just a single dimer at the center of the "sb" feature. This means a total of 5 dimers or 10 Si atoms within the non-standard longer building block, as opposed to just 3 dimers or 6 Si atoms within the standard building block of the c(8 × 8) superstructure. The common feature of both building block types is the edge dimer "ed", whose packing relative to the central part is non-dense. The "ed" dimers display a lower brightness in the occupied states (hence, a lower density of states) than other dimers of the building block, most probably due to the specific local bonding configuration (proximity to the "di" vacancy group).

5. Discussion

Although our present work agrees with the initial STM observation of Murray et al. [8] on the Cu contamination, which causes the c(8 × 8) reconstruction of the Si(001) surface, we arrive at different conclusions about the constituents of this superstructure. The atomic resolution capability of the STM technique in our experiments has allowed for the direct observation of Si atoms within the basic building block of the Si(001)-c(8 × 8), indicating the presence of only 6 Si atoms forming 3 not densely packed epitaxial ad-dimers in contrast to 12 initially suggested Si atoms forming 6 densely packed epitaxial ad-dimers [8]. Likewise, our STM data are not consistent with 12 Si atoms forming 6 not densely packed

ad-dimers per building block proposed by Zilani et al. [10] or 8 Si atoms forming 4 epitaxial ad-dimers with a dense/loose packing combination proposed by Arapkina et al. [11].

Our results are in the striking "geometric" agreement with the Si(001)-c(8×8) structure proposed by Liu et al. [9] in terms of the number of atoms constituting the basic "sb" building block and the number of vacancies (4 Si atoms missing) belonging to the "di" features. Identically to our conclusion, three epitaxial ad-dimers with the loose packing are ascribed to the "sb" surface feature. However, a major discrepancy deals with the chemical identity of the ad-dimers, which are suggested to be Cu ad-dimers due to the large Cu amount (measurable by electron spectroscopy) used to induce the given reconstruction [9]. Since Cu is already firmly confirmed to produce the Si(001)-c(8×8) nanostructure by several authors [8, 10], there is no wonder that Cu has performed its job, when being present in excess of the minimum required amount. Since no direct elemental identification is possible by the STM technique, a possibility arises that Si atoms were mistaken for Cu atoms by Lie et al. in their STM images.

6. Conclusions

A high spatial resolution achieved in the present voltage-dependent STM investigation of the Si(001)-c(8×8) reconstruction, has allowed us to directly observe the atomic constituents of the basic building blocks of the given nanostructure. We arrive at the conclusion that it consists entirely of the Si adatoms forming 3 non-dense epitaxial ad-dimers per single block. Although the trace amounts of Cu are used to stabilize this reconstruction, probably, due to a stress in the near-surface region, the Cu atoms cannot be involved in every c(8×8) unit cell. Further experimental and theoretical investigations are required to unearth the exact stabilization mechanism by Cu impurities, as well as to establish a complete atomic model (involving at least several atomic layers below the surface) of the Si(001)-c(8×8) structure.

All STM data processing was performed using the Gwyddion software package, which is available as "open source" and can be downloaded from the gwyddion.net website.

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Received 30.10.14

А. Горячко, С.П. Кулик, П.В. Мельник, М.Г. Находкін

ДОСЛІДЖЕННЯ НАНОСТРУКТУРОВАНОЇ ПОВЕРХНІ Si(001)-c(8×8) МЕТОДОМ СКАНУЮЧОЇ ТУНЕЛЬНОЇ МІКРОСКОПІЇ

Р е з ю м е

Реконструкція Si(001)-c(8×8), що спостерігається в деяких випадках, є унікальним наноструктурованим станом поверхні Si(001). Він був одержаний внаслідок внесення домішок Cu в концентраціях нижче межі чутливості електронної спектроскопії. Детальні СТМ зображення демонструють, що в стані c(8×8) поверхня не є атомарно гладкою, натомість складається із основних елементів, які належать двом послідовним атомним шарам. Цими елементами є епітаксійні аддимери Si в першому (поверхневому) шарі та подвійні димерні вакансії в другому (приповерхневому) шарі кремнієвого субстрату.