Photoemission spectroscopy and electron diffraction study of Pd/tungsten oxide/W(110) epitaxial system

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Abstract. Epitaxial thin films of tungsten oxide were prepared by radio-frequency plasma oxidation of the W(110) surface followed by thermal annealing. Reflection High-Energy Electron Diffraction (RHEED) showed that the films were composed of crystal grains having a pseudo-cubic structure and (111) epitaxial plane. The re-crystallisation process led to the reduction of the tungsten oxide films. A lack of oxygen atoms was compensated by a formation of crystallographic shear planes (CSP). Deposited Pd atoms formed three-dimensional clusters with a (111) epitaxial plane reflecting the hexagonal symmetry of the tungsten oxide surface lattice. Electronic structure of the Pd/tungsten oxide/W(110) was investigated by means of X-ray Photoelectron Spectroscopy (XPS) and Synchrotron Radiation Photoelectron Spectroscopy (SRPES) methods. The epitaxial tungsten oxide thin film exhibited well-defined oxidation states indicated by narrow components in the W 4f spectrum which were not observed in amorphous phase. The deposition of Pd led to significant changes in the valence band structure but the detailed analysis of W 4f and Pd 3d lines did not show a direct interaction of Pd and W species.

1. Introduction
Tungsten oxide plays an important role in a variety of electrochromic devices, catalysts and chemical sensors. Doping the surface of these devices by an active metal can be used to control their sensitivity and selectivity [1, 2]. Chemical properties of real catalysts and gas sensors are strongly dependent on their structure. Although the gas sensors were developed and used for variety of gases the principles of gas sensing mechanisms and their structural dependence are not understood so far. The main goal of our research is to prepare a well-defined model system and to investigate the above mentioned fundamental properties and dependences.

Tungsten oxide thin films have been prepared by different deposition techniques including thermal evaporation [3], chemical vapor deposition, sputtering [4, 5], sol-gel method [6] and oxidation of tungsten thin film [7]. Unfortunately, only a few articles report a successful preparation of high-quality tungsten oxide layers [8, 9]. In addition, low electric conductivity of nearly stoichiometric tungsten trioxide leads to a significant charging during spectroscopic measurements limiting a precise evaluation of the results.
In this paper we report on the preparation of epitaxial tungsten oxide layers of high quality on W(110) single-crystal by RF oxidation. A small thickness of the layers avoids charging effects during measurements. The crystallographic structure, chemical composition and state were investigated by means of Reflection High-Energy Electron Diffraction (RHEED), Synchrotron Radiation Photoelectron Spectroscopy (SRPES) and X-ray Photoelectron Spectroscopy (XPS) methods. Epitaxial clusters of Pd were deposited in-situ afterwards on the surface.

2. Experimental details
The investigation of structural and electronic properties of the Pd/tungsten oxide/W(110) was performed by using RHEED, XPS and SRPES analysis in Surface Science Laboratory in Prague and at the Materials Science Beamline at the synchrotron Elettra in Trieste. Tungsten single-crystal supplied by MaTecK with a miscut below 0.1° was cleaned by repeated cycles of ion bombardment and annealing at 1050°C in ultra high vacuum (UHV). The surface cleanliness and structure was checked by XPS and diffraction methods. RF oxygen plasma was used to oxidize the surface at room temperature followed by heating at 630°C in UHV. Pd was deposited from electron-heated Pd evaporation source permitting the deposition of high purity thin layers. XPS measurements were performed at room temperature with photon energies 1254, 43 and 85 eV and the total resolution 0.75 and 0.15 eV, respectively. Low photon energies provided well-resolved photoemission data with high surface sensitivity. The spectra were normalised to primary photon beam current.

3. Results and discussion
The example of the surface structural analysis performed by RHEED is shown in figure 1. The diffraction pattern was taken at primary electron beam energy 25 keV and thus it represents nearly plane cut of the reciprocal lattice perpendicular to the substrate surface. The similar diffraction pattern was reported on tungsten single-crystal annealed at very high temperatures in oxygen [10]. The results show the presence of epitaxial WO$_3$ crystal grains having pseudo-cubic crystal lattice [7] and (111) epitaxial plane. The diffraction pattern is composed of two (110) reciprocal planes having common [111] direction perpendicular to the W(110) substrate surface and rotated by 180° with respect to each other.

Although further heating of the sample at 630°C under UHV led to a partial surface reduction the WO$_3$ structure was preserved and the lack of oxygen atoms in the layer was compensated by formation of crystallographic shear planes (CSP) along <120> and <001> crystallographic directions (the CSP are indicated by transversal lines in the pattern).

The typical RHEED diffraction pattern is presented in figure 2. The round diffraction spots and diffraction circles indicate three-dimensional growth of Pd. The same diffraction pattern was observed for each 60° during the rotation of the sample around the surface normal indicating a hexagonal symmetry of this structure corresponding to the same symmetry of the tungsten oxide surface. Two
phases of metal clusters, (111) epitaxial and randomly oriented were found. The epitaxial phase is composed of two populations of clusters rotated by 90° and exhibited so-called “double positioning” [11]. The similar structure was observed in the case of the growth of Pd or Rh clusters on other substrates [11, 12].

**Figure 2.** RHEED diffraction pattern of Pd deposited on tungsten oxide and its interpretation.

The electronic structure was investigated by XPS and SRPES methods. XPS measurements revealed no charging effects of this thin oxide film.

**Figure 3.** W 4f photoemission spectra (SRPES) from tungsten oxide layer prepared on the W(110) single-crystal after oxidation (c), after the formation of the epitaxial layer by annealing at 630 °C (b) and after the deposition of Pd (a). The spectra are compared to that ones from amorphous tungsten oxide layers as prepared on W polycrystalline foil (d) and annealed at 630 °C (e). Photon energy was 85 eV.

The electronic structure was determined mainly from the shape of W 4f and valence band spectra. The example of the evolution of W 4f spectra at different steps of the experiment is shown in figure 3. The different oxidation states of tungsten and their evolution after the redox treatments are illustrated by sets of arrows in the figure. Mainly the W$^{6+}$, W$^{5+}$, W$^{4+}$ and W$^{0}$ states were found. The states are labelled according to [13]. In this case the presence of W$^{0}$ and W$^{2+}$ species can be attributed to the tungsten substrate and substrate-oxide interface, respectively. The relatively narrow peaks marked as W$^{5+}$ correspond probably to the tungsten atoms at CSP. These conclusions are supported by the fact that the intensity of W$^{0}$ and W$^{2+}$ peaks increases with increasing photon energy (i.e. increasing information depth) while the relative intensity of W$^{5+}$ peak decreases. The spectra from epitaxial system are compared to that ones of amorphous tungsten oxide layers prepared by a similar oxidation of metallic tungsten foil. One can see that the amorphous system is less stable towards annealing than the epitaxial one. The W 4f spectra after Pd deposition did not change significantly indicating a weak interaction between tungsten oxide and the Pd deposit.

Reactivity of the surface can be deduced from the valence band spectra. Evolution of valence band spectra after different treatments is presented in figure 4. The spectra exhibit a presence of three main features corresponding to the W5d, O2p and hybridized states [14]. In addition, other states can be observed near the Fermi edge. These states are generally attributed to oxygen vacancies and they are considered as catalytically active sites. Comparing these spectra to that ones from amorphous tungsten
oxide (e) a special shape of states near Fermi edge was observed on epitaxial tungsten oxide layer (b). Combining the RHEED and photoemission observations it can be attributed to well-arranged oxygen vacancies at the CSP. A further increase of the intensity in the gap after the Pd deposition is caused by the presence of metallic Pd clusters on the tungsten oxide surface (Pd 4d states). It should be noted that the measurements taken at energy 43 eV of primary photons are extremely surface sensitive.

**Figure 4.** Valence band photoemission spectra (SRPES) from tungsten oxide layer prepared on W(110) single-crystal after oxidation (c), after the formation of the epitaxial layer by annealing at 630 °C (a) and after the deposition of Pd (b). The spectra are compared to that ones from amorphous tungsten oxide layers as prepared on W polycrystalline foil (d) and annealed at 630 °C (e). Photon energy was 43eV.

4. Conclusion
The results presented in this paper show that it is possible to prepare a well-defined Pd/tungsten oxide epitaxial system Pd(111)/WO$_3$(111)/W(110) which can be used as an excellent model system for investigation of fundamental catalytic and gas sensing properties of pure and/or Pd doped tungsten oxide. Thermal annealing of RF oxidized (110) tungsten single-crystal surface led to a formation of a high quality sub-stoichiometric epitaxial thin film. The lack of oxygen atoms in the structure was compensated by a formation of CSP. After the growth of Pd non-oriented and (111) epitaxial phases of Pd three-dimensional clusters were found. The valence band and W 4f spectra measured using SRPES showed well-defined states which can be attributed to the well-arranged oxygen vacancies at the CSP.

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