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STM INVESTIGATIONS OF CONTAMINATED AND CLEAN V(100) SURFACE

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Dedicated to Professor Boran Leontić on the occasion of his 70$^{\mathbf{th}}$ birthday

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Scanning tunneling microscopy is used to characterize different states of the V(100) surface during the cleaning procedure in an ultrahigh vacuum apparatus, starting with the "as received" sample and finishing with an almost perfectly clean surface. We show, for the first time, STM images of the clean V(100) surface and with atomic resolution.

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1. Introduction

Vanadium (100) surface has been a subject of numerous experimental and theoretical studies [1]. There are several reasons for this. The first one relates to theoretically predicted magnetism of the topmost V(100) layer as well as of the ultra-thin vanadium films [2] of the same or similar structure. The second one is connected with the use of vanadium oxides in design of various catalysts, whereas clean vanadium surfaces are prerequisite for the preparation of the so-called "inverted" catalysts which in turn serve to study and model more complex systems. Vanadium has also been frequently studied with respect to trends in electronic properties of the first-row transition metals. It is worth to mention that a study [3] of vanadium Auger transitions, within its valence band, has shown how important it is to perform experiments on clean surfaces of transition metals. Impurities, even

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at very small concentrations, can severely affect electronic and magnetic properties of a transition metal. Moreover, the structural properties may also be significantly affected by impurities and are sometimes misinterpreted as the features of clean surfaces. Vanadium (100) is also an example in this respect [4–7].

It has to be emphasized at this point that the cleaning of any of transition metal surfaces is a very involved process, in particular so in the case of the V(100) surface. In the last couple of years, several methods have been described that, eventually, produce clean V(100) surface [5,8,9].

The electronic properties of the clean V(100) surface are well documented by results obtained using angle-resolved ultraviolet photoemission spectroscopy (ARUPS) [1,3], inverse photoelectron spectroscopy (IPES) [10] and electron-loss spectroscopy (ELS) [11]. Its structural properties have been studied by low-energy electron diffraction (LEED) [4–8] and photoemission from adsorbed xenon (PAX) [8] while no scanning tunnelling microscopy (STM) investigation have been, to our best knowledge, published until now [12].

In this work we characterize, using an STM microscope, different states of the (100) surface of a vanadium monocrystal inserted into an ultra high vacuum environment, starting from the "as received" state and finishing with an almost perfectly clean surface.

2. *Experimental*

The experiments have been performed in Bonn and Zagreb using the same vanadium monocrystal, two almost identical STM microscopes and two very similar vacuum systems equipped with STM, LEED and Auger electron spectroscopy (AES). The base pressure was in the low 10^{-10} mbar region. The technical details about the STM apparatus are given in Ref. [13]. Typical bias voltages and tunneling currents were for wide scans (of the order of hundred nm) in the range of 60 – 500 mV and 4 – 10 nA, respectively. Atomically resolved images were taken typically with a bias voltage of 20 mV and a tunneling current of 3 – 10 nA. The detailed cleaning procedure is given in Ref. [8].

3. *Results and discussion*

A vanadium crystal, that had already been cleaned and used in previous experiments, was inserted into the vacuum chamber after being exposed to air for several days. After a bake-out procedure the base pressure in the chamber reached low 10^{-10} mbar and the first STM images of the "as received" surface were taken. A typical image is shown in Fig. 1. It is dominated by large cloud-like features, which cover the vanadium surface completely. These features are three-dimensional and of the order of 100 nm $\times$ 100 nm $\times$ 10 nm. The height (10 nm in our case) can be extracted from an STM measurement by performing the so-called profile scans across a selected surface feature. The line profiles give information about the cor-

rugation of the surface electronic density. The Auger spectra of this surface show a large carbon peak while the vanadium signals are barely discernible. This suggests that the features are some kind of hydrocarbon compounds adsorbed from the air.

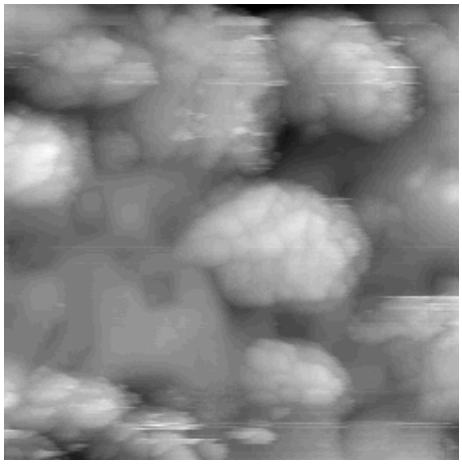

Fig. 1. STM image (334 nm × 334 nm) *of the "as received"* V *(100) surface.*

In order to remove these adsorbates, one has to sputter them off while keeping the sample at or below the room temperature. Any heating of the sample at this stage of the cleaning procedure would result in a massive diffusion of impurities into the vanadium bulk. After several minutes sputtering with a beam of argon ions, most of impurities are removed. A typical Auger spectrum shows prominent V signals and also strong signals of carbon and oxygen. After a short annealing of the sample at 800 K to heal the defects induced by the ion bombardment, the Auger spectra do not change significantly. An STM image after such a treatment reveals the basic mesoscopic characteristics of the V(100) surface. In Fig. 2a one clearly sees terraces of the V(100) surface and islands of adsorbed impurities. While Fig. 1 is dominated by three-dimensional (3-D) structures, these islands are 2-D. This information is obtained from the profile scan shown in Fig. 2b, made along the white line in Fig. 2a. The profile scan shows that the impurity island is approximately 0.6 nm thick while it covers an area of approximately 100 nm^2. In addition, the shape of these islands suggests that they might be fractals. In order to estimate the fractal order of the islands, we calculated their Haussdorff's dimension [15] and obtained 1.8 ± 0.1. This value suggests that indeed these islands have partially fractal structure.

Further sputtering removes these islands completely. The chemical composition of the surface is still a mixture of vanadium, carbon and oxygen, the amount of oxygen being increased with respect to carbon. A typical STM image is shown in Fig. 3. The surface is on the microscopic scale dominated by hills and valleys. They are the result of the surface polishing in the early stages of the surface preparation as well as of the not properly healed defects induced by ion sputtering. On the

nanoscopic scale, the hills and valleys are layered structures of the (100) planes. Figure 3 shows large terraces in valleys and on top of the hills and a large number of very narrow terraces along the hills. These two kinds of terraces may give rise to two different growth modes of a metal deposited on such a surface. By combining sputtering and very long, high temperature annealing, one can reduce the concentration of narrow terraces and significantly increase the amount of very large, 2-D, terraces. Figure 4 shows an STM image taken after such treatment of the V(100)

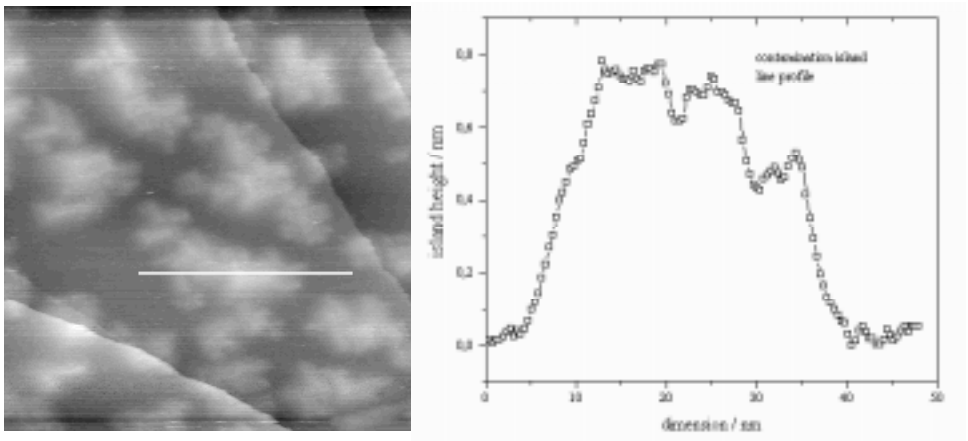

Fig. 2. STM image (100 nm × 100 nm) *of the* V*(100) surface obtained (a) after initial steps in the cleaning procedure and (b) (right) a profile scan across one of the impurity islands.*

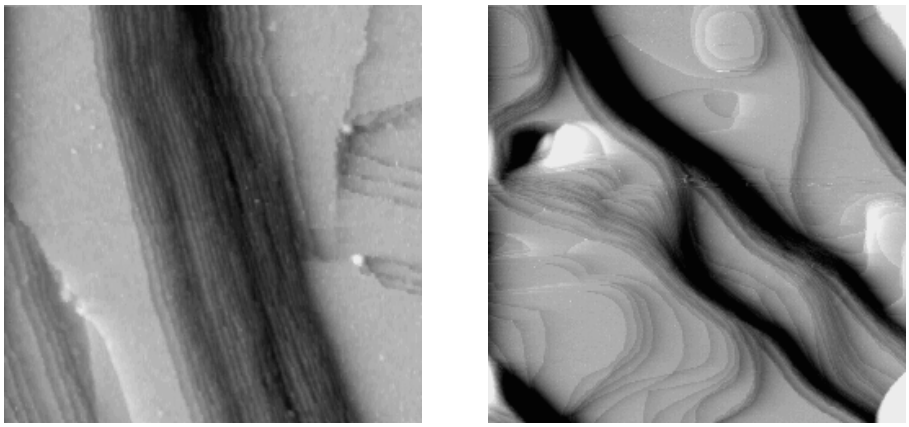

Fig. 3. STM image (100 nm × 100 nm) *of the* V*(100) surface covered with carbon and oxygen, both in sub-monolayer range of coverage.*

Fig. 4 (right). The same surface as in Fig. 3. This image (200 nm × 200 nm) *was taken after a very long annealing at 1000* K.

surface. Terraces of 100 nm × 100 nm size now dominate the surface. There are still narrow terraces as Fig. 5 shows but their total contribution to the macroscopic surface area is very small, mostly due to the fact that high hills with very steep slopes (Fig. 3) do not exist any more. While this surface treatment affected the structure, the chemical composition of this surface remained in essence unaffected: carbon and oxygen signals in the Auger spectra were of similar intensity as before the treatment.

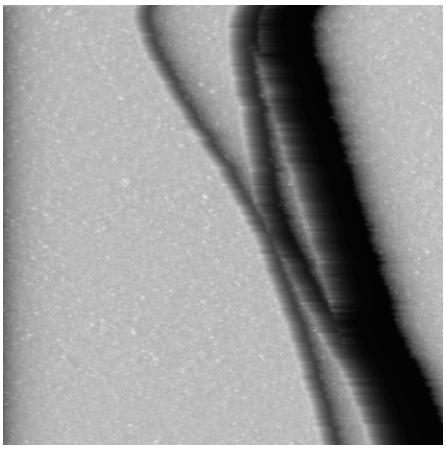

Fig. 5. One detail (50 nm × 50 nm) *scanned within the area shown in Fig. 4.*

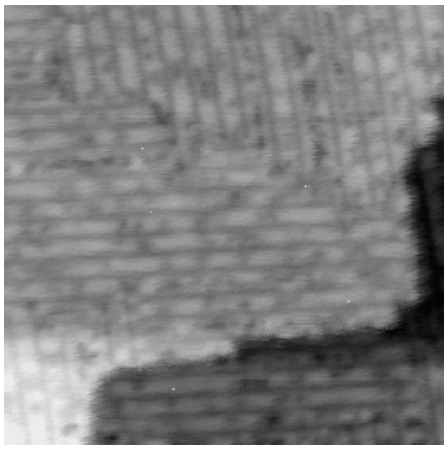

Fig. 6 (right). One detail (10 nm × 10 nm) *scanned in the high-resolution mode of the STM chosen in the area shown in Fig. 4.*

These two impurities cover the vanadium surface completely as one can reveal from the STM image shown in Fig. 6. This image is a result of scanning the tip across a large terrace boundary and in atomic-resolve mode. Two terraces and a mono-atomic step are clearly visible. The upper terrace shows two domains of regular structures of bright and dark spots. Based on the work by Koller et al. [12], we can safely interpret these ordered features as a mixture of carbon (bright) and oxygen atoms (dark). These authors also suggest that V(100) surface is reconstructed at these concentrations of carbon and oxygen. Our data can not be used to support or deny this suggestion. It should be pointed out that this image does not show individual atoms but clearly resolves monoatomic one-dimensional structures. In order to achieve total atomic resolution, one should apply biases close to zero, the request that can not be fulfilled by our technical setup. However, in the case of clean vanadium surface, there was no problem to achieve atomic resolution. This is shown in Fig. 7a. It was taken after a successful cleaning procedure [8] was completed and neither of our spectroscopies showed any traces of contaminants on this surface. The image displays typical topography, as tested at many different surface points, of a clean, non-reconstructed and well ordered bcc (100) surface, as expected for the V(100) surface.

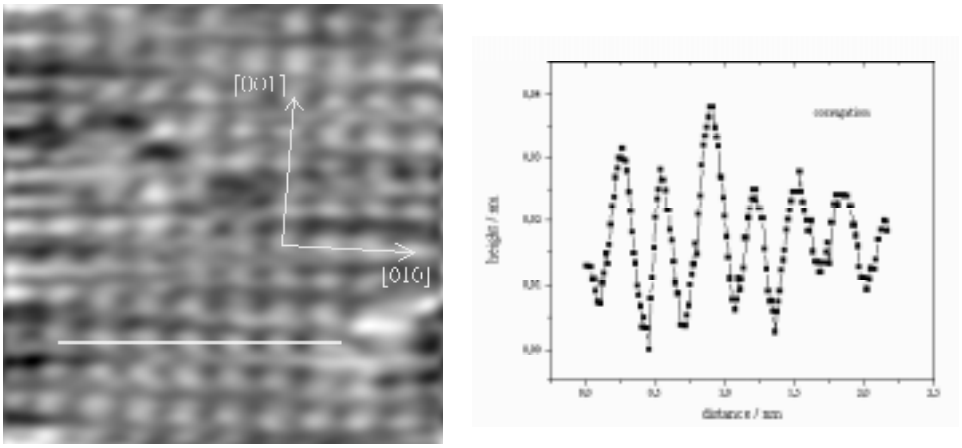

Fig. 7. STM atomic resolution mode image (3.05 nm × 3.05 nm) *(a) of the clean* V*(100) surface and (b) (right) a profile scan across a chain of* V *atoms along one of the high-symmetry axes.*

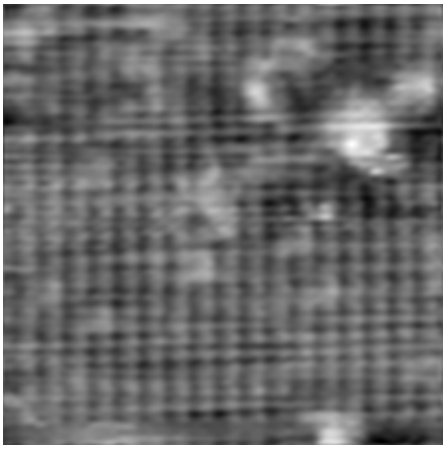

Fig. 8. The clean V*(100) surface* (5.34 nm×5.34 nm) *after being exposed to residual gas atmosphere of the ultrahigh vacuum chamber* $(1 - 2 \cdot 10^{-10}$mbar) *for several hours.*

The profile scan along a chain of vanadium atoms along one of the high symmetry axes (white line in Fig. 7a) is shown in Fig. 7b. The separation of maxima in the line-scan clearly shows the typical value for the vanadium lattice constant (0.301 nm). This finding confirms, for the first time by a real space image, that the V(100) surface does not reconstruct. Also, the corrugation of 0.04 nm, as revealed in Fig.7b, is a typical value found for transition metal surfaces.

The vanadium surface is extremely reactive and gets contaminated easily even in very good ultrahigh vacuum conditions. In our case, after several hours of resting,

the surface was again investigated by STM in atomic resolution mode. A representative image is shown in Fig. 8. On top of an atomically resolved surface patch, islands of impurities are detected. These impurities are adsorbed from the residual gas in the vacuum chamber. Therefore, it is absolutely necessary to work fast when experimenting with clean vanadium surfaces, because already small concentration of impurities may significantly affect the electronic and structural properties of the substrate as well as of the particles that were deliberately deposited on the surface.

4. Conclusions

Scanning tunneling microscopy provides valuable information about surface topography already at early stages of surface cleaning procedure. In this work, we have shown that in spite of its high reactivity, the initially heavy contaminated V(100) surface can be prepared so as to reveal large patches of impurity-free surface. These are the very first STM images of the clean V(100) surface published so far.

Acknowledgements

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ISTRAŽVANJE NEČISTE I ČISTE (100) POVRŠINE VANADIJA STM-om

Primijenili smo skenirajući tunelirajući mikroskop (STM) za topografsku karakterizaciju površine V(100) prije i tijekom čišćenja u aparaturi za ultravisok vakuum, počevši s "dobivenim" uzorkom i nakon pojedinih postupaka čišćenja. Po prvi puta se pokazuju slike potpuno čiste površine V(100) s atomskim razlučivanjem, snimljene STM-om.