

## Chapter 5

# Growth of thin vanadium oxide films and adsorption of pentacene

In this chapter, the formation of thin vanadium oxide films on  $\text{Cu}_3\text{Au}(100)$  and the adsorption of pentacene molecule on these films are investigated.

Metal oxides, like vanadium oxide, are of considerable interest in terms of technological applications and have been intensively studied in the last decades, for example as support for metal particles in catalysis, as gas sensors, or for the passivation of metal surfaces against corrosion [96].

In this work, thin vanadium oxide films are used as spacer layers, with the aim of electronically decouple adsorbed molecules from the metal substrates. In terms of the development of molecular electronics, STM has the drawback to operate only on conductive substrates, where the electronic coupling between an adsorbed molecule and the substrate is strong. For example, in the case of a molecular wire, the charge flowing through a molecular wire would easily dissipate into the conductive substrate.

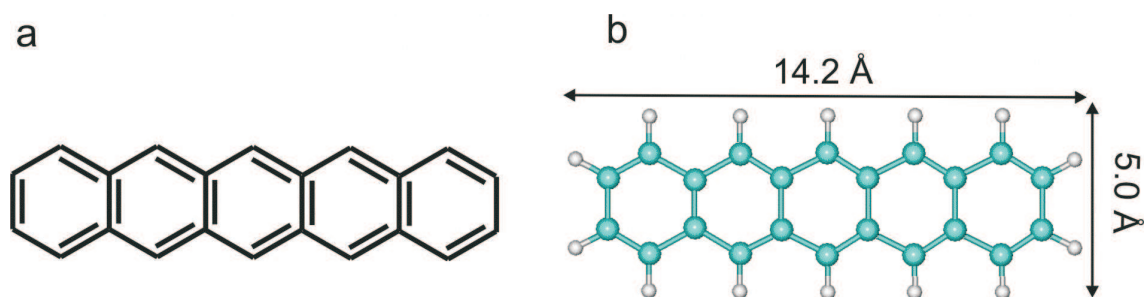
In Chapter 4 the decoupling of the Lander polyaromatic molecular board from the surface has been realized by spacer groups which elevate the board from the metal surface and reduce its electronic interaction with the substrate. However, we have seen (see Chapter 4) that the interaction of the central board with the surface is still relevant, since it is responsible for the molecular adsorption conformations and for induced surface reconstructions [84,90]. Moreover, it has been demonstrated by L. Gross *et al.* [87] that the molecular board contributes decisively to the scattering of the surface state electrons of  $\text{Cu}(111)$ .

A promising new approach, followed in this chapter, is to adsorb molecules on thin insulating films grown on metallic substrates, in order to reduce the interaction between the molecule and the substrate more significantly. Intensive surface science studies have been performed during the last years on thin metal oxides films and on ionic crystal layers in order to understand their surface structure and electronic properties at the microscopic level. The growth of NaCl layers on Al(111) was first studied by STM in the group of P. Varga [97] and atomic resolution was obtained. Furthermore, J. Repp et al. [98] studied NaCl layers on Cu surfaces. In particular, they found that single gold atoms on a thin NaCl film show two differently charged states, stabilized by the large polarizability of the film [99]. Such charged states have been controlled by adding or removing a single electron with the STM tip. Moreover, pentacene molecules have been adsorbed on ultrathin NaCl films. The NaCl film decouples electronically the molecule from the metallic substrate, allowing the imaging of individual molecular orbitals [100]. Ultrathin MgO films, grown on Ag(001), were investigated at low temperature in the group of W.-D. Schneider using scanning tunnelling microscopy and spectroscopy [101]. By determining the electronic and atomic structure of the films layer by layer, they found that even at a film thickness of only three monolayers a band gap of about 6 eV is formed. This corresponds to that of the MgO(001) crystal surface. Moreover, Al<sub>2</sub>O<sub>3</sub> films growth on NiAl(110), have been characterized in the group of H.-J. Freund [102]. The same system has been used in the group of W. Ho to excite the fluorescence of single adsorbed molecules by LT-STM [103].

Because of their electronic and catalytic properties and the large variety of structures and phase transitions they exhibit, growth and surface properties of thin vanadium oxide films have been intensively investigated [96, 104]. Thin vanadium films were grown on Cu<sub>3</sub>Au(100). The growth of thin vanadium films involved three steps. First, a clean and ordered Cu<sub>3</sub>Au(100) surface was prepared. Afterwards, an oxygen layer was formed at the metal surface. Finally, vanadium was deposited and oxidized on the surface.

In this chapter, the adsorption of pentacene molecule on thin vanadium oxide films is investigated. In order to facilitate this investigation, the adsorption of pentacene was first studied on Cu<sub>3</sub>Au(100) and then on the oxidized Cu<sub>3</sub>Au(100).

## 5.1 Pentacene molecule



**Figure 5.1:** (a) Chemical structure and (b) sphere model of pentacene molecule. In the structural model larger spheres represent carbon atoms, while smaller ones represent hydrogen atoms.

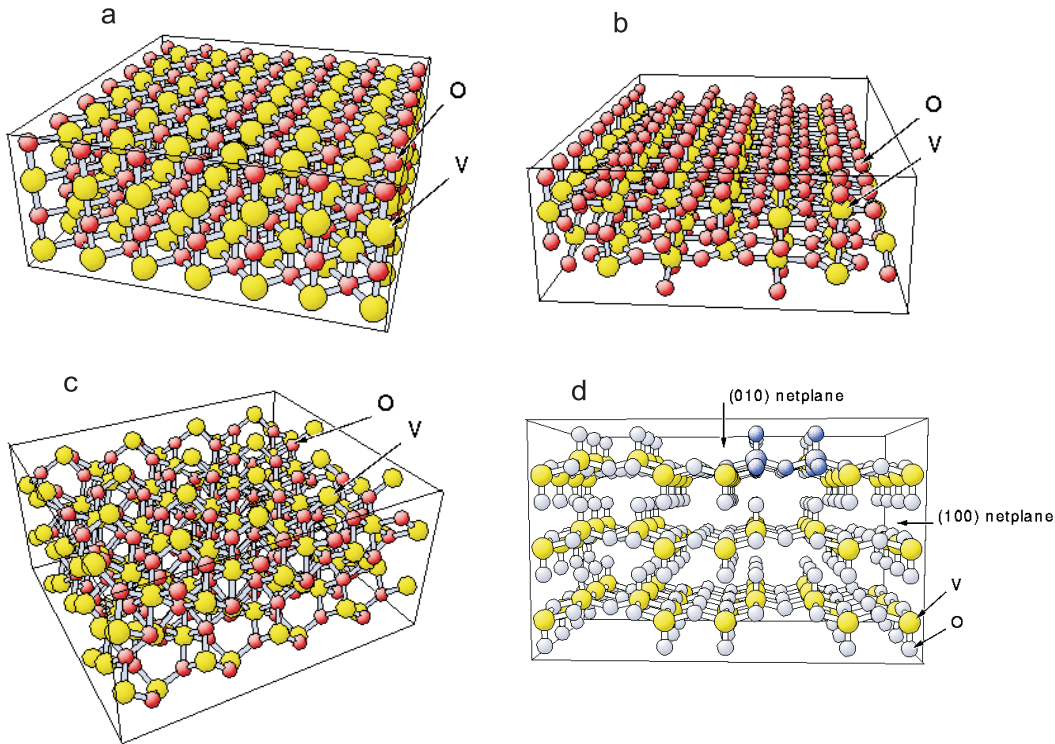
Pentacene is a 14.21 Å long and 5.02 Å wide linear hydrocarbon molecule, consisting of five benzene rings (Fig. 5.1). It is a very intensively studied molecule due to its promising bulk properties as an organic semiconductor [105–107]. Pentacene thin film transistors with room temperature mobilities as high as 1,5 cm<sup>2</sup>/V s have already been fabricated [108]. Furthermore, the unit cell of the crystal structure is composed of two molecules which are not parallel to each other, but are packed in a herringbone structure [109]. Since transport occurs mainly through the molecular  $\pi$ -systems, the conductivity of pentacene crystal depends strongly on the crystallographic directions [107, 110].

On metal surfaces, the bonding of the pentacene molecule to the surface is expected to be facilitated primarily through the overlapping of the delocalized  $\pi$ -electrons systems to the surface. Thus pentacene molecules in the submonolayer regime are expected to adsorb planar, excluding complicated molecular conformations. STM studies of pentacene adsorption [111–114] and manipulation [114] in the sub-monolayer regime on copper surfaces indeed show a planar adsorption geometry. However, it has recently been shown that the interaction strength of the pentacene  $\pi$  system with the substrate is controlled by the local density of states of the substrate surface at or near the Fermi energy [115]. Especially in the case of surfaces with a low electron density near the Fermi energy, the  $\pi$ - $\pi$  interactions between molecules are stronger than the interactions with the substrate. Thus the molecules stand up on the surface. As the LDOS is increased, the molecule-substrate interactions become stronger and the molecules lie planar on the surface.

An important work in the way of molecular decoupling of pentacene molecule, has been done by J. Repp *et al.* [100]. The authors were able to image the unperturbed HOMO

and LUMO of pentacene by decoupling the molecule from the substrate using insulating thin NaCl films.

## 5.2 Preparation of thin vanadium oxide films on $\text{Cu}_3\text{Au}(100)$



**Figure 5.2:** Calculated structures of vanadium oxide bulk phases from reference number [116]. (a) VO structure ((001) orientation). (b) Monoclinic (rutile) structure of  $\text{VO}_2$  ((011) orientation). (c) Rhombohedral (corundum) structure of  $\text{V}_2\text{O}_3$  ((111) orientation). (d)  $\text{V}_2\text{O}_5$  structure ((010) orientation).

The vanadium-oxygen system exhibits a multitude of discrete bulk phases whose stoichiometry influences their chemical and physical properties. This diversity in properties makes the vanadium-oxygen system highly interesting for solid-state physics. The main technological interest in these oxides comes from their particular catalytic properties [96]. In the main phases, vanadium exhibits the different oxidation states VO ( $\text{V}^{2+}$ ),  $\text{VO}_2$  ( $\text{V}^{4+}$ ),  $\text{V}_2\text{O}_3$  ( $\text{V}^{3+}$ ), and  $\text{V}_2\text{O}_5$  ( $\text{V}^{5+}$ ). The structures and the electronic properties of the main vanadium oxide phases are summarized in the following.

- VO has a NaCl-like cubic structure and a metallic character [96]. The structure of VO is shown in Fig. 5.2(a)<sup>1</sup>.

<sup>1</sup>The pictures in Fig. 5.2 are taken from the "Gallery of BALSAC" by K. Hermann of the Theory De-

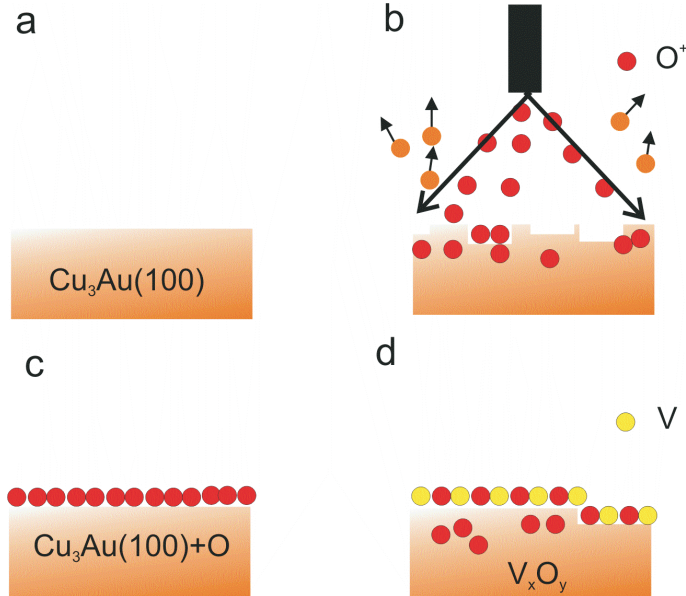
- VO<sub>2</sub> has a metal-semiconductor transition at 341 K. Above this temperature it forms a tetragonal rutile structure and is metallic, while below it has a semiconductor character in a monoclinic structure [96]. The rutile structure is shown in Fig. 5.2(b).
- V<sub>2</sub>O<sub>3</sub> shows a metal-insulator transition at 150 K. Above this temperature it occurs in a corundum structure (Fig. 5.2(c)), while below 150 K is monoclinic [96].
- V<sub>2</sub>O<sub>5</sub> (supported on TiO<sub>2</sub>) is a well known catalyst for the reduction of nitrogen oxides and for the oxidation of hydrocarbons. V<sub>2</sub>O<sub>5</sub> forms an orthorhombic, layered structure (Fig. 5.2(d)) and is an insulator. The building blocks of a vanadium pentoxide layers are distorted trigonal bipyramids formed by a vanadium atom surrounded by five oxygen atoms. The apical oxygen atom of the bipyramid, called vanadyl oxygen in the literature, forms a double bond to the vanadium atom. Adjacent bipyramids share edges and form zigzag chains in the [001] direction. The chains are linked via common corner oxygen atoms. The resulting layers are stacked along the [010] direction [117].

The fabrication of perfect vanadium oxide crystals is extremely difficult [96]. However, uncontaminated surfaces can be obtained more readily by preparing thin metal oxide films by means of epitaxial methods. The growth of thin vanadium oxide layers on single-crystal metal surfaces has many advantages. For example, by controlling the oxide thickness, the oxygen quantity during the oxidation, or the substrate temperature and structure, new oxide phases of varying stoichiometry and structure can be formed that exhibit novel, non-bulk-like properties [104]. Thin vanadium oxide films were obtained by evaporating vanadium on the Au(111) and subsequently oxidizing it in the group of G.A. Somorjai [118]. It was found that metallic vanadium deposited on Au(111) is unstable because vanadium and gold interact readily: vanadium diffuses irreversibly into the bulk of the gold crystal forming an inter-metallic compound. Kishi et al. [119] have prepared vanadium oxide films on Cu(100) by first exposing the surface to oxygen followed by vanadium deposition in a O<sub>2</sub> atmosphere. However, the obtained vanadium films were rough and highly defective.

A different approach, developed by H. Niehus and co-workers [120], has been fol-

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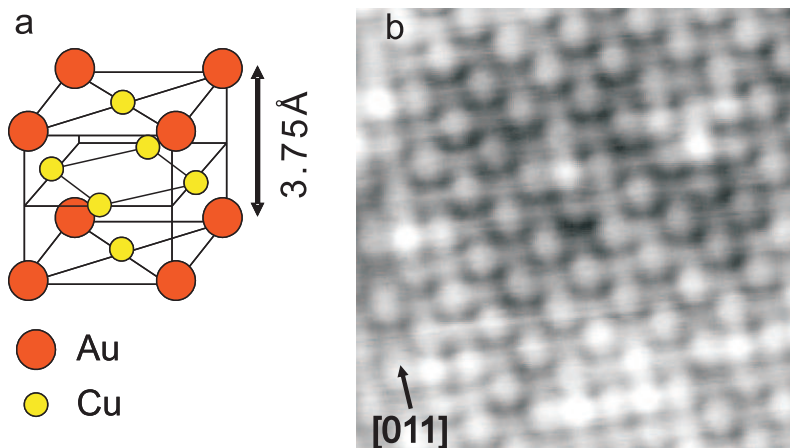
**Figure 5.3:** Preparation of thin vanadium oxide films. (a) The substrate is cleaned in UHV by cycles of Ne sputtering and annealing. (b) Oxygen is implanted into the surface by sputtering. (c) The formation of an ordered oxygen layer is obtained by annealing the surface. (d) Vanadium is deposited and then the surface is annealed.

lowed in this work. The steps for the growth of vanadium oxide films are schematically presented in Fig. 5.3. A  $\text{Cu}_3\text{Au}(100)$  substrate is used. After the preparation of a clean  $\text{Cu}_3\text{Au}(100)$  surface (a), oxygen atoms are implanted into the surface using an ion sputter gun (b). The subsurface oxygen, accumulated in this way, serves as an oxidation medium for the growing oxide film. The method of implantation is used because  $\text{Cu}_3\text{Au}(100)$  is rather inert to gas exposure, behaving more like Au than Cu, and oxygen is not directly adsorbed from the gas phase [121, 122]. After the implantation, the sample is annealed to obtain an ordered and flat oxide topmost layer (c). This oxide layer prevents alloy formation when vanadium is deposited on the metallic surface. In the final preparation step, vanadium is deposited and the surface is annealed in an oxygen atmosphere (d). Using this method, H. Niehus and coworkers have obtained vanadium oxide films of various stoichiometry and structure which maintain the bulk structure at the surface. This has been confirmed by room temperature STM studies [120].

Another important work on the growth of thin vanadium oxides films has been performed in the group of F.P. Netzer [104, 123–127]. The authors have grown very well ordered thin vanadium oxide films on Pd(111) and Rh(111) with various stoichiometry and with structures very similar to those of the bulk. Notably, the structure of ultrathin oxide films differs from those of the bulk phases, because the proximity of the metal substrate perturbs the oxide electronic structure.

In our case, the formation of ultrathin films is of particular interest, because films in the sub-monolayer regime (very low coverage of vanadium) facilitate the experimental measurements. In fact, oxide free regions guarantee the possibility of reforming the tip by gently crashing it into the metallic substrate. Moreover, islands of thin vanadium oxide films grown on a metal could be used to explore the contact at the atomic scale of a single molecule (adsorbed on the thin oxide films and isolated from the metallic surface) with a metallic electrode (like a surface step edge).

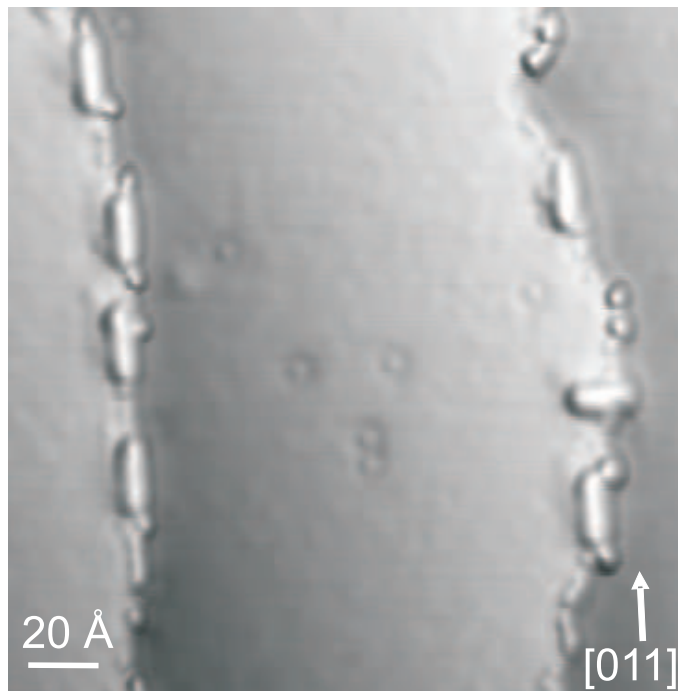
### 5.3 $\text{Cu}_3\text{Au}(100)$ and adsorption of Pentacene



**Figure 5.4:** (a)  $\text{Cu}_3\text{Au}(100)$  crystallographic structure. (b) Atomically resolved STM image of  $\text{Cu}_3\text{Au}(100)$ . STM parameters:  $U = 0.01$  V,  $I = 3$  nA; Image dimension  $= (40 \times 40)$  Å<sup>2</sup>.

The  $\text{Cu}_3\text{Au}(100)$  sample was prepared by several cycles of 2 keV  $\text{Ne}^+$  sputtering, followed by annealing at 810 K. Thereafter the sample was kept at 540 K for 10 hours to allow bulk and surface ordering. The  $\text{Cu}_3\text{Au}$  alloy has an order-disorder transition phase at a bulk temperature of  $T_c = 660$  K [128]. Above this temperature the crystal has a fcc unit cell where each lattice site is occupied randomly by Cu or Au atoms with probability of 75% and 25%, respectively. The crystallographic structure for the ordered phase of  $\text{Cu}_3\text{Au}(100)$  (known as L12 structure) is shown in Fig. 5.4(a). It can be described as a fcc lattice with gold atoms at the cubic corners and copper atoms at the center of the cubic faces. In a (100) bulk truncation, the outermost surface layer might be terminated by a pure Cu or a mixed Cu-Au composition. In agreement with the work of H. Niehus [120], we found that the composition of the first layer of the  $\text{Cu}_3\text{Au}(100)$  surface consists of the 50%Au-50%Cu plane. In such a surface, every Cu atoms finds itself surrounded by

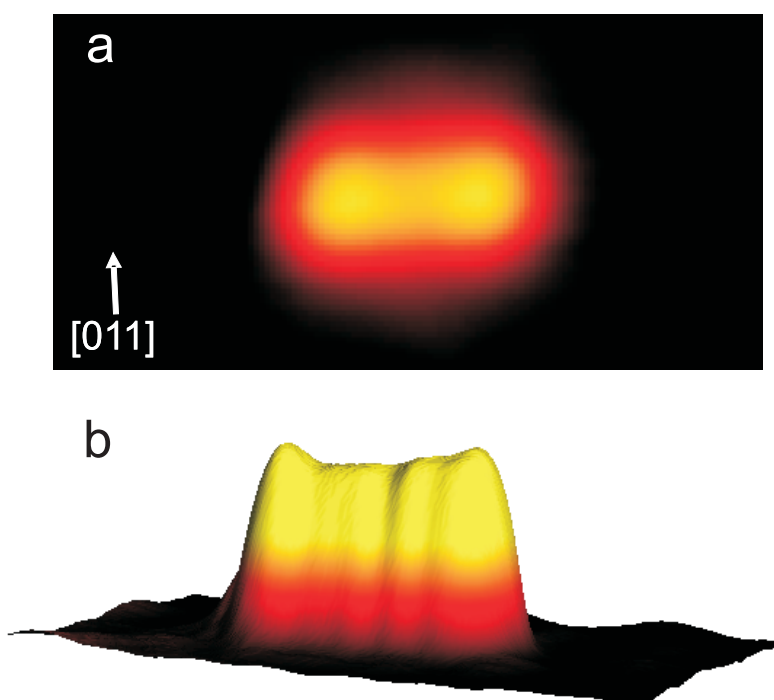
Au atoms and viceversa. Fig. 5.4(b) shows an atomic resolution STM image of a clean  $\text{Cu}_3\text{Au}(100)$  surface at about 7 K. In the image it is possible to distinguish between the different atomic species at the surface, in that one species appears brighter than the other in the image. However, the assignment to the specific atomic species is not possible based on STM imaging measurements alone.



**Figure 5.5:** Overview STM image of pentacene molecules on  $\text{Cu}_3\text{Au}(100)$  for a sample temperature of 340 K during deposition: the molecules are adsorbed on step edges. STM parameters:  $U = 1.3$  V,  $I = 0.3$  nA.

Pentacene molecules were evaporated on the  $\text{Cu}_3\text{Au}(100)$  surface from a home built Knudsen cell, described in Chapter 3, at a temperature of about 440 K. The deposition rate was monitored via a quartz crystal microbalance. The coverage was in the order of  $10^{-3}$  monolayer (ML), as checked by STM, where one monolayer is defined as the amount of molecules which cover the first substrate layer completely. The  $\text{Cu}_3\text{Au}(100)$  sample was kept at 340 K during the molecules deposition. After deposition, pentacene molecules are found to be preferentially adsorbed at step edges and rarely at surface defects on terraces, indicating that the molecules diffuse on the  $\text{Cu}_3\text{Au}(100)$  surface at room temperature. In Fig. 5.5, an overview STM image is shown. Seven pentacene molecules are adsorbed on step edges of  $\text{Cu}_3\text{Au}(100)$ , six of them are oriented along [011], while





**Figure 5.6:** (a) Single pentacene molecule on a  $\text{Cu}_3\text{Au}(100)$  terrace. STM parameters:  $U = -0.5$  V,  $I = 0.5$  nA,  $T = 7$  K; Image dimension =  $(50 \times 25)$  Å<sup>2</sup>. (b) Three dimensional representation of a pentacene molecule on  $\text{Cu}_3\text{Au}(100)$  imaged with submolecular resolution by means of a modified tip. STM parameters:  $U = 2$  V,  $I = 0.2$  nA,  $T = 7$  K.

one lies parallel to the  $[0\bar{1}1]$  direction.

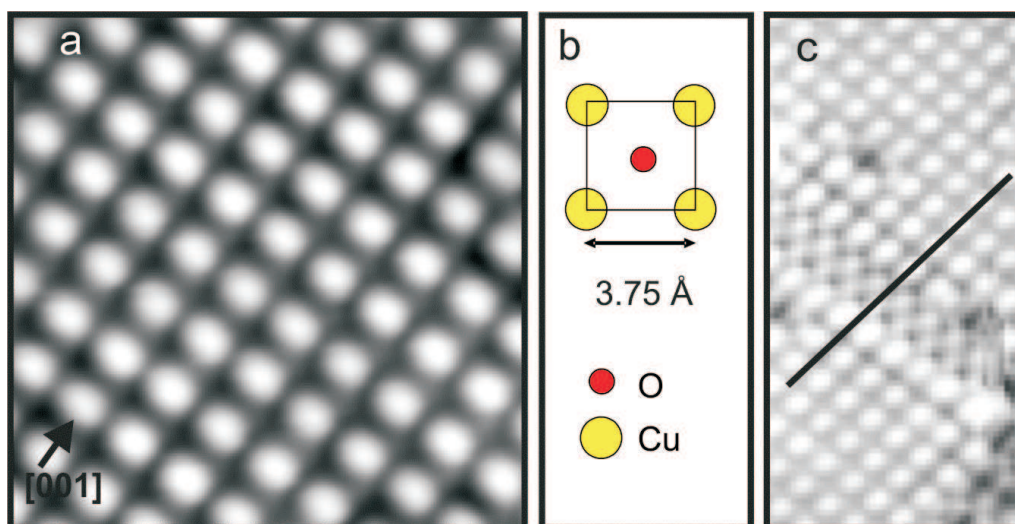
In general, at the step edges, the molecules lie on the upper plane and are oriented parallel to the step edges. Rarely, molecules are found perpendicular to a step edge half on the upper terrace and half on the lower terrace. The preference of the molecules to adsorb on step edges arises from the interaction of induced molecular dipoles with intrinsic dipoles present at steps of metal surfaces due to *Smoluchowski* effect of electron charge smoothing [129].

When molecules are adsorbed on terrace defects they are oriented either parallel to the  $[011]$  direction or perpendicular to it (with equal probability). Single pentacene molecules appear in the STM images as rod-like protrusions with brighter lobes at the ends (Fig. 5.5 and 5.6(a)). This shape remains unchanged for the entire bias range investigated (from  $-2$  V to  $+2$  V). The distance between the two lobes is  $(9.3 \pm 0.6)$  Å which matches the distance between the two outer phenyl rings of  $9.9$  Å [130], confirming that the molecules adsorb in a planar configuration on the surface. The apparent molecular height amounts to

1.2 Å for positive sample voltages, while for negative voltages it linearly increases from 0.9 Å to 1.2 Å. Notice that the appearance of pentacene on Cu<sub>3</sub>Au(100) resembles the one observed on other metal surfaces, in which the molecule was observed in a planar geometry [111, 114].

Submolecular resolution (as shown in Fig. 5.6(b)) has been obtained with modified tips, probably after a molecule or part thereof has been picked up to the tip.

#### 5.4 Oxygen on Cu<sub>3</sub>Au(100) and adsorption of Pentacene

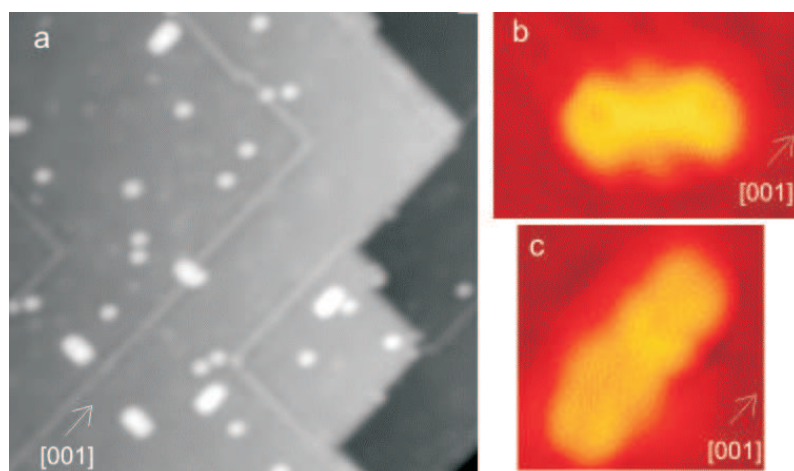


**Figure 5.7:** (a) Atomic resolution image of the Cu<sub>3</sub>Au(100)+O; STM parameters:  $U = +0.06$  V,  $I = 1.5$  nA,  $T = 7$  K; Image dimensions =  $(30 \times 30)$  Å<sup>2</sup>. (b) Schematic of the Cu-O  $c(2 \times 2)$  structure on the topmost layer. (c) Atomic resolved image of an antiphase domain boundary. Notice the phase shift along the line crossing the domain boundary. STM parameter:  $U = +0.06$  V,  $I = 1.5$  nA,  $T = 7$  K; Image dimensions =  $(60 \times 30)$  Å<sup>2</sup>.

Oxygen was implanted into the Cu<sub>3</sub>Au(100) surface by sputtering with 1 keV O ions ( $4 \times 10^{-5}$  mbar O<sub>2</sub>, 4 mA emission current, sample current density of about  $2 \mu\text{A}/\text{cm}^2$ ) for 10 min with a normal ion sputter gun (Varian). Thereafter, the sample was annealed at 800 K for 4 minutes in order to smooth the surface. The surface prepared in this way is expected to have a topmost layer consisting of a Cu-O structure, while having additional oxygen stored in the subsurface region which serves as an oxygen reservoir [120]. Compared to the preparation of Niehus [121, 122], a lower subsurface oxygen concentration is expected, due to the higher annealing temperature (800 K in this work and 650 K by H. Niehus).

STM measurements show that the prepared surface is ordered and flat. Steps run along the [001] or [0 $\bar{1}$ 1] surface directions and are very straight. An atomic resolution image is presented in Fig. 5.7(a). The image reveals rows of bright protrusions running along the [001] direction separated by a distance of 3.7 Å. The atomic corrugation is in this case five times greater than the one observed for the bare Cu<sub>3</sub>Au(100) surface. It has been found by H. Niehus and collaborators [121, 122], that the topmost layer of the oxygen saturated Cu<sub>3</sub>Au(100) surface consists of a Cu-O structure. The adsorption of oxygen induces a rearrangement of the alloy surface driven by the greater affinity of O for Cu than for Au. Therefore gold atoms segregate from the first surface layer and a c(2×2) Cu-O structure is formed (see Fig. 5.7(b)). The bright protrusions in the image in Fig. 5.7(a) are attributed to the positions of the Cu atoms, while, similar to the case of oxygen adsorption on pure copper surfaces, oxygen itself is not visible in the STM images [131, 132]. Because of the equal height of all the Cu atoms in the STM images, the proposed position for the oxygen atoms is the fourfold hollow site in the center of the (100) unit cell of the copper atoms (see 5.7(b)). The measured corrugation enhancement is attributed to the influence of oxygen on the local electronic distribution. It turns out that domains, having the positions of copper atoms shifted by half a lattice constant, are formed for Cu<sub>3</sub>Au(100)+O. The domains boundaries run straight and appear as zig-zag chains slightly underneath the Cu<sub>3</sub>Au(100)+ O (see Fig. 5.7(c)) for positive sample voltages, while for negative sample voltages they are imaged as ridges. In Fig. 5.7(c) it is possible to see a domain boundary for a positive sample voltage where the line drawn on the STM image indicates the atomic shift between the two domains.

Pentacene molecules were deposited onto the Cu<sub>3</sub>Au(100)+O surface using the same procedure as described in Sec. 5.3. After deposition, the molecules were found on terraces (see Fig. 5.8(a)), and not at the step edges. This finding is an indication that surface diffusion is hindered on the Cu<sub>3</sub>Au(100)+O surface at room temperature. The lateral dimension of a single pentacene on Cu<sub>3</sub>Au(100)+O measured from half maximum to half maximum is about 20 Å. In the sample voltage range of ±1 V, the apparent molecular height is voltage dependent: for negative polarities it amounts to 1.9 Å, while for positive voltages the apparent height slowly decreases until at U = +1 V it reaches a value of 1.1 Å. In the favorite adsorption geometry, the orientation of the molecules is either parallel to



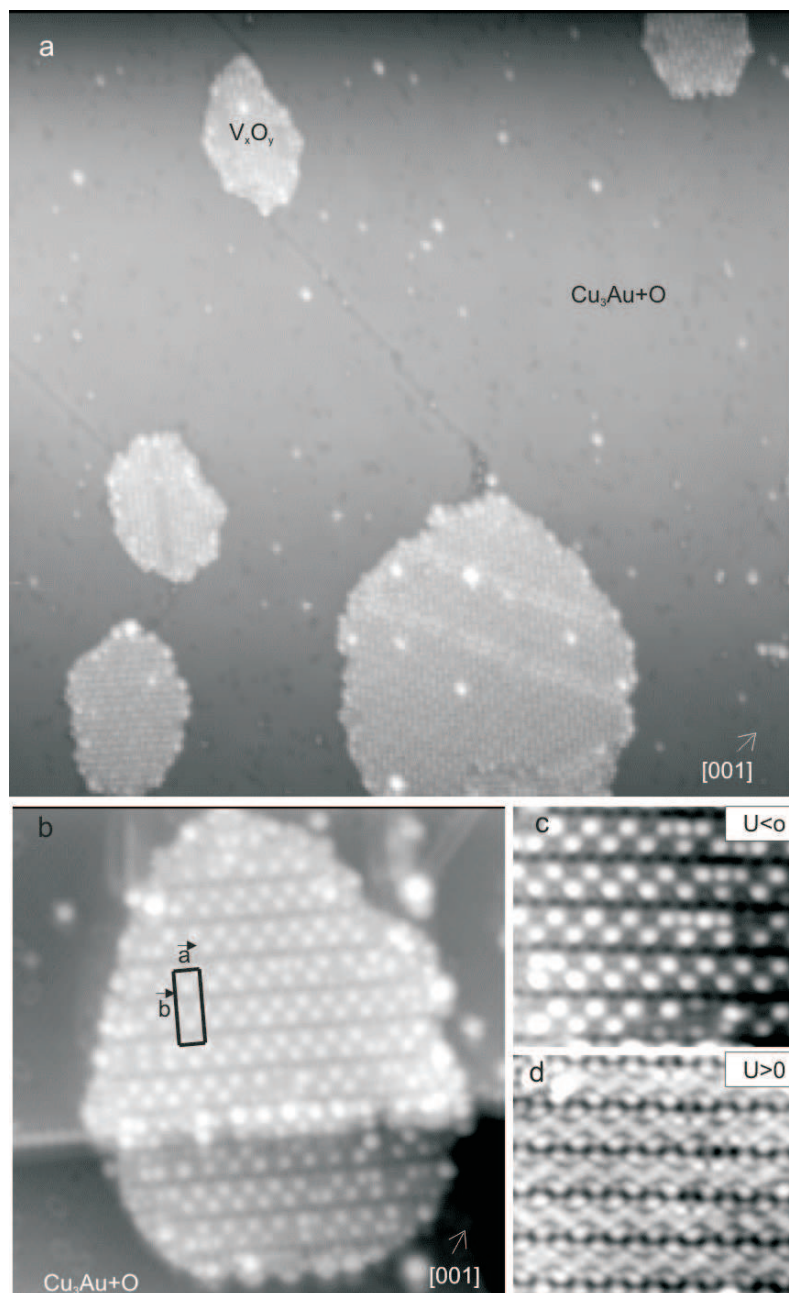
**Figure 5.8:** (a) Overview image of pentacene adsorbed on  $\text{Cu}_3\text{Au}(100)+\text{O}$ . STM parameters:  $T = 7 \text{ K}$ ,  $U = -0.8 \text{ V}$ ,  $I = 0.2 \text{ nA}$ . Image dimension  $= (350 \times 350) \text{ \AA}^2$ . (b) Single pentacene molecule oriented  $45^\circ$  with respect to the  $[001]$  direction. STM parameters:  $U = +0.3 \text{ V}$ ,  $I = 0.4 \text{ nA}$ ,  $= (30 \times 20) \text{ \AA}^2$ ; (c) Single pentacene molecule oriented parallel to the  $[001]$  direction. STM parameters:  $U = +0.5 \text{ V}$ ,  $I = 1 \text{ nA}$ ; Image dimensions  $= (20 \times 20) \text{ \AA}^2$ .

the  $[001]$  direction or perpendicular to it. Only 1/5 of the molecules are found at  $\pm 45^\circ$  with respect to the  $[001]$  direction. The two orientations of the molecules correspond to two different adsorption geometries on the surface. In the first case the molecule is adsorbed on a row of atoms of the same species, which corresponds to a lower adsorption energy, while in the second case atoms of different species alternate. This difference in the adsorption geometry is directly transferred to the appearance of single molecules which differs between the case of adsorption parallel/perpendicular to the  $[001]$  direction and in the case of adsorption at  $\pm 45^\circ$  with respect to the  $[001]$  direction. In Fig. 5.8(b),(c) one can see how the intermolecular modulation in the STM images differs for the two molecular orientations.

## 5.5 Thin $V_xO_y$ films and adsorption of Pentacene

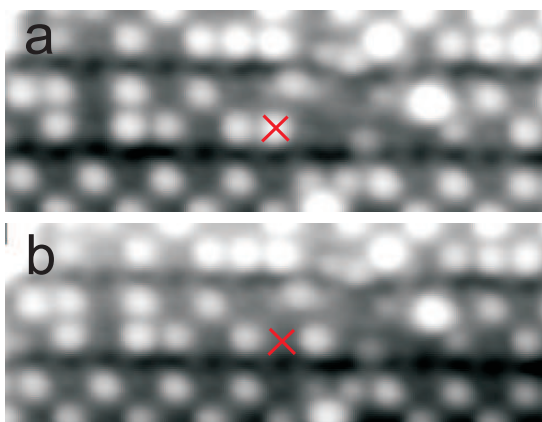
The preparation of vanadium oxide films is rather complex because it is influenced by several growth parameters, i.e. (i) the amount of oxygen already present at the surface (which depends on the oxygen implantation time, on the annealing temperature and the annealing time), (ii) the amount of vanadium evaporated and (iii) the temperature in the final annealing step. In this study, the  $Cu_3Au(100)+O$  surface was always prepared in the same way, so that one can consider the amount of oxygen stored in the sample to be constant and lower than in the work of H. Niehus et al. (as discussed in Sec. 5.4). In contrast, the dosage of vanadium deposited and the temperature of final annealing were varied. In particular, the amount of vanadium was varied between 1/12 and 1 monolayer equivalent (MLE), where one monolayer is defined with respect to the  $Cu_3Au(100)$  atomic surface density. The very low coverages were used in order to form vanadium oxides in the sub-monolayer regime. The final temperature of annealing was varied in the range between 600 K and 800 K. Once a smooth  $Cu_3Au(100)+O$  was prepared, vanadium was evaporated onto the substrate at room temperature, by using an electron beam evaporator (see Chapter 3), the process being monitored via a quartz crystal microbalance. Thereafter, the sample was annealed at diverse temperatures for 3 min in an oxygen atmosphere ( $1.4 \times 10^{-8}$  mbar of  $O_2$ ), cooled down, and transferred into the STM.

In a first preparation, about 1/12 MLE of vanadium was deposited onto the substrate and then the sample was annealed at 700 K for 3 minutes. The results are shown in Fig. 5.9. Islands of vanadium oxides were formed on the bare  $Cu_3Au(100)+O$  substrate, which can be recognized in atomic resolved images. The islands exhibit zig-zag stripes which run  $\pm 45^\circ$  with respect to the [001] direction and extend to lengths of about 350 Å. The apparent height of the vanadium oxide islands with respect to the  $Cu_3Au(100)+O$  surface varies between  $-2.2$  Å and  $+4.4$  Å at fixed tunneling conditions, which indicates that islands of different thickness are formed. In Fig. 5.9(b) an atomically resolved image of the oxide film is shown and the lattice vectors  $\vec{a}, \vec{b}$  are indicated. Their moduli are  $|\vec{a}|=10.6$  Å and  $|\vec{b}|=26.0$  Å (accuracy  $\pm 0.3$  Å) which correspond to a  $(2\sqrt{2} \times 5\sqrt{2})R45^\circ$  superstructure with respect to the  $c(2 \times 2)$  structure of  $Cu_3Au(100)$ . As shown in Fig. 5.9(c), a strong voltage dependence is observed in the atomic resolution images. The obtained oxide has a large unit cell and its structure differs from those of



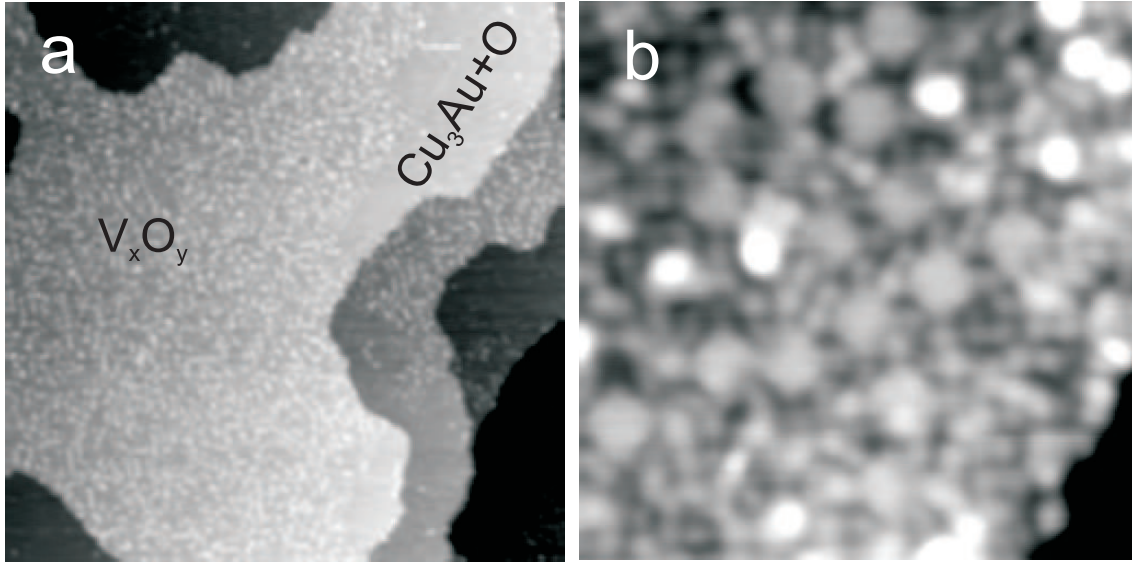
**Figure 5.9:** Thin vanadium oxide films formed after depositing 1/12 MLE of vanadium and subsequent annealing at 700 K for 3 minutes. (a) Overview image with vanadium oxide islands on  $\text{Cu}_3\text{Au}(100)+\text{O}$ . (b) Zoom on an island where the oxide structure is visible and where the lattice vectors are indicated. (c) Voltage dependence of the observed structure. STM parameters:  $T = 6.5$  K; (a)  $U = 1.5$  V,  $I = 0.3$  nA; Image dimension =  $(675 \times 675) \text{ \AA}^2$ ; (b)  $U = -1.7$  V,  $I = 0.1$  nA; Image dimension =  $(190 \times 190) \text{ \AA}^2$ ; (c) (top)  $U = -1.7$  V, (bottom)  $U = 0.7$  V;  $I = 0.1$  nA; Images dimensions =  $(80 \times 70) \text{ \AA}^2$ .

vanadium oxide bulk phases, as expected for very thin oxide films (few monolayers). The proximity of the metal substrate perturbs in fact the oxide electronic structure and influences the growth mechanism, as observed in References [104, 123, 124]. Without theoretical calculations it is not possible to assign the species observed in the STM image to vanadium or oxygen atoms. Interestingly, we found that it is possible to induce local modifications on the position of the surface bright atoms. This was realized by approaching the STM tip towards the surface about  $2 \text{ \AA}$  with respect to the normal scanning tip position (where the tip is about  $4$  to  $5 \text{ \AA}$  above the surface) and applying a voltage of  $2 \text{ V}$ , as shown in Fig. 5.10.



**Figure 5.10:** Manipulation of atoms of a vanadium oxide film. (a) STM image before the manipulation. The cross indicated the position of the tip during the application of a voltage pulse (tip height about  $4 \text{ \AA}$ ,  $U = 2 \text{ V}$  for 2 seconds). (b) STM image after the manipulation. One can see that the atom under the tip is moved to the right. STM parameters:  $T = 7 \text{ K}$ ; (a)  $U = -1.6 \text{ V}$ ,  $I = 0.1 \text{ nA}$ ; Image dimensions =  $(80 \times 30) \text{ \AA}^2$ .

The dependence of the oxide growth on the amount of vanadium deposited has been investigated. In particular, amounts of vanadium between  $1/12$  MLE and one MLE were evaporated on the  $\text{Cu}_3\text{Au}(100)+\text{O}$  surface prepared as in Sec. 5.4 and then annealed at  $700 \text{ K}$  for  $3 \text{ min}$ . It turned out that by increasing the deposited amount of vanadium, the films become more and more rough and highly defective. An example is shown in Fig. 5.11(a), where  $1/3$  MLE was deposited. In this case it is possible to recognize an ordered structure only for small oxide regions, as shown in Fig. 5.11(b). Even after annealing the surface at higher temperatures (up to  $800 \text{ K}$ ) and for a longer time (up to  $15 \text{ min}$ ) the films remain disordered. These results indicate that the crucial parameter for the the growth of ordered thin vanadium oxide films is the balance between the oxygen concentration already present at the surface and the amount of vanadium deposited. When

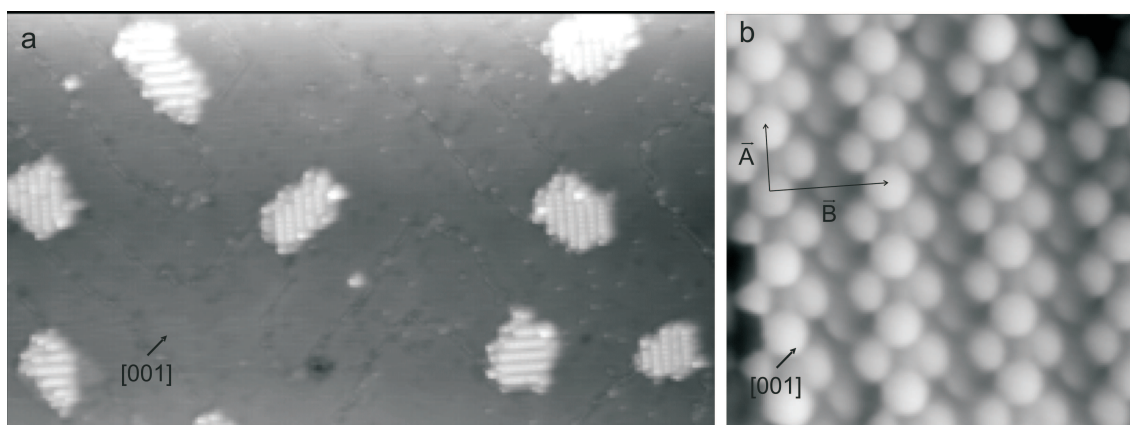


**Figure 5.11:** After depositing 1/3 MLE of vanadium and subsequent annealing at 700 K for 3 minutes, disordered oxide films are formed. (a) Overview image with vanadium oxide islands on  $\text{Cu}_3\text{Au}(100)+\text{O}$ . (b) Detail of an oxide island with an ordered structure of the observed structure. STM parameters:  $T = 7 \text{ K}$ ; (a)  $U = -1.3 \text{ V}$ ,  $I = 0.1 \text{ nA}$ ; Image dimension =  $(780 \times 780) \text{ \AA}^2$ ; (b)  $I = 1 \text{ nA}$ ; Image dimension =  $(98 \times 98) \text{ \AA}^2$ .

the amount of vanadium exceeds a critical value (which depends on the oxygen amount on the surface) it can no longer form ordered and stable oxide structures. In this study, surfaces with low oxygen content were used. Thus, to obtain ordered films the amount of vanadium had to be very small.

Once the right balance of oxygen and vanadium is deposited on the surface (as in the case of depositing 1/12 MLE), changes in the final annealing temperature influence the structure of the oxides films formed. The results obtained after depositing 1/12 of a MLE and annealing the surface at 600 K (for 3 min in  $1.4 \times 10^{-8}$  mbar of  $\text{O}_2$  atmosphere) are shown in Fig. 5.12(a). Ordered islands of vanadium oxides are formed. These islands are small and have very similar dimensions (on average they are 80  $\text{\AA}$  long and 50  $\text{\AA}$  wide), while they can have different thicknesses (their apparent height is either at the level of the surface or above 4  $\text{\AA}$ ). The atomically resolved image in Fig. 5.12(b) reveals the atomic structure of this new vanadium oxide phase which corresponds to a  $(\sqrt{2} \times 2\sqrt{2})\text{R}45^\circ$  superstructure with respect to the  $c(2 \times 2)$  structure of  $\text{Cu}_3\text{Au}(100)$ . The lattice vectors  $\vec{A}$  and  $\vec{B}$  are indicated in the image. In this case the structure of the vanadium oxide islands remains unchanged by varying the voltage in the range between +2 V and -2 V. The





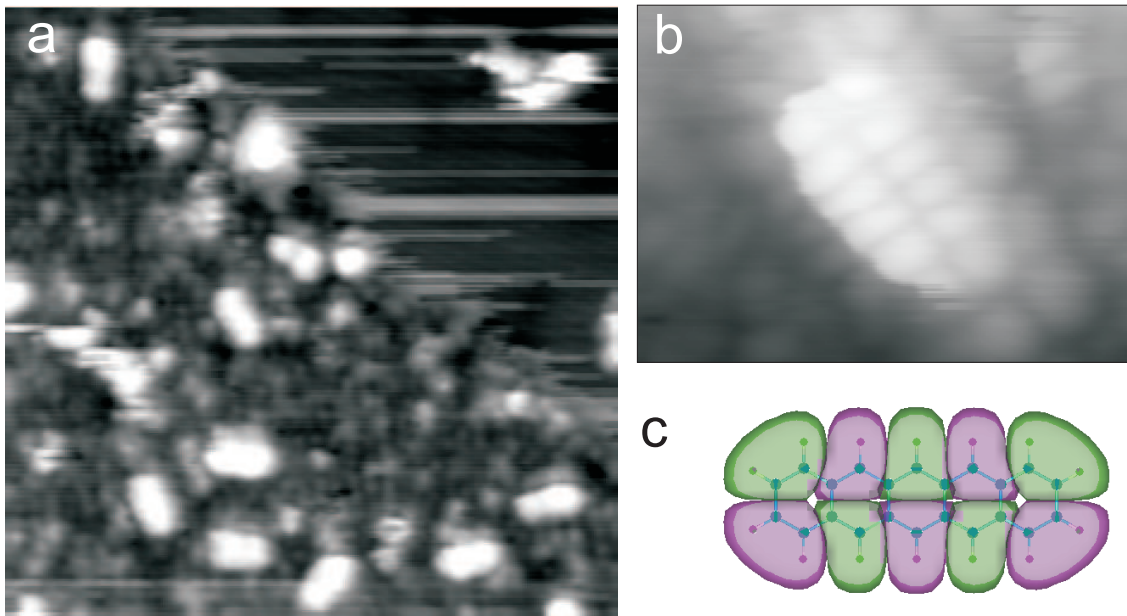
**Figure 5.12:** Thin vanadium oxide films formed after depositing 1/12 MLE of vanadium and subsequent annealing at 600 K for 3 minutes. (a) Overview image with vanadium oxide islands on  $Cu_3Au(100)+O$ . (b) Zoom out of an island where the oxide structure is visible and the lattice vectors are indicated. STM parameters:  $T = 6$  K; (a)  $U = 1.6$  V,  $I = 0.1$  nA; Image dimension  $= (675 \times 675) \text{ \AA}^2$ ; (b)  $U = 0.2$  V,  $I = 1$  nA; Image dimension  $= (35 \times 35) \text{ \AA}^2$ .

obtained structure does not resemble a surface plane of any of the known bulk vanadium oxide phases.

Pentacene molecules were deposited on a disordered vanadium oxide phase (obtained after evaporating 1/3 MLE vanadium and annealing at 700 K and shown in Fig. 5.11) with the substrate at about 50 K during deposition in order to facilitate molecular adsorption. It turned out that pentacene molecules do adsorb on vanadium oxide.

A typical overview image is shown in Fig. 5.13(a). The molecules are found to be oriented in random directions. They often rotate under scanning conditions, indicating a weak interaction with the oxide film. Because of the roughness and non-stability of the film, it is impossible to give precise values of the molecular dimensions. However, it was possible to image single molecules with an internal structure. In Fig. 5.13(b) an image of an isolated molecule is shown. The molecular appearance is very similar to the electron density of the HOMO, which is presented in Fig. 5.13(c) for comparison.

This result can be explained by the electronic decoupling from the metallic substrate caused by the oxide film, which preserves the electronic properties of the molecule, allowing the imaging of the molecular LDOS. Probably, the oxide film exhibits a gap in the negative voltages polarities investigated and thus its LDOS does not mix with the molecular states. The situation is different when molecules are adsorbed on bare metal surfaces,



**Figure 5.13:** Adsorption of pentacene on vanadium oxide. (a) Overview image where pentacene molecules are adsorbed on vanadium oxides. (b) Single pentacene molecule on vanadium oxide. (c) HOMO of pentacene molecule in the gas phase cut in the molecular plane (calculated with the program for molecular modeling, Hyperchem7). STM parameters: = 6 K; (a)  $U = 0.5$  V,  $I = 0.1$  nA; Image dimension  $= (195 \times 195) \text{ \AA}^2$ ; (b)  $U = -1$  V,  $I = 0.1$  nA; Image dimension  $= (35 \times 25) \text{ \AA}^2$

whose LDOS influences the one of the molecules, as it has been explained in Chapter 2.

## 5.6 Conclusion

The study of the formation of thin vanadium oxides films on  $\text{Cu}_3\text{Au}(100)$  has been presented. First, the bare metallic  $\text{Cu}_3\text{Au}(100)$  surface has been studied by STM. Then oxygen has been implanted into the surface in order to act as a reservoir for the oxidation of vanadium and the surface has been annealed to form an ordered oxygen layer on the substrate to avoid alloy formation when vanadium is adsorbed. Different preparations of the vanadium oxide films have been performed and for each preparation atomically resolved images have been obtained allowing the investigation of the oxide structure. The formation of ordered vanadium oxides phases depends on the balance between the amount of vanadium evaporated and the concentration of oxygen already present at the surface. If the amount of vanadium exceeds a critical value, disordered oxide phases are formed. Regarding the oxide formation, it turned out that the obtained oxides structures differ from

those of the bulk phases, due to the proximity of the metal substrate which perturbs the oxide electronic structure and influences the growth mechanism. Thus, new non bulk-like structures with complicated and large unit cells are formed. Moreover, the oxide structures can present a strong voltage dependence. Therefore it was not possible on the basis of STM studies, which probe the electronic structure of the oxide surface rather than the atomic arrangement, to determine the stoichiometry and exact structures of the oxides formed.

Thin vanadium oxides films have been used to decouple pentacene molecule from the metal surface. In order to facilitate the study of the adsorption of pentacene on thin vanadium oxide films, the molecular adsorption was first investigated on the  $\text{Cu}_3\text{Au}(100)$  surface, thereafter on the  $\text{Cu}_3\text{Au}(100)+\text{O}$  surface and finally on thin vanadium oxide films. It was found that the molecular appearance changes in each case, demonstrating the effect of the variation of molecule-substrate interactions. In particular, when pentacene is adsorbed on thin vanadium oxide films, its appearance resembles the electron density of the HOMO molecular orbital, which is an indication of the electronic decoupling from the metal surface.

