

Deposition of Titanium–Vanadium Oxide Thin Films on Organic Self-Assembled Monolayers: Role of Complexing Agents[†]

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Titanium–vanadium oxide films were co-deposited from aqueous solutions on organic self-assembled monolayers (SAMs) with alkylammonium or amine surface functional groups. The chemical composition of the films was manipulated via the use of lactic acid and oxalic acid as complexing agents. From solutions with [oxalate]:[vanadium] < 1:1, titanium-enriched films were formed. However, with [oxalate]:[vanadium] > 1:1, the Ti:V ratio dropped back to that of films deposited in the absence of complexing agents. Therefore, it is concluded that oxalic acid chelates both titanium and vanadium, but preferentially vanadium. At high concentrations of oxalic acid, no films formed, indicating that both titanium and vanadium were chelated strongly. Lactic acid, in contrast, was oxidized by pentavalent vanadium. When [lactate]:[vanadium] < 1:2, the resulting V⁴⁺ increased the deposition rate of vanadium, and vanadium-rich films were formed. For [lactate]:[vanadium] > 1:2, the remaining (i.e., unoxidized) lactic acid preferentially complexed vanadium and showed effects comparable to those seen with oxalic acid. The thickness of films formed on the alkylammonium SAMs increased with increasing vanadium content in the films, whereas film composition had little or no effect on the thickness of films formed on amine SAMs.

Introduction

Vanadium-oxide-based catalysts are used in oxidation reactions, such as the conversion of SO₂ to SO₃ in the production of sulfuric acid,^{1,2} partial oxidation of methanol to formaldehyde,³ and oxidation of butene to acetic acid.⁴ They are also used in reduction reactions, such as selective catalytic reduction of NO_x by NH₃ (SCR process).⁵

Methods for preparing supported vanadium oxide catalysts include impregnation, grafting, chemical vapor deposition (CVD), atomic layer deposition (ALD), equilibrium adsorption, sol–gel synthesis, and thermo spreading. Almost all of these methods consist of exposing the support material (prepared separately) to a vanadium-containing environment. The present work reports a method of co-deposition of Ti–V oxide films from aqueous solution, that is, a new potentially catalytic material with active phase and support prepared in a single step.

Titania films and vanadia films deposit individually on certain organic self-assembled monolayers (SAMs) via forced hydrolysis of acidic aqueous solutions.⁶ The deposition of

mixed titanium–vanadium oxidic films was recently reported by our group⁷ and by Hoffmann et al.⁸ From mixed aqueous peroxide precursor solutions at 80 °C and pH of 0.85, Hoffmann et al. deposited films 0.15 μm thick in two consecutive 3-h immersions on silicon wafers with and without sulfonate-terminated SAM surfaces. Our work⁷ used a solution of ammonium metavanadate, ammonium hexafluorotitanate (Ti:V = 2:1), and boric acid at pH 2.5 and 45 °C. Films grew to thicknesses of 1.5–1.8 μm on sulfonate- or alkylammonium-terminated SAMs and 1.2–1.5 μm on amine- or carboxylic acid-terminated SAMs, on silicon in single 24-h immersions.

Synthesis of vanadium–titanium oxide catalysts, whether by conventional methods or by co-deposition, requires a means of controlling the vanadium loading in the solid product. Because each metal oxide typically precipitates under different solution conditions,^{9,10} solution deposition of multicomponent materials can be difficult to control. Complexing agents are frequently used in aqueous deposition of sulfide and selenide films^{10–13} to stabilize the metal ion in aqueous solution and thereby control the growth rate of films. Without complexing agents, solutions for co-deposition usually must be enriched in the more slowly hydrolyzing

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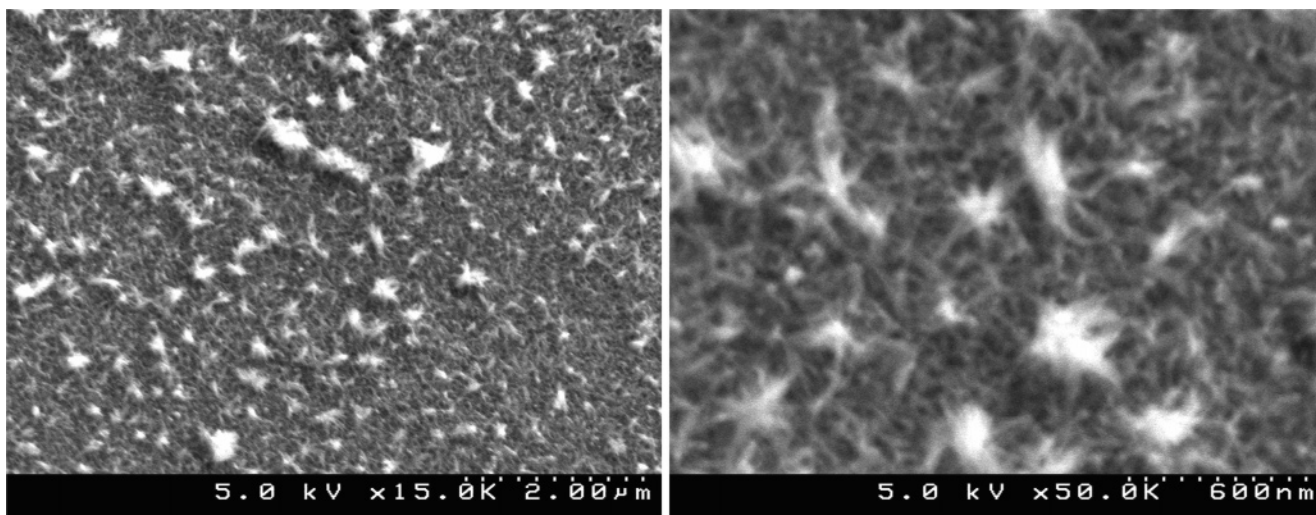


Figure 1. Typical SEM topography of films grown with oxalic acid on amine SAM. Solution contained 50 mM Ti as $(\text{NH}_4)_2\text{TiF}_6$, 25 mM V as NH_4VO_3 , 20 mM oxalic acid, pH initially 2.5, held for 24 h at 45 °C. Ti:V ratio = 48:52 cat. % at film–substrate interface, 53:47 cat. % average over the film thickness; (1060 ± 100) nm thick.

metal to obtain a homogeneous film of the desired composition. By adding a ligand that preferentially complexes with the faster-depositing ions, it should be possible to avoid this divergence in composition between solution and film. The present work examines the effects of complexing agents on the growth rates and compositions of mixed titanium–vanadium oxide films formed on amine and alkylammonium SAM surfaces on silicon wafers.

Baskaran et al.¹⁴ reported growing titania thin films from a commercially available titanium lactate, $(\text{NH}_4)_2(\text{OH})_2\text{Ti}(\text{C}_3\text{H}_4\text{O}_3)_2$. This suggests that lactic acid can complex titanium in aqueous solutions. Vanadia monolayer catalysts can be made from NH_4VO_3 dissolved in oxalic acid.¹⁵ The resulting deep blue solution contains ammonium vanadyl-oxalate, $(\text{NH}_4)_2[\text{VO}(\text{C}_2\text{O}_4)_2]$.¹⁵ This indicates that oxalic acid can complex vanadium in aqueous solution. (Note that although vanadium is in the tetravalent oxidation state in ammonium vanadyl-oxalate, the solution yields crystalline V_2O_5 even at low vanadium contents.)

Experimental Procedures

Deposition of Titanium–Vanadium Oxide Films. The preparation of SAM-modified Si single-crystal substrates with amine ($-\text{C}_{11}-\text{NH}_2$) and alkylammonium ($-\text{C}_{11}-\text{N}^+(\text{CH}_3)_3$) surface functionalities was identical to that reported before.¹⁶

Ammonium metavanadate (NH_4VO_3 , 0.2925 g, 2.5 mmol, Strem, 99%) and boric acid (H_3BO_3 , 0.93 g, 15 mmol, Fisher, certified ACS) were dissolved in 80 mL of distilled water at 80 °C. After the solution cooled to room temperature, ammonium hexafluorotitanate ($(\text{NH}_4)_2\text{TiF}_6$, 0.9890 g, 5 mmol, Aldrich, 99.99%) was added. Desired amounts of anhydrous oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$, 9.093 mg/mL, Acros, 98%, or Fluka, >99%) or 85% aqueous solution of DL-lactic acid ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, 8.83 $\mu\text{L}/\text{mM}$, Aldrich) was added. The pH was adjusted to 2.5 by adding either 1 N HCl or 1 N NaOH aqueous solution dropwise. The whole solution was then diluted to 100 mL, giving 50 mM [Ti] and 25 mM [V].

The SAM-coated substrates were immersed in this deposition solution. The dish was covered and then placed in an oil bath at 45 °C for 24 h. The coated samples were then rinsed with distilled water and dried with a stream of dry argon. The samples were then ultrasonically cleaned in absolute ethanol for 20 min.

Film Characterization. Chemical composition and thickness of films were determined from X-ray photoelectron spectroscopy (XPS, PHI Model 5600 MultiTechnique system) and sputter depth profiles (PHI 04-303 sputter gun) using 25 mPa ultrapure argon with 4 kV accelerating voltage at 1-min intervals and rastered over a 2 mm \times 3 mm area. The sputtering rate, calibrated against cross-sectional scanning electron microscope (SEM) images of four films ranging in thickness from 250 to 1400 nm,⁷ was 1.8 nm/s. The uncertainty in determining the film thickness was estimated as ± 1 min sputter interval, i.e., ± 100 nm. XPS peaks from Ti_{2p} (450–470 eV), V_{2p} (510–530 eV), and Si_{2p} (95–105 eV) (referenced to the Si 2p peak of single-crystal (100) silicon at 99.7 eV) were analyzed at 30 to 60 positions across the thickness of each film to determine the relative concentrations of Ti and V at each depth. Other than a tendency for films to exhibit somewhat lower V concentrations at the surface than at the film–substrate interface, there were no pronounced variations in the composition of the films with depth; the variations in vanadium and titanium concentrations across a film typically were ± 5 (cation %). In continuous films, XPS detected essentially no carbon, suggesting that neither complexing agent was appreciably entrained in the growing films. Trace amounts of fluorine were detected in most films.

SEM images (Hitachi S-4500) were taken using 5 kV accelerating voltage at 45° tilt. Grazing-incidence X-ray diffraction (GIXRD, Scintag Advanced Diffraction System) was performed with $\text{Cu K}\alpha$ X-rays, fixing the X-ray source at 1° with 0° sample tilt and varying the angle of the detector. NMR spectra (Varian XL-300, 300 MHz) were recorded in D_2O solvent.

Results and Discussion

Figure 1 and Figure 2 show the typical surface morphology of these films after 24 h of growth on SAMs. As with the films deposited without chelating agents,⁷ all of the present films covered the SAM-modified substrates uniformly without cracks. Pure titania films grown under similar conditions exhibit drying cracks when the thickness exceeds a few

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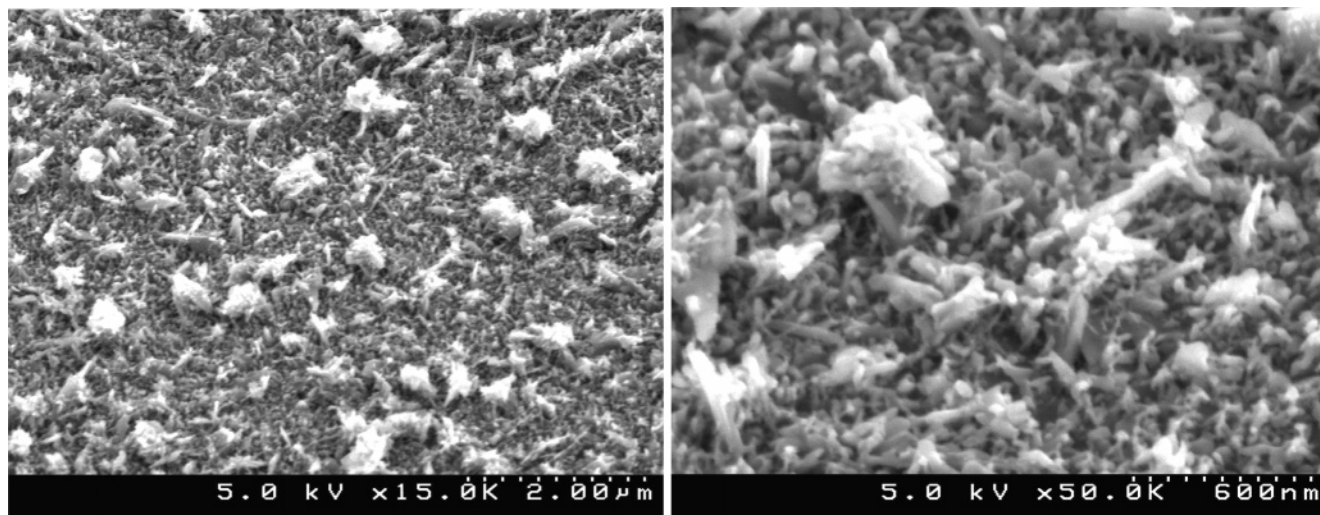


Figure 2. Typical SEM topography of films grown with lactic acid on amine SAM. Solution contained 50 mM Ti as $(\text{NH}_4)_2\text{TiF}_6$, 25 mM V as NH_4VO_3 , 10 mM lactic acid, pH initially 2.5, held for 24 h at 45 °C. Ti:V ratio = 33:67 cat. % at film–substrate interface, average 45:55 cat. %; (1314 ± 100) nm thick.

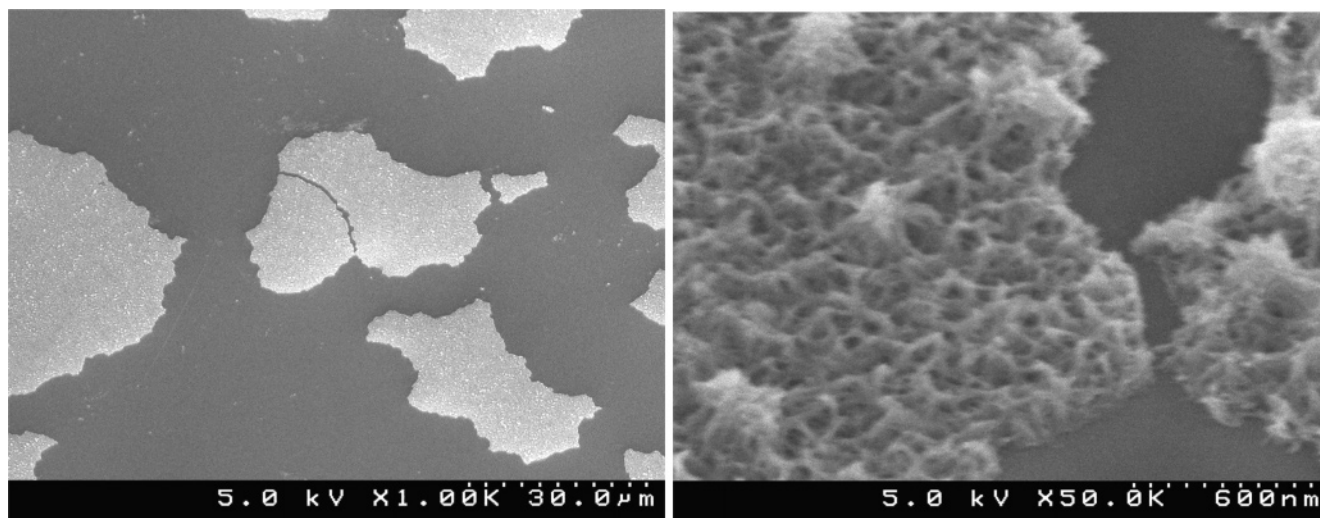


Figure 3. SEM topography of discontinuous film deposited on oxidized Si substrate without SAM. Ti:V ratio = 49:51 cat. %. Thickness: (125 ± 55) nm.

hundred nanometers.¹⁷ Without SAMs, only discontinuous films $\sim 0.12 \mu\text{m}$ thick with Ti:V $\cong 1:1$ formed on the oxidized, hydrolyzed, bare Si surface (Figure 3). This contrasts with the results of Hoffmann et al.,⁸ who reported that film deposition was successful on bare silicon as well as on sulfonate SAM at their lower pH (0.85).

Our earlier work⁷ concluded that the growth mechanism for these films involves attachment of existing particles rather than surface nucleation. That is, hydrated vanadia and titania particles first formed in the aqueous solution and attracted each other due to their oppositely charged ionic double layers at the prevailing pH of 2.5. (The results of Hoffmann et al.⁸ that the isoelectric points of oxidic powders precipitated from acidic solutions were 3.5 for titania and 2.0 for hydrated vanadia support this interpretation.) The resulting Ti–V oxide aggregates would have net surface charge that would depend on the relative surface concentrations of Ti (positive) and V (negative). These particles could then be attracted to the substrate by a combination of electrostatic, van der Waals,

and induced dipolar/electrostatic forces. The more highly charged SAM surfaces (sulfonate and alkylammonium salt) would induce stronger dipolar attractions, which resulted in thicker films than on less strongly charged surfaces such as amines and carboxylic acids. That van der Waals forces alone were insufficient to form continuous films in this case is indicated by the patchy and much thinner films (Figure 3) deposited on bare Si (near its isoelectric point under these deposition conditions, compared to zeta potentials of 70 mV for amine SAMs and 100 mV for alkylammonium SAMs¹⁶).

Oxalate and Titanium. The formulation of a solution for deposition of the titania component of the films was based on a reported liquid-phase deposition recipe.¹⁸ Solutions of 150 mM H_3BO_3 , 50 mM TiF_6^{2-} , $2.5 < \text{pH} < 3.0$ at 45 °C became visibly cloudy within 24 h when the concentration of the oxalate ion was 0–30 mM. For oxalate concentrations higher than 35 mM, the solutions remained clear (indicating the absence of precipitation) and colorless (indicating the absence of reduction of $\text{Ti}^{(\text{IV})}$ ¹⁹) under these conditions.

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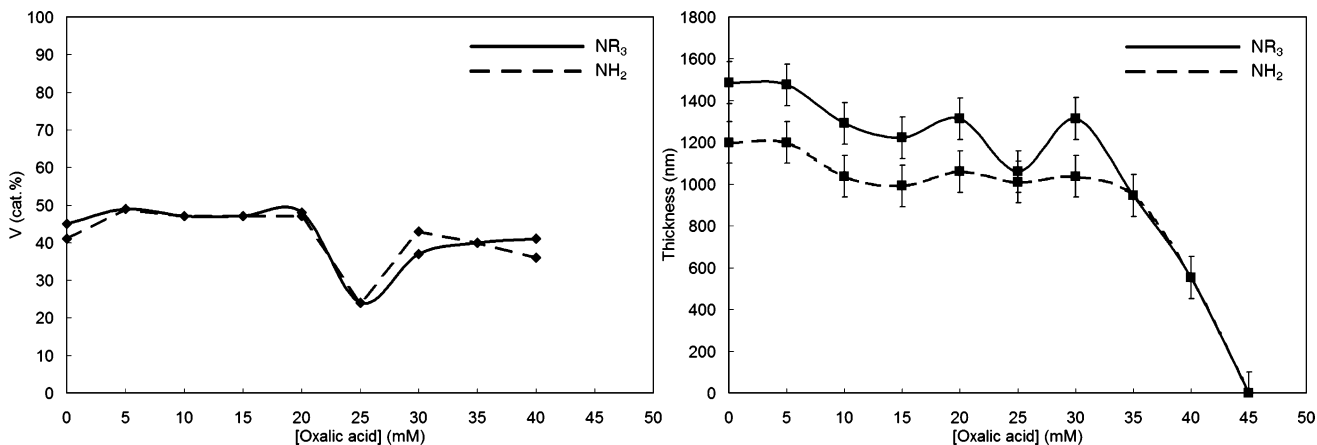
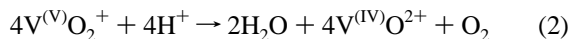
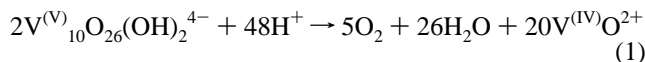
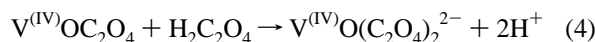
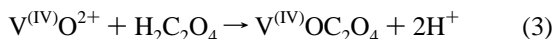


Figure 4. Effect of oxalic acid on the average composition (left) and thickness (right) of Ti–V oxide films deposited on amine and alkylammonium SAMs on (100) silicon. Solutions contained 50 mM Ti as $(\text{NH}_4)_2\text{TiF}_6$, 25 mM V as NH_4VO_3 , pH initially 2.5, held for 24 h at 45 °C.

Oxalate and Vanadium. Solutions of 25 mM [V] at 2.4 < pH < 2.9 and 45 °C remained free of visible precipitates for oxalate concentrations ranging from 5 to 200 mM. However, different oxalate concentrations led to differences in color (both initial and final) and a rise in pH (to 2.6–3.6) in the solutions. The direction of the color change with time (from yellow to green at low oxalate concentrations, from green to blue at higher oxalate concentrations) suggested a shift from $\text{V}^{(\text{V})}$ (characteristically yellow-orange in aqueous solution) to $\text{V}^{(\text{IV})}$ (blue, in the form of $\text{V}^{(\text{IV})}\text{O}(\text{C}_2\text{O}_4)_2^{2-}$).¹⁵ Given that the dominant vanadium species in aqueous solutions are VO_2^+ and $\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-}$ (i.e., both containing pentavalent vanadium²⁰) with the latter species being predominant under the conditions used here,^{20,21} these observations suggest that the following equilibria were at work:



(Additional qualitative evidence for the occurrence of such reactions was the formation of bubbles in these solutions and a buildup of pressure when the solutions were placed in sealed vials, neither of which occurred with titanium–oxalate solutions.) Oxalate could then stabilize the reduced vanadium by complexation:



Similar trends were observed under the same conditions but with a higher initial vanadium concentration (50 mM instead of 25 mM), with the only difference being that a yellow precipitate formed at the lower oxalate concentrations (0–15 mM).

It thus appears that both vanadium and titanium can be chelated by oxalic acid and stabilized in solution. Moreover, oxalic acid complexed vanadium more strongly than it did titanium: only 20 mM of oxalate ion was needed to keep 50 mM vanadium ions in solution, whereas 35 mM of oxalic acid was needed to keep 50 mM titanium ions in solution.

Oxalate and Mixed Titanium–Vanadium. Solutions containing 50 mM Ti and 25 mM V with pH = 2.5 at 45 °C were prepared with varying amounts of oxalic acid. Amine- and alkylammonium-functionalized SAMs were immersed in this solution (unstirred) for 24 h. Figure 4 shows that low concentrations of oxalate had no effect on the film composition and little effect on the film thickness. However, at about 1:1 vanadium:oxalic acid, the vanadium content in the films reached a minimum, indicating that the vanadium ions were preferentially kept in solution by the oxalate. Increasing the concentration of oxalic acid chelated the titanium ion also, and the vanadium content rose to the earlier levels. Beyond 40 mM oxalate, no film or precipitates formed.

The film thickness decreased gradually with oxalate concentration at first, then more rapidly as complexation of both cations became more complete (Figure 4, right). For the alkylammonium surface, for oxalate concentrations up to 30 mM, films were thicker than on amine surfaces, and tracked the vanadium content. This reflects the behavior of the single-oxide films on these surfaces: vanadium oxide films deposit, and titania films do not, on alkylammonium,⁶ whereas both titania and vanadia films deposit on amine surfaces, but the vanadia films are thinner than those on alkylammonium.^{6,22,23} Vanadia films exhibit an intrinsically higher growth rate ($\sim 0.3 \mu\text{m}/\text{h}$ on amine SAMs)²² than those of titania ($\sim 0.02 \mu\text{m}/\text{h}$ on amine SAMs)⁶ under these conditions of temperature and pH. The average growth rate for the mixed oxide films was maximum with no complexing agent, $0.050 \mu\text{m}/\text{h}$ on amine and $0.062 \mu\text{m}/\text{h}$ on alkylammonium surfaces.

At all but the highest concentrations of complexing agent (see also the results on lactic acid below), these films grew

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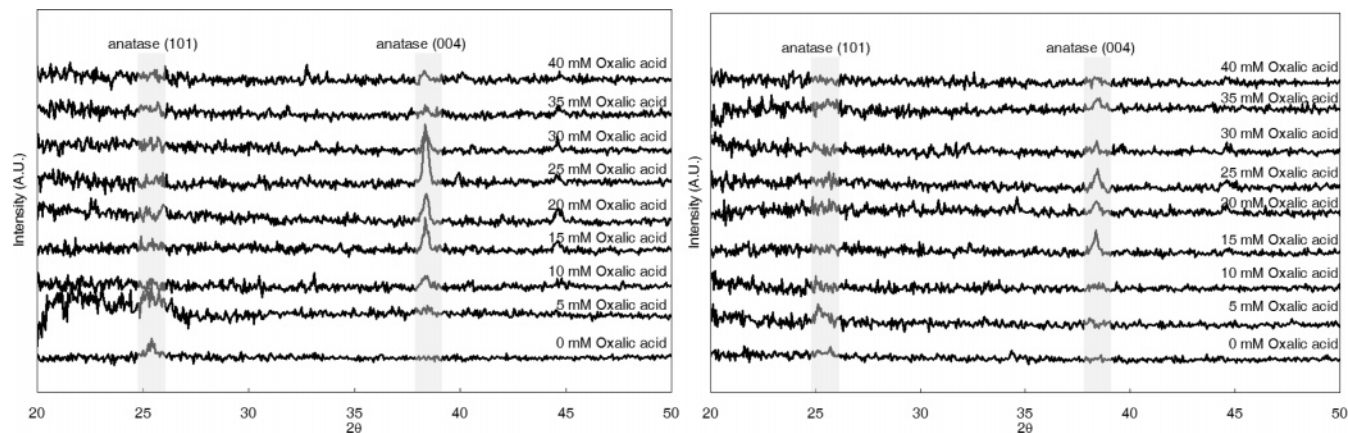


Figure 5. GIXRD of Ti-V oxide films deposited in 24 h from solutions containing oxalic acid. Left: films on amine SAM. Right: films on alkylammonium SAM. Oxalate concentration increases from 0 in the bottom pattern to 40 mM in the top pattern. Shaded bars indicate the locations of the (101) (at 25.3°) and (004) (at 37.8°) peaks of anatase.

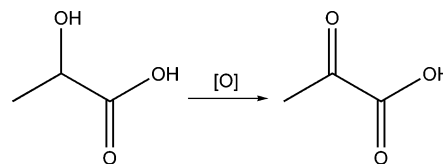
faster than those reported by Hoffmann et al.⁸ (0.025 $\mu\text{m}/\text{h}$). Compared to the present work, their conditions were quite different: lower pH (0.85 vs 2.5), higher temperature (80 vs 45 °C), peroxide ions (as opposed to ammonium and fluoride ions and boric acid), lower metal concentrations (each 10 mM or less, vs $[\text{Ti}] = 50 \text{ mM}$ and $[\text{V}] = 25 \text{ mM}$ here), and sulfonated SAM (vs alkylammonium or amine here). It is notable that their films were all enriched in Ti relative to the solution, whereas the opposite was usually the case here ($\text{Ti}:\text{V} = 2:1$ in solution, lower in the films). This suggests that peroxide may be a more selective complexing agent for V than either oxalate or lactate (see below).

Figure 5 shows that the films grown with oxalic acid consisted in part of anatase with (00 ℓ) texturing (as evidenced by the intensity of the (004) peak at 37.8° relative to the normally strongest (101) peak at 25.3°, which is virtually absent in many of these patterns). This phase may be a solid solution of $(\text{Ti},\text{V})\text{O}_{2+\delta}$.²⁴ Bulk precipitate from these solutions could be identified as $(\text{Ti},\text{V})\text{O}_{2+\delta}$ on the basis of its lattice parameters, but more and stronger XRD peaks would be needed to check this possibility in the films. The amount of the anatase phase was highest for intermediate oxalate concentrations. No known vanadium-containing crystalline phase could be identified from the diffraction patterns.

Lactate and Titanium. Solutions of 75 mM H_3BO_3 , 25 mM $(\text{NH}_4)_2\text{TiF}_6$, $2.5 < \text{pH} < 2.8$ at 45 °C formed visible colloids within 24 h at low concentrations of added lactate (0–15 mM lactic acid). For lactate concentrations higher than 20 mM, the solutions remained clear (indicating the absence of precipitation) and colorless (indicating the absence of reduction of $\text{Ti}^{(\text{IV})}$)¹⁹ under these conditions. When the titanium concentration was raised to 50 mM, heavy precipitation was observed for low concentrations of added lactate (0–15 mM), a mixture of solid and suspended colloid for 20–30 mM added lactate, and clear colorless solutions for lactate concentrations higher than 35 mM. In all solutions but one (out of 28) the pH rose slightly with time to 2.8–3.0. This indicated that titanium ions were complexed and retained in solution by the lactate ion.

Lactate and Vanadium. Solutions of 25 mM vanadium (as NH_4VO_3), $2.2 < \text{pH} < 2.9$, 45 °C, initially orange-yellow to yellow, formed yellow solid precipitate for low concentrations of added lactate (0–15 mM) with a rise in pH to 2.6–2.9. For 20–280 mM added lactate, yellow-green to green to blue-green solutions formed with increasing lactate concentration, and pH rose to 3.1–3.5. Blue solutions with a final pH of 2.9–3.1 resulted for 320–480 mM added lactate. Similar trends were observed under the same conditions but with a higher initial vanadium concentration (50 mM instead of 25 mM), with the main difference being that a green precipitate formed at the lower lactate concentrations (5–40 mM).

From these results, it was clear that lactate could complex vanadium. However, the interaction was more complicated than simple complexation. The alcohol group on the second carbon of lactic acid is a reductive group that can be oxidized to a ketone group:



$\text{V}^{(\text{V})}$ conversely is an oxidative ion (standard reduction potential²⁵ is 0.991 V for $\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$), which is capable of oxidizing such an alcohol group. On the other hand, such a redox reaction is not expected with the $\text{Ti}^{(\text{IV})}$ system (standard reduction potential²⁵ is -0.055 V for $\text{TiOH}^{3+} + \text{H}^+ + \text{e}^- \rightarrow \text{Ti}^{3+} + \text{H}_2\text{O}$). Furthermore, as mentioned above, the Ti-lactate (and Ti-oxalate) solutions exhibited no color change, as would occur on reduction of $\text{Ti}^{(\text{IV})}$ to $\text{Ti}^{(\text{III})}$;¹⁹ lactic acid is not oxidized by TiO_2 in the absence of vanadium²³ and there was no evidence of $\text{Ti}^{(\text{III})}$ in the XPS depth profiles.

To look for evidence that this reaction had taken place, the organic part of the reacted solution was extracted using diethyl ether. The ^1H NMR (Figure 6) (using H_2O as internal standard at 4.76 ppm) showed diethyl ether [^1H NMR (300

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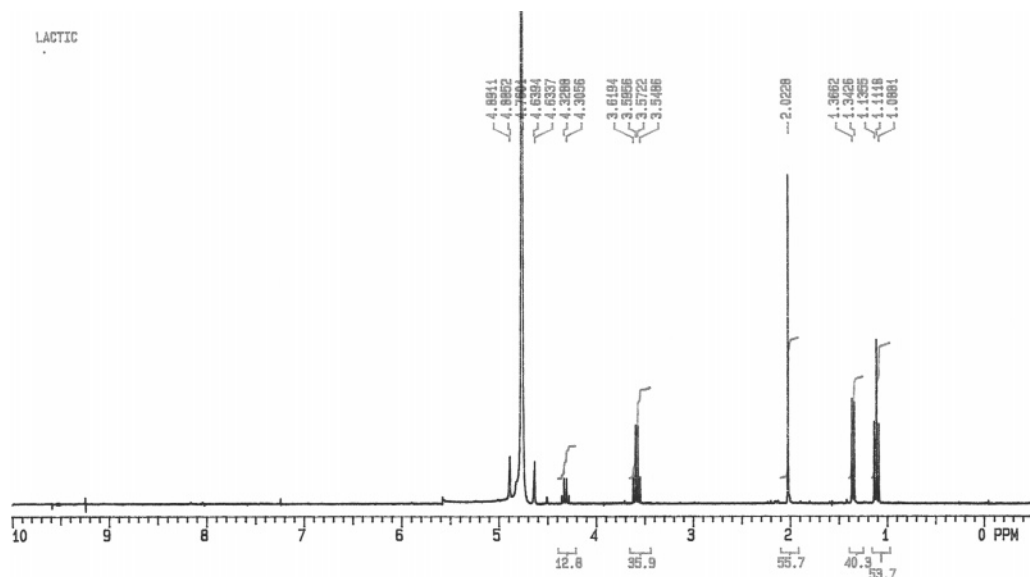


Figure 6. ^1H NMR of lactic acid reacted with vanadium.

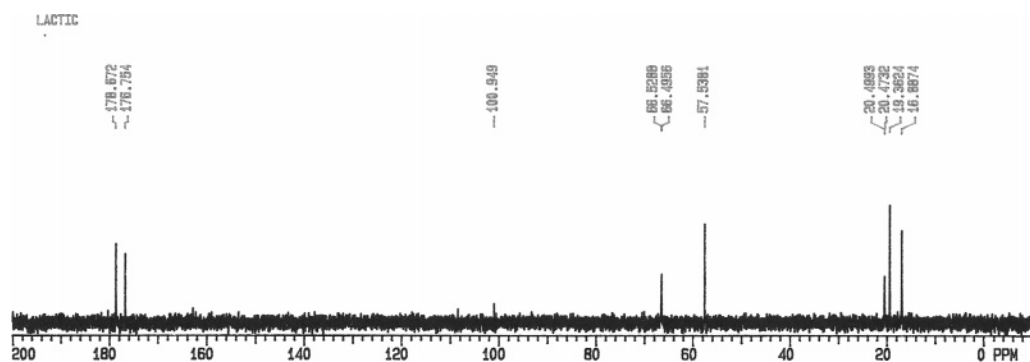
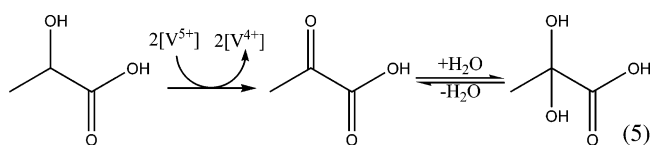


Figure 7. ^{13}C NMR of lactic acid reacted with vanadium.

MHz, D_2O): δ 1.11 (t, $J = 7$ Hz, 6H) 3.58 (q, $J = 7$ Hz, 4H)], unreacted lactic acid [^1H NMR (300 MHz, D_2O): δ 1.35 (d, $J = 7$ Hz, 3H) 4.31 (q, $J = 7$ Hz, 1H)], and oxidized lactic acid [^1H NMR (300 MHz, D_2O): δ 2.02 (s, 3H)]. The integration suggested that 58% of the lactic acid was oxidized.

The ^{13}C NMR (Figure 7) showed diethyl ether [^{13}C NMR (75 MHz, D_2O): δ 16.9, 57.5], unreacted lactic acid [^{13}C NMR (75 MHz, D_2O): δ 19.4, 66.5, 178.5], and an oxidized form of lactic acid [^{13}C NMR (75 MHz, D_2O): δ 20.5, 100.9, 176.8]. The peak at ~ 100 ppm suggested that this oxidized product contained an acetal group instead of a carbonyl group (140–180 ppm).

Therefore, the reaction of lactic acid in the presence of vanadium ions was



Indirect evidence for this reaction also came from experiments on the deposition of mixed Ti–V oxide films in the presence of lactate (discussed next).

Lactate and Mixed Titanium–Vanadium. Figure 8 shows the effect of lactic acid on Ti–V oxide films deposited on amine- and alkylammonium-SAM surfaces on (100) silicon.

Due to the additional oxidation–reduction reaction between vanadium and lactic acid, the effect of lactic acid was more complicated than that of oxalic acid (cf. Figure 4).

At low lactic acid concentrations (0–15 mM), the vanadium content in the film increased with increasing lactate, the film thicknesses increased, and $\text{V}^{(\text{IV})}$ was detected in the films via XPS during sputter depth profiling.²⁶ Considered together with the observations of solutions containing lactate and $\text{V}^{(\text{V})}$, these results indicate that the lactate reduced the $\text{V}^{(\text{V})}$ to $\text{V}^{(\text{IV})}$, decreasing the amount of lactic acid available to complex the vanadium and titanium. Meanwhile, $\text{V}^{(\text{IV})}$, known as a polymerization initiator in the formation of pentavalent vanadia solid,^{27,28} increased the solidification rate of vanadia in the films, raising the maximum average growth rate to 0.10 $\mu\text{m}/\text{h}$ on alkylammonium surfaces and 0.060 $\mu\text{m}/\text{h}$ on amine surfaces. Although the solutions with oxalate

(26) XPS detected $\text{V}^{(\text{IV})}$ after sputter depth profiling in films deposited both from solutions containing lactate and from those containing oxalate, but it is possible that some of the $\text{V}^{(\text{IV})}$ resulted from the sputtering itself. Before sputter depth profiling, no $\text{V}^{(\text{IV})}$ was detected in the films via XPS, but XPS detects species only within a few atomic distances of the surface, and any $\text{V}^{(\text{IV})}$ this close to the surface would be expected to have oxidized to $\text{V}^{(\text{V})}$ when exposed to air. Therefore, XPS is not definitive in establishing the presence of $\text{V}^{(\text{IV})}$ in the films, but the color changes described in the text strongly indicate its presence in the solutions.

(27) Gharbi, N.; Sanchez, C.; Livage, J.; Lemerle, J.; Nejem, L.; Lefebvre, J. *Inorg. Chem.* **1982**, *21*, 2758–2765.

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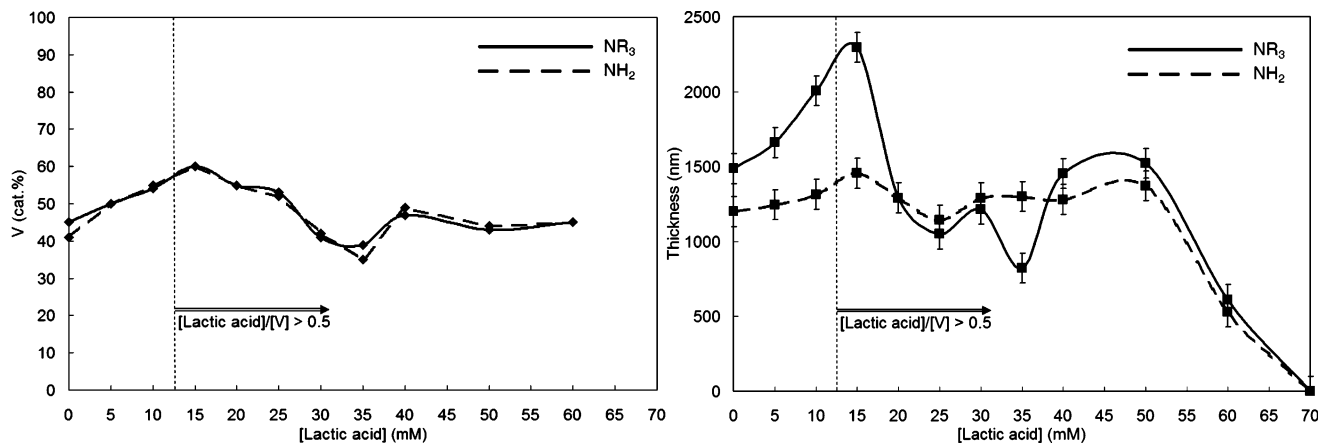


Figure 8. Effect of lactic acid on the average composition (left) and thickness (right) of Ti–V oxide films deposited on amine and alkylammonium SAMs on (100) silicon. Solutions contained 50 mM Ti as $(\text{NH}_4)_2\text{TiF}_6$, 25 mM V as NH_4VO_3 , pH initially 2.5, held for 24 h at 45 °C.

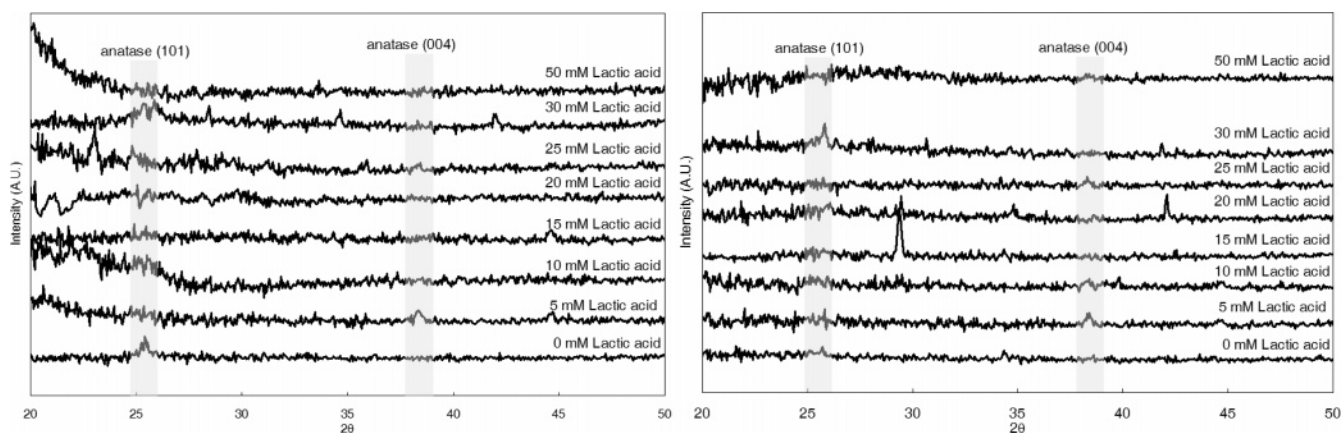


Figure 9. GIXRD of Ti–V oxide films deposited in 24 h from solutions containing lactic acid. Left: films on amine SAM. Right: films on alkylammonium SAM. Lactate concentration increases from 0 in the bottom pattern to 50 mM in the top pattern. Shaded areas indicate the locations of the (101) (at 25.3°) and (004) (at 37.8°) peaks of anatase.

also evolved $\text{V}^{(\text{IV})}$, oxalate did not increase the thickness and vanadium content of those films (cf. Figure 4), because oxalate strongly chelates $\text{V}^{(\text{IV})}$, preventing it from participating in the formation of vanadia¹⁵ (eqs 1–4).

At slightly higher lactate concentrations, when the [lactate]/[vanadium] exceeded 0.5 (which is the stoichiometry of the redox reaction), there was lactic acid left to complex the vanadium ions. As a result, the vanadium content in the films, and the film thickness, decreased. As the [lactate]/[vanadium] exceeded 1.5 (at which point the solution composition would be [vanadium]:[lactate]:[oxidized lactate] = 1:1:0.5), the lactate began to complex titanium (as seen with oxalic acid, above), and the vanadium content and film thickness increased again slightly. Beyond 50 mM added lactate, film thickness decreased dramatically, and no film formed for 70 mM lactate, indicating that sufficient lactate remained after reducing V^{5+} to complex all of the metal ions and keep them in solution.

As with oxalic acid, the film thickness of mixed Ti–V oxide films deposited in the presence of lactate on alkylammonium SAMs tracked the vanadium content quite closely. Parallel but less pronounced variations were seen on amine SAMs. The topography of films in this series (Figure 2) was not markedly different from that of the films deposited in the presence of oxalic acid (Figure 1).

With lactate as a complexing agent, there was much less of the anatase phase (Figure 9), and when it was detected, it

exhibited less (00 ℓ) texturing than when oxalate was used (Figure 4). Many of the films from these lactate-containing solutions showed no GIXRD peaks, as do films grown without complexing agent.⁷ No known vanadium-containing crystalline phase could be identified from the diffraction patterns.

Conclusions

Titanium–vanadium oxide films were formed via co-deposition from aqueous solution on alkylammonium and amine SAMs in a single step. In contrast to traditional ways of preparing titania-supported vanadium oxide catalysts, this illustrates the potential of synthesizing the support and the active component of a titanium–vanadium oxide catalyst simultaneously.

Both oxalic acid and lactic acid acted as complexing agents for titanium and vanadium. Oxalic acid preferentially chelates vanadium ions and stabilizes V^{4+} ions in the solution. Therefore, oxalic acid is able to lower the vanadium content in the vanadium–titanium oxide films. Such films contained (00 ℓ)-textured anatase (possibly $(\text{Ti},\text{V})\text{O}_{2+\delta}$) on both amine and alkylammonium SAMs. Since oxalic acid also chelated titanium ions, there was no film formation at high oxalate concentration.

Lactic acid reduced the V^{5+} to V^{4+} . Since V^{4+} works as a catalyst in the formation of vanadia, it enriched the

vanadium content in the film. With increasing amounts of lactic acid, the unoxidized lactic acid worked as a chelating agent, particularly on vanadium ions. As a result, the vanadium content of the films decreased. The resulting films were largely amorphous with some untextured anatase-structured phase. Since lactic acid also complexed titanium ions, there was no film formation at high lactate concentration.

The film thickness on alkylammonium SAMs ranged from 1.1 to 2.3 μm , increasing with the vanadium content. On

amine surfaces, the films were usually thinner (1.2–1.5 μm), though the compositions were essentially the same as those on alkylammonium SAMs.

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