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On the preparation and electronic properties of clean W(1 1 0) surfaces

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Abstract

We have studied the influence of oxygen pressure during the cyclic annealing used for the cleaning of W(1 1 0) surfaces. For this purpose the surface morphology and electronic properties are measured by means of scanning tunneling microscopy (STM) and spectroscopy (STS), respectively. It is found that the surfaces with impurity atom densities as low as 2×10^{-3} can be obtained by gradually reducing the oxygen pressure between subsequent annealing cycles down to about 2×10^{-8} mbar in the final cycle. Only on the clean surface a bias-dependent spatial modulation of the local density of states (LDOS) is observed at step edges and around impurity sites by STS. In addition, we find a pronounced peak in the occupied states. In combination with density functional theory calculations these features can be traced back to a dispersive p_z–d_{xz}-type surface resonance band and the lower band edge of a surface state, respectively. Published by Elsevier B.V.

Keywords: Scanning tunneling microscopy; Scanning tunneling spectroscopies; Tungsten; Tungsten oxide; Single crystal surfaces; Surface segregation; Surface electronic phenomena

1. Introduction

Among the refractory metals which are very popular substrates for thin film experiments because – in contrast to many noble metals – the problem of intermixing between film and substrate is strongly reduced, the densely-packed (1 1 0) surface of tungsten is most-widely used. In order to clean the dense-packed W(1 1 0) surface from its main impurity, carbon (C), a variety of processes have been proposed [1–19]. Common to these cleaning procedures are cycles of prolonged annealing in an oxygen atmosphere and subsequent short high-temperature treatments, so-called flashes. During the annealing in oxygen, C is removed from the surface by the formation of CO and CO_2, which are both gaseous substances and can be pumped after thermal desorption. Simultaneously, however, the tungsten surface oxidizes. The resulting tungsten oxides can only be removed by thermal desorption at $T \geqslant 2300$ K [20,21].

Comparison reveals that the actual parameters of the duration d, the oxygen partial pressure p_{ox}, the annealing temperature T_{ann}, and the flash temperature T_f strongly vary between the above mentioned cleaning procedures [1–19,22]. For example, the values of p_{ox} range from 2×10^{-8} mbar [14] up to 4×10^{-6} mbar [1], T_{ann} is between 1000 K [15] and 2000 K [6,8,12], and T_f is anywhere between 2000 K [2,3,12] and 3000 K [6]. Although several criteria have been proposed as indicators of a high surface quality, such as the sharpness and low background intensity in low-energy electron diffraction (LEED) [3,17,22], the absence of C-related peaks in Auger electron (AES) or X-ray photo-emission spectra (XPS) [14,17,19], the absence of H-specific peaks in electron-energy loss spectra (EELS) [14,19], or the intensity of an occupied surface resonance at 1.4 eV below the Fermi level in photo-emission spectra (PES) [23,18], it remains unclear under which conditions the best W(1 1 0) surface quality can be obtained.

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While keeping the duration of annealing d fixed at about 30 min we have experimentally studied the topography and electronic properties of W(1 1 0) surfaces in dependence of the oxygen pressure p_{ox} during annealing by means of scanning tunneling microscopy (STM) and spectroscopy (STS). These experimental results are compared with band structures obtained by first-principles calculations based on density functional theory. Our results show that a clean surface with a defect density below 2×10^{-3} can be obtained if p_{ox} is gradually reduced during the sequence of annealing and flash cycles down to 2×10^{-8} mbar in the final cycle.

Characteristic for a clean W(1 1 0) surface with defect densities below 1% is the presence of an interference pattern in STS experiments. It originates from the reflection of electronic states at step edges and dilute impurity atoms. The dispersion of the involved band is measured by constant-separation tunneling spectroscopy. The experimentally determined upper band edge energy is $E_0 = 314 \pm 12$ meV and an effective mass of $m_{eff} = -1.15 \pm 0.05 m_e$ is obtained, where m_e is the electron rest mass. A comparison with the calculated band structures reveals that this band is a downwards dispersing surface resonance of p_z–d_{xz}-type character. Further, a pronounced peak in the occupied part of the measured tunneling spectra is identified as the lower band edge of a surface state. This surface state shows an unusual charge distribution in the vacuum with enhanced LDOS between the surface atoms and has previously been predicted to result in a bias-voltage dependent corrugation reversal [24].

2. Experimental setup and procedures

The STM experiments were performed in an ultra-high vacuum (UHV) system with four separate chambers for cleaning tips and substrates, thin film growth, standard surface analysis, and cryogenic STM [25]. The pressure in each chamber is in the low 10^{-11} mbar range and probably significantly lower within the dewar used for cryogenic STM measurements. During STM measurements tip and sample are at $T = 13 \pm 1$ K. All STM data presented here were obtained with flashed W tips. Topographic STM images are recorded in the constant-current mode. The differential conductance dI/dU, which is proportional to the electronic local density of states (LDOS) [26], is measured by lock-in technique. The dI/dU signal can be acquired in two measurement modes: if the feedback loop, which keeps the tunneling current at a previously selected set-point, remains active, dI/dU maps at one particular bias voltage can be measured simultaneously with topographic images; alternatively, the tip-sample distance may be fixed at certain set-point values for the tunneling current and the gap voltage, and full dI/dU spectra may be measured over a wide voltage range after the feedback loop has been deactivated.

The terrace width of the W(1 1 0) substrate amounts to 50 nm on average but strongly varies depending on the precise location. The surface is cleaned by cycles of annealing ($T \approx 1500$ K for about 30 min) in oxygen and a subsequent high-temperature flash ($T \approx 2300$ K for 15 s) in UHV ($p \leqslant 1 \times 10^{-9}$ mbar). Temperatures are measured with an infrared pyrometer using an emission coefficient $\epsilon = 0.43$. Oxygen (99.999% purity, delivered by Messer Griesheim) is dosed with a leak valve. The total pressure is measured by using a standard Beyard–Albert manometer with a thorium-oxide–coated Ir filament. The chemical composition of the residual gas in the preparation chamber is analyzed with a quadrupole mass-filter (C100M from Inficon). Our analysis indicated that at any step of the oxygen treatment p_{ox} is at least 500 times higher than any other partial pressure.

3. Theoretical methods

The electronic structure of the W(1 1 0)-surface has been calculated with the full-potential linearized augmented plane-wave method (FLAPW) in film geometry as implemented in the FLEUR-code [27]. The calculations apply density functional theory in the local density approximation of Barth and Hedin [28] using the parameterization by Moruzzi, Janak and Williams [29]. A symmetric film consisting of 19 layers has been chosen to simulate the surface using the experimental W lattice constant of $a_0 = 5.972$ a.u. No vertical relaxation of the surface has been included, since it has been experimentally determined to be less than 2% [30]. The W 5p semi-core states have been described by local p orbitals added to the LAPW basis set consisting of about 100 basis functions per atom. Non-spherical terms in the potential, charge density, and wave functions are expanded within the muffin-tin spheres with radius $R_{MT} = 2.456$ a.u. up to $l_{max} \leqslant 8$. Integrations over the 2 D Brillouin-zone (2D-BZ) have been performed using 42 special $\mathbf{k}_{\|}$-points in the irreducible wedge of the 2D-BZ (I2D-BZ) while the local density of states in the vacuum has been analyzed using 814 $\mathbf{k}_{\|}$-points in the I2D-BZ.

4. Results and discussion

4.1. Experiment

Fig. 1 shows constant-current STM images of the W(1 1 0) surface obtained after several dozens of cleaning cycles consisting of oxygen annealing (duration $d =$ 30 min) and a subsequent high temperature flash. In each case the initial oxygen partial pressure was $p_{ox} = 2 \times 10^{-6}$ mbar. Between two successive annealing cycles p_{ox} was typically reduced by 30–50%. The cleaning process was stopped at different values of p_{ox} in the final cycle. Fig. 1a shows a W(1 1 0) surface which was heated in $p_{ox} = 1 \times 10^{-6}$ mbar in the final cycle. Numerous point-like depressions with an apparent depth of 0.1–0.3 Å and a typical diameter of 0.5–1 nm can be recognized. Analysis reveals that after annealing at $p_{ox} = 1 \times 10^{-6}$ mbar about 2% of the surface atoms are impurities, probably C. As the oxygen partial pressure during the final cycle is lowered, the number of depressions in the STM images