The Influence of Surface Structure on the Photoelectrochemistry of Polycrystalline n-TiO_2-Films

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The relationship between the surface structure, film thickness and the photoelectrochemical behaviour (photocurrent, corrosion and stability) of n-TiO_2-films produced by controlled thermal oxidation of titanium foils is carefully investigated. X-ray surveys, optical and scanning electron microscopical observations were performed to elucidate the surface structure. It is established that a special etching procedure of Ti-metal foils, followed by controlled oxidation at 600 to 700 °C for 10 to 30 min in the presence of sufficient oxygen results in n-TiO_2 layers with a defined surface structure and high photoactivity. As charge transfer through the Schottky barrier is decisive for the photoefficiency, the formation kinetics of the oxide layer is the most influencing factor.

1. Introduction

Photoactive polycrystalline films of n-TiO_2 can be used as photoanode in cells of the Fujishima-Honda type [1] for the splitting of water or the production of electricity by sunlight. A feasible production of photoactive n-TiO_2 layers can be achieved by thermal oxidation of Ti-foils [2–6]. Recently [2] it has been shown that n-TiO_2-semiconductors with high photoefficiency can be produced by a controlled thermal oxidation procedure. Thereby it was established that changes in the experimental parameters, e. g. surface pretreatment of the metal foil, heating time, temperature and partial pressure of oxygen strongly influence the photoelectrochemical behaviour of the semiconductor film and its mechanical stability. The above mentioned factors are known to affect the metallurgical properties of the oxide crystalls on the titanium surface [7–10]. There are a number of titanium-oxide-phases, and is possible to produce a mixture of them during the thermal oxidation process [11–13]. By reducing the oxygen pressure different Magneli-phases appear [14]. The first step of oxygen uptake consists in the formation of a solid solution, where oxygen atoms become inserted in the octahedric gaps of the metal lattice. This content of dissolved oxygen can be quite high at elevated temperatures [7]. Simultaneously oxidation of titanium occurs as a competing process. Three polymorphic forms: anatase, brookite and rutile can be formed, where of the latter is the most stable form with tetragonal symmetry ($(P4_2)_{mnm}$, $a_0 = 4.593$ Å, $c_0 = 2.959$ Å) and is photoactive. Some authors claim the same photoefficiency for anatase [15, 16]. It should be mentioned that n-TiO_2 films produced by anodic oxidation lack the remarkable mechanical and corrosive stability, compared with these obtained by thermal oxidation [17]. However, a subsequent heating over a longer period leads to better photoelectrochemical properties [18, 19]. From previous metallurgical investigations it is known that anatase produced in aqueous media (below 400 °C [20, 21]), can be transformed to rutile at temperatures about 600 °C [16, 19].

As the Schottky barrier at the metal/semiconductor interface is authoritative for the photoelectrochemical behaviour [22–24], the electric conductivity of the nonstoichiometric n-TiO_2 is due to ionized interstitial Ti-atoms and anionic vacancies in the crystal lattice [9]. This is indicated by measurements of the anisotropic electric conductivity at various oxygen pressures and of the Hall and Seebeck effects [25–27]. The photoconductivity of samples obtained by thermal oxydation at temperatures below 800 °C is based on oxygen vacancies, whereas on heating above 1000 °C interstitial Ti-

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atoms are dominating. This transition seems to be due to defect diffusion in rutile. As the oxygen concentration decreases, the crystal arranges itself, so that extra Ti-atoms can be located [27]. A time dependend decrease in electric conductivity has also been revealed [28].

Different titanium oxides, dopants, various surface structures and possible surface states play an important role in the absorption of the photochemically generated intermediates (mainly OH, H and $-$OH-sites) on the TiO_2-surface [29 – 32]. These intermediates influence the flatband potential, the band-bending and the electrical conductivity through the bilayer [33]. In addition to this, charge transfer processes are essentially bound to the overlap of the relevant energetic levels and to the potential gradient in the Helmholtz layer.

The aim of the presented work was to investigate thoroughly the relationship between the metallurgical observations (crystal structure, composition, etc.) and the photoelectrochemical behaviour (e. g. photocurrent, corrosion, etc.) of *n*-TiO_2 films produced by controlled thermal oxidation of metallic titanium foils. The morphology and the structure of the *n*-TiO_2-surface layer and the composition of the oxide films were studied by scanning electron- and optical microscopical methods combined with X-ray investigations. Further, photoelectrochemical measurements were performed with each TiO_2-sample as previously described [2]. Based on these results an interdependence of the kinetic performance of the oxidation, the spatial distribution of growth centers, the photoefficiency and the stability of the semiconducting oxide layers was established.

2. Experimental

The titanium sheets (Goodfellow metals, Cambridge, GB), consisting of 99.7% Ti (with 300 ppm Al, 20 ppm Ca, 50 ppm Cr, 5 ppm Cu, 1500 ppm Fe, 100 ppm Mn, 50 ppm Ni, 300 ppm Si, 200 ppm Sn, 300 ppm C, 60 ppm H, 150 ppm N, and 2000 ppm O), were first cleaned and etched as described before [2]. Immediately after the last washing step they were evacuated and treated thermally in a quartz tube in a thyristor steered oven. Table 1 gives the parameters of treatment for the different probes.

Photoelectric measurements were carried out by means of cyclic current voltage curves. The experimental equipment was a wave form generator, a potentiostat and an *X-Y*-plotter. The thickness of the TiO_2-layer has been determined by capacitance measurements in a standardized phase sensitive impedance bridge [2, 34]. Subsequently the oxide layers were characterized through an optical microscope (Reichert, type "Zetopan"), and photographs were taken before and after operation in the electrochemical cell, usually with a magnification of 800 *. In addition to this, the detailed structure of selected samples was observed by scanning electron microscopy (type: Leitz AMR 1600). Afterwards the oxide layer of these samples was scratched off by a quartz rod and the crystal structure was studied by X-ray diffraction methods (Siemens Kristalloflex Cr-K_α and Cu-K_α radiation, 1 rad camera).

Table 1. Experimental parameters of the thermal oxidation of Ti-foils. The given series indications are used throughout this work.

Series	Etching	Atmosphere	Temperature (°C)	Time (min.)
1	yes	oxygen	400 — 800	10 — 180
2	yes	air	600 — 1000	1 — 120
3	no	air	600 — 1100	10 — 120
4	yes	air (5×10^{-2} torr)	600 — 1100	10 — 120

3. Results

3.1. Titanium-Oxide Films Prepared in Pure Oxygen (Series 1)

First, optical microscope photographs were taken from all samples to observe the characteristics of the surface. In order to obtain comprehensive information from each sample and to correlate their various characteristics, also cyclic current-voltage curves and the thickness of the layer were determined. The thin oxide films show interference colours, changing, from blue to yellow and red, depending on the temperature and heating time. Thicker layers appear greyish and finally white as the thickness increases, and the surface becomes more and more homogenous and the photoactivity decreases (Figure 1). For more exact investigations with greater magnification of the surface structure a scanning electron microscope method was employed in addition to the above mentioned measurements. Photographs of typical samples of the observed series show these differences more clearly (Figure 2). It can be seen that in pure

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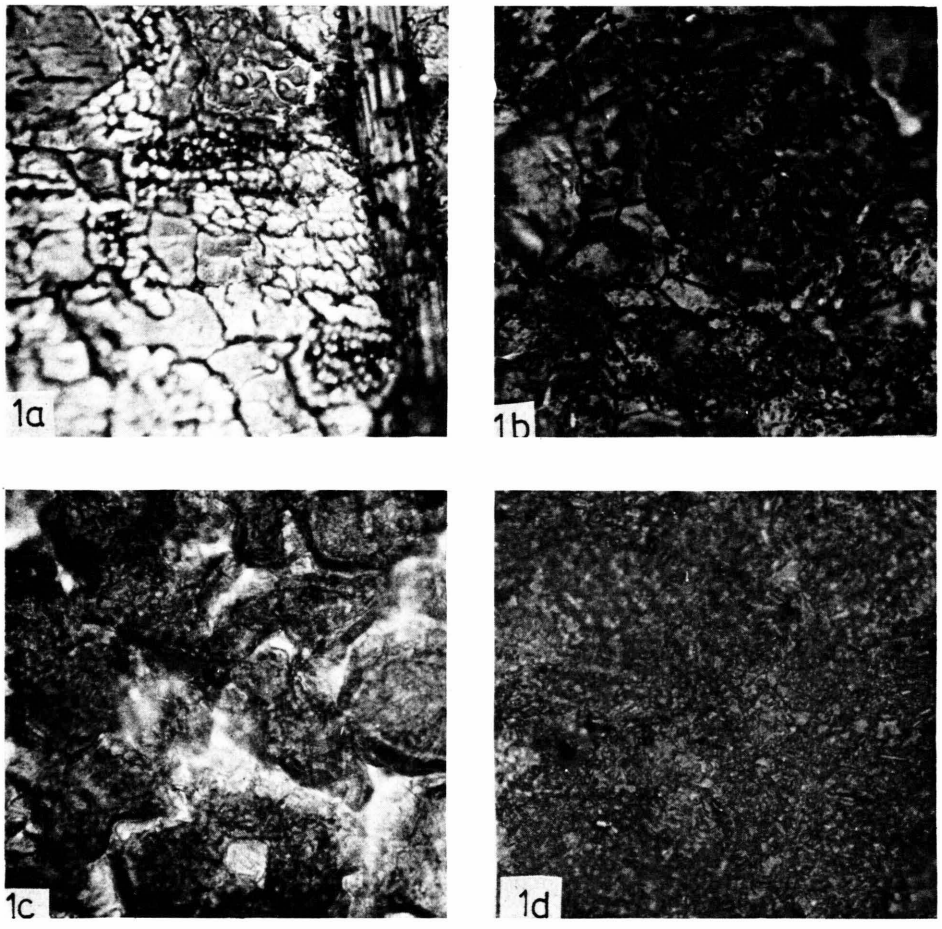

Fig. 1. Optical microscope pictures for increasing film thickness (series 1, magnification (f) = 800). The parameters of the samples, i. e. temperature (T), time (t) of thermal oxidation, photocurrent with a 300 W Xe-lamp at zero bias in 0.1 m KCl (i) and the filmthickness (d), were
1a: $T = 600\,°C$, $t = 10$ min, $i = 2.1$ mA/cm², $d = 0.35$ μm;
1b: $T = 600\,°C$, $t = 120$ min, $i = 1{,}8$ mA/cm², $d = 3{,}80$ μm;
1c: $T = 700\,°C$, $t = 10$ min, $i = 0.8$ mA/cm², $d = 0.80$ μm;
1d: $T = 800\,°C$, $t = 120$ min, $i = 0{,}04$ mA/cm², $d = 5.90$ μm.

oxygen atmosphere a quite rapid oxide layer growth occurs at activation centers, building up a sort of oxide layer islands (Figure 2 a). With increased time and/or temperature of oxidation the crystallite grains are growing from in between and on the surface of the islands and their photoactivity decreases. The thin film in Fig. 2 b shows mainly the contours of the grains of the substrate (ca. 1 – 10 μm). Similar islandlike structures were previously found by other authors [35], but with samples produced under quite different experimental conditions. The samples in this series have the best mechanical stability and a photocurrent maximum (2.4 mA/cm²) if the layer is 1 μm thick. These results confirm our previous observations [2].

By means of X-ray methods it has been established that all foils of series 1 have rutile as predominant component. No anatase could be found at the employed temperatures (from 400 to 1100 °C). Only Ti and a small amount of TiO_2 was detected with X-ray diffraction of samples showing interference colours, in general by heating at temperatures below 500 °C. In oxide layers produced up to 700 °C and below 800 °C traces of Ti_3O_5 were found, at higher temperatures pure TiO_2 is again the main component.

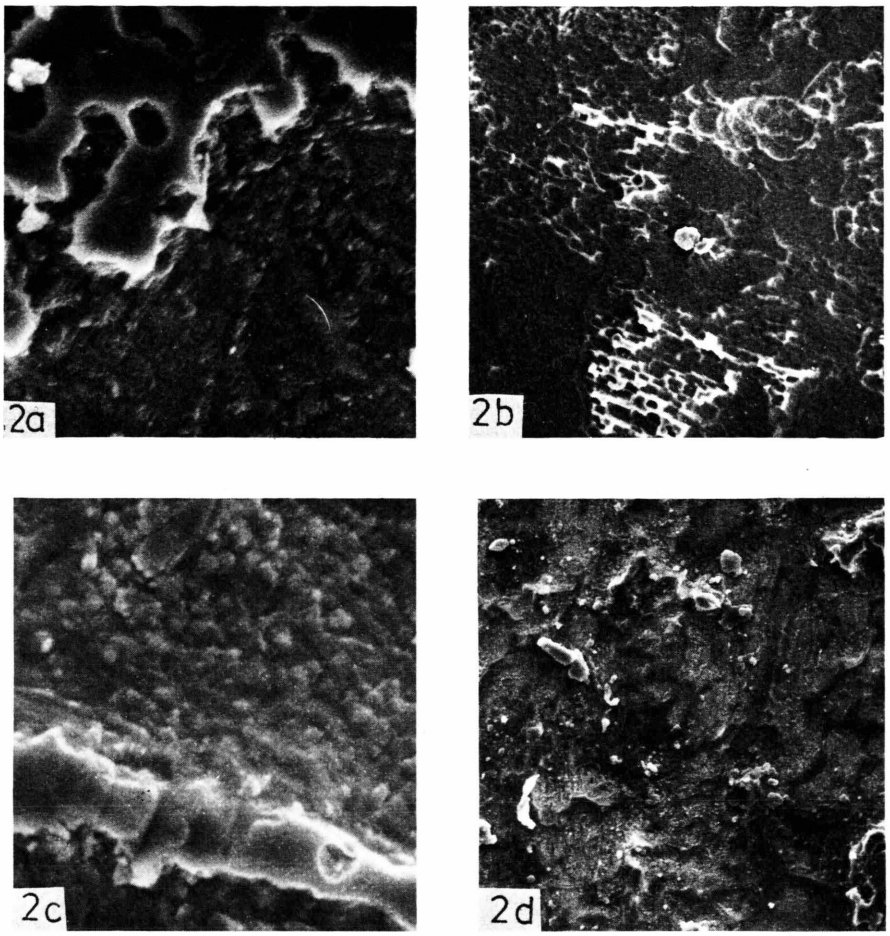

Fig. 2. Scanning electron microscopical photographs of samples of series. The parameters of the samples and the magnification (f) of the pictures were
2a: $T = 600\,°C$, $t = 10$ min, $i = 2.1$ mA/cm^2, $d = 0.35$ μm, $f = 5000$.
2b: $T = 500\,°C$, $t = 10$ min, $i = 1.2$ mA/cm^2, $d = 0.16$ μm, $f = 1000$.
2c: $T = 700\,°C$, $t = 30$ min, $i = 1.0$ mA/cm^2, $d = 1.50$ μm, $f = 2200$.
2d: $T = 800\,°C$, $t = 10$ min, $i = 0.5$ mA/cm^2, $d = 0.38$ μm, $f = 1040$.

3.2. Titanium-Oxide Films Prepared in Air at Normal Pressure (Series 2)

Quite similar optical microscope pictures were obtained for samples of series 2, therefore they are not presented (cf. Figure 1). However, these samples were photographed by scanning electron microscope, and the images for some of them (Figs. 3 a and 3 b) exhibit structures which are looking more like "mountain ridges". This structure can be explained by the fact that by the thermal oxidation in air the partial pressure of oxygen is lower at the active centers on the surface than in series 1. The structure in Fig. 3 a shows about the same photoresponse as series 1, which decreases with the time and/or temperature of the oxidation, as crystallites grow from in between the primary structure (Figure 3 b). Further oxidation leads to a basalt like structure with quite long facetted crystallites with a preferred orientation (Figures 3 c and 3 d). This effect was previously described by Motte et al. [36].

For the X-ray observations the same statements as before can be made, fixing TiO_2-rutile as the main component. In general, the samples of this series are characterized by a good mechanical stability and a maximum photocurrent (e. g. for heating at 600 °C for 30 min and $d = 0.08$ μm a

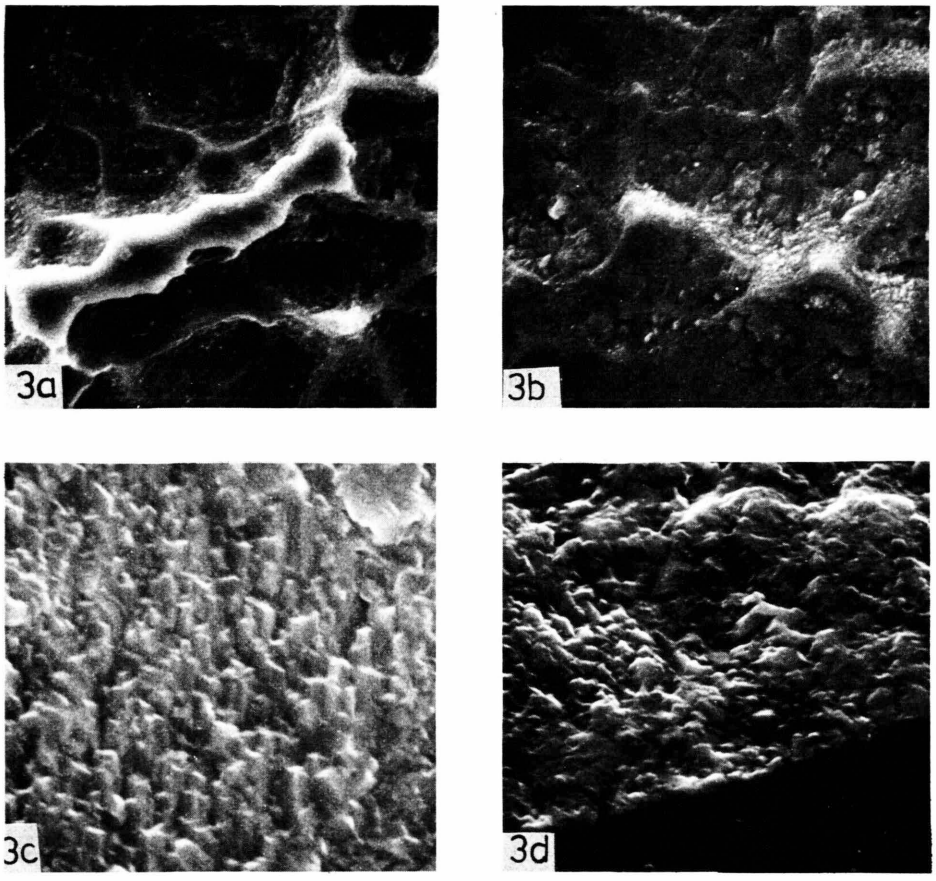

Fig. 3. Scanning electron microscopical photographs of samples of series 2 with the parameters
3a: $T = 600\,°C$, $t = 10$ min, $i = 1.00$ mA/cm², $d = 0.02$ μm, $f = 5080$,
3b: $T = 700\,°C$, $t = 120$ min, $i = 0.43$ mA/cm², $d = 0.50$ μm, $f = 4920$,
3c: $T = 800\,°C$, $t = 10$ min, $i = 0.12$ mA/cm², $d = 0.14$ μm, $f = 4990$,
3d: $T = 800\,°C$, $t = 60$ min, $i = 0.04$ mA/cm², $d = 2.00$ μm, $f = 1950$.

current of 2.3 mA/cm² was obtained). Similar observations were made previously [2].

3.3. Titanium-Oxide Films Prepared Without Previous etching (Series 3)

The aim of these experiments was mainly to demonstrate the effect of the absence of the etching process. The optical photographs of the surface look similar as described before (cf. Fig. 1), but these samples have much less photoactivity (e. g. 0.7 mA/cm² at a layer of 0.1 μm, obtained at 700 °C and 60 min). The mechanical stability of the layer is not satisfactory, since the oxide flakes off easily. This behaviour seems to be due to the omission of the etching process prior to the thermal oxidation procedure.

Scanning electron microscopical photographs were taken and are presented in Figure 4. Figure 4 a reveals a more or less homogenous oxide layer with a few crystallite clusters. It can be seen that from the cold rolling of the Ti-foil during manufactoring a texture appears, covered with a very thin oxide film. The metal surface texture can influence the oxidation, which was pointed out before [35]. Longer times and/or higher temperatures of heating show a corresponding growth of the oxide layer in a quite unique way in one direction (Figure 4 b). The high resistance at the Schottky barrier : metal substrate/semiconducting oxide leads to the assumption that there are frequent holes in the oxide/metal interface, so that the mechanical instability and the poor photoresponse can be explained as well (Figure 4 d).

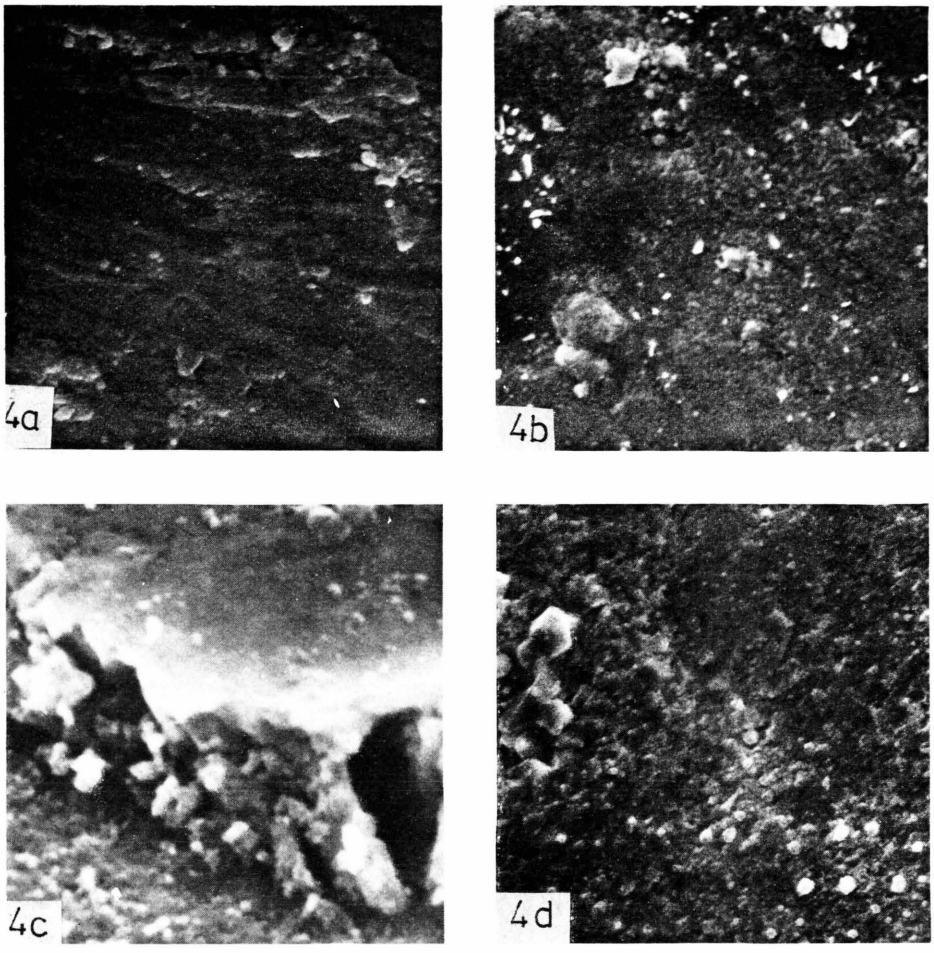

Fig. 4. Scanning electron microscopic photographs of samples from series 3 with the parameters
4a: $T = 600\,^{\circ}C$, $t = 10$ min, $i = 0.23$ mA/cm², $d = 0.015$ µm, $f = 5010$,
4b: $T = 700\,^{\circ}C$, $t = 120$ min, $i = 0.10$ mA/cm², $d = 1.30$ µm, $f = 5080$,
4c: $T = 800\,^{\circ}C$, $t = 60$ min, $i_2 = 1.10$ mA/cm², $d = 1.15$ µm, $f = 5800$,
4d: $T = 800\,^{\circ}C$, $t = 120$ min, $i = 0.03$ mA/cm², $d = 2.10$ µm, $f = 4920$,
(i_2 means photocurrent of the second oxide layer, see text).

A remarkable effect was observed for the samples of this series, namely the formation of a second thin TiO_2-film beyond the primary thick oxide layer. After removing the latter, the remaining thin oxide film shows a high photoactivity ($\geqq 1$ mA/cm², Figure 4 c).

The X-ray findings show no deviation from the above mentioned characteristics, e. g. rutile is the main component.

3.4. Titanium-Oxide Films Prepared under Reduced Pressure (Series 4)

These samples are a special case, since the oxygen concentration during the oxidation was extremely low, the X-ray observations were not able to reveal TiO_2-lines. On the contrary, small amounts of TiO could be found besides the main component Ti. TiO-phases were observed before [37] in vacuum at much higher temperatures. The lines of TiO vanish at higher oxidation temperature, so that pure Ti was established by heating the metal foil at 1000 °C.

These samples show neither a noticeable photocurrent nor a thickness of the oxide, measurable by capacitance methods, even if a sort of crystallite structure can be seen in optical and scanning electron microscopical photographs (Figure 5 a). Photographs of the surface prepared at elevated temperatures (Fig. 5 b) reveal only etching figures

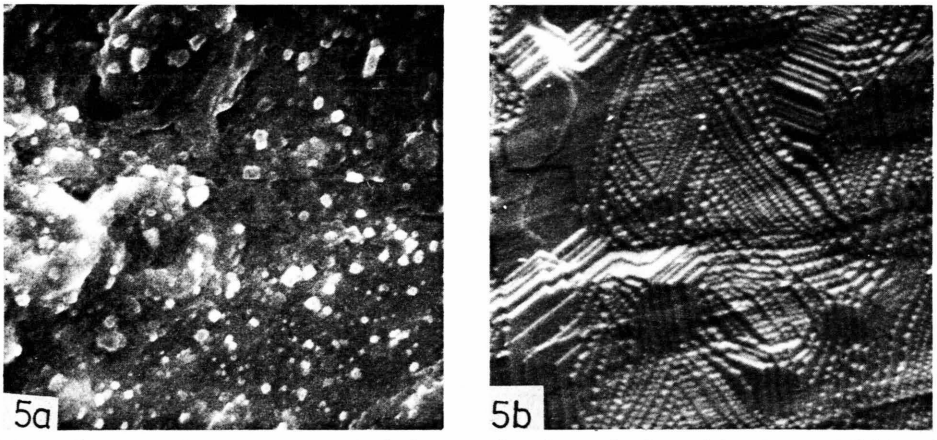

Fig. 5. Scanning electron microscopical photographs of samples heated in air at 5.10^2 Torr. Neither photocurrent nor thickness were measurable.
5a: $T = 900\,^{\circ}C$, $t = 120$ min, $f = 5050$, 5b: $T = 1000\,^{\circ}C$, $t = 10$ min, $f = 2040$.

of titanium metal. The surface layer of these foils becomes very hard, mechanically.

4. Discussion

Attempts have been made to correlate the structure of thermally produced *n*-TiO_2-photoanodes with their photoactivity, resistance against corrosion and long time stability during operation. From the optical investigations it can be concluded that photocurrents above 1 mA/cm² in 0.1 KCl are strictly bound to such surface structures as shown in Figures 1 a and 1 b. With increasing thickness of the TiO_2-layers the surface becomes more and more homogenous and the photoefficiency decreases sharply. This effect is in accordance with previous observations [2].

Comparing the results of optical and scanning electron microscopical observations with the achieved photocurrent of the four investigated series it can be stated that *n*-TiO_2 layers with relatively high photoefficiency (>1 mA/cm²) can be obtained only if the metal foil is etched and sufficient oxygen (offered as air or pure oxygen) is available during the oxidation. In this case the surface of the TiO_2-films is rather similar (series 1 and 2). The importance of the etching procedure is demonstrated by comparing the results of series 3 with those of series 1 and 2. The obtained surface structure (samples of series 3) differs from that in the prior series and the oxide film is flaking off easily. Below their porous surface (Fig. 4 c) a second oxide film is built with quite high photoactivity. This phenomenon has been observed earlier for long time oxidation [10, 36] and for electrochemically produced oxide films [3, 17], where single oxide layers of approximately 3 µm have been found. Finally, by the lack of etching, absorbed impurities on the surface of the titanium foils can contribute to the film instability [17].

Although thermodynamically a sequence of different titanium-oxide-phases could be expected [11 – 13], nearly pure rutile form of TiO_2 was established by X-ray surveys of Ti-foils obtained in series 1, 2 and 3. This observation was previously made in the frame of metallurgic investigations [37]. It might be mentioned that samples, heated from 700 °C up to 800 °C (series 1, 2 and 3) reveal a small amount of Ti_3O_5. This oxygen-deficit-phase occurs only in samples heated for a short time period ($\leqq 30$ min) in the mentioned temperature range. However, samples prepared in the same temperature range, but for longer time of thermal oxidation show preferred orientation of the crystallites of pure TiO_2. All the other oxide phases, e. g. TiO, Ti_2O_3 etc., can only occur below a few percent, as confirmed by the X-ray investigations of series 1, 2 and 3.

Totally different is the behaviour of titanium foils oxidated under reduced oxygen pressure. TiO and pure Ti are the main components. At temperatures above 880 °C α-Ti changes its modification into β-Ti, where the oxygen uptake is enhanced through a higher diffusion rate [7]. Oxygen stabi-

lizes the α-form (up to $TiO_{0,35}$), so that between 900 and 1000 °C dissolution in the β-phase and growth of the α-phase will take place and all the oxygen is dissolved and no TiO is left. The hardness is thereby increased very much as an effect of the oxygen content [8]. This was observed, however, for TiO_2-layers at higher temperatures [7] and may be the cause of some uncertainties in film thickness measurements at higher temperatures, too. The intermediate TiO is only detected when the rate of oxidation is completely governed by the supply of gaseous oxygen to the surface. This fact is also indicated by the linear oxidation rate [2] due to absorption at the surface as rate determining step [38].

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