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Communications

Deposition of Composite Titania/Vanadia Thin Films by Chemical Bath Deposition

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Titania/vanadia composites are of industrial importance as oxidation catalysts.¹ Numerous publications deal with the grafting of titania carrier materials with vanadia surface coatings.² The suitability of sol-gel procedures for the preparation of powders, which consist of titania and vanadia particles beside each other, was also investigated.^{3–5} Sol-gel derived thin films were fabricated and tested for their potential use as antireflective coatings in solar cells.⁶ An alternative to sol-

gel techniques could be chemical bath deposition (CBD), which was recently introduced for the deposition of ceramic thin films from aqueous solutions at low temperatures. CBD here refers to the thermohydrolysis (or "forced hydrolysis") of metal salts for the fabrication of oxidic films. The deposition of multicomponent systems, however, can be difficult to control, since the different metal oxides form under specific conditions (pH, metal ion concentration, temperature). Without the help of complexing agents, the more easily hydrolyzable metal ions deposit first and thus will lead to the formation of a concentration gradient within the film or even to the subsequent deposition of the various oxides.⁷

The work presented here investigates the preparation of mixed titania/vanadia thin films via CBD. The deposition of films consisting of the single components titania and vanadia is well understood.^{7,8} While titania thin films were prepared from a peroxo complex,^{9,10} hydrated vanadia films ($V_2O_5 \cdot nH_2O$) were deposited from vanadic acid.¹¹ Since the synthesis of vanadia particles from sols containing hydrogen peroxide^{12,13} is also known, it could be possible to fabricate multicomponent films using a mixture of the educts for the single component films.

Solutions of the titanium peroxo complex were prepared by addition of titanium tetrachloride to an aqueous solution of hydrogen peroxide. For the synthesis of vanadic acid a solution of ammonium vanadate was

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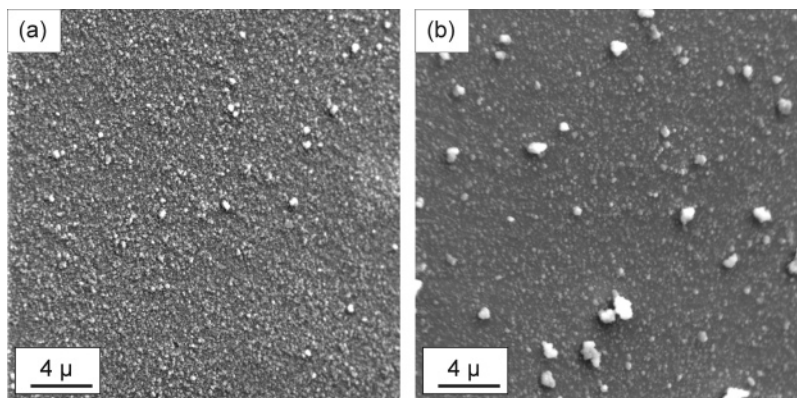


Figure 1. SEM micrographs of as-deposited films grown on SO_3H -modified wafers in 2×3 h at 353 K from solutions containing (a) 10 mM [Ti], 10 mM [V], 140 mM HCl or (b) 7.5 mM [Ti], 2.5 mM, [V] 140 mM HCl, respectively.

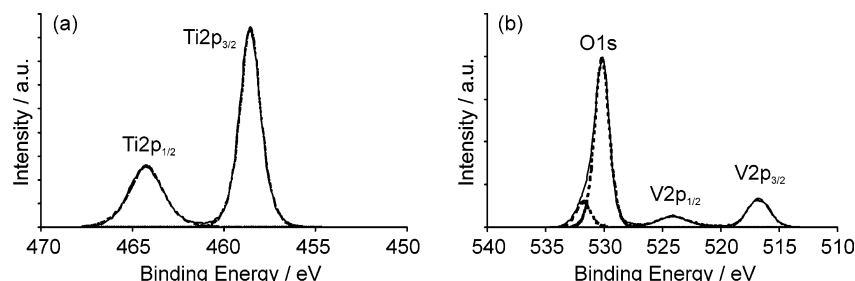


Figure 2. Background-corrected XPS spectra and resolved oxidic main peaks of the as-deposited films grown on SO_3H -modified wafers in 2×3 h at 353 K from solutions containing 10 mM [Ti], 10 mM [V], 140 mM HCl. Resolved (a) Ti $2p$ main peaks and (b) O $1s$ and V $2p$ main peaks, as obtained by constrained peak fitting.

passed through an ion-exchange resin. The reaction solution was fabricated by mixing the appropriate amounts and adjusting the pH with hydrochloric acid. Films could be grown from solutions containing ratios of Ti/V from 1:10 to 10:10. Silicon substrates were functionalized by sulfonate terminated self-assembled monolayers (SO_3H -SAMs) according to known procedures.^{14,15} Deposition was successful on surface-oxidized silicon as well as on SO_3H -SAM modified substrates.

The films are adherent in a tape peel test and show interference colors in dependence of their thickness. Typical surface morphologies are shown in Figure 1. The SEM micrographs show uniform surfaces without cracks. Larger colloidal particles, however, were observed in some cases (Figure 1b).

X-ray photoelectron spectroscopy (XPS) analysis of the prepared oxide films revealed the presence of both Ti-oxide and V-oxide within the film (Figure 2). A constrained curve-fitting of the Ti $2p$ and V $2p$ spin-orbit doublet (i.e., taking the same Gauss-Lorentz fractions and a fixed area ratio of 0.5 for the $2p_{3/2}$ and $2p_{1/2}$ main peaks in the doublets) was performed on the measured XPS spectra after subtraction of a Shirley background. The binding energies of the thus-resolved Ti $2p_{3/2}$ and Ti $2p_{1/2}$ main peaks (458.63 ± 0.05 eV and 464.31 ± 0.05 eV, respectively), as well as the associated value for the spin-orbit splitting of the Ti $2p$ doublet ($5.68 \text{ eV} \pm 0.01$ eV), are in agreement with corresponding literature values^{16,17} for TiO_2 (Figure 2a). The obtained binding

energies of the resolved V $2p_{3/2}$ and V $2p_{1/2}$ main peaks (516.4 ± 0.3 eV and 523.8 ± 0.3 eV, respectively), as well as the associated splitting of the V $2p$ doublet (7.5 ± 0.2 eV), comply with the corresponding literature values¹⁷ for $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (Figure 2b). No other Ti or V oxidic species are evident from the analysis of the measured Ti $2p$ and V $2p$ XPS spectra. The corresponding O $1s$ spectra could be accurately fitted with only two components (see Figure 2b), attributed to TiO_2 (lower-BE peak at 530.1 ± 0.1 eV) with a variable degree of hydroxylation at its surface (i.e., Ti-hydroxide, higher-BE peak at 531.7 ± 0.1 eV).

The formation of titanium peroxides from solutions of titanium peroxo complexes has to be suppressed by choice of an appropriate pH value.^{9,10} Only hydrated vanadium oxide, however, could be obtained from vanadium peroxo complexes.¹² Therefore, no deposition of peroxides is to be expected in the films investigated here. There is further no evidence for the presence of solid solutions.

So far films with Ti/V compositions from 10:1 to 1:1 were obtained, which could be easily adjusted by changing the ratio of the titanium and vanadium component in reaction solution. The films presented in Figure 1a and b had compositions of Ti/V of 2.85:1 and 7.5:1, respectively.

Sputter-depth profiles were recorded using auger electron spectroscopy (AES) to determine the concentrations of Ti, V, O, and Si as a function of depth below the oxide surface (i.e., to investigate whether any changes in the composition of the oxide film have

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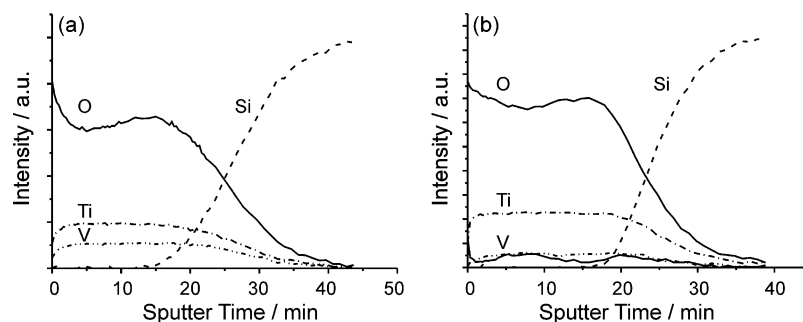


Figure 3. Auger sputter depth profiles acquired from as-deposited films grown on SO_3H -modified wafers in 2×3 h at 353 K from solutions containing (a) 10 mM [Ti], 10 mM [V], 140 mM HCl or (b) 7.5 mM [Ti], 2.5 mM [V], 140 mM HCl, respectively.

occurred during the course of deposition). The resulting concentration–depth profiles (Figure 3), as obtained for different positions on the sample surface, show that the prepared oxide films are homogeneous of composition, both lateral and perpendicular to the sample surface. The film can therefore be considered as a composite of titania and hydrated vanadia nanoparticles. The thickness of the prepared oxide films is approximately 150 nm (as estimated from the corresponding sputter-rate of a Ta_2O_5 film of known thickness on a Ta substrate).

The current model for film deposition via CBD suggests that the colloidal particles, which are generated in the solution, deposit on surfaces through attractive electrostatic interactions between particles and substrates, which can be estimated from the corresponding zeta potentials.¹⁸ For a more detailed view, van der Waals interactions and other contributions have to be included which are subsumed by the DLVO theory.^{18,19}

The pH dependence of the zeta potentials of titania and hydrated vanadia powders from the above-men-

tioned reactions were determined separately giving isoelectric points of 3.5 and 2.0, respectively. Since the pH in the film deposition reaction described above is about 0.85, both titania and vanadia particles will bear a positive charge in solution. They will therefore be attracted by a negatively charged surface like oxidized^{20,21} or SO_3H modified¹⁹ silicon. Since the formation of the films is straightforward for a range of Ti and V concentrations in the reaction solution, strong van der Waals interactions might exist between titania and hydrated vanadia particles, which together form the film. This was suggested for composite titania/vanadia films fabricated via a sol–gel process.³

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Supporting Information Available: Detailed experimental procedure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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