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XPS study of vanadium surface oxidation by oxygen ion bombardment

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Abstract

Oxidation of vanadium metal surfaces at room temperature by low-energy oxygen ion beams is investigated by X-ray photoelectron spectroscopy (XPS). It is observed that ion-beam irradiation of clean V results in formation of thin oxide layer containing vanadium in oxidation states corresponding to VO, V_2O_3 , VO_2 and V_2O_5 oxides. The composition of the products of ion-beam oxidation depends markedly on oxygen ion fluence. The results of angle-resolved XPS measurements are consistent with a structure of oxide film with the outermost part enriched in V_2O_5 and VO_2 oxides and with V_2O_3 and VO oxides located in the inner region of the oxide layer. © 2006 Elsevier B.V. All rights reserved.

Keywords: Vanadium oxide; Oxide film; Ion-beam oxidation; X-ray photoelectron spectroscopy

1. Introduction

Vanadium oxides play an important role in a number of modern technological applications. For example, they are active as catalysts for many of industrially important reactions including oxidation of sulphur dioxide, partial oxidation of hydrocarbons and selective reduction of nitric oxide [1,2]. Thin films of V oxides are employed as electro-optical switching devices, light detectors and temperature sensors [2,3]. Vanadium oxides exhibit interesting electronic properties. For example, in V₂O₃ metal–insulator transition occurs at 160 K and in VO₂ semiconductor–metal transition at 340 K was reported [4]. The unique physical and chemical properties of supported vanadium oxide films were observed and interpreted in terms of interaction of oxide layer with the supporting material [4].

Oxide films are most frequently prepared by evaporation and sputtering. Another perspective method of growing oxide film on a metal consists in irradiation of metal sur-

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face by low-energy (0.1–10 keV) oxygen ions under high-vacuum conditions [5–8]. Up to now, relatively little attention has been paid to oxide phases produced by bombarding metal surfaces with oxygen ions. This method allows growing of thin layers of various oxides, the composition of which can be varied by varying the ion flux, ion energy and target temperature. The thickness of oxide layer can be easily controlled even if it is limited by simultaneous ion sputtering of the oxide produced and by depth of oxygen ion penetration into the oxidized material. Oxidation can be carried out at low temperatures and selective oxidation of a metal component in alloy is possible. Using the focused ion beams oxide nanostructures can be fabricated on metal or semiconductor surfaces.

In this paper we report on the possibility of preparing vanadium oxide films by oxygen ion-beam irradiation of metallic vanadium target. To determine the population of individual oxidation states of vanadium in the oxide layer and to assess their depth distribution angle-resolved Xray photoelectron spectroscopy (ARXPS) was employed. This method is ideal tool for in situ monitoring the chemical composition of produced oxide films. For the purpose

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of comparison the oxide films were also grown by thermal oxidation of vanadium by molecular oxygen.

2. Experimental

The experiments were carried out using a VG ESCA 3 Mk II and Gammadata Scienta ESCA 310 electron spectrometers equipped with a source of AlKa (1486.6 eV) radiation, hemispherical electron analyzer and a VG AG 2 cold cathode ion gun. The pressure in the analyzer chamber during spectra acquisition was 10^{-8} Pa. Polycrystalline vanadium foil 0.127 mm thick (99.7%, Aldrich Chemical Co.) was used as a starting material. Prior to oxidation the vanadium surface was cleaned by sputtering with argon ions (E = 6 keV, $I = 40 \mu$ A). No annealing was applied after sputtering. The oxide layers were grown in the preparation chamber of the spectrometer. In the present experiments molecular oxygen ion bombardment was carried out with ion energy of 6 keV and fluence ranging from 10^{15} to 10^{17} ions/cm². The ion beam was directed normal to the sample surface. The projected range of 3 keV oxygen atoms produced by surface neutralization and dissociation of 6 keV molecular oxygen ions into vanadium metal and calculated using TRIM code is ~ 6 nm. During oxygen ion bombardment the sample was kept at room temperature. The purity of oxygen used (Linde AG) was 99.998%. The samples with oxide layer were transferred into the analyzer chamber of the spectrometer under ultrahigh vacuum. The spectra of V 2p and O 1s electrons were measured at several different detection angles. The electron analyzer was operated in the fixed transmission mode. The energy scale of the spectrometer was calibrated to the Au $4f_{7/2}$ binding energy fixed at 84.0 eV. No static charging of oxide layer was observed; the spectra measured with flood gun on and off coincided. The estimated error in the determination of the binding energies was ± 0.1 eV. Fitting of the V 2p–O 1s spectra was essential for determination of oxidation states of V present in the oxide layer. This was done after subtraction of Shirley background using Gaussian-Lorentzian sum function and XPSPEAK 4.1 software [9].

3. Results and discussion

Fig. 1 shows the high-resolution spectra of V 2p–O 1s electrons of clean vanadium surface and surface oxidized with oxygen ion beam using low and high ion fluence, respectively. The fits of the spectra show in addition to V $2p_{3/2}$ line located at 512.4 eV and belonging to metallic V the presence of components centered at 513.6, 515.2, 515.8 and 517.2 eV. Comparison of these values with the data found in the literature [10–15] allows attributing these components to V²⁺, V³⁺, V⁴⁺ and V⁵⁺ oxidation states of vanadium, respectively. The binding energy of the peak located at 513.6 eV compares to value 513.5 and 513.7 eV published for thin films of VO [10–12]. The binding energy of the peak centered at 515.2 eV is in the range of the values reported for bulk V₂O₃ oxides (515.2–515.7 eV)



Fig. 1. Fitted spectra of V 2p and O 1s core electrons taken from clean V surface (a), after oxidation by molecular oxygen ions (E = 6 keV) with fluence $D = 9.4 \times 10^{14} \text{ ions/cm}^2$ (b) and $D = 1.7 \times 10^{17} \text{ ions/cm}^2$ (c). Detection angle is 45°.

[12–15]. The binding energies of the peaks located at 515.8 eV and 517.2 eV are close to those published for bulk VO₂ oxides (515.7–516.2 eV) [12–15] and bulk V₂O₅ oxides (516.9–517.2 eV) [12–15], respectively.

The dependence of the population of individual oxidation states of vanadium on the oxygen ion fluence is given in Fig. 2. It follows from this figure that with increasing



Fig. 2. The population of different oxidation states of vanadium as a function of oxygen ion fluence calculated from the fitted XP spectra.

fluence of irradiation the overall thickness of oxide layer increases (intensity of the component belonging to metallic V decreases). In the initial stages of oxidation the population of all oxidation states of V increases while at higher ion fluence the relative amounts of V_2O_3 and VO start to decrease and the relative population of V_2O_5 and VO_2 continues to increase.

There are two competing processes taking place during irradiation of a metal surface by oxygen ions that determine the thickness and composition of oxide layer: production of oxides and their sputtering [5–8]. For understanding the relationships between the oxidation parameters (energy of ions, fluence, and temperature) and the layer composition and for determination of absolute cross-sections for beam-surface reaction [16] additional and more detailed studies are required.

For the purpose of comparison we studied also the composition of the oxide layers produced by oxidation of V with molecular oxygen at room temperature and at 673 K. The spectra of V 2p–O 1s electrons of vanadium oxidized by molecular oxygen along with the spectra of sample oxidized by oxygen ion beam are displayed in Fig. 3. It follows from the comparison of the spectra in Fig. 3 that qualitatively the same oxidation states of V are most likely produced by both methods, thermal oxida-



Fig. 3. Fitted spectra of V 2p and O 1s core electrons taken from V surface oxidized by 100 Langmuir exposure of molecular oxygen at room temperature (a), 1.2×10^4 Langmuir at 673 K (b) and after oxidation by molecular oxygen ions (E = 6 keV, $D = 1.1 \times 10^{15}$ ions/cm²) (c). Detection angle is 45°.



Fig. 4. The population of individual oxidation states of vanadium obtained from the fitted spectra of the V 2p electrons as a function of detection angle defined from the sample surface.

tion and ion-beam oxidation. However, the population of individual oxidation states of vanadium is different. The chemical composition of oxide surface layer already in the initial stage of the ion-beam oxidation is comparable with that obtained after heavy thermal oxidation. At higher fluences the efficiency of the ion-beam oxidation increases considerably.

To get insight into the depth distribution of individual oxidation states of vanadium the spectra of V 2p electrons were measured at several different detection angles. The dependence of the population of individual oxidation states as a function of the detection angle (defined from the sample surface) is given in Fig. 4. It is seen from this figure that the angle dependence of individual oxidation state populations is different. With detection angle increase the population of V^0 , V^{2+} and V^{3+} oxidation states increases while the population of V^{4+} and V^{5+} oxidation states decreases. This finding indicates that the outer part of the oxide film is enriched in V^{5+} and V^{4+} oxidation states while V^{3+} and V^{2+} oxidation states are located in the inner region of the film.

4. Conclusions

Oxidation of vanadium by molecular oxygen ion bombardment at room temperature has been studied in situ by angle-resolved X-ray photoelectron spectroscopy. The four different oxidation states of vanadium, namely V^{5+} , V^{4+} , V^{3+} and V^{2+} were identified in the oxide film and dependence of their population on ion fluence has been determined. The results of angle-resolved measurements are consistent with a structure of the oxide film with the outermost part enriched in V^{5+} and V^{4+} oxidation states while V^{3+} and V^{2+} oxidation states are located in the inner region.

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References

- [1] B.M. Weckhuysen, D.E. Keller, Catal. Today 78 (2003) 25.
- [2] V.E. Henrich, P.A. Cox, The Surface Science of Metal Oxides, Cambridge University Press, Cambridge, 1996, p. 211.
- [3] M.G. Krishna, Y. Debauge, A.K. Bhattacharya, Thin Solid Films 312 (1998) 116.
- [4] S. Surnev, M.G. Ramsey, F.P. Netzer, Prog. Surf. Sci. 73 (2003) 117.

- [5] K.S. Kim, W.E. Baitinger, T.W. Amy, N. Winograd, J. Electron Spectrosc. Relat. Phenom. 5 (1974) 351.
- [6] N.V. Alov, G.B. Petrov, G.A. Grigorev, Dokl. Akad. Nauk. 294 (1987) 623.
- [7] L.D. Lopez-Carreno, G. Benitez, L. Viscido, J.M. Heras, F. Yubero, J.P. Espinos, A.R. Gonzalez-Elipe, Surf. Sci. 402–404 (1998) 174.
- [8] N.V. Alov, Poverkhnost (No. 3) (2005) 6.
- [9] www.phy.cuhk.edu.hk/~surface/XPSPEAK.
- [10] M. Della Negra, M. Sambi, G. Granozzi, Surf. Sci. 436 (1999) 227.
- [11] M. Petukhov, G.A. Rizzi, G. Granozzi, Surf. Sci. 490 (2001) 376. [12] G. Silversmit, D. Depla, H. Poelman, G.B. Marin, R. De Gryse,
- J. Electron Spectrosc. Relat. Phenom. 135 (2004) 167.
- [13] G.A. Sawatzky, D. Post, Phys. Rev. B 20 (1979) 1546.
- [14] J. Mendialdua, R. Casanova, Y. Barbaux, J. Electron Spectrosc. Relat. Phenom. 71 (1995) 249.
- [15] M. Demeter, M. Neumann, W. Reichelt, Surf. Sci. 454-456 (2000) 41.
- [16] H.-K. Hu, T. Murray, Y. Fukuda, J.W. Rabalais, J. Chem. Phys. 74 (1981) 2247.