

IR AND X-RAY PHOTOELECTRON SPECTROSCOPY OF V₂O₅, TiO₂ AND V/Ti-OXIDE SOL-GEL DERIVED FILMS

INFRARDEČA IN RENTGENSKA FOTOELEKTRONSKA SPEKTROSKOPIJA V₂O₅, TiO₂ IN V/Ti-OKSIDNIH SOL-GEL FILMOV

ĐORDE MANDRINO¹, M. JENKO^{1,*}, A. ŠURCA², B. OREL²

¹Institute of Metals and Technology, Lepi pot 11, SI-1000 Ljubljana

²National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana

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V/Ti-oxide films were prepared by dip-coating from sols made by mixing of V-oxoisopropoxide and Ti-propoxide in V:Ti molar ratio in precursors 3:1, 1:1 and 1:3. Amorphous films were obtained after annealing at 300°C (1 h). IR spectroscopic analysis revealed that V=O stretching modes appeared at 1020 cm⁻¹ in the IR spectrum of powder (V:Ti=1:1). However, in the IR spectra of a film with the same molar ratio the bands at 1008 and 914 cm⁻¹ appeared suggesting the presence of V⁴⁺-O bonds. The new band at 790 cm⁻¹ signalled the V-O-Ti bridging bonds connecting V-O and Ti-O polyhedra. XPS measurements confirmed that initial-state films contained V³⁺, V⁴⁺ and Ti⁴⁺ species, but at the film surface only V³⁺ species existed. Sequential depth analysis of films performed with Ar⁺ sputtering showed that the vanadium is reduced to 3+ oxidation state with progressive exposure while titanium is not affected.

Key words: electrochromic (EC) devices, oxide films, IR spectroscopy, XPS, oxidation states, sputtering, sol-gel

V/Ti-oksidge filme smo pripravili iz koloidnih raztopin V-oksioizopropoksida in Ti-propoksida v 2-propanolu s tehniko potapljanja. Molska razmerja V:Ti v prekurzorjih so znašala 3:1, 1:1 in 1:3. Amorfní filmi so nastali po segrevanju na 300°C (1h). V IR spektru praškastega vzorca (V:Ti = 1:1) so se valenčna nihanja V=O pojavila pri 1020 cm⁻¹. V IR spektru filma z istim molskim razmerjem pa se pojavita trakova pri 1008 cm⁻¹ in 914 cm⁻¹, kar kaže na prisotnost V⁴⁺-O vezi v filmih. Novi trak pri 790 cm⁻¹ kaže na V-O-Ti vezi, ki povezujejo poliedre V-O in Ti-O. XPS meritve so potrdile, da filmi vsebujejo V⁴⁺, V³⁺ in Ti⁴⁺, medtem ko je na njihovem površju prisoten le V³⁺. Profilna analiza filma s pomočjo Ar⁺ ionskega jedkanja je pokazala, da se vanadij tekom jedkanja reducira do oksidacijskega stanja 3+, medtem ko jedkanje ne vpliva na oksidacijsko stanje titana.

Ključne besede: elektrokromne (EC) naprave, oksidni filmi, IR spektroskopija, XPS, oksidacijska stanja, ionsko jedkanje, sol-gel

1 INTRODUCTION

Sol-gel processing is a rapidly growing field of material chemistry with applications in synthesis of glasses, ceramics, organic-inorganic hybrid materials and thin films¹. Thin films for window glazings were one of the first commercial products of sol-gel processing and can be easily made by using a dip-coating deposition¹. The main advantage of the dip-coating is the possibility of the preparation of large-area films with only a fraction of cost needed for the production of sputtered or evaporated films. Dip-coating is performed by pulling a substrate slowly from aqueous or alcoholic sols¹. During pulling solvent evaporates from the deposited thin layer of the sol on the glass substrate allowing the reactions between colloidal species. These condense in larger aggregates which results in a formation of a compact xerogel film. Its annealing at elevated temperatures (up to 500°C) brings about metal oxide film with an amorphous or crystalline structure, desired surface texture and porosity. The deposition of multicomponent films is easy to perform because precursors are mixed at the molecular level, i.e. in solution. High homogeneity of films is therefore obtained.

In this paper we report investigations of V/Ti-oxide films which were made from alkoxide precursors of vanadium and titanium after annealing at 300°C. Sputter-deposited V/Ti-oxide films with an amorphous structure exhibit intercalation properties and are currently used in electrochromic (EC) devices². In EC devices they function as counter-electrodes assuring the balance of the charge which is transported from the active colouring films (WO₃ in most cases) through the lithium ionic conductor (electrolyte) which glues both parts of the EC device together to the counter-electrode film³. To achieve electronically balanced EC device ion-storage capacity of the counter-electrode should be nearly the same as that of WO₃ film (40 - 50 mCcm⁻²). Sputtered V/Ti-oxide exhibit ion-storage capacity in the range 30 - 40 mCcm⁻² (4), i.e. close to that of WO₃ films. Additionally, the optical modulation of V/Ti-oxide counter-electrodes is small, they are highly transparent (>70%) in both charged and discharged states contributing to the total transmittance of the EC device. This property is particularly important for "smart" window applications³.

Preliminary studies of sol-gel derived V/Ti-oxide films (300°C) revealed that films were amorphous and formed solid solutions in the whole concentration range

* To whom the correspondance should be adressed.

(0 - 100% of V or Ti)⁵. IR spectroscopy combined with electrochemical (CV)⁶ and in-situ UV-VIS spectroelectrochemical measurements^{2,5} revealed that in initial-state films vanadium could be either in 5+, 4+ or both oxidation states, while the oxidation state of titanium was proposed to be 4+.

Accordingly, in this work we undertook X-ray photoelectron spectroscopy (XPS) investigations of V/Ti-oxide films aiming to evaluate the oxidation states of V and Ti ions and to compare these results to those gathered from our previous IR spectroscopic and electrochemical investigations^{2,5}. We then made a sequential depth analysis of the same films by using Ar⁺ sputtering. Correct assignment of XPS spectra of films containing V and Ti is not trivial because both elements show tendency to become reduced due to the Ar⁺ sputtering during XPS measurements. We explain the XPS results on the basis of known binding energies of various V and Ti compounds and by using a standard deconvolution procedure available at our XPS spectrometer.

2 EXPERIMENTAL

Amorphous V/Ti-oxide films with V:Ti molar ratios in precursors 3:1, 1:1 and 1:3 were prepared via a sol-gel alkoxide route⁷. A titanium (IV) propoxide and vanadium (V) oxoisopropoxide were added into 2-propanol while atmospheric water was sufficient to initiate the hydrolysis reactions. The V₂O₅ and TiO₂ sols were prepared by

adding the appropriate amount of corresponding alkoxide into 2-propanol. The films were deposited by dip-coating on SnO₂:F glass substrates or silicon wafers and annealed at 300°C for 1 hour in air. The approximate thickness of V/Ti-oxide films was 80 nm. The V₂O₅, TiO₂ and V/Ti-oxide powders were prepared by first drying the sol in air and annealing the residue at various temperatures for 1 h⁵.

FT-IR spectroscopic measurements were obtained using a Perkin Elmer System 2000 spectrometer. The resolution was 4 cm⁻¹. V/Ti-oxide powders were pressed in KBr pellets and the IR spectra were recorded between 4000 and 400 cm⁻¹. The V/Ti-oxide films were deposited on silicon wafers for FT-IR absorbance measurements⁸.

Films to be examined by XPS were deposited on SnO₂:F glass substrates with the area of about 1 cm². This was enough to ensure that all signal in XPS spectra was due to X-ray irradiation of the film under investigation since the irradiated area of the sample is about 3x6 mm². XPS measurements were obtained using a VG Microlab 310-F system equipped with an XPS facility. Mg K_α radiation (1253.6 eV) was used. Carbon 1s peak at 284.8 eV was used as an internal standard. Pressure in the analysis chamber was below 10⁻⁹ mbar. During the sputtering the pressure did not exceed 10⁻⁷ mbar due to the differentially pumped ion gun. Sputtering rate (≈ 1 nm/min) was partly controlled by argon influx into the ion gun and partly by focusing of the ion beam. XPS spectra were processed by Eclipse Data System v 2.1 software package. SIMPLEX fitting algorithm with linear combination of Gaussian and Lorentzian peak shapes was used in deconvolution subroutine of the software.

3 RESULTS AND DISCUSSION

3.1 FT-IR spectra of powders and films

Bands at 1018, 990, 806 and 535 cm⁻¹ in the IR spectrum of a V/Ti-oxide powder with the molar ratio V:Ti = 3:1 (300°C, 1 h) resemble those observed in the IR spectrum of a V₂O₅ powder (200°C, 1 h), (**Figure 1**). Certain bands, i.e. 1018, 806 and 535 cm⁻¹, also coincide with transversal (TO) optical modes in the IR absorbance spectrum of the crystalline V₂O₅ films annealed at 300 or 400°C^{8,9}: the V=O (vanadyl) stretching at 1016 cm⁻¹, the bridging V-O_B-V stretching at 795 cm⁻¹ and the 3V-OC stretching mode at 475 cm⁻¹. In the IR spectrum of V/Ti-oxide powder (V:Ti=1:3) in **Figure 1** the Ti-O stretching mode is predominant, however, the band at 1018 cm⁻¹ confirms the presence of V=O groups (V⁵⁺-O bonds). The Ti-O stretching (601 cm⁻¹) can neither be ascribed to anatase nor rutile. This agrees with the fact that crystalline TiO₂ (anatase) does not appear below 500°C.

The IR spectrum of the V/Ti-oxide powder (V:Ti = 1:1; 300°C) differs considerably from the IR spectra of V₂O₅ (200°C), TiO₂ and V/Ti-oxide powders (V:Ti=3:1 and 1:3), (**Figure 1**). The presence of a strong band at 823 cm⁻¹ suggests that V/Ti-oxide at 300°C forms a solid

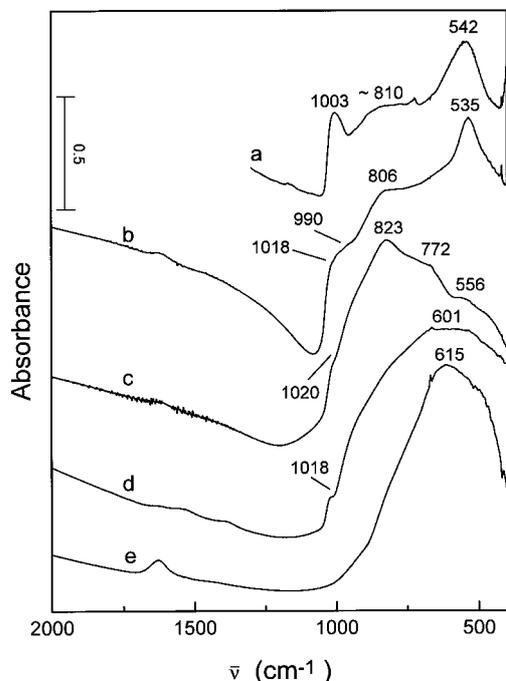


Figure 1: IR absorbance spectra of powders: a) V₂O₅, 200°C (1h), b-d) V/Ti-oxide, 300°C (1h) and e) TiO₂, 300°C (1h). Molar ratios V:Ti in precursors are: b) 3:1, c) 1:1 and d) 1:3

Slika 1: IR absorbcijnski spektri prahov: a) V₂O₅, 200°C (1h), b-d) V/Ti-oksidi, 300°C (1h) in e) TiO₂, 300°C (1h). Molska razmerja V:Ti v prekurzorjih so: b) 3:1, c) 1:1 in d) 1:3

solution. Weak 1020, 772 and 556 cm^{-1} bands indicate the presence of V=O and 3V-O_C modes typical of edge-sharing V-O pyramids⁸. The strong band at 823 cm^{-1} undoubtedly reveals the V-O-Ti groups which link the polyhedra of V and Ti together.

FT-IR absorbance spectra of TiO₂ and V/Ti-oxide film with a molar ratios of V:Ti = 3:1 and 1:1 (300°C) are depicted in **Figure 2**. The IR spectra of an initial-state V/Ti-oxide films (**Figure 2**) and powders (**Figure 1 b, c**) reveal similar features. However, the bands in the IR absorbance spectrum of the initial-state film are systematically shifted to lower frequencies. The reason is the polarisation effect¹⁰, which shifts the IR bands of powders in the frequency range between the transversal (TO) and longitudinal (LO) optical modes. The former are observed in IR absorbance spectra of films while the latter are detected in near-grazing incidence angle (NGIA) IR spectra⁷ (not shown here).

In the IR spectrum of an initial-state V/Ti-oxide film with the V:Ti molar ratio 1:1 (**Figure 2**) - contrary to the strong band at 823 cm^{-1} in the IR spectrum of the powder in **Figure 2** (V-O-Ti stretching) - a less distinct band at 790 cm^{-1} is observed. We did not detect any band around 500 cm^{-1} due to the 3V-O_C mode. Obviously Ti modifies the structure of the V/Ti-oxide film by forming V-O-Ti bonds. However, the 3V-O_C mode appears in the IR spectrum of the V/Ti-oxide film (V:Ti = 1:1) prepared at 400°C² and signals the segregation to V₂O₅ and TiO₂

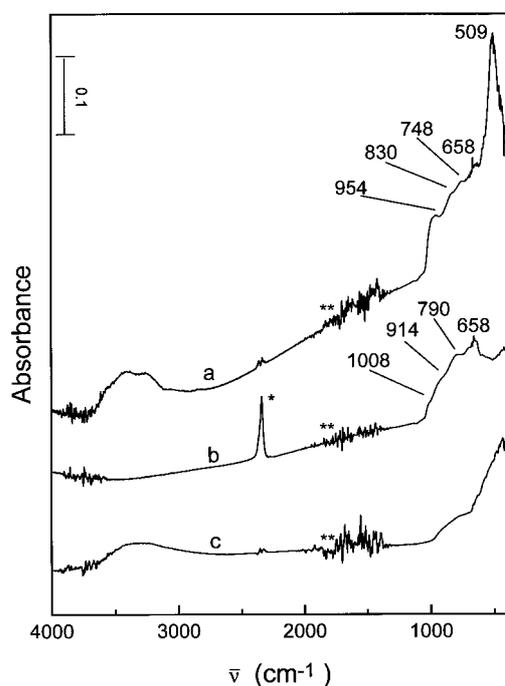


Figure 2: FT-IR absorbance (TO) spectra of: a, b) V/Ti-oxide films and c) TiO₂ film annealed at 300°C for 1h. The molar ratios V:Ti are: a) 3:1 and b) 1:1. * and ** denote CO₂ and water absorption band due to insufficient purging

Slika 2: FT-IR absorpcijski (TO) spektri: a, b) V/Ti-oksidičnih filmov in c) TiO₂ filmov segrevanih 1h na 300°C. Molska razmerja V:Ti so: a) 3:1 in b) 1:1. * in ** označujeta absorpcijske trakove CO₂ in vode zaradi nezadostnega čiščenja

phases. The 658 cm^{-1} band in **Figure 2** is an artefact from the Si substrate.

3.2 XPS measurements

XPS spectra of V₂O₅, TiO₂ and V/Ti-oxide films (V:Ti=1:1) annealed at 300°C are shown in **Figure 3**. Peaks at 458.4 eV observed in XPS spectra of TiO₂ and V/Ti-oxide films correspond to Ti 2p_{3/2} peaks of Ti⁴⁺. The V 2p_{3/2} peaks corresponding to V⁵⁺ appeared at 517.2 eV in XPS spectra of V₂O₅ and V/Ti-oxide films. Surprisingly, XPS spectrum of initial-state V/Ti-oxide film did not show the presence of V⁴⁺ phase as we expected from the IR spectra of V/Ti-oxide films (**Figure 2**). However, IR spectrum of the powder (**Figure 1c**) showed the V=O stretching band (V⁵⁺ sites). At 1020 cm^{-1} which occur due to the oxidation of the large surface of the powder grains. To prove the presence of the surface rich V⁵⁺ states the argon sputtering with sputtering rate of 1 nmmin⁻¹ was used for the removal of the surface layer of the film. Corresponding XPS spectra measured after 3, 4,

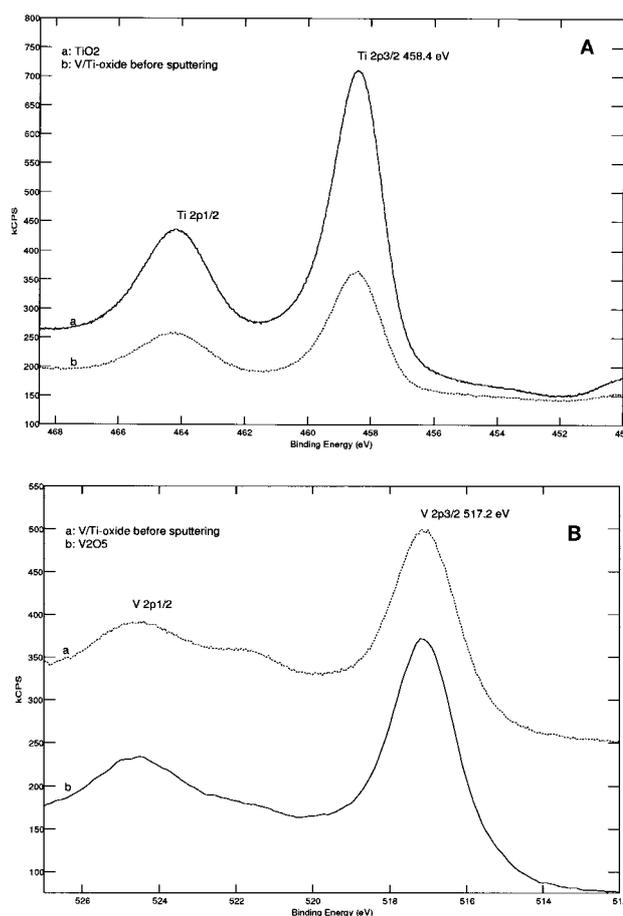


Figure 3: XPS spectra of the initial-state of: A) V/Ti-oxide and TiO₂ films (Ti 2p_{3/2}) and B) V/Ti-oxide and V₂O₅ films (V 2p_{3/2}). The V/Ti-oxide film with a V:Ti molar ratio 1:1 was annealed at 300°C for 1 h

Slika 3: XPS spektri začetnih stanj: A) V/Ti-oksidičnih in TiO₂ filmov (Ti 2p_{3/2}) in B) V/Ti-oksidičnih in V₂O₅ filmov (V 2p_{3/2}). V/Ti-oksidični film z V:Ti molskim razmerjem 1:1 je bil 1 h segrevan na 300°C

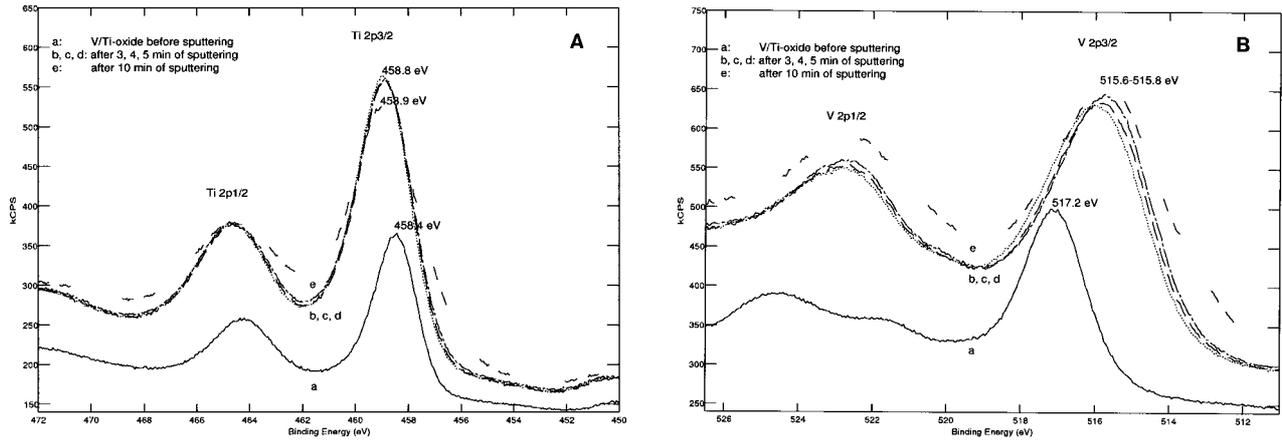


Figure 4: XPS spectra of V/Ti-oxide film: A) Ti 2p_{3/2} and B) V 2p_{3/2} peaks. The XPS spectra were taken: a) before sputtering and after sputtering for: b) 3 min, c) 4 min, d) 5 min and e) 10 min. V/Ti-oxide film with a V:Ti molar ratio 1:1 was annealed at 300°C for 1 h

Slika 4: XPS spektri V/Ti-oksidičnih filmov: A) Ti 2p_{3/2} in B) V 2p_{3/2} vrhov. XPS spektri so bili posneti: a) pred ionskim jedkanjem in po: b) 3 min jedkanja, c) 4 min jedkanja, d) 5 min jedkanja in e) 10 min jedkanja. V/Ti-oksidični film z V:Ti molskim razmerjem 1:1 je bil 1 h segrevan na 300°C

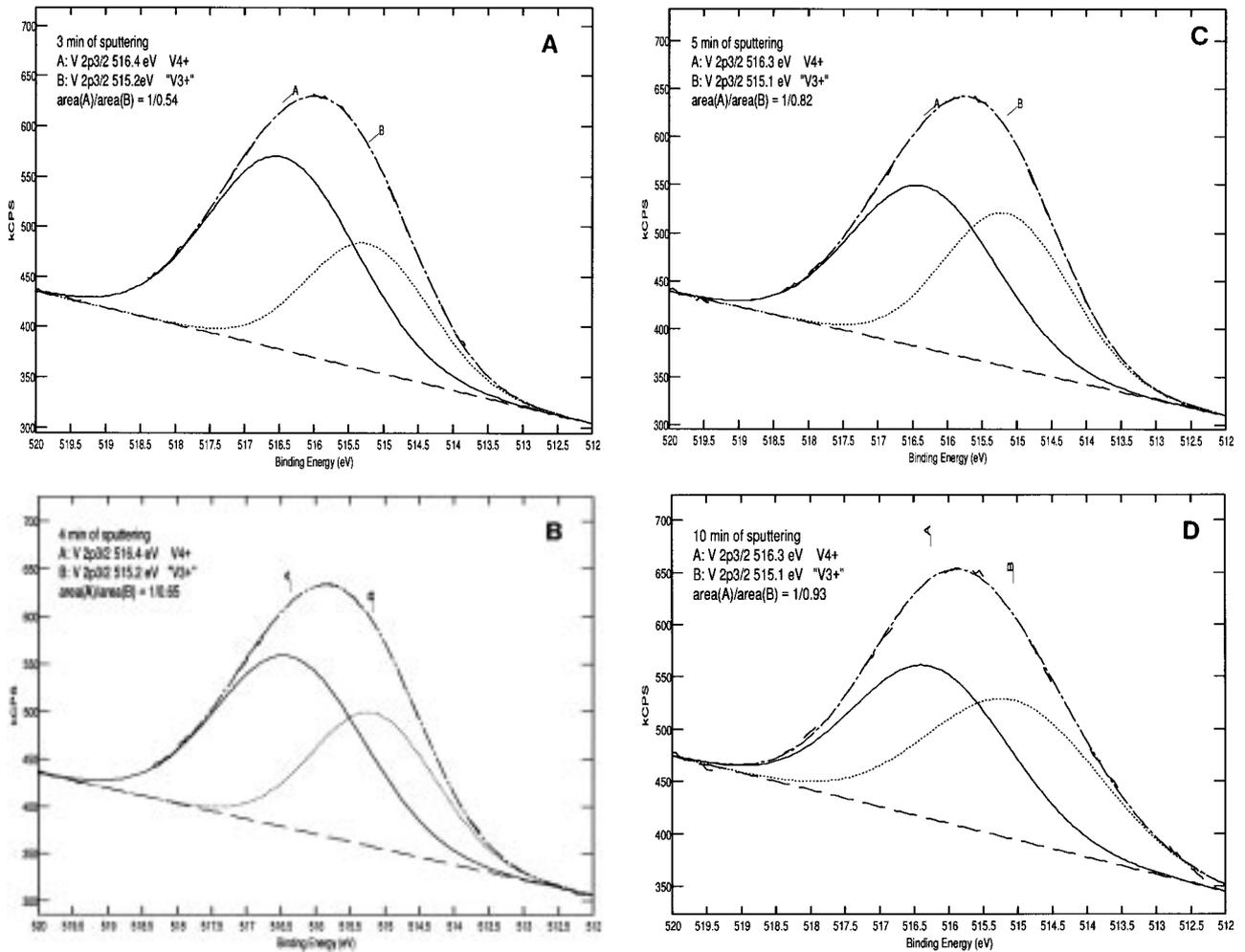


Figure 5: Deconvolution of V 2p_{3/2} peaks in XPS spectra of V/Ti-oxide film obtained after sputtering for: A) 3 min, B) 4 min, C) 5 min and D) 10 min. V/Ti-oxide film with a V:Ti molar ratio 1:1 was annealed at 300°C for 1 h

Slika 5: Dekonvolucija vrhov V 2p_{3/2} v XPS spektrih V/Ti-oksidičnega filma po ionskem jedkanju: A) 3 min, B) 4 min, C) 5 min in D) 10 min. V/Ti-oksidični film z V:Ti molskim razmerjem 1:1 je bil 1 h segrevan na 300°C

5 and 10 minutes of sputtering showed that Ti $2p_{3/2}$ peaks shifted 0.4 to 0.5 eV towards higher binding energies with respect to the non-sputtered V/Ti-oxide film (**Figure 4a**). In addition, the shift of this peak towards higher binding energies ruled out the expected change in oxidation state of Ti from 4+ to 3+ which would result in a shift towards lower binding energies. This could be due to the presence of V-O-Ti bonds in the structure of V/Ti-oxide film.

Contrary to Ti $2p_{3/2}$ peak V $2p_{3/2}$ peaks of Ar⁺ sputtered V/Ti-oxide film (V:Ti=1:1) were shifted 1.4 to 1.6 eV towards lower binding energies (**Figure 4b**). Nevertheless, this energy shift is somewhat too large to be attributed unequivocally solely to a difference between V⁵⁺ (517.2 eV) and V⁴⁺ (516.3 eV) phases. It was therefore assumed that the observed V $2p_{3/2}$ peaks in Ar⁺ sputtered V/Ti-oxide film consist of two overlapping peaks, the first one belonging to the V⁴⁺ component and the additional one originating from V species in oxidation states lower than 4+. To verify this idea we made the deconvolution analysis of V $2p_{3/2}$ peaks in XPS spectra obtained after different sputtering times (**Figure 5**). Deconvolution analysis show that the $2p_{3/2}$ peaks are actually composed of two components: the first located at higher binding energy of 516.3 - 516.4 eV undoubtedly corresponds to V⁴⁺ species while the second with the binding energy of 515.1 - 515.2 eV could be assigned to V³⁺ species. However, the position of the latter peak is about 0.3 eV too low to be due solely to the V³⁺ species. It is likely that the additional component stemming from the V reduction to oxidation states lower than 3+ is present in the second peak. However, any attempt to deconvolute the V $2p_{3/2}$ peaks into more than two components resulted in worse fitting (higher χ^2 values) indicating that the energy peak of the second component is the characteristic feature of the V/Ti-oxide structure. Without knowing the binding energy values of $2p_{3/2}$ peaks of V/Ti-oxide more detailed deconvolution analysis of the experimental XPS spectra could not be done. We also tried to deconvolute the V $2p_{3/2}$ peak of non-sputtered V/Ti-oxide film to check the possible presence of the V⁴⁺ component in the surface layer. However, very high χ^2 values were obtained suggesting that such a fit was unrealistic. The deconvolution analysis proved that the structure of the inner part of the V/Ti-oxide films consists also of V⁴⁺ species and that the sputtering increases the amount of V³⁺. The latter was also judged from the increase in the ratio of the respective areas of V³⁺ and V⁴⁺ peaks with sputtering time (**Figure 5**).

4 CONCLUDING REMARKS

XPS spectra of V/Ti-oxide films revealed the binding peak of V $2p_{3/2}$ at 517.2 eV¹¹ which undoubtedly confirmed the presence of V⁵⁺ species in the upper layer of initial-state films. This agrees with the fact that the upper part of the V/Ti-oxide film has been completely oxidised

during the annealing at 300°C (1 h). Like the binding energy peak of V⁵⁺ also Ti⁴⁺ peak at 458.4 eV observed in XPS spectra of the upper part of the films did not show considerable deviation¹² from the binding energy expected for Ti in 4+ oxidation state. In Ar⁺ sputtered film Ti peak shifts to higher energies contrary to the expected shift of Ti in 3+ oxidation state¹². The positive energy shift of the Ti $2p_{3/2}$ peak clearly signalled the electron band structure around titanium in the V/Ti-oxide film and therefore could not be ascribed to a simple sum of XPS spectra of segregated V₂O₅ and TiO₂ phases. This result agrees with results of IR spectra analysis exhibiting the V⁴⁺-O mode at 914 cm⁻¹ contrasting the V=O stretching mode which was found in IR spectra of V₂O₅ films⁸. The presence of the 790 cm⁻¹ band gave evidence of the edge and/or corner-shared V- and Ti-octahedra with at least one well defined V-O-Ti connecting bond.

The behaviour of the V $2p_{3/2}$ binding energy peak at 517.2 eV changed drastically with Ar⁺ sputtering. Already after first 3 nm of etching the peak is shifted to 515.6 eV. The observed energy shift is quite large and is higher than that which could be expected for the pure V⁴⁺ states. Deconvolution of V $2p_{3/2}$ peaks revealed two well defined components: the first one appearing at 516.4 eV and the second one at much lower energies (515.1 eV). The first was assigned to V⁴⁺ states¹¹ while the second very likely corresponds to the mixed V³⁺ and lower V states. This proved that amorphous V/Ti-oxide films prepared via the sol-gel synthesis are not homogeneous with respect to the composition of V ions. Annealing at 300°C is sufficient to oxidise to 5+ state only those vanadium ions which are present in the upper layer of the film while the rest of the film interior contains V⁴⁺ and V⁵⁺ ions together with Ti⁴⁺ species. Slower sputtering rates with very low Ar⁺ current density is planned to be done to decrease the sputtering-induced reduction of V. This is prerequisite before the XPS measurements of electrochemically charged and discharged films will be performed.

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