

Enhanced contamination of Si(001) when analyzed by AES with respect to XPS

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Clean Si(001) single crystal surfaces are obtained by cycles of long (30 mins.) annealings in ultrahigh vacuum (fairly below 1×10^{-9} mbar). The surface reconstruction is investigated by low energy electron diffraction (LEED). This paper reports, in addition to the well-known $p(2 \times 1)$ reconstruction, the first observation of $c(4 \times 2)$ at room temperature and also the completely new $c(6 \times 2)$ reconstruction. The *in situ* oxidation of these surfaces was investigated by Auger electron spectroscopy (AES) and by X-ray photoelectron spectroscopy (XPS). It is found that, in similar ultrahigh vacuum conditions (6×10^{-10} mbar), much faster contamination (about 500 times) occurs when the samples are investigated by AES than by XPS, owing mainly to the interaction of the electron beam with the sample surface. Also, much gentler surface bombardment with electrons, such as in LEED, still enhances sample oxidation. Therefore, XPS proves to be a much more convenient technique for non-destructive assessment of the surface composition. When the surface is subjected to the AES investigation, we found that the contamination occurs by forming $>\text{Si}_2\text{C}=\text{O}$ complexes based on the Si dimers.

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1. Introduction

A key test of most surface science ultrahigh vacuum (UHV) apparatuses, and especially of molecular beam epitaxy (MBE) installations is the cleaning of semiconducting samples, of which Si(111) and Si(001) are the most used examples. This allows the setup and commissioning of standard characterization devices, such as (i) for structural characterization: low-energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED); (ii) for chemical characterization: Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS). In this paper we present the first consistent results obtained by using the LEED, AES and XPS techniques when dealing with a surface which is relatively difficult to achieve without contamination, but also of high technological interest, Si(001).

Usually, silicon substrates are prepared by flashes at very high temperatures (1200 – 1400°C) [1-3], cycles of Ar^+ sputtering and annealing [4-6], cleavage under UHV [7], RCA (Radio Corporation of America) method and other wet chemical methods [8-9], gas source MBE [10], laser ablation [11-12]. Any of these methods has disadvantages. Very high temperature flashes require special sample manipulators and heating procedures. Cleavage cannot be performed on any surface, it also produces dust, defects, fractures and the results of a cleavage are uncertain. The wet chemical methods are unable to completely remove the ambient contamination [8], the gas-source MBE requires special care to work with harmful gases (silanes); also, laser ablation is an expensive technique. It is therefore desirable to set up a method allowing the preparation of silicon samples at lower

temperatures, with the required degree of purity in order to proceed to molecular beam epitaxy of such surfaces. Low temperature sample preparation are well known in the case of MgO(001) substrates [13-15], GaAs(011) and GaAs(001) substrates [16-20], or InAs(001) substrates [21-27] and this facility allows quick preparation and achievement of a wide variety of studies in a relatively short time and without a considerable effort.

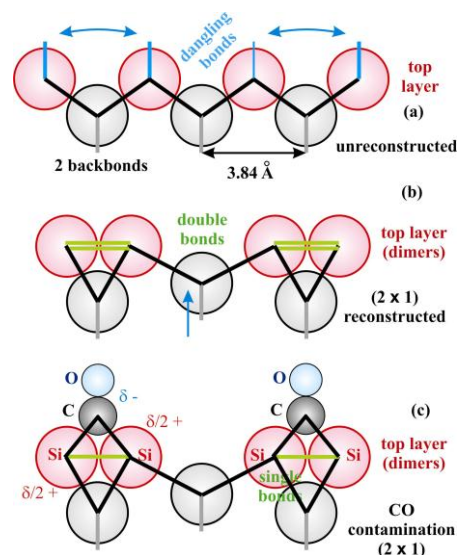


Fig. 1. Side views of the (110) plane of a (001)-oriented Si crystal: (a) Ideal structure (no reconstruction). Dimer formation by completion of the dangling bonds is figured; (b) (2 x 1) reconstructed surface; (c) Model proposed for adsorption of carbon monoxide from the residual gas. The (2 x 1) reconstruction is preserved.

In this paper we firstly present a novel and cheap method for preparing atomically clean samples of Si(001) just by annealing in ultrahigh vacuum. The method may be repeated several times with reproducible results in obtaining low-contamination, well characterized surfaces of Si(001). The atomically clean Si(001) provided not only the 'standard' $p(2 \times 1)$ - (1×2) , reconstruction, but also some more reconstructions which are briefly discussed in the following.

The well-known $p(2 \times 1)$ reconstruction is formed by Si dimers at the surface, such as represented in Fig. 1(b). Recently, $c(4 \times 2)$ was evidenced at low temperatures, below 40 K [28,29], then below 150-200 K [30,31], but to date no report of the room temperature observation of this reconstruction is available. For flat Si(001) surfaces, the $p(2 \times 1)$ reconstruction coexists with the $p(1 \times 2)$ one, on domains whose shape may be visualized e.g. by low-energy electron microscopy (LEEM), see Fig. 2.

High resolution X-ray photoelectron spectroscopy (XPS) evidenced a wide variety of surface states [30,32], whereas a study by scanning tunneling microscopy (STM) of the *in situ* oxidation in ultrahigh vacuum (UHV) revealed the high reactivity of the step edges [33]. However, to date no *in situ* survey of the oxidation of ultraclean Si(001) was published by using the standard methods in surface science: XPS and AES, although it was recognised that the electron beam may affect strongly the surface reconstruction, by low energy electron diffraction (LEED) experiments [29]. Hence, apart for presenting the observation of new reconstructions provided by clean Si(001), this paper presents also a comparative survey of the *in situ* contamination of atomically clean Si(001) followed by AES and XPS.

We will also present very first results from our laboratories obtained on clean Si(001) by LEEM, a technique which allows separate visualisation of the reconstructed $p(2 \times 1)$ or $p(1 \times 2)$ domains [34].

2. Experimental

All experiments are performed in an UHV cluster (Specs) comprising a molecular beam epitaxy (MBE), communicating with an STM and with a photoemission chamber. The latter is equipped with a dual Al/Mg K_{α} X-ray source, an X-ray monochromatized source (for the present experiments we used only Al $K_{\alpha 1}$ line, $h\nu = 1486.74$ eV) and a 150 mm radius Phoibos hemispherical electron energy analyzer. The combined energy resolution due to both the X-ray source and to the electron energy analyzer is below 0.5 eV with still a considerable counting rate ($> 10,000$ cps on test samples such as Ag 3d).

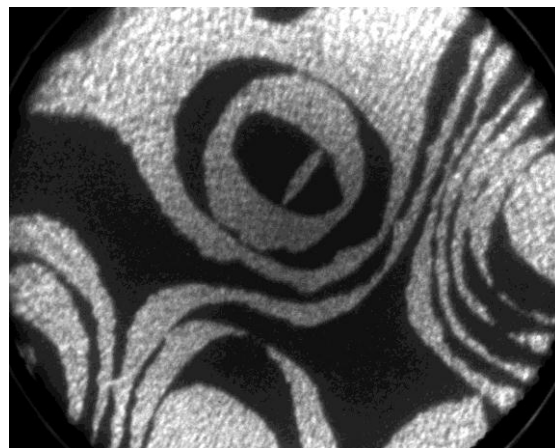


Fig. 2. Dark field low-energy electron microscopy (LEEM) on a Si(001) surface, obtained by selecting one of the $p(2 \times 1)$ spots from the diffraction plane. The field of view (FOV) is $2 \mu\text{m}$.

The MBE chamber is equipped with a Specs LEED-Augur system. All chambers operate at base pressure below 1.5×10^{-10} mbar. n-doped Si(001) wafers were cleaned by three cycles of annealing at 1200 ± 30 °C, in a pressure of 10^{-10} mbar range.

During the LEED investigation, the pressure rises at 5×10^{-10} mbar, during AES and XPS at 6×10^{-10} mbar. The clean samples did not show contamination, i.e. the C contamination level, if any, is below 0.001 of a single atomic layer, as investigated by both AES and XPS. During AES and XPS measurements, the vacuum composition was permanently controlled with a quadrupole mass spectrometer - residual gas analyzer. The setting up of the cleaning procedure lasted several months, including vacuum conditioning, manipulator outgassing, etc. During this time, RHEED was very often used rather than LEED to investigate the sample cleanliness and the surface reconstruction. However, it appeared that the LEED technique is much more sensitive to the surface reconstructions and also involves electrons of lower energy interacting with the surface. Therefore, in all the experiments discussed here, LEED was the principal structural technique utilised.

A separate experiment with a new setup for photoemission electron microscopy and low-energy electron microscopy (PEEM-LEEM) [34] was conducted on Si(001) in order to visualise the domains $p(2 \times 1)$ and $p(1 \times 2)$. These experiments will be described in more detail in a forthcoming publication. For the present study, we just present in Fig. 2 a dark-field image obtained by selecting one (2×1) spot from the diffraction plane [34]. This allows to clearly see the reconstructed domains of the clean Si(001). Also, the LEEM experiments allowed us to affirm that practically the whole surface of the Si(001) is reconstructed and also to infirm the presence of any contamination on the clean Si(001) once the surface was prepared in ultrahigh vacuum (10^{-10} mbar).

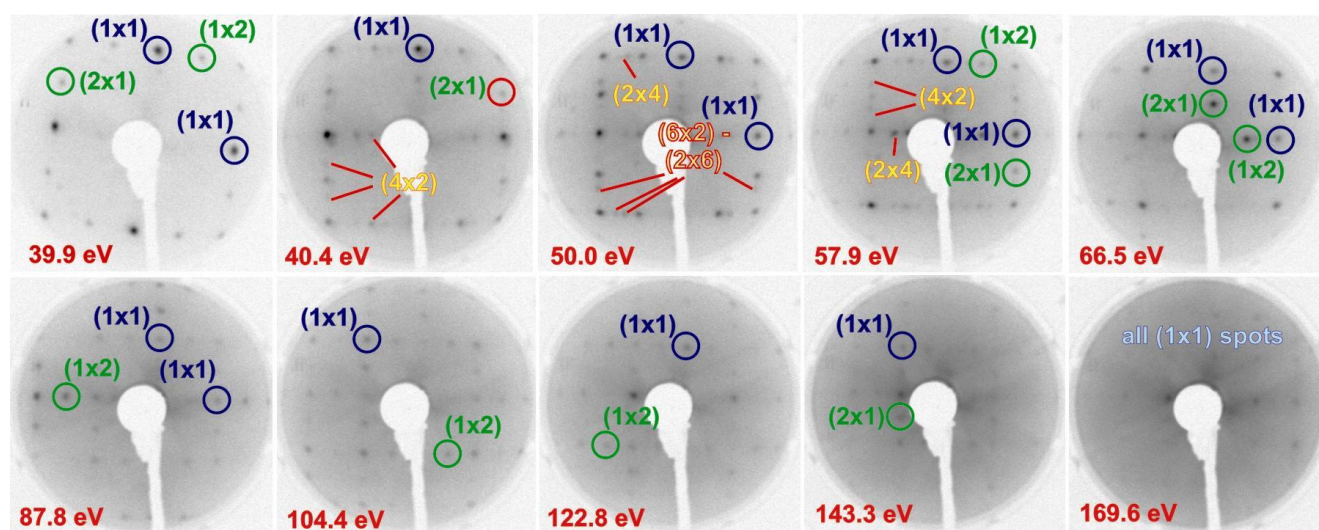


Fig. 3. Low-energy electron diffraction (LEED) images recorded at several incident electron energies (figured on graphs). For better clarity, negatives of the obtained images are shown. Also, the spots belonging to several reconstructions (1×1) , (2×1) - (1×2) , (4×2) - (2×4) , (6×2) - (2×6) are indicated.

3. Results and discussion

3.1 LEED

Fig. 3 presents LEED patterns obtained at different energies, at room temperature (RT). One easily identifies the $p(2 \times 1)$ reconstruction, well defined $c(4 \times 2)$ spots (at energies between 40-58 eV) and also some traces of $c(6 \times 2)$, visible at 50.0 eV. This last reconstruction was never reported so far for clean Si(001), but only for submonolayer Yb/Si(001) [35]. Note also that this is the first observation of the $c(4 \times 2)$ reconstruction at room temperature.

After AES measurements, the sample was again investigated by LEED and the $p(2 \times 1)$ - (1×2) reconstructins were still visible, but the $c(4 \times 2)$ and the $c(6 \times 2)$ disappeared. In view of the AES observations which will be presented in the following paragraph, that means that extremal cleanliness of the Si(001) surface might be probed by the existence of higher order reconstructions [$c(4 \times 2)$ and $c(6 \times 2)$], but not compulsory by the 'usual' $p(2 \times 1)$ - (1×2) .

Since here we report the first observation of the $c(4 \times 2)$ and of the $c(6 \times 2)$ reconstructions at room temperature, forthcoming experiments are planned in order to investigate the domains formed by these reconstructions, by LEEM. The advantage of the LEEM system stems in the possibility of high temperature flashing of Si(001) in extremely high vacuum conditions, low than 10^{-10} mbar.

3.2 AES

Fig. 4 presents the evolution of the AES signals of Si LVV, C and O KLL with time, during a continuous

measurement. The electron current on the sample was 20 μ A and the kinetic energy 1.1 keV. Clear evidence of oxidation is present from both the occurrence of the C and O KLL lines and of the 'reacted' Si LVV feature at about 84 eV. The atomic percentages, represented in the inserts of Fig. 4, are obtained by normalising with extrapolated AES sensitivity factors [36]. These data were fitted as:

$$I(\text{Si}^0) = 1 - 0.773 \times [1 - \exp(-0.0052 t)]$$

$$I(\text{Si}^{\delta+}) = 0.546 \times [1 - \exp(-0.0046 t)]$$

$$I(\text{C}) = 0.108 \times [1 - \exp(-0.0105 t)]$$

$$I(\text{O}) = 0.159 \times [1 - \exp(-0.0033 t)]$$

where the time t is expressed in minutes. From here, it follows that the installation of the 'reacted' Si component $\text{Si}^{\delta+}$ is accompanied by the increase of both C and O, with a ratio of roughly two reacted Si atoms per C and O, since $0.546 \approx 2 \times (0.108 + 0.159)$. This yields the very simple model proposed in Fig. 1, where a $(=\text{CO})^{\delta-}$ radical is bonded to a surface dimer. Note that residual gas analysis (RGA), represented in Fig. 5, reveals a partial pressure of 1.4×10^{-10} mbar of 'mass 28' = CO^+ during the AES measurement. Also, structures such as those from Fig. 1(c) keep the $p(2 \times 1)$ reconstruction. This was checked several times: the LEED of contaminated samples still present well-defined (2×1) spots. Consequently, as mentioned in the above paragraph, the existence of $(1, 1/2)$ or $(1/2, 1)$ spots is not an absolute proof of the surface cleanliness.

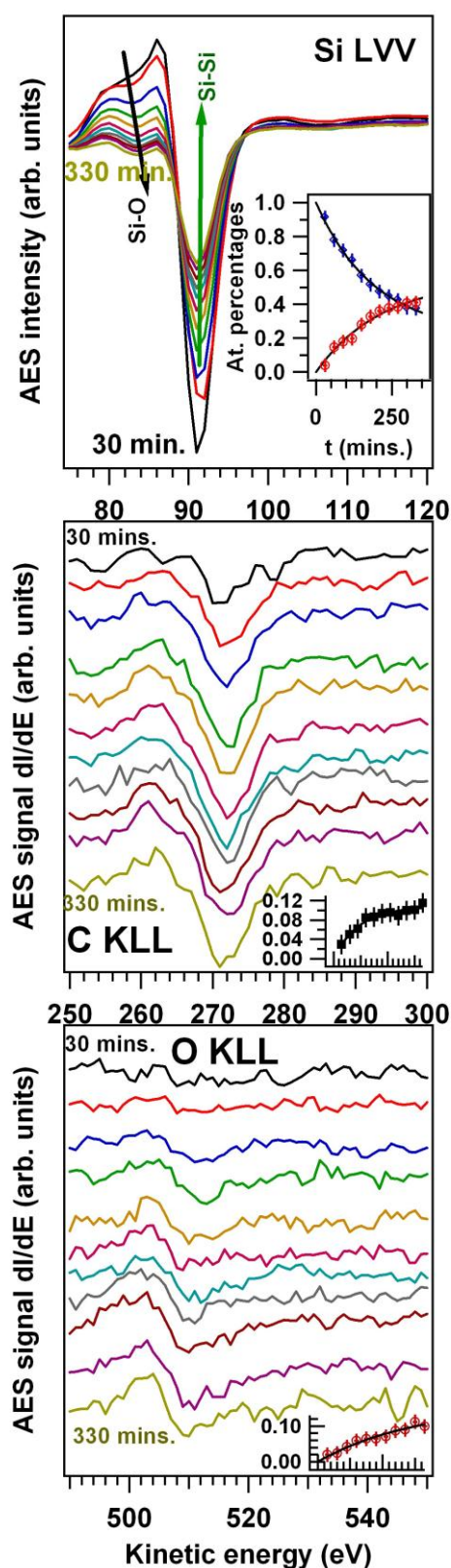


Fig. 4. Auger electron spectroscopy (AES) of Si LVV, C KLL and O KLL. Insert in all figures: the time evolution of atomic percentages (see text for details).

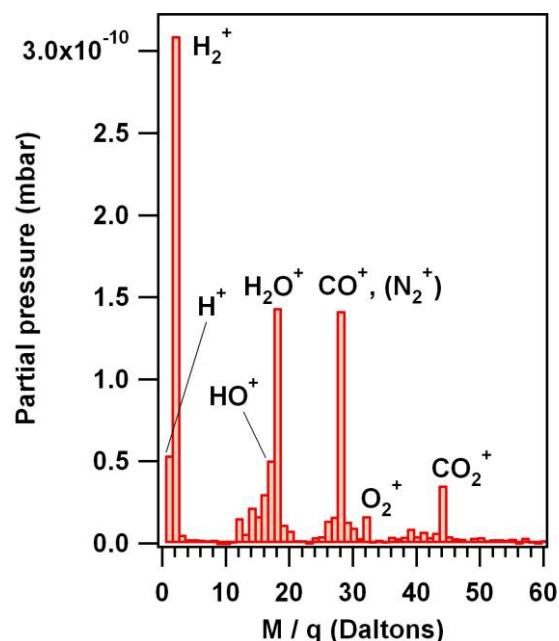


Fig. 5. Residual gas analysis, recorded during an AES measurement.

3.3 XPS

Fig. 6 presents a series of XPS spectra recorded on clean samples ($t = 0$), then after a short (15 min.) LEED check (yielding already some contamination of the surface), and after 20 hours of continuous measurement. From the general aspect of the spectra, it is found that, although the XPS measurements are performed in similar vacuum conditions as for AES, the contamination rate is significantly lower in this case. Practically, the short LEED check of the sample is responsible for more contamination than the whole XPS measurement of 20 hours. An estimate of the contamination rate from the decay of the Si $2p$ signal is on the order of $0.976 \times 10^{-5} \text{ min}^{-1}$. The C contamination after 20 h of measurements is estimated at 0.107 ± 0.012 single carbon atomic layers, from the C $1s$ XPS spectrum (not shown). Therefore, the surface is about $(5.2 \times 10^{-3} / 0.976 \times 10^{-5} = 532) \approx 500$ times more stable in absence of the electron beam.

Fig. 6 presents also curve fits, usually called 'deconvolutions' of the Si $2p$ signals, by using Voigt lines and their integrals [37]. Our laboratory photoemission setup did not allow to retrieve all fine details exhibited by third generation synchrotron radiation XPS data [32]; however, it exhibits clearly surface components of higher binding energy (BE) for clean Si signal. The spin-orbit splitting was 0.424 eV and the branching ratio was fixed to its theoretical value of 2. Allowing the branching ratio to vary did not improve significantly the quality of the fit. The spin-orbit splitting was initially allowed to vary, then it was fixed for all spectra to the average of all previously obtained values. This value is different from the value reported in Ref. [35] (0.605 eV), but let us also remark that the branching ratios in the curve fitting from this paper

were variable, between 1.96 and 2.05. The spin-orbit splitting derived in the present simulation is much closer to the commonly assessed value of 0.40 eV for Si 2p [38].

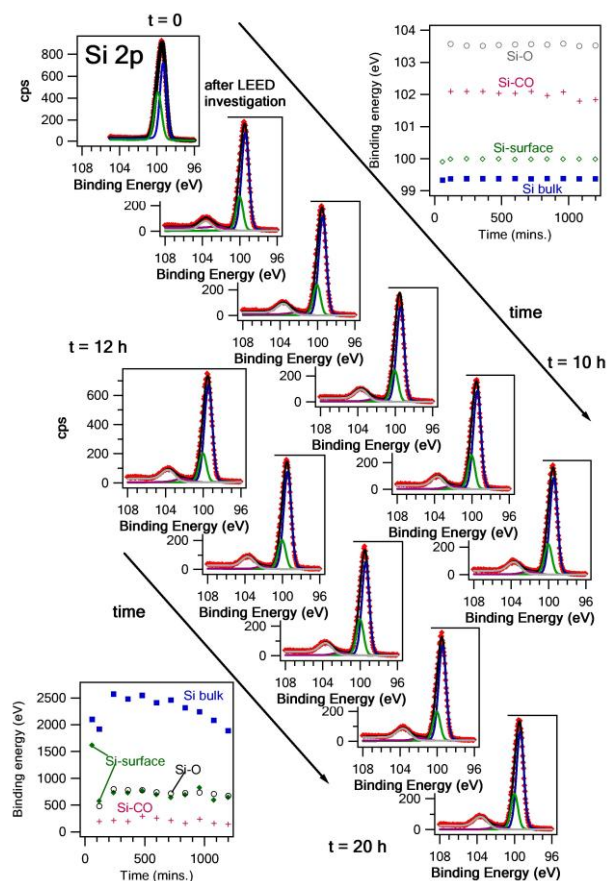


Fig. 6. Survey of sample contamination by X-ray photoelectron spectroscopy. The second spectrum is recorded after a short LEED investigation, then the measurements were undertaken continuously during 20 hours. The main contamination comes from the LEED investigation. The upper-left graph presents evolution of the binding energies of the four separate components used in the fit. The lower-right graph presents the evolution of their intensities. The XPS spectra are fitted using Voigt profiles (see text for details).

In addition to the 'clean' Si⁰ signal (together with its surface component), the 'reacted' signal present two additional lines, one which is attributed to Si-O (BE around 103.5 eV [39]) and another attributed to Si-C or Si-CO (BE around 102 eV [39]). The time evolution of the line intensities from Fig. 6 allows a simple derivation that both Si-O and (Si-C or Si-CO) components are developed on the expense on the 'surface' component of the clean Si spectrum; therefore, the reaction involves only the Si dimers at the surface. The model from Fig. 1(c) is valid also in this case. Let us also note that a final LEED check after the whole 20 hours of measurements still exhibited the $p(2 \times 1) - (1 \times 2)$ reconstruction, with somehow more diffuse spots.

4. Conclusions

We report here for the first time the room temperature observation of the the Si(001) $c(4 \times 2)$ reconstruction, and also some traces of the $c(6 \times 2)$ reconstruction, which was never reported on clean Si(001). It might be that the $c(6 \times 2)$ arrangement of the Yb/Si(001) interface, reported last year in Ref. [35], is more a fundamental property of the Si surface than an effect of the adatoms.

Clean Si(001) samples are quite stable in UHV (6×10^{-10} mbar) while analyzed by XPS. A contamination of 1 % from a single atomic layer is expected to occur in about two hours. When analyzed by AES with relatively low energy electrons (1.1 keV) and 20 μ A electron current, the contamination rate is about 500 times faster. Also, LEED investigation with electrons whose energy is considerable lower (50-100 eV) induces significant contamination.

The contamination proceeds mainly by forming $>\text{Si}_2\text{C}=\text{O}$ complexes based on the Si dimers, therefore preserving the $p(2 \times 1)$ reconstruction. In view of these findings, observation of a (2×1) LEED pattern is not a straightforward proof of sample cleanliness, as commonly assessed in the surface science community. A better sign of surface cleanliness would be the occurrence even of some traces of the $c(4 \times 2)$ or $c(6 \times 2)$ reconstructions at room temperature.

The LEEM investigations allowed us to derive that practically the whole sample surface presents one of the $p(2 \times 1) - (1 \times 2)$, $c(4 \times 2) - (2 \times 4)$ or $c(6 \times 2) - (2 \times 6)$ reconstructions, so the procedure described in this work allows synthesis of extended atomically clean, well-ordered, Si(001) surfaces.

Finally, we remark once more the much higher non-invasive character of X-ray (structural and chemical) investigation, as compared with investigations involving interaction with a flux of external electrons, no matter which is the energy of these electrons.

Acknowledgements

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