

INTERACTION OF OXYGEN WITH V (111) SURFACE

LIDIJA ŠILLER, PETAR PERVAN and MILORAD MILUN*

Institute of Physics of the University Zagreb, Bijenička 46, Zagreb, Yugoslavia

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XPS, UPS and AES have been used to study oxygen adsorption on V (111) surface at 90 K and 300 K sample temperature. At $T_{ad} = 90$ K surface saturation was observed at exposure of 1.5 L and at $T_{ad} = 300$ K at 10 L O_2 . Surface oxygen penetrates into the bulk already at 200 K but the penetration rate is highest at 500 K. Oxygen exposures >10 L result with appearance of V^{+4} surface species.

1. Introduction

Despite its present and prospective technological importance vanadium has not been very intensively studied in the surface science sense. The main reason for this situation lies in the difficulties to prepare a clean vanadium surface. The main impurities originating from the vanadium bulk are sulphur and oxygen. While sulphur may be removed and a surface maintained sulphur-free for a long time the oxygen removal is much harder task. It already caused discussions¹⁻⁴⁾ in the interpretation of LEED structures of clean V (100) surface. A clean V (110) surface has been reported⁵⁾ as well as the polycrystalline vanadium surface⁶⁾. To our best knowledge there is no study published on the interaction of oxygen with V (111) surface. We used the UPS, XPS and AES to study the oxygen/V (111) system in a temperature range 90—760 K. In the following sections we present the results of our cleaning procedure⁷⁾ (and other relevant experimental information) and the UPS and XPS results obtained after oxygen adsorption on the V (111) surface at 90 K and 300 K.

* To whom the correspondence should be addressed.

2. Experimental

A V(111) oriented and mechanically polished monocrystal of 2 mm thickness and 7 mm diameter was mounted to the sample-holder attached to the x , y , z -rotary manipulator. The crystal was spot-welded to two W-wires of 0.25 mm dia. which in turn were spot-welded to two Mo rods fixed to two Cu blocks. The two Cu blocks were fixed to a sapphire plate and mutually isolated. The sapphire plate was connected to the cold finger of a closed loop helium cryostat via a Cu-braid. In the same time, each of the Cu-blocks was connected via Cu braids to a Cu U-shaped tube for liquid nitrogen cooling. The sample could be oriented towards UPS He lamp, XPS dual anode (Mg and Al) gun, mass spectrometer, electron and/or ion gun. The outcoming electrons were analyzed by the use of Vacuum Science Workshop hemispherical analyzer HA 100. The XPS and UPS spectra have been recorded with the fixed analyzer transition of 50 eV and the fixed retard ratio of 5, respectively.

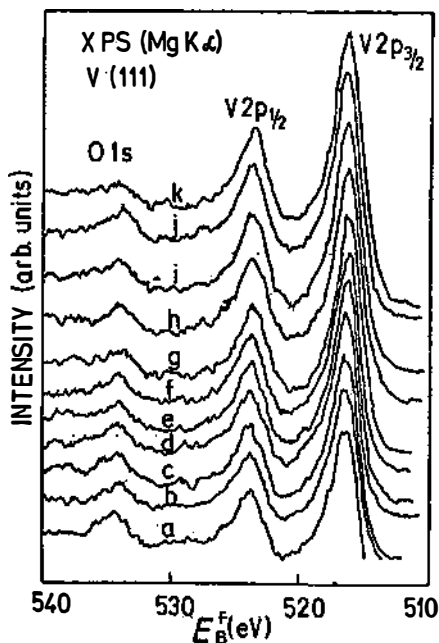


Fig. 1. XPS (MgK) spectra of V(111) taken during cleaning procedure: a—2' Ar (500 V) at 300 K; spectra b, d, f, h and j—flash to 700 K; c—3' Ar (500 V) at 300 K; e—2' Ar (600 V) at 300 K; g—3' Ar (600 V) at 300 K; i—4' Ar (600 V) at 300 K; k—3' Ar (640 V) at 300 K.

The base pressure in the chamber was typically 3×10^{-8} Pa. The maximal oxygen partial pressure during exposure was 4×10^{-5} Pa. The apparatus was pumped out by a 360 l/s Balzers turbopump and a titanium sublimation pump with a liquid nitrogen cooled shield. The bakeout temperature was around 180 °C.

Very long Ar⁺ sputtering (typically 8–10 hours) at 3 kV ion energy and 1100 K sample temperature was sufficient to remove sulphur from the surface. After this treatment the only surface impurity as judged by the AES and XPS was oxygen. In order to remove oxygen we followed several procedures described in the literature^{1–6)} but have not obtained satisfactory results. We finally find out that the best results were obtained by the following procedure: the sample was repeatedly ion sputtered with the ions of kinetic energy 500–600 eV at the room temperature and subsequently annealed to 700 K. A progress in surface cleanness thus achieved is shown in Fig. 1. A spectrum k represents the »clean« surface as compared to some published XPS⁴⁾ and AES⁸⁾ spectra. However, UPS spectrum of the »clean« surface still contained O (2p) emission peak. Further treatment as described above reduced this emission band significantly but it never disappeared completely. Foord et al.⁴⁾ published the UPS spectra of clean V (100) surface which contained no O (2p) emission. Our UPS spectra differ very much from those by Foord et al. and in particular with respect to the V (3d) emission band. The origin of these differences is not clear to us. However, based on the UPS spectra we do not consider our V (111) surface completely free from oxygen. Since water⁶⁾, and carbon monoxide³⁾ from the residual gas as well as the bulk of vanadium are always present as the possible sources of surface contamination with oxygen we believe that a completely oxygen free vanadium surface may be (if at all) prepared and preserved for only very short period of time. Therefore, it seems that a small amount of surface oxygen is unavoidable in the time consuming experiments. In the following we refer to the clean V (111) surface as to the one which exhibits an XPS spectrum similar to the k spectrum in Fig. 1.

3. Results

3.1. Oxygen adsorption at 90 K

Fig. 2 shows a set of HeI UPS spectra obtained after the clean V (111) surface had been exposed to a given amount of oxygen. The spectra have been taken with the fixed retard ratio (FRR) = 5 which caused stronger reduction of the intensity of the electrons of higher binding energies. Although the absolute signal intensities of the O (2p) peak at 6 eV and V (3d) at the Fermi edge may not be used to estimate oxygen surface concentration their ratio certainly reflects a change in oxygen surface coverage as probed within the HeI information depth. The saturation exposure (see Fig. 3) was found to be 1.5 L (1 L = 1×10^{-6} Torr \times \times 1 s; 1 Torr = 133.322 Pa). This saturated surface was then annealed at different temperatures, each time 30 s. Thermal desorption measurements have shown that no oxygen desorption took place during annealing procedure. The first changes in area ratio of the peaks at 1 eV and 6 eV have been observed already at 200 K which means that it presents the temperature at which oxygen starts to penetrate the bulk. However, it may be noted that the penetration process rate is highest at 500 K annealing temperature. This is in accord with the SIMS results of Welter and Wachendorf⁶⁾ obtained for V (poly).

Even prolonged annealing at 760 K did not result with restoration of the clean surface. It rather looks like so as an equilibrium between the in- and from-bulk processes has been established.

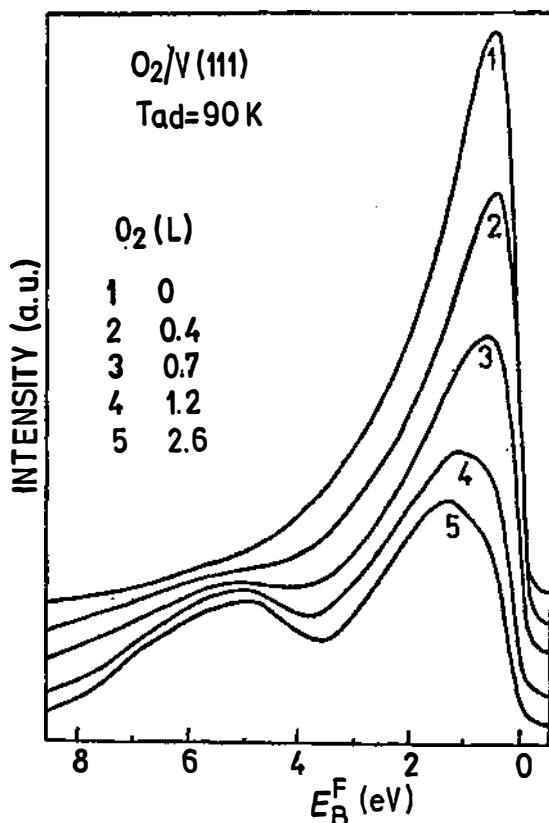


Fig. 2. UPS (HeI) spectra from clean and at $T_{ad} = 90$ K oxygen covered V (111) surface.

3.2. Oxygen adsorption at 90 K

Room temperature adsorption resulted in a set of UPS spectra displayed in Fig. 4. Same as in the case of the low temperature spectra a decrease of the intensity at E^F is clearly observed accompanied with a corresponding increase of the 2p oxygen emission at 6 eV. Surface saturation is also observed, this time at 10 L oxygen exposure (see Fig. 5). However, there is an important difference between the results obtained for the two adsorption temperatures. While the XPS spectra at $T_{ad} = 90$ K (not shown here) of the V (111) surface exposed to O₂ quantities several times greater than the saturation one exhibit only V (2p) levels of the »metallic« vanadium surface, the ones recorded at $T_{ad} = 300$ K show, beyond the saturation exposures (10 L N Fig. 5), additional V (2p) signals. This is shown in Fig. 6: The clean surface (a) was exposed to 2 L (b), 5 L (c), 10 L (d) and 40 L (e) oxygen at $T_{ad} = 300$ K. A permanent increase of O (1s) intensity is clearly seen as well as a decrease in V (2p) intensities. However, the trace d shows additional signals accompanying the V (2p) signals. These two groups of signals are separated by 3.3 eV. According to Brundle⁹⁾, trace c would correspond to a monolayer of oxygen. The appearance of new V (2p) states shifted 3.3 eV indicates

formation of V^{+4} species⁹). Under similar conditions, Brundle⁹) reported the formation of V^{+5} species but on the evaporated polycrystalline vanadium films. Nevertheless, the new peaks are very broad and certainly contain other oxidation states^{9,10}). Still, our results do not enable one to conclude that the V (111) surface is covered by the VO_2 layer: a 5 min. annealing of the surface, whose XPS

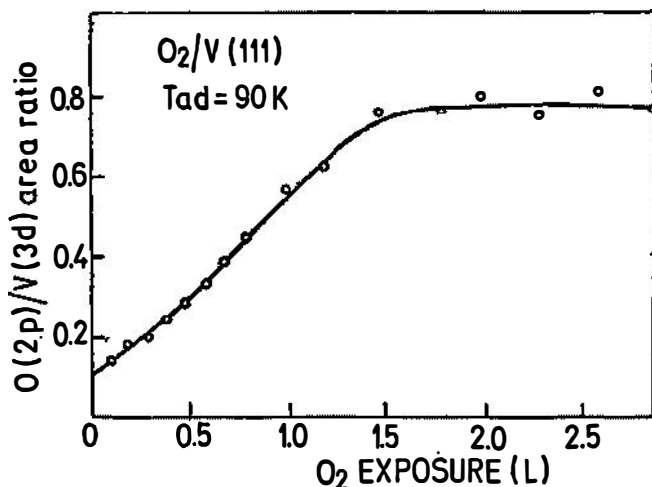


Fig. 3. Plot of O(2p)/V(3d) area ratios versus O_2 exposures. The experimental points are obtained from the UPS (HeI) spectra of the $O_2/V(111)$ system at 90 K.

spectrum is e in Fig. 6, at 500 K reduces the oxygen surface concentration and remove V^{+4} features from the XPS spectrum. The effect of annealing is at best followed with UPS: Fig. 7 shows area ratios of the O(2p) and V(3d) bands as a function of annealing temperatures: V(111) surface was exposed to 40 L oxygen at $T_{ad} = 300$ K and subsequently annealed for 5 min. to 400 K, then to 425 K, etc. up to 760 K. A strong reduction of oxygen signal is observed for annealing temperatures up to 600 K. Higher annealing temperatures affect the oxygen surface concentration only slightly. Similar results have also been obtained from the corresponding set of XPS spectra. The observed decrease of oxygen surface concentration is exclusively due to penetration of oxygen atoms in the bulk.

4. Conclusions

At the 90 K sample temperature oxygen saturates the V(111) surface after 1.5 L exposure.

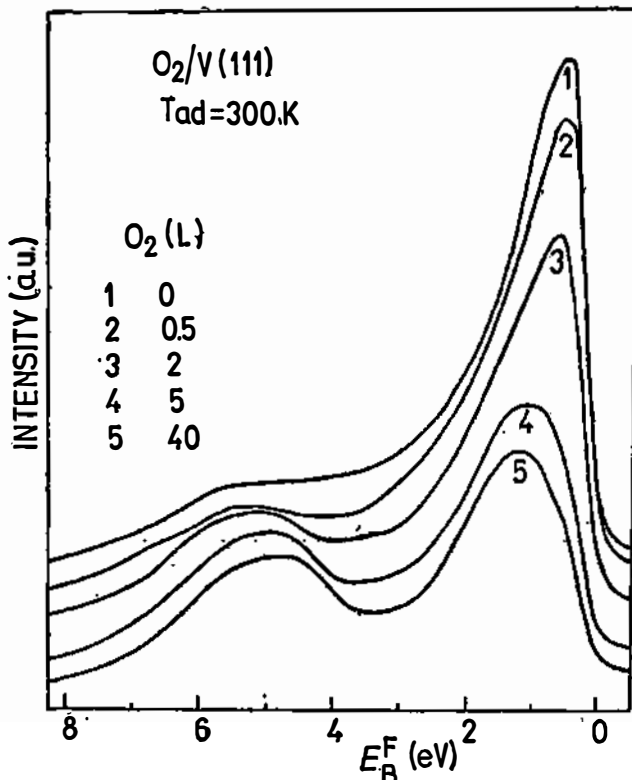


Fig. 4. UPS (HeI) spectra of $O_2/V(111)$ at $T_{ad} = 300$ K.

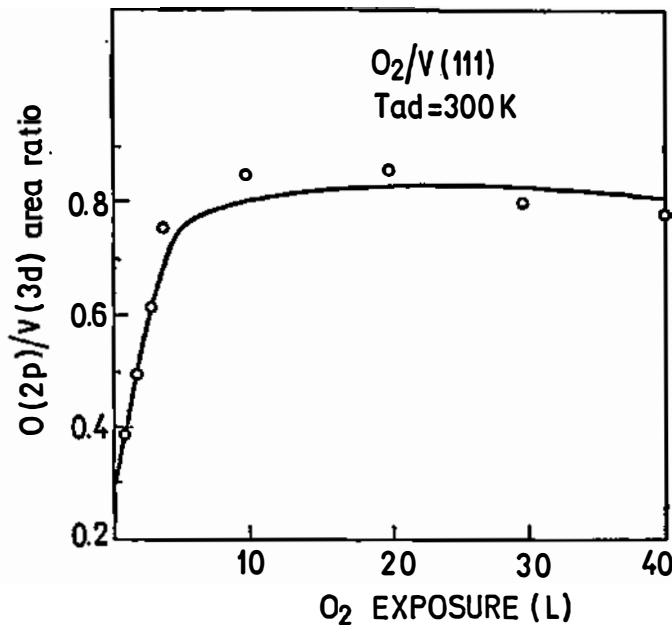


Fig. 5. UPS (HeI) $O(2p)/V(3d)$ area ratios versus O_2 exposure at $T_{ad} = 300$ K.

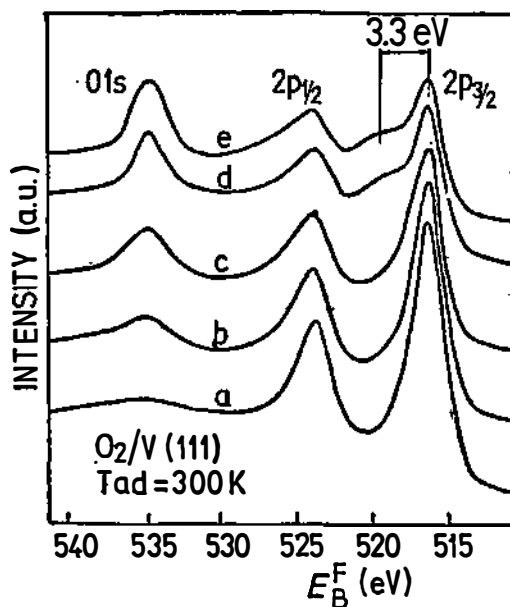


Fig. 6. XPS (MgK) spectra of V (111) exposed at 300 K to: a — 0 L, b — 2 L, c — 5 L, d — 10 L, e — 40 L oxygen.

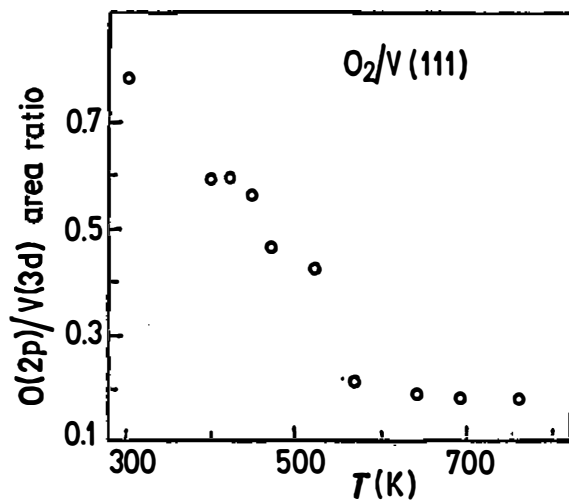


Fig. 7. UPS (HeI) O (2p)/V (3d) area ratio as a function of annealing temperature. Each point is obtained after 5' annealing at a given temperature. The first point corresponds to V(111) surface exposed to 40 L O₂ at 300 K and annealed for 5' at the same temperature. All other points are obtained without additional oxygen supply.

At the 300 K sample temperature saturation is reached after 10 L oxygen. Additional exposures produce V-oxide features in the XPS spectra. These oxide states are rather unstable and disappear completely after an annealing at 760 K. Surface oxygen penetrates the vanadium bulk at temperatures above 200 K.

Acknowledgements

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References

- 1) P. W. Davies and R. M. Lambert, *Surface Sci.* **107** (1981) 391;
- 2) V. Jensen, J. N. Andersen, H. B. Nielsen and D. L. Adams, *Surface Sci.* **112** (1981) L785;
- 3) V. Jensen, J. N. Andersen, H. B. Nielsen and D. L. Adams, *Surface Sci.* **116** (1982) 66;
- 4) J. S. Foord, A. P. C. Reed and R. M. Lambert, *Surface Sci.* **129** (1983) 79;
- 5) D. L. Adams and H. B. Nielsen, *Surface Sci.* **107** (1981) 305;
- 6) J.-M. Welter and H.-N. Wachendorf, *Appl. Surf. Sci.* **14** (1982/83) 173;
- 7) This work was in part presented at the XI Yugoslav Vacuum Congress, G. Martuljak, April 1990;
- 8) J. Kasperkiewicz, J. A. Kovacich and D. Lichtman, *J. Electron Spectr.* **32** (1983) 123;
- 9) C. R. Brundle, *Surface Sci.* **52** (1975) 426;
- 10) F. J. Szalkowski and G. A. Somorjai, *J. Chem. Phys.* **56** (1972) 6097.

INTERAKCIJA KISIKA S POVRŠINOM V(111)

LIDIJA ŠILLER, PETAR PERVAN i MILORAD MILUN

Institut za fiziku sveučilišta u Zagrebu, Bijenička 46, Zagreb, Jugoslavija

UDK 538.971

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Fotoelektronskim spektroskopijama XPS i UPS te Augerovom spektroskopijom studirana je interakcija kisika s V(111) površinom na temperaturama uzorka 90 i 300 K. Na 90 K nađeno je zasićenje površine nakon ekspozicije od 1.5. Na 300 K površina se zasiti nakon 10 L kisika. Dodatne količine kisika ne povećavaju intenzitet signala u UPS spektrima ali znatno mijenjaju izgled XPS spektara ukazujući da nastaju nova oksidna stanja vanadija. Također je nađeno da penetracija kisika u volumen uzorka počinje kod 200 K.