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Ultra thin V_2O_3 films grown on oxidized Si(1 1 1)

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ABSTRACT

The growth of V_2O_3(0 0 0 1) has been investigated by scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). Direct evaporation of vanadium onto the Si(1 1 1)-7 × 7 substrate gives rise to massive surface intermixing and consequent silicide formation. In order to obtain the vanadium oxide with good quality, the 7 × 7 surface was initially partially oxidized which leads to a smooth oxygen–silicon surface layer which in turn prevents a complete vanadium–silicon alloy formation. Finally a vanadium oxide film of V_2O_3 stoichiometry was created. The grown film exposes single crystalline areas of stepped surfaces which appear azimuthally randomly-oriented.

1. Introduction

The growth of ultra thin films of transition metal oxides to act as model catalysts appears of remarkable significance in surface science studies [1]. In particular vanadium oxide is of interest in the field of heterogeneous catalysis. It operates as a redox catalyst [2–4] and also serves for oxidative dehydrogenation, i.e. the propane to propene (ODP) reaction [5]. Among the different vanadium oxides V_2O_5 has gained the most impact in catalytic processes either as a single active phase or in combination with other metals to form mixed oxides. It has been recently shown [6] that during catalytic processes at elevated temperature also vanadium oxide reduction may occur leading to lower oxidation states (e.g. VO_2, V_2O_3). Obviously, the oxidation state of vanadium plays an important role for the catalytic activity and selectivity. In addition, supported vanadium oxide catalysts have been found to be more selective than the unsupported bulk V_2O_5 material because of the interactions of VO_x with the oxide support substrates (e.g. SiO_2). In order to prove simple catalytic reactions, model catalysts can play an important role. In literature we can find already some studies of thin *vanadia* films grown either on solid oxide substrates as Al_2O_3 [7], TiO_2 [8], CeO_2 [9] and SnO_2 [10], or on metal substrates as Au(1 1 1) [11], Cu(1 0 0) [12], Pd(1 1 1) [13,14], Rh(1 1 1) [15], Re(0 0 0 1) [16], Cu_3Au(1 0 0) [17,18] and W(1 1 0) [19]. In addition oxide nanoclusters have been grown on metal surfaces which might serve as an *inverse model catalyst* [20]. In any case, conducting and semiconducting substrates make also thin insulating oxide films accessible to usual surface science tools depending on charge transfer.

Furthermore, in the perspective of development of new catalyst materials it seems to be appropriate not only to consider the catalyst-support influence but also to take the role of the surface morphology in the catalytic process into account. The surface morphology is expected to play a decisive role in catalytic reactivity. In particular surface defects (point defects, steps, etc.) are supposed to enhance chemical reactivity considerably. In the following we propose a method to grow single phase ordered V_2O_3(0 0 0 1) which exposes a highly stepped surface expected to be catalytic more active as compared with the plain defect free V_2O_3(0 0 0 1) surface. In order to grow a *vanadia* film with such particular surface morphology oxidized Si(1 1 1) appeared as an appropriate substrate. As we have shown recently [21], direct evaporation of vanadium onto the Si(1 1 1)-7 × 7 surface gives rise to massive silicide formation and subsequent oxygen exposure leads only to the formation of rough $V_xSi_yO_z$ films of unknown structural and chemical composition. In order to prevent initial vanadium silicide formation the Si(1 1 1)-7 × 7 surface was oxidized prior to vanadium evaporation. The vanadium film was converted into a thin vanadium oxide layer by annealing the sample in oxygen ambiance.

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2. Experimental

The experiments have been carried out in two different ultra-high vacuum chambers (base pressures < 2×10^{-10} mbar) both equipped with an e-beam evaporator (EFM3-OMICRON) and a home-made 6 MHz quartz micro-balance using an INFICON controller [22] which serves to verify the same amount of evaporated vanadium on the sample in the two vacuum systems.

All STM data have been obtained in a system equipped with a variable-temperature STM (OMICRON), low energy electron diffraction (LEED) optics and an Auger electron spectrometer (SPECTALEED). The STM images were recorded in the constant current mode at room temperature using electrochemically etched W tips. The tunnelling gap voltages presented in the figures below refer to the applied sample bias.

Detailed X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) measurements were carried out in the second system equipped with LEED and a hemispherical electron analyser EAC 2000-SPHERA (OMICRON). All XPS data were acquired at room temperature for electrons leaving the surface at 60°. The primary X-ray beam (Al Kα) impinges the surface at an incidence angle of 90°. For spectrum calibration the Si_{2p} line at 99.15 eV has been used. The oxidation state of vanadium was determined by analysing in detail the V_{2p} envelopes after subtraction of a Shirley type background with the help of the peak-fitting procedure of the CasaXPS software package [23].

Clean Si(1 1 1)-7 × 7 surfaces have been prepared after keeping the crystal in an overnight degassing stage at 900 K by several short annealing cycles with temperatures up to ~1400 K in UHV (maintaining the pressure at $p < 1 \times 10^{-9}$ mbar). Oxidation of the clean surface was achieved by annealing the sample at 920 K in 2×10^{-7} mbar oxygen atmosphere for about 90 min. The corresponding AES data of the Si $L_{2,3}VV$ lines reveal a change in the silicon valence band as expected for silicon-oxidation [24].

In order to obtain continuous VO_x films a quantity of more than 4 ML vanadium has to be evaporated. The film was produced by vanadium deposition (rate of 0.2 ML/min; 1 ML = 7.83×10^{14} atoms/cm^2) onto the oxidized Si(1 1 1) surface at room temperature in an oxygen atmosphere of 2×10^{-7} mbar. The VO_x was then reformed by subsequent annealing at 600 K in UHV by 30 min. Finally the specimen was annealed at 600 K in oxygen atmosphere (2×10^{-7} mbar) by 5 min in order to restore possible oxygen vacancies.

3. Results

After silicon-oxidation a thin oxide layer (<0.5 nm) composed mainly by intermediate silicon-oxidation states appeared, similar as already reported in the literature [25,26]. The corresponding STM images of the oxidized surface are presented in Fig. 1. In the large scale image (Fig. 1a) several flat terraces can be recognized which are separated by monoatomic steps. In Fig. 1b two terraces are shown in a close up. The geometrical structure of the oxidized surface follows the registry of the Si(1 1 1)-7 × 7 substrate as can be seen in the Fast Fourier Transform (FFT) of the STM image (not presented here) showing clearly the six spots arising from the 7 × 7 periodicity.

The VO_x film was created by evaporation of 5 ML of vanadium onto the oxidized surface and subsequent oxidation as described above. The typical surface morphology shown in the survey STM image in Fig. 2a indicates that still monoatomic steps of 0.3 nm height are present originating from the Si(1 1 1) surface. The film exposes an overall grainy structure divided by several trenches with a depth about 1.2 ± 0.2 nm. The related grains appear azimuthally not well ordered (cf. Fig. 2b). However, preferential orientation of steps can be noticed. Hence, on top of the surface these grains expose favoured azimuthal directions at ±30°; ±60° and ±120°.

The grains consist of oxide terraces coming to the surface under an oblique angle (cf. Fig. 3). The terraces with a mean terrace width of 1.5 ± 0.3 nm are ending at the surface in such a way that the overall top plane becomes parallel to the Si(1 1 1) substrate. The height profile (Fig. 3b) measured on top of one grain reveals an oblique angle of 7 ± 0.3° of the oxide terraces with respect to the Si [1 1 1] direction.

The atomic structure of the distinct oxide terraces can be seen in the high resolution STM image shown in Fig. 4. Many small terraces separated by single steps can be recognized. From the atomic structure visible in the STM images we may now conclude that the grains are composed of crystalline VO_x. The prominent structure element at the terraces appears to be a hexagon exposing point distances of 0.5 nm. Similar hexagonal structures showing the same point distance in STM are already identified for surfaces of V_2O_3(0 0 0 1) films grown on metal surfaces [27]. Due to of the corundum crystal structure V_2O_3(0 0 0 1) expose alternating layers of oxygen and rumpled vanadium layers. A similar layered structure of the terraces can be recognized in Fig. 4. Also the measured step height of 0.2 ± 0.02 nm is in good agreement with the V_2O_3(0 0 0 1) crystallography. Consequently, on the basis of the

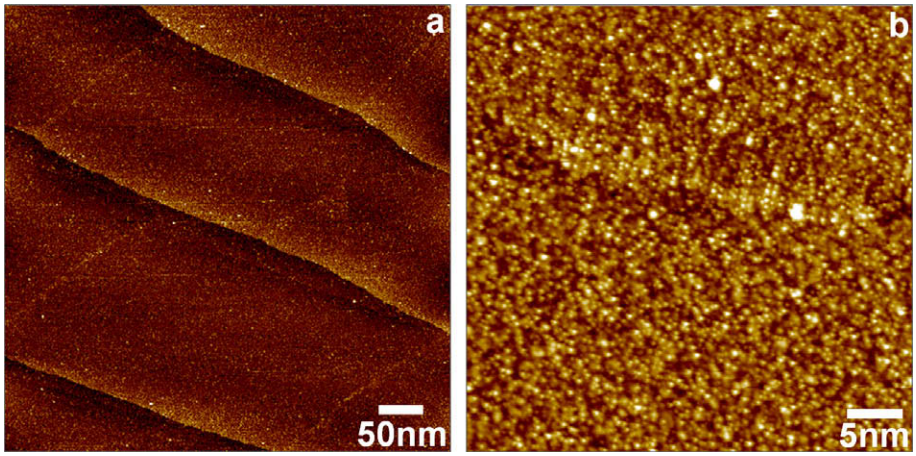

Fig. 1. STM images of the oxidized Si(1 1 1) surface (empty-states, I_t = 1nA, U_{sample} = 2.6 V). (a) Survey to show the flat terraces which are separated by monoatomic steps, (b) the close up illustrates the granular structure of the surface.