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Oxidation of vanadium with reactive oxygen plasma: A photoelectron spectroscopy study of the initial stages of the oxide growth process

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Abstract

We report on the oxidation of vanadium surface in a low-temperature oxygen plasma studied by in-situ photoelectron spectroscopy (XPS, UPS). Pure vanadium foil was exposed to the oxygen plasma for different time intervals allowing to investigate early stages of the oxide–metal interface formation process and the oxide film growth. Upon increasing the exposure time to the oxygen plasma we identify two regimes with respect to the vanadium oxidation state: formation of 4+ state on the early stages of growth and in saturated regime vanadium was found to be predominantly in the 5+ oxidation state. Angle-resolved XPS was used to perform an in-depth distribution analysis of chemical composition in outermost layers of the oxide. We found that plasma oxidation produces a well-pronounced interface with a transition layer thickness of about 1.3 nm.
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Keywords: Vanadium oxide; Oxidation; Plasma processing and deposition; XPS

1. Introduction

Thin films of vanadium oxides possess a great technical relevance because of their electro- and thermochromic properties as well as catalytic activity in many oxidation reactions [1–3]. In spite of many works devoted to the determination of binding energies of core levels related to different oxidation states, there is still a large spread in the reported values [4–6].

Ultrathin oxide films on metallic substrates are widely used as a model system to study the properties of highly insulating oxides [7,8]. The synthesis of such films could be performed by various methods, such as sputtering deposition, molecular beam epitaxy, sol–gel deposition, plasma-enhanced chemical vapor deposition etc. Most frequently the preparation of ultrathin oxide films is performed by oxidizing a metal surface resulting in formation of a thin layer of native oxide. Oxidation of vanadium in atomic in molecular oxygen was already studied before [9,10] however the results on oxide growth kinetics and metal–oxide interface formation have not been yet reported. Over the last years novel methods of ultrathin metal oxide film preparation such as ion beam and plasma oxidation have attracted considerable attention [11–13]. In the case of plasma oxidation the metal surface is exposed to highly reactive low energy oxygen species resulting in formation of thin oxide film. It is expected that such method can be beneficial compared to other oxidation techniques due to its higher degree of controllability and superior oxidation rate at room temperature.

In the present work we report on the oxidation of vanadium surface in a low-temperature oxygen plasma studied by in-situ photoelectron spectroscopy (XPS, UPS). The stepwise oxidation allows to study the band structure and the film composition at different stages of growth process. Analysis of angle-resolved photoemission spectra offers a clearer view on transition layer composition and width of the metal–oxide interface.

2. Experimental details

Substrate of polycrystalline vanadium foil ($10 \times 10 \times 0.05$ mm^3 from Goodfellow, 99.95% pure) was polished using a standard electrochemical mechanical polishing procedure described elsewhere [14] resulting in surface roughness value of ~ 2 nm as measured by atomic force microscopy. Prior to oxidation the sample was successively subjected to Ar^+ sputtering and heating at 800 °C in order to remove surface contamination. The sample was put on water cooled grounded electrode and was then

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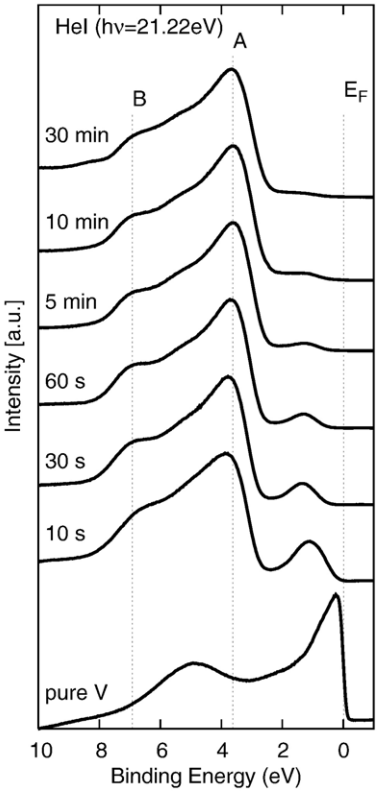

Fig. 1. Evolution of the valence band spectra (HeI) as a function of the oxidation time. The bottom most spectrum corresponds to the original vanadium substrate.

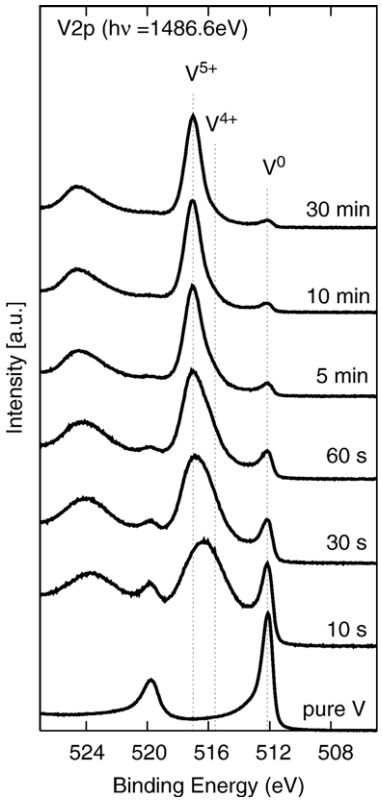

Fig. 2. The V 2p core-level spectra taken at normal emission for different oxidation times. The positions of oxidation states are marked with dashed lines.

oxidized in a low-temperature reactive oxygen r.f. plasma for different time intervals at pressure of 0.5 Pa and r.f. power 50 W. The bias voltage on electrode to which the power was applied was equal to 175 V. The sample was then transferred into the UPS/XPS analyzing chamber without breaking the vacuum under a background pressure below 1×10^{-7} Pa.

The photoelectron spectroscopy analysis was performed on a VG ESCALAB 210 spectrometer equipped with a monochromatized Al *K*α (1486.6 eV) radiation source and helium discharge lamp emitting in ultraviolet range (HeI, 21.22 eV). The typical resolution was 0.1 eV for UPS and 0.35 eV for MXPS measurements. The energy position of the spectra presented below is given with respect to the Au $4f_{7/2}$ core-level line of a clean gold sample positioned at 84.0 eV binding energy.

3. Results and discussion

Fig. 1 shows the valence band spectra (HeI) measured as a function of the exposure time to the oxygen plasma. The bottommost spectrum corresponds to pristine (unexposed) polycrystalline vanadium and is dominated by emission from the vanadium d band with minor contribution from s and p bands. A broad peak around 5 eV stems from the surface contamination with residual oxygen (<2% according to XPS). The short (10 s) exposure of the vanadium surface to the oxygen plasma leads to a remarkable change of shape of V 3d band accompanied by formation of two broad features denoted on Fig. 1 as "A" and "B" and centered at 4.3 eV and 7 eV respectively. According to previously published results [15] and band calculations of Gupta et al. [16] the A-band could be assigned to nonbonding oxygen band (O 2pπ) whereas B-band is related to bonding of oxygen 2pσ orbitals with vanadium d band. The drastic decrease in the intensity at the Fermi edge and shift of V 3d band from the Fermi level indicate the insulating character of the obtained film. This trend is continued with increasing

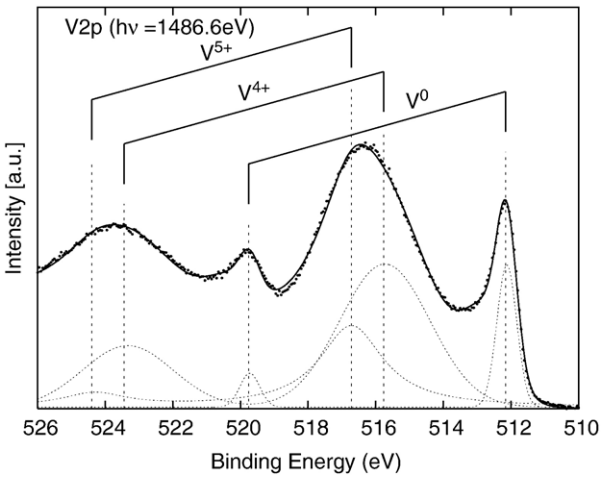

Fig. 3. The V $2p_{3/2}$ core-level spectrum measured after 10 s oxidation run. Dashed lines represent the chemically shifted components after core-line decomposition.

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