



Deposition and characterization of stoichiometric films of V_2O_5 on Pd(111)



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ARTICLE INFO

Keywords:

Vanadium pentoxide
X-ray photoelectron spectroscopy
Reflection adsorption infrared spectroscopy
Low energy electron diffraction

ABSTRACT

A simple and efficient method has been used to grow V_2O_5 thin films on Pd(111) at a substrate temperature of 300 K through physical vapor deposition by heating a fine powder of V_2O_5 in a non-oxidative, UHV environment. X-ray photoelectron spectroscopy (XPS), reflection absorption infrared spectroscopy (RAIRS) and low energy electron diffraction (LEED) were used to characterize the thin films. When the as-grown films exceed a minimum thickness, characteristic features of V_2O_5 were revealed by XPS and RAIRS, which confirms the presence of stoichiometric V_2O_5 . LEED indicates no long range order of the as-grown films at 300 K. Annealing to temperatures between 600 and 700 K causes a reduction of V_2O_5 to VO_2 as identified by XPS and the formation of ordered structures as determined by LEED, and VO_2 is predominant after annealing to 800 K. After further annealing to 1000 K, only an ordered form of V_2O_3 is present on Pd(111).

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1. Introduction

The wide range of oxidation states of vanadium among its oxides and the ability to switch between these multiple oxidation states from V^{5+} (V_2O_5) to V^{2+} (VO) gives the vanadium oxides vast potential in heterogeneous catalysis. Oxide supported V_2O_5 catalysts have been applied in industrial catalytic processes for decades, such as the oxidation of SO_2 to SO_3 in the production of sulfuric acid, the oxidation of *o*-xylene to phthalic anhydride, and the reduction of NO_x with NH_3 to N_2 [1–3]. In recent years, they have also been promoted for oxidative desulfurization (ODS) in oil refining [4].

V_2O_5 has also attracted great interest in electrochemistry due to its multiple accessible vanadium oxidation states and layered structure. Carbon-coated V_2O_5 nanocrystals have been investigated as a high performance cathode material for Li-ion batteries [5]. In addition, V_2O_5 gels are considered as a promising cathode material for rechargeable Mg batteries, which is a competitive alternative to Li-ion batteries [6].

To understand the basic structural and electronic properties of V_2O_5 and its interfacial behavior in both catalysis and electrochemistry, investigation of well-defined and characterized model systems is highly desirable. The preparation of model V_2O_5 surfaces is therefore of great interest. V_2O_5 single crystals generally exhibit surface charging problems in spectroscopic measurements, thus various methods have been used in an attempt to grow V_2O_5 thin films, which can be summarized into three categories. The first approach is the oxidation of vanadium during or following vanadium metal deposition [7–15]. Netzer and co-workers [7–9] applied reactive evaporation of vanadium onto Pd(111)

in 2×10^{-7} mbar of O_2 , but could only achieve mainly a stoichiometry of V_2O_3 . Wong et al. [10,11] studied the post-oxidation of vapor-deposited vanadium on $CeO_2(111)$ and $TiO_2(110)$ by X-ray photoelectron spectroscopy (XPS). They found on both surfaces that the oxidation in 10^{-7} Torr of O_2 produces primarily V^{3+} , while oxidation in 10^{-3} Torr of O_2 yields primarily V^{5+} , though it is always accompanied by some V^{4+} species. Guimond et al. [14,15] reported the first and only growth of well-ordered $V_2O_5(001)$ thin films on Au(111), however it requires post-oxidation of vanadium layers under an oxygen flow of 50 mbar in a high pressure cell, which is not suitable for common UHV systems.

Chemical vapor deposition has also been used to prepare V_2O_5 thin films. Wang and Madix [16] simultaneously dosed $VOCl_3$ (5×10^{-7} Torr) and water (5×10^{-6} Torr) onto a $TiO_2(110)$ surface at room temperature and produced sub-monolayer to multilayer V_2O_5 thin films as verified by XPS. However this method also has to be carried out in a high pressure preparation chamber attached to a UHV system.

Another approach is physical vapor deposition from a V_2O_5 source. Silversmit et al. [17] prepared fully oxidized V_2O_5 up to 30 Å in thickness on a $TiO_2(001)$ -anatase substrate with reactive DC magnetron sputtering of a polycrystalline V_2O_5 target in 1 Pa of flowing O_2 . In another attempt, Julien et al. [18,19] applied flash evaporation of polycrystalline V_2O_5 powder to grow amorphous V_2O_5 films on silicon substrates at room temperature, however the stoichiometry of the as-grown films was not characterized. Ramana et al. [20] have grown V_2O_5 thin films on glass and Si(100) substrates at room temperature by the evaporation of V_2O_5 powders in a molybdenum crucible in high vacuum (10^{-6} Torr). The authors found that the as-grown films are nearly stoichiometric V_2O_5 as indicated by XPS and electron probe micro-analysis

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(EPMA), and are completely amorphous at room temperature. However, the V_2O_5 source temperature was not mentioned. Wu et al. [21–23] have deposited V_2O_5 thin films on highly ordered pyrolytic graphite (HOPG) at room temperature by the evaporation of V_2O_5 powders in a boron nitride crucible in UHV, with the source temperature at 670 °C. Amorphous, nearly stoichiometric V_2O_5 thin films were identified by XPS, ultraviolet photoelectron spectroscopy and low energy electron diffraction (LEED). However, a small amount of V^{4+} species is always present at various coverages as revealed by XPS, which suggests a slight reduction of V_2O_5 during the deposition process.

Although most successful cases of growth of stoichiometric V_2O_5 thin films were carried out under extreme conditions for a UHV system – either ambient pressure oxidation treatment, or high pressure water vapor dosages – direct evaporation from V_2O_5 powder offers an attractive alternative method for surface science studies in UHV. Here we demonstrate the successful growth of stoichiometric V_2O_5 thin films on Pd(111) by this method and have characterized the films with XPS, reflection absorption infrared spectroscopy (RAIRS) and LEED. By growing the V_2O_5 films on a Pd(111) substrate by this physical vapor deposition (PVD) method, we are able to make direct comparison with the extensive existing literature on the growth and characterization of vanadium oxides on Pd(111) by other methods.

2. Experimental

All experiments were carried out in a stainless steel ultra-high vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. The chamber is equipped with an ion gun for Ar^+ sputtering (Physical Electronics, PHI 04–161), a Fourier transform infrared (FTIR) spectrometer (Mattson Instruments, RS-10,000), a hemispherical electron energy analyzer (VG Microtech, CLAM 2) with a dual Mg/Al anode X-ray source, and reverse view low energy electron diffraction (LEED) optics (Princeton Research Instruments, RVL 8–120SH).

The Pd(111) single crystal was spot-welded to two tantalum wires mounted on a LN_2 -cooled sample holder. A type K thermocouple was spot-welded to the edge of the crystal for temperature measurement. The sample can be resistively heated to 1200 K and cooled with LN_2 to 90 K. The Pd(111) surface was prepared by Ar^+ bombardment (1 keV, 5 μA) and annealing to 1200 K in UHV. The cleanness of the surface was examined by XPS, LEED and O_2 TPD.

V_2O_5 (VWR, 99.99%) powder was placed in an alumina coated tungsten basket (Midwest Tungsten Service) and was evaporated onto the sample by resistively heating to 675 °C. A type K thermocouple was pasted to the external surface of the tungsten basket by Aremco Ceramabond 569 cement for temperature measurement.

All XPS spectra were acquired at 50 eV pass energy using Mg $K\alpha$ radiation corresponding to a nominal resolution of 1.32 eV at a sample temperature of 300 K. XPS data analysis, including subtraction and deconvolution, was performed with eXPFit15.xlsm (www.chem.qmul.ac.uk/software/eXPFit15.xlsm). All XPS spectra shown in this work have been corrected by satellite and Shirley background [24] subtraction. The film thickness was estimated based on the attenuation of the Pd 3d XPS intensity due to V_2O_5 deposition using the equation:

$$\frac{I}{I_0} = \exp\left(-\frac{d}{\lambda}\right),$$

where d is the film thickness, λ (2.1 nm) is the inelastic mean free path (IMFP) of a photoemitted Pd 3d electron in bulk V_2O_5 calculated via the NIST Electron Inelastic-Mean-Free-Path Database [25], and I_0 and I are the integrated intensities of the Pd 3d peaks before and after V_2O_5 deposition, respectively. The V/O ratios were determined from the integrated XPS intensity of the deconvoluted V 2p and O 1s peaks corrected by atomic sensitivity factors estimated by

$$\frac{S_1}{S_2} \approx \frac{\sigma_1 \lambda_1 / KE_1}{\sigma_2 \lambda_2 / KE_2}$$

as described elsewhere [26], where σ is the photoionization cross section of the element core level found in published data [27], KE is the kinetic energy of the photoemitted electron, and λ is its inelastic mean free path. The ratio of atomic sensitivity factors for V 2p and O 1s was estimated to be 3.34, while a similar value of 2.98 was calculated from the Perkin-Elmer XPS Handbook [28]. This comparison indicates that the sensitivity factor that we use is unlikely to be in error by more than ~ 10%.

All RAIR spectra were acquired using 1024 scans and 2 cm^{-1} resolution with a LN_2 -cooled mercury-cadmium-telluride (MCT) detector at a sample temperature of 300 K. When using triangle apodization, significant interference fringes were observed. Therefore, all RAIR spectra shown have been processed with cosine 4th apodization, which smooths the spectra but also reduces the effective resolution. The corresponding RAIR spectra processed with triangle apodization are shown in the Supporting Information. Reported full width at half maxima (FWHM) were measured from the triangle apodized spectra.

All LEED patterns were taken using a beam energy of 138 eV at a sample temperature of 300 K. For the annealing experiments, the sample was heated from 300 K then held at the annealing temperature for 60 s, then cooled down to 300 K for data acquisition.

3. Results

3.1. As-grown thin films at various coverages

3.1.1. XPS

Fig. 1(a) displays the XP spectra of the sample in the V 2p, O 1s and Pd 3p_{3/2} regions after successive V_2O_5 depositions on Pd(111) up to a film thickness of 3.8 nm. The Pd 3d peak, not shown, was also monitored and was used to determine the film thickness as described in the experimental section. For a clean Pd(111) surface, only the Pd 3p_{3/2} feature is present in Fig. 1(a). For the 0.07 nm thick oxide films, a V 2p_{3/2} peak appears at 515.7 eV, and an O 1s peak at 529.6 eV is seen as a weak shoulder on the lower binding energy side of the Pd 3p_{3/2} peak, which is slightly attenuated. With increasing film thickness up to 0.6 nm, the V 2p_{3/2} and O 1s peaks grow while the Pd 3p_{3/2} peak is further suppressed. The V 2p_{3/2} binding energy shifts to higher values up to 516.9 eV, while the O 1s peak shows only a small shift to 529.8 eV. For oxide films from 0.6 to 3.8 nm thick, the V 2p_{3/2} and O 1s peaks continue to grow accompanied by significant suppression of the Pd 3p_{3/2} peak. However, the V 2p_{3/2} and O 1s binding energies remain at about the same values.

In addition, Fig. 1(b) displays plots of the V 2p_{3/2} binding energy, as well as the difference in binding energy between O 1s and V 2p_{3/2} (ΔE) and the V/O ratio obtained from the XPS data in Fig. 1(a), as a function of film thickness. The value of ΔE decreases from 13.9 eV for a 0.07 nm film to 12.9 eV for a 0.6 nm film then shows no change for thicker films, which is similar to the trend in the V 2p_{3/2} binding energy. Unlike the V 2p_{3/2} binding energy and ΔE , the V/O ratio is fairly constant at around 0.40 over the full range of film thickness from 0.07 to 3.8 nm.

3.1.2. RAIRS

Fig. 2 displays the RAIR spectra of the sample after successive V_2O_5 depositions on Pd(111) up to a film thickness of 2.3 nm. For oxide films of 0.4 nm on Pd(111), a weak and broad vibrational feature at 940 cm^{-1} and an intense peak at 1034 cm^{-1} are present. The 940 cm^{-1} feature grows without change in peak position with increasing film thickness up to 2.3 nm. The 1034 cm^{-1} peak shifts to 1039 cm^{-1} and sharpens for a 0.8 nm film. A new feature appears at 1026 cm^{-1} for a 1.2 nm film and becomes predominant for a film thickness of 2.3 nm.

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