# TiO$_2$ thin films grown on SiO$_2$–Si(111) by the reactive evaporation method

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TiO$_2$ thin films were grown on silicon substrates using an electron-beam evaporator. Grainy TiO was used as the evaporation material. Temperature substrate during TiO$_2$ growth was relatively low (about 150 °C), what is important for many optoelectronic devices and multilayers mirrors. High vacuum condition allows to maintain clean surfaces substrates before and during oxide growth. The morphology of titanium oxide thin films was *ex situ* investigated using atomic force microscopy operating in contact mode, X-ray photoelectron spectroscopy, X-ray powder diffractometry, and by means of a contact angle analyzer. The influence of annealing treatment and exposure to UV–VIS radiation on the morphology has been also discussed.

Keywords: titanium oxide, wettability, X-ray photoelectron spectroscopy, UV radiation.

## 1. Introduction

Titanium dioxide (TiO$_2$) based thin films are widely used in industry. The compound is utilized in protective coatings against harsh environment, self-cleaning hard coatings, personal care products. The unique properties, such as an excellent optical transparency, high refractive index and thermal stability, make the coatings also attractive to industry of photoelectric devices [1–3]. The quality of coatings and devices essentially depends on, apart from the optical properties of TiO$_2$, the structural features of the material such as grain size, *etc*. [4]. Surface protection is extremely important for high efficiency solar cells [5] as well as for Mo/Si multilayer mirrors used in extreme ultra lithography [6]. Features of thin films are heavily dependent on deposition techniques and substrate temperature, hence the choice of preparation procedures is difficult. Anyway, sputtering and sol–gel synthesis are the most employed means of TiO$_2$ deposition [7].

Another interesting technique, which is not widely used to prepare the thin films and has been employed in this study, is the direct electron-beam evaporation. It is difficult to produce titanium dioxide thin films using this method which was previously investigated by Dongjin Byun *et al.* [8]. Powdered $TiO_2$ cannot be evaporated due to thermal dissociation and reactions with the crucible. Because of those problems, titanium monoxide TiO was used as evaporation material for which additional high purity oxygen had to be transported from the gas phase in order to get formation of stoichiometric $TiO_2$ thin films on slightly heated Si-substrate. In this paper, thin films of $TiO_2$ grown on Si substrate, prepared by the reactive electron beam evaporation technique are presented, and the morphology and quality of the obtained layers are discussed.

## 2. Experimental details

The $TiO_2$ thin films were grown on silicon substrates, with an oxidized native Si(111) surface, using a homemade electron-beam evaporator, where grainy TiO was used as evaporation material. Processes were carried out in a technological vacuum reactor chamber which consisted of the gas supply- and dynamic pumping system. Base pressure before deposition was $5 \times 10^{-8}$ torr. Evaporation of TiO was made at pressures up to $5 \times 10^{-5}$ torr, in a reactive atmosphere using high purity 99.999% $O_2$ as a working gas. During deposition the temperature of the substrate was about 150 °C. The morphology of the $TiO_2$ thin films grown was *ex situ* investigated in an ultrahigh vacuum (UHV) apparatus by atomic force microscopy (AFM; Omicron) operating in contact mode, and also X-ray photoelectron spectroscopy (XPS; Specs) using a non-monochromatized Mg K$\alpha$ radiation ($hv = 1253.6$ eV). Recorded spectra of all samples were referenced to the C-1$s$ line of the residual carbon set at 284.6 eV. Additionally, the analysis of the thin films was carried out with an X-ray powder diffractometer (XRD; Siemens) using Co K$\alpha$ radiation ($hv = 6930.32$ eV). The samples were also examined by water contact angle measurements using a contact angle analyzer (CAA; Krüss DSA 100) and exposures to UV–VIS radiation (450 W xenon lamp) ranging from 2 min to 2 hours. $TiO_2$ samples were heated in air at a temperature of 650 °C for 4 hours. All measurements were performed at room temperature.

## 3. Results and discussion

To examine the $TiO_2$ thin films grown on the $SiO_2$–Si(111) surface, a series of measurements was carried out before and after heating them in air at 650 °C for 4 hours. A wide XPS spectrum of the as-prepared thin films of $TiO_2$ is presented in Fig. 1; a similar spectrum of the heated samples was recorded. The intensity of the spectral lines O-1$s$, Ti-2$p$, C-1$s$ was equal in both cases. A subtle difference appeared between O-1$s$ and C-1$s$ peaks at a closer inspection. Ti-2$p$ peak doublets with
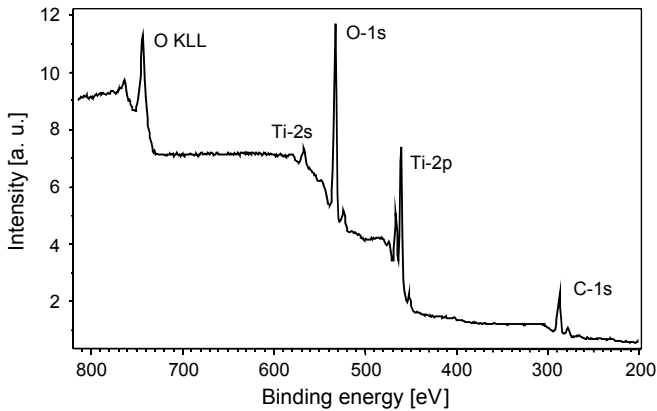
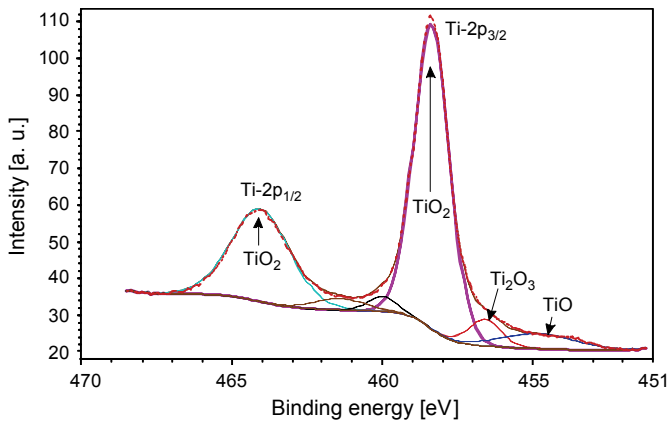Fig. 1. A wide XPS spectrum of the as-prepared thin films of TiO$_2$.



Fig. 2. Ti-2*p* XPS spectrum recorded from the as-prepared thin films of TiO$_2$ (dotted line). Solid-line curves through the data points show the results of deconvolution procedure.

a binding energy (BE) of 458.07 eV for the Ti-2$p_{3/2}$ appeared on both the as-prepared samples and the heated ones, whereas the splitting of the 2*p* doublet amounted to 5.7 eV, which indicated that, in addition to a Ti$^{+4}$ oxidation state, there were oxygen-deficient oxides [9–11]. A detailed analysis of the peak deconvolution is shown in Fig. 2. The full width at half-maximum (FWHM) amounts to 1.38 eV for the Ti$^{+4}$-2$p_{3/2}$ core-level peak and 2.2 eV for the Ti$^{+4}$-2$p_{1/2}$. Also two peak doublets could be assigned to intermediate oxidation states (Ti$^{+3}$ and Ti$^{+2}$): one with a binding energy of 457.3 eV and the FWHM 1.2 eV for the core-level peak Ti$^{+3}$-2$p_{3/2}$ (with 462.12 eV and the FWHM 1.94 eV for Ti$^{+3}$-2$p_{1/2}$) and second with an energy of 455.54 eV and the FWHM 2.9 eV for the core-level peak Ti$^{+2}$-2$p_{3/2}$ (with 460.7 eV and the FWHM 1.1 eV for Ti$^{+2}$-2$p_{1/2}$) for a small fraction of Ti$_2$O$_3$ and TiO oxides,

respectively. A distance of 1.97 eV between $Ti^{+4}$-$2p_{3/2}$ and $Ti^{+3}$-$2p_{3/2}$, and another of 3.5 eV between $Ti^{+4}$-$2p_{3/2}$ and $Ti^{+2}$-$2p_{3/2}$ are in good agreement with earlier data of the literature [10, 12].

Oxygen is a common bulk and surface contaminant in titanium and titanium compounds. The deconvolution of O-1$s$ peaks is shown in Fig. 3. The O-1$s$ spectrum for as-prepared sample can be fitted by four peaks: the one of 529.728 eV with FWHM equal to 1.3 eV, and another of 531.15 eV with FWHM equal to 1.9 eV, and 532.3 eV with FWHM 2.0 eV, and 528.8 with FWHM 1.5 eV. The former peak is related to oxygen chemically bound to Ti [13, 14], the second peak is assigned to ad-sorbed water or a fraction of $Ti_2O_3$ [15, 16]. The third peak is assigned to a C–O-type surface impurity. The last one corresponds to a fraction of TiO [12, 17], which were used as evaporation material. For the samples heated in the air, the position and shape of the O-1$s$ peak did not change significantly, see Fig. 3**b**. It can be fitted also by four peaks: the one of 529.88 eV with FWHM equal to 1.4 eV, another of 531.24 eV
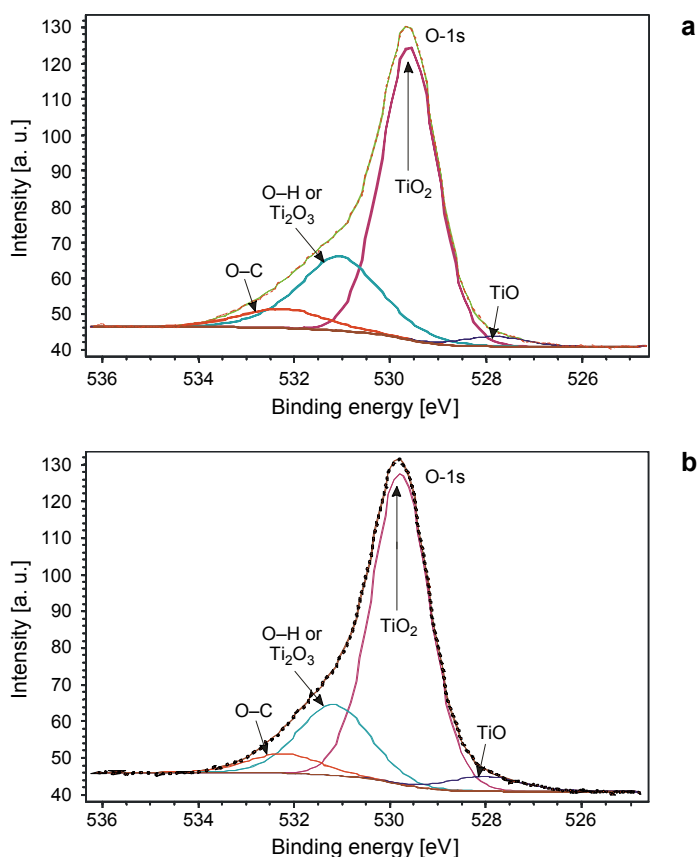


Fig. 3. O-1$s$ XPS spectrum recorded from (**a**) the as-prepared thin films of $TiO_2$ (dotted line) and (**b**) the samples heated in air. Solid-line curves through the data points show the results of deconvolution procedure.

with the FWHM 1.7 eV, and 532.27 eV with the FWHM 1.7 eV, and 528.14 eV with the FWHM 1.78 eV. The nature of those peaks is similar as for as-prepared sample. Considering only the contributions of that peak at 529.8 eV, the O/Ti ratio for the as-prepared samples amounts to 2.2 and comes close to the stoichiometric value. The ratio for samples after heating increases to 2.6.

The C-1*s* spectrum for the as-prepared samples can be fitted by two peaks, which is shown in Fig. 4**a**. The peak at 284.6 eV with FWHM equal to 1.46 eV is related to a C–C type surface carbon impurity, and the one at about 286.0 eV with FWHM equal to 1.5 eV corresponds to a C–O type carbon. For the samples heated in the air, the C–1*s* spectral line consists of three peaks, see Fig. 4**b**. One lies at 284.6 eV with FWHM equal to 1.38 eV, second at 285.81 eV with the FWHM 2.00 eV and the third at 282.88 eV with the FWHM 1.38 eV. The latter peak is characteristic of a titanium carbide. It is worth noting that we are dealing with surface grain boundary carbides rather than the ones of the bulk [18]. Formation of carbides of this type clearly depends
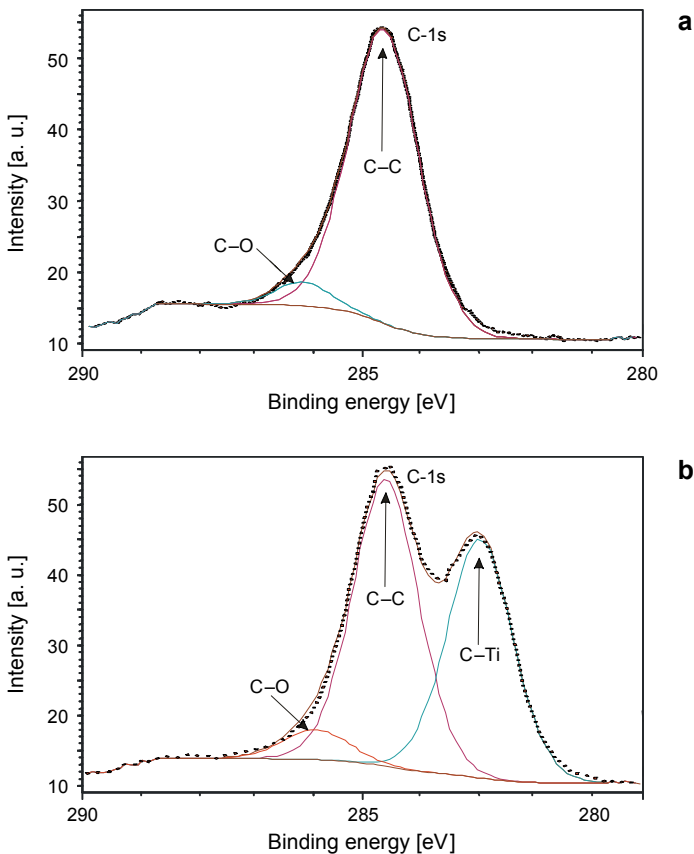


Fig. 4. C-1*s* XPS spectrum recorded from (**a**) the as-prepared thin films of $TiO_2$ (dotted line) and (**b**) the samples heated in air. Solid-line curves through the data points show the results of deconvolution procedure.
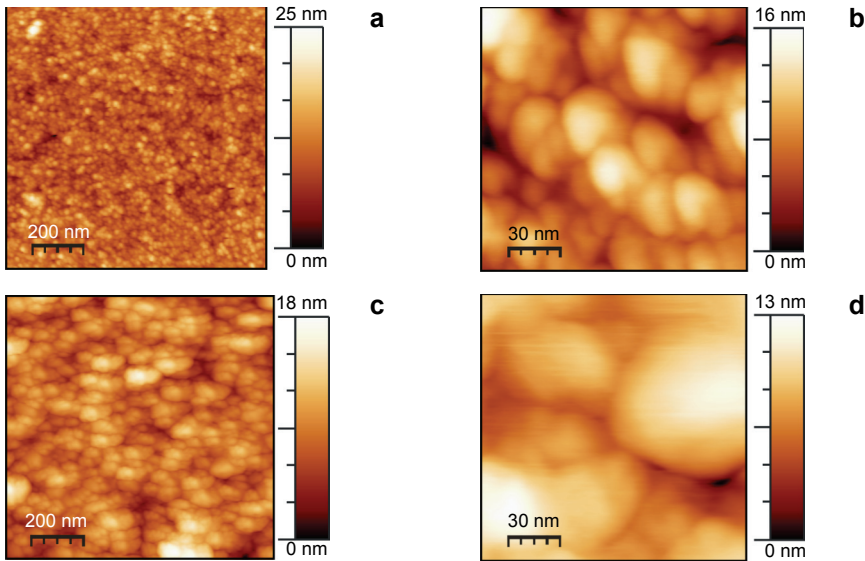
Fig. 5. AFM images of TiO$_2$ thin films (**a**, **b**) as-prepared, and (**c**, **d**) after heating in air at 600 °C for 4 hours.

on the size of crystallites composing a thin layer; the smaller the grains are, the easier carbides appear.

A typical topography of an as-prepared sample with a uniform structure is shown in Figs. 5**a** and 5**b**. Regularity in TiO$_2$-grain size is visible. Figure 6 shows the result of analysis of the distributions of grain diameters without taking account of the scanning-tip size. Local population maxima appear for the grains of 6 and 36 nm diameter, while the largest diameter is 100 nm. XRD patterns taken for as-deposited sample do not show any peaks apart from the spectral line from the Si(111) substrate. This
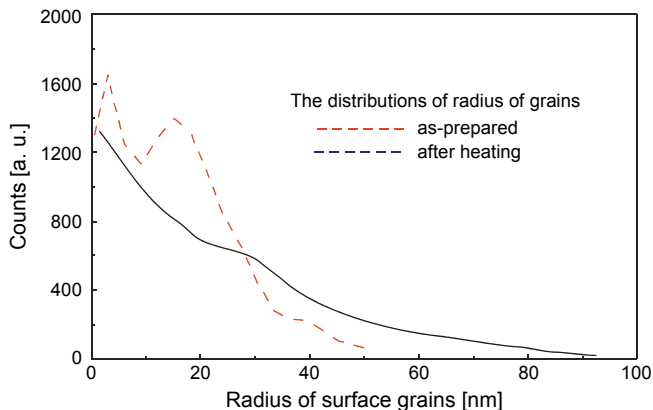


Fig. 6. Distribution for grain radii on as-prepared thin films of TiO$_2$ (dashed line) and on samples heated in air (solid line).

indicates that during the growth of $TiO_2$ thin films on the substrate a strong strain forced the growth of small and randomly oriented and distributed nanocrystalline grains. The changes in surface topography appeared after heating the sample in the air. The grains grew larger leading to coalescence, which is clearly seen from Figs. 5**c** and 5**d**. The grain-diameter distribution curve exhibits no prominent diameters. The biggest grains had a diameter as high as 180 nm, almost twice that for the non-heated samples. In Fig. 7 XRD patterns reveal the occurrence of a preferential crystallographic direction perpendicular to the (110) surface, which can be attributed to the signals of the rutile phase. Also, a weak signal from the (101) orientation of $TiO_2$ is seen.
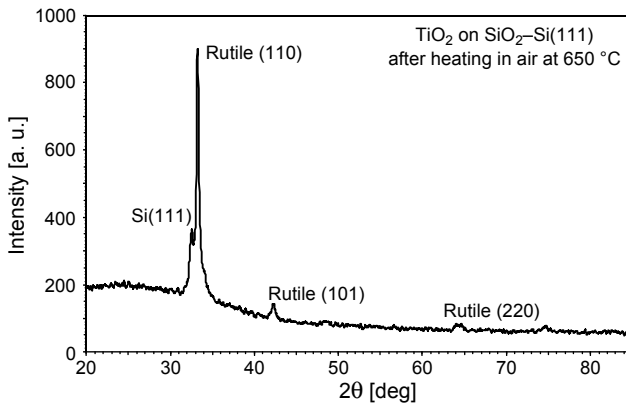


Fig. 7. X-ray diffraction patterns of the $TiO_2$ thin films on the $SiO_2$–Si(111) after heating in air at 600 °C show the grain orientation distribution while XRD patterns taken after deposition exhibit only the peak of the substrate (data not presented).

Rutile (110) and (100) faces are known for their strong hydrophilic properties, which is in contrast to the (001) surface with its hydrophobic behavior [13]. Wettability of the specimen surfaces was checked by the measurement of the water drop shape, which droplets were deposited onto the surface under investigation before and after irradiation with UV–VIS. The as-prepared samples appeared to be hydrophobic; the samples poorly wetted the surface, even after exposures to UV radiation. Samples in-the-air heated showed a strong wettability effect which was still stronger after UV irradiation. The angle data before and after UV–VIS irradiation are collected in

T a b l e  1.  Surface wettability inspection through water-contact angle measurements on the as-prepared $TiO_2$ thin films and the ones after heating in air at 600 °C for 4 hours before and after 10 minute UV radiation.

| | Water-contact angle [deg] | |
|---|---|---|
| $TiO_2$ thin film | Before UV radiation | After 10 minute UV radiation |
| As deposited | 86±3 | 83±3 |
| After heating | 55±3 | 26±3 |

Table 1. The UV-radiation promoted mechanism of the hydrophobic–hydrophilic transition for the rutile surface properties, which is connected with the reduction of surface Ti-cations from an oxidation degree +4 to +3 as well as oxidation of the oxygen anions –2 leading to their desorption. As a result of this process, the oxygen vacancies promote the dissociative adsorption of water molecules, what is observed as the increase in surface wettability [11, 16].

## 4. Conclusions

$TiO_2$ thin films have successfully been grown by reactive evaporation on Si substrate. The calculated O/Ti ratio is almost 2, or consistent with stoichiometric $TiO_2$ grown thin films. The topography of the $TiO_2$ films exhibits a high-quality nanocrystalline structure with uniformly distributed grains. The surface roughness is uniform on the whole area in question. On the as-prepared samples, the grains are randomly oriented, and XRD patterns taken do not show any peaks of the films. Heated samples show a reconstruction of the grains and their coalescence.

The as-prepared samples exhibited hydrophobic behavior, and no marked changes were observed after UV irradiation. In contrast, the heated samples revealed strong hydrophilic properties which increased after UV irradiation.

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