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# Spin coated titanium-ruthenium oxide thin films

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### ABSTRACT

Substrates of different roughness spin coated with  $Ti_{0.7}Ru_{0.3}O_2$  films have been evaluated as model system for fundamental studies of the industrially and scientifically interesting  $(Ti,Ru)O_2$  based electrodes. The approach allowed for much more accurate control over the material synthesis than the traditionally used brush-, dip-, or spray-coating, on titanium-metal substrates. It moreover yielded well-defined samples suitable for basic studies of the surface properties that are of fundamental importance for understanding the electrochemical functionality of the electrode. We have compared the films on silicon substrates to films prepared by spin coating the same material on titanium-metal substrates. Samples have been characterized using atomic force microscopy (AFM), X-ray diffraction, scanning electron microscopy (SEM), and cyclic voltammetry. The samples displayed a uniformity of the films appropriate for AFM characterization. The smoother the substrate the less cracks in the coating. Using easily broken silicon wafers as substrate, a straightforward sample preparation technique was demonstrated for cross-section SEM. In addition, using high spinning velocities we have deposited the oxide films directly on silicon-nitride grids, thin enough to allow for studies with transmission electron microscopy without further sample preparation.

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#### 1. Introduction

Ruthenium-containing metal-oxide films have been widely investigated for their industrially important and scientifically interesting electrocatalytic activity [1,2] and good perspective of application as electrochemical supercapacitors [3]. The electrocatalytic properties of a metal oxide depend on its electronic and geometric parameters [4]. The electronic parameters are related to the physical and chemical properties of the material, such as electronic structure and crystallinity etc, whereas the geometrical parameters are linked to the morphology of the film. There is both a micro- and a nano-structure, which in turn depends on the preparation process [5,6]. Characterization of the surface properties of electrodes covered with catalytic metallic oxide films is of fundamental importance for understanding their electrochemical behavior [4].

The most common preparation method for industrial applications, as well as electrochemical studies, consists of a pyrolytic treatment of a gel-like precursor solution deposited on a metal substrate [7], where common coating processes [8] include spray-, brush- or dip-coating. The production method is simple, economical and offers tuning of a wide range of parameters [9]. An essential point is that the substrate is also involved in the calcination process as metal ions from the substrate enter the coating film and affect its electrochemical properties [10]. This effect decreases the possibility to investigate

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the electrochemical properties intrinsic to the coating, but can be circumvented by replacing the metal substrate with an inert one. Ferro and DeBattisti [11], used boron doped diamonds on a silicon support as substrate for RuO<sub>2</sub>, thus avoiding contamination from the substrate. Contamination from the substrate has also been suggested as cause for deactivation or passivation of the electrode during long time use [12].

Another characteristic of a metal substrate is surface roughness on the microscale. This roughness is often wanted, helping the adhesion of the coating to the substrate [13], but can be a limitation when investigating physical properties, such as viewing the nanoscaled grains [5], using for example an atomic force microscope (AFM) [14]. It is also difficult to define and measure the obtained coating thickness if the substrate is rough, e.g. when films are synthesized using the common wet-chemistry methods. The roughness often results in a non-uniform film thickness across the sample. The coating thickness becomes a matter of definition, depending on which part of the sample that is scanned, and an average value over the whole electrode does not say very much about the actual case.

Spin coating is a technique where a liquid is deposited onto a solid, flat substrate, placed horizontally and subsequently rotated with a high speed. The liquid is in this way distributed in an even, uniform layer across the substrate surface [15]. Spin coating is an attractive alternative to the commonly used spray-, brush- or dip-coating for preparation of oxide-coated electrodes, offering the possibility of substantially enhanced reproducibility and detailed control over the application of the coating precursor. This method is widely used for

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e.g. application of photo resist in semiconductor processing, and has proved a good technique for making long lasting electrodes for oxygen evolution [8]. The film thickness can be controlled by the spin velocity and accurate predictions of it may be done. Schubert and Dunkel [16] have derived a model for prediction of the film thickness in spin coating,

$$h_{\infty} \sim \omega^{-1/2} \eta^{1/3} c_0, \tag{1}$$

where  $h_{\infty}$  is the coating thickness after infinite spinning time,  $\omega$  is the spinning velocity,  $\eta$  the viscosity of the solution, and  $c_0$  the concentration of film-forming material in the initial coating solution. For a given solution, the film thickness is proportional to  $\tilde{\omega}^{-1/2}$ . Moreover, problems associated with surface roughness of metal substrates can be circumvented by instead using silicon wafers, as they offer a very well defined, extremely flat, inert surface at low cost. When films are synthesized using the common wet-chemistry methods, the uncertainties of the actual coating thickness, together with a possible high roughness due to the microstructure, makes fundamental studies complicated. The advantages of the spin coating techniques have not been fully utilized in the case of catalytic electrode coatings, only a few studies [17-19] have been found in the subject. In addition to providing a good model system for studies of electrocatalytic oxides as such, it is our belief that spin coating on a well defined substrate can be suitable for materials chemistry studies to understand the different steps in the formation of the complex oxide materials.

We here describe spin coating of an electrocatalytic metal oxide on silicon wafers and polished titanium discs in an attempt to construct a suitable model system for fundamental studies. The spinning speed was varied to confirm that the film thickness could be controlled with high precision, the samples also displayed a uniformity of the films appropriate for AFM characterization. By breaking the silicon samples, a straightforward sample preparation technique for crosssection scanning electron microscopy (SEM) was demonstrated, facilitating accurate film-thickness determination. By increasing the spinning velocity, thin enough films were produced showing the electron transmission needed for transmission electron microscopy (TEM). This allowed the coating to be studied as-prepared without need for elaborate sample preparation.

#### 2. Material and methods

A coating solution was prepared using titanium(IV)n-butoxide (TBOT) and RuCl<sub>3</sub>  $\cdot$  nH<sub>2</sub>O (35.51 wt.% Ru) as metal precursors. 14.93 g of TBOT and 5.351 g RuCl<sub>3</sub>  $\cdot$  nH<sub>2</sub>O were dissolved in n-propanol to a final volume of 50 ml, giving a molar ratio between titanium and ruthenium of 7:3. The solution was stirred for 48 h to assure complete dissolution of the salts.

We used three different kinds of substrates; highly doped (resistivity: 0.01  $\Omega$  cm) silicon wafers, mirror polished titanium discs and silicon nitride TEM grids. The silicon wafers were as-delivered coated with a 8  $\mu$ m thick epitaxial layer of low doped (resistivity: 15  $\Omega$  cm) silicon. They also had as-delivered a thick silicon dioxide layer on the back and a thin, spontaneously formed silicon dioxide layer on the front. First, the thin silicon oxide layer on the front was removed by dipping the wafer in 1 wt.% HF, at room temperature, for 15 s. The epitaxial layer was then etched away in 25 wt.% KOH, 80 °C for 15 min. Finally the silicon dioxide on the back was removed in 10 wt.% HF, at room temperature, for 6 min. Between each etching step the wafer was thoroughly rinsed in distilled water. The coating solution was applied to the silicon wafer, which was subsequently spun using a standard photo-resist spinner (Electronic Micro Systems) at 550 rpm for 30 s to distribute the liquid in a uniform layer. The coating was thereafter dried at 90 °C for 10 min with the wafer in horizontal position and calcined at 450 °C for 10 min with the wafer standing vertically. Prior to the coating, 150 nm of titanium was evaporated onto the silicon wafer, using an electron beam evaporator. This step was necessary to assure adhesion of the oxide film. For SEM sample preparation the wafer was broken using a diamond drawing point.

For estimates of coating thickness based on weight increase, the obtained oxide was assumed to be pure dioxide with a molar ratio between titanium and ruthenium of 7:3. The density of this mix was assumed to be 5076 kg/m<sup>3</sup>, based on calculation from individual densities of TiO<sub>2</sub> ( $\rho = 4230$  kg/m<sup>3</sup> [20]) and RuO<sub>2</sub> ( $\rho = 7050$  kg/m<sup>3</sup> [20]) as follows: 0.7 · 4230 kg/m<sup>3</sup> + 0.3 · 7050 kg/m<sup>3</sup> = 5076 kg/m<sup>3</sup>.

The titanium discs (59 mm in diameter, 2.5 mm thick) were mechanically polished and etched for 20 min in boiling HCl (18 wt.%). Coating solution was spun onto them at 1400 rpm, the discs were dried in 80 °C for 10 min and then calcined in 470 °C for 10 min. The samples were prepared with one, two or three layers of coating and thereafter final-calcined for 50 min in 470 °C. From these discs smaller discs (area = 1 cm<sup>2</sup>) were punched for rotating-disc cyclic voltammetry.

TEM samples were made by gluing two silicon nitride TEM grids (Ted Pella) at equal distance from and on opposite sides of the center of a silicon wafer. A drop of coating solution was placed on each grid and subjected to spinning at 5500 rpm. The grids were then removed from the wafer and placed in a crucible for drying and calcination using the same procedure as described above for the wafers.

We used a Digital Instruments Dimension 3100 AFM (tapping mode), a LEO 1450 EP SEM (acceleration voltage: 20 kV) and a JEOL 2000 FX TEM (acceleration voltage: 160 kV) to study the samples. X-ray diffraction (XRD) measurements were performed using a Philips PW3040 diffractometer. The experiments were performed in  $\theta$ -2 $\theta$  geometry using Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 1.54 Å).

The voltammetric charge, q\*, was determined from cyclic voltammograms measured in deaerated 1 M NaOH at 25 °C. Charges from anodic currents, q\*+, and cathodic currents, q\*-, were evaluated and the reported q\* was calculated as their average value  $(q^{*+} - q^{*-})/2$ . A 1 cm<sup>2</sup> rotating disc electrode was used at 3000 rpm. A platinum mesh served as the counter electrode and the reference electrode was a saturated calomel electrode (SCE) from Radiometer Copenhagen. The voltammograms were, in accordance with Burke et al. [21], measured between -0.77 and +0.18 V vs. SCE at different sweep rates between 20 and 200 mV/s. The voltammetric charge for the "inner" and "outer" electrochemically active area was extracted from q\* values for different sweep rates according to Ardizzone et al. [22].

### 3. Results and discussion

Five silicon wafers were coated at different spinning velocities and the coating weight (taken as the weight increase of the sample) was plotted as a function of  $\omega^{-1/2}$  (Fig. 1). Assuming that the calcined coating of all the samples displays equivalent composition, the weight increase of the wafers is proportional to the coating thickness. Although the n-propanol based ruthenium-titanium solution in this work was of significantly lower viscosity than the polymer solutions typically used for spin coating, the results agree very well with the model of Schubert and Dunkel [16], as the obtained coating weight forms a straight line versus  $\omega^{-1/2}$ .

The typical dimensionally stable anode cracked-mud structure appears during heat-treatment (drying and calcination), most likely due to thermal expansion of the substrate. The almost atomically flat surface of the silicon substrate gives a coating with very few cracks and the areas between the cracks (the "plaquettes") in this case become several millimeters across. Fig. 2A shows a portion of a surface where two cracks meet. On a polished titanium plate (Fig. 2B) the plaquettes are also large, but not as large as in the coated silicon wafer case. Typically, coating plaquettes on a polished titanium substrate are about 100 µm across. On a rough surface, e.g. a grit blasted metal plate, coating solution will accumulate in the valleys



**Fig. 1.** Coating weight controlled by spinning velocity. Total weight increase of a coated 4-inch silicon wafer as a function of reciprocal square root of spinning speed. Spin velocities ( $\omega$ ) given in revolutions per minute (rpm) are indicated for each data point. The line is a linear regression fit to data.

resulting in non-uniform thickness and, consequently, areas with more or less cracked-mud microstructure. The coating plaquettes also becomes quite small, see Fig. 2C. If the coating is not very thin, the AFM is limited to study the top of the plaquettes since the cracks are too deep and narrow for the tip to reach the bottom. As can be seen in Fig. 2, the smoother the substrate is, the lower the crackdensity in the coating becomes.

In contrast to titanium metal, silicon wafers are easily broken. Provided that the breaking of the coating to a reasonable degree follows the breaking direction of the wafer, the broken silicon substrate electrode displays a nice cross section of the coating. This provides a convenient route to perform cross-sectional microscopy investigations. When using metal substrates, cross-section sample preparation involves moulding in epoxy and several grinding/polishing steps. It is in addition usually difficult to obtain a good result due to the very different mechanical properties of the brittle, porous oxide coating and the ductile substrate. Fig. 3 shows a cross-sectional SEM image of a coated silicon wafer. The coating was about 450 nm thick, with the 150 nm titanium layer underneath clearly visible as a brighter line in between. Calculations of film thickness based on weight increase for this sample results in 414 nm. The difference most likely originates from porosity in the coating and uncertainty of the density of the mixed oxide. Knowledge about the actual film thickness makes studies on loading versus activity as well as electrolyte penetration depth less complicated.

With high spinning velocity the coating could be made thin enough to be examined in TEM without need of tedious sample preparation. We spin coated silicon-nitride TEM grids at 5500 rpm, which on a silicon wafer resulted in a coating that was about 90 nm thick. After drying and calcination, the thin coating on the grid could be examined as whole in the TEM. Two example images are displayed in Fig. 4. The image reveals that the coating is made up of individual grains a few tens of nanometers across. The grains are closely packed together and under low magnification (Fig. 4A) it looks like a smooth dotted surface. The coating has somewhat detached from the grid and there is no coating to the far right in the image. Higher magnification (Fig. 4B) allow for the grains to be seen individually. The facets on the larger ones (marked by an arrow in the image) are visible, in agreement with our previous study [5].

To compare coatings on silicon and titanium substrates, XRD patterns of samples on the two substrates were measured. The results are shown in Fig. 5. Both patterns demonstrate clearly diffraction peaks originating from the rutile structure. The rutile peaks have similar intensities and widths in the two samples. As expected, both patterns display strong reflections from the respective substrate materials. Reflections originating from the metallic titanium interlayer can be seen





**Fig. 2.** SEM images of plaquettes created by different substrate roughnesses. The cracked-mud structure of a spin coated (A) silicon wafer (spin velocity 550 rpm), (B) polished titanium disc (spin velocity 1400 rpm) and for comparison (C) blasted titanium disc (spin velocity 1500 rpm). The coating weight is approximately the same for all three samples.

on the sample prepared on silicon substrate. These peaks are wider, with different relative intensities, and somewhat shifted towards lower diffraction angles as compared to the titanium peaks from the sample on metal substrate. The shift of the peaks presumably indicates an expansive strain in the titanium lattice deposited on silicon. The broader peaks could indicate higher disorder and/or smaller crystal-lites. The different intensity ratios (with the 002 peak around 38° dominating the collection of titanium peaks from the silicon-substrate sample) are most likely explained by a preferred direction of the



**Fig. 3.** Cross-section SEM image of thin film coating, measurement of film thickness. Cross-section of 450 nm of  $Ti_{0.7}Ru_{0.3}O_2$  coating with 150 nm titanium deposited on the wafer prior to the coating.

titanium with the c-axis parallel to the normal of the silicon substrate. In any case, the presence of a titanium diffraction pattern showed us that the titanium metal on the silicon substrate was not transformed (at least not fully) to titanium dioxide in the process. It can moreover be noted that none of the patterns display any reflection attributable to  $TiO_2$  in anatase form.

The similarity of the appearance of the rutile reflections indicates that the physical properties of the coating, such as crystallite size and composition, were preserved independently of the substrate. This is in agreement with the XRD study of Gerrard and Steele [23], where RuO<sub>2</sub>-TiO<sub>2</sub> (30:70) brush-painted on flat titanium and on silica were compared and it was shown that the crystallite size is not affected by the substrate. It is also in agreement with Shrivastava and Moats [8], who conclude that the nanostructure of the coating is independent of the technique used to apply the solution to the substrate. Average crystallite size derived from the Scherrer equation is about 30 nm for both substrates. It must however be noted that there is a slight difference that can be seen when comparing the profiles around the first rutile peak at about 27°-28°, as shown in the magnified view in Fig. 5B. There is an indication of a shoulder on the high-angle side of the peak in the titanium substrate sample data. Even if the shoulder is weak it is tempting to speculate about its origin. A double peak could indicate the presence of two rutile phases, due to either phase separation of the coating material or due to oxidation of the substrate yielding a second source of oxide material. Since the shoulder appears at the position of RuO<sub>2</sub> it is not easily explained by oxidation of the substrate and the phase-separation explanation is also unlikely since Gerrard and Steele [23] report phase separation only for annealing temperatures above 700 °C. In either case, more studies are needed to reveal the impact of the substrate material on the coating composition.

The cell parameters, assuming a tetragonal rutile structure, derived from the peak positions in the diffractograms are a = 4.57 Å and c = 3.01 Å for the coating on the titanium substrate and a = 4.55 Å and c = 3.01 Å for the coating on silicon. This can be compared with a = 4.575 Å and c = 3.003 Å as expected from Vegard's law assuming a molar ratio of 30:70 between RuO<sub>2</sub> (a = 4.4968 Å, c = 3.1049 Å [24]) and TiO<sub>2</sub> (a = 4.5937 Å, c = 2.9587 Å [24]). This could indicate a slightly higher titanium dioxide concentration in the coating on the titanium substrate, which in turn could be explained by titanium migrating into the coating from the substrate. However, some caution must be taken when evaluating the cell parameter values derived from Vegard's law as the cell parameters deviate from the straight line in for example the Sn<sub>x</sub>Ti<sub>1</sub> – xO<sub>2</sub>-system [25].





**Fig. 4.** TEM image of coating in transmission. Approximately 90 nm thick  $Ti_{0.7}Ru_{0.3}O_2$  film spin coated onto a silicon nitride TEM grid. (The black elliptic dot is an imaging artifact.) (A) Grains are closely packed together and under low magnification it looks like a smooth dotted surface. (B) The individual grains can be seen and moreover, the facets of the larger ones (marked by an arrow).

Using AFM, the topography of the sample surface can be seen. The technique also gives an indication of grain size (quantitative grain size measurements are preferable performed using XRD, as described previously). Comparing the two samples, on silicon and polished titanium substrates, a noticeable difference is the cracking structure on the micrometer scale. As seen in the SEM images (Fig. 2), the crack-density is much lower on the silicon substrate than on the titanium substrate, which makes the AFM imaging less complicated on the former. However, when investigating the top of a plaquette, the packing of the coating grains (visible as dots) is similar in both samples (Fig. 6).

An indication of the mechanical integrity of the coating is also given by the AFM technique. A coating with poor adhesion might be damaged by the AFM tip, scratched, or even detached from the substrate. A coating containing loose particles, or particles with poor



**Fig. 5.** XRD patterns of  $Ti_{0.7}Ru_{0.3}O_2$  coating on titanium and silicon substrates. (A) Full patterns, showing reflections from the rutile structure of the coating and strong reflections from the respective substrate materials. (B) Magnification of the first rutile peak and expected  $TiO_2$  and  $RuO_2$  rutile peaks marked with vertical lines. An indication of a shoulder on the high-angle side of the peak is visible in the titanium substrate sample data.

adhesion, might cause imaging artifacts, as loose particles cling to the tip. None of the above was noticed in neither of the two samples, leading to the conclusion that the coatings of both samples have good adhesion to the substrate and between the grains.

We only performed electrochemical measurements on the polished titanium disc electrodes, due to contact problems with the silicon wafer electrodes. The contact problems can be solved by making a proper ohmic contact on the back-side of the wafer [26,27]. For electrodes prepared by spin coating on polished metal, the coating weight corresponds to a calculable coating thickness [16]. The voltammetric charge ( $q^*$ ) is an established technique to measure the active area of oxide electrodes [28]. During a potential sweep the electrode surface is oxidized and reduced according to reaction 2, with the oxide coating acting as an electrochemical capacitor.

$$\operatorname{RuO}_{x}(\operatorname{OH})_{y} + \delta \operatorname{H}^{+} + \delta e \quad \leftrightarrow \operatorname{RuO}_{x-\delta}(\operatorname{OH})_{y+\delta}$$

$$\tag{2}$$

Reaction (2) is believed to take place only on surface of the grains and the voltammetric charge, calculated from potential sweeps using reaction (3), is then a measure of the real active surface area of the electrode.

$$q^* = \int i dt \tag{3}$$

The active area of the electrodes should increase with increasing coating thickness until the electrolyte penetration limit is reached. The results of the electrochemical measurements are displayed in





**Fig. 6.** AFM images of coating grains. Topography of the top of a coating plaquette on (A) silicon substrate and (B) titanium substrate, respectively. The variation in color represents height differences according to the scale bar to the right. Imaged area:  $500 \text{ nm} \times 500 \text{ nm}$ .

Fig. 7. As seen in Fig. 7B the voltammetric charge decreases with increasing sweep rate. This has been interpreted as diffusion limitations of electroactive species in the electrolyte within the fine pores of the coating. A technique has been proposed to evaluate the "outer" and "inner" surface area of a coating, where the "outer" area is easy to reach for the electrolyte species, whereas the "inner" area relates to fine pores associated with diffusion limitations [22].

The voltammetric charge of  $RuO_2$  coatings on titanium substrates is generally proportional to the catalyst loading [22,29] though at low loadings deviations from linearity have been observed [30]. Our data in Fig. 7 show an increase in voltammetric charge with increasing coating weight, in agreement with earlier studies mentioned. Analysis of data from varying sweep rates in Fig. 7B shows an approximately constant ratio between "inner" and "outer" surface areas for the different loadings, see Table 1. This indicates a relatively homogeneous morphology with coating depth.



#### Table 1

Ratio of the inner and the total surface areas as determined by the voltammetric charge, for different loadings. Coating weight given for the original titanium disc, 59 mm in diameter.

Number of layers	Coating weight [mg]	$\mathbf{q}_i^*/\mathbf{q}_t^*$
1	7.04	0.30
2	13.35	0.34
3	20.20	0.32

### 4. Conclusions

Spin coated silicon wafers and polished titanium discs have been compared and evaluated as model system for (Ti, Ru)O<sub>2</sub> based electrodes with the purpose to facilitate surface characterization. This model system showed thin uniform films where the film thickness could be controlled by the spinning velocity, and where the uniformity of the films enabled proper AFM characterization. By breaking the silicon samples, a straightforward sample preparation technique was shown for cross-section SEM, and estimates of the film thickness from weight-increase data were in agreement with SEM data. SEM images also showed that the smoother the substrate is, the lower the crack-density in the coating becomes. AFM images and XRD measurements show the size and packing of the coating grains with no interference of the substrate. High spinning velocity (>5000 rpm) was used to produce films thin enough to be studied by TEM directly as-prepared without need of tedious sample preparation. The morphology was shown to be relatively homogeneous with the coating depth, as the ratio between "inner" and "outer" surface areas for different loadings was approximately constant.

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#### **Author contribution**

Conceived and designed the study: CH, HO, JB. Performed the experiments: CH, JG. Analyzed the data: CH, JG, AC, HO, JB. Wrote the paper: CH, JG, AC, HO, JB.

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**Fig. 7.** Results from cyclic voltammetry measurements. (A) Cyclic voltammograms measured using a sweep rate of 200 mV/s. Results for three different loadings; one, two or three layers of  $T_{10,7}Ru_{0,3}O_2$  spun onto polished titanium. (B) Voltammetric charge (q\*) as a function of coating weight on the original titanium disc (59 mm in diameter). Values are integrated from cyclic voltammograms measured at different scan rates as indicated in the figure. (C) Total, outer and inner q\* as indicated. Values are derived from extrapolations to infinite and zero scan rates following published methods [22]. Estimated coating thickness corresponding to each coating weight is given in brackets.

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