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THERMAL STABILITY OF CV DEPOSITED TiO_2 THIN FILMS. XPS AND AES CHARACTERIZATION

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Thermal stability of TiO_2 thin polycrystalline films obtained by the very simple chemical vapour deposition method on the quartz, molybdenum and gold substrates have been examined by X-ray photoelectron and Auger spectroscopy (XPS and AES), respectively, before and after annealing in vacuum at temperatures from 298 K to 1200 K. In this temperature range we have found carbon, water, and O-H groups as the impurities at the surface of the films. The possible influence of both the annealing and the impurities on the film stoichiometry is discussed.

1. *Introduction*

Titanium dioxide films are extensively used in the optical thin film devices because of their desirable optical properties and good stability in adverse environments. We have produced TiO_2 thin films by a very simple chemical vapour deposition (CVD)$^{1)}$ method and used them$^{2)}$ as intercalation electrodes for Ag/Agl/TiO_2, SnO_2 rechargeable, photosensitive galvanic cells. The Ag^+ ion diffusion in TiO_2 and thus the kinetics of the electrochemical intercalation reaction are greatly influenced by the properties of the oxide electrode. In order to achieve understanding of its performance we have performed a series of measurements of optical and electrical properties of TiO_2 thin films in different environments: X-ray diffraction[3)], Raman spectroscopy[3,4,6)], thermally stimulated currents (TSC)[4)], photoresistance – wavelength dependence in the range 250 – 350 nm[7)] and Fourier transform infra red (FTIR)[8)]. All of these bulk sensitive methods indicated the existence of carbon and oxygen containing impurities in the films. Moreover, in our work[3)] on Raman of TiO_2 thin films produced by the chemical vapour deposition (CVD) method[1)], we had observed two extra lines at 1358 cm^{-1} and 1598 cm^{-1}. These two lines may be attributed to the up to 3 nm large microcrystalline graphite[9)]. It is important to emphasize that the CVD method used has been simplified[1)] in order to be practical and possibly used in commercial CVD reactors for producing solar cells. The whole procedure is performed in a normal atmosphere, not in a vacuum chamber.

In this work we use the X-ray photoelectron spectroscopy (XPS) and Auger electron spectrocsopy (AES) in order to prove the presence of carbon at or within the surface of the samples as probed by these methods. Beside this, we wanted to examine the behaviour of surface impurities as well as the stoichiometry of the film itself as a function of annealing in the temperature range 300 K – 1200 K. These temperatures are below the anatase-rutile phase transition temperature (1200 K – 1470 K).

After an annealing of 15 minutes at a given temperature, the samples were characterized by the XPS and AES, while during the annealing the partial pressures of water, carbon monoxide, hydrogen, carbon dioxide and oxygen were monitored. In such a way it was possible not only to prove the existence of carbon as an impurity but also to get an idea on its influence on the surface properties of our films.

Since the CVD method required heating of the substrate during deposition, we tested three different materials (quartz, gold and molibdenum sheets) in order to see if any correlation between the carbon concentration and the choice of the substrate existed.

2. *Experimental*

We have described in detail the CVD method of preparation of TiO_2 thin films elsewhere[1,2)]. A schematic diagram of the apparatus used is shown in Fig. 1. Air was used as a carrier gas flow through pipe (1) at a rate of 10 ml/min. The sublimation vapour $TiCl_4$ is carried away through pipe (2) to a clean substrate (quartz, Mo, Au) placed on a plate heated at 650 K. At the heated substrate, $TiCl_4$ molecules receive enough energy to interact with moisture from air

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl. \tag{1}$$

The growth rate of the films was typically 5 nm/s. The thickness of the films was approximately 300 nm. Since the samples have been produced by the CVD method in atmospheric conditions, they have been transported without any special treatment and inserted in an ultrahigh vacuum apparatus equipped for the XPS, AES and thermal desorption spectroscopy (TDS) measurements. The samples were mounted on the sample holder whose detailed description is given elsewhere$^{19,11)}$. X-ray excitation source was a Mg anode (Mg K_α line). The measured spectra were referenced to the Fermi level which was determined using a gold foil mounted parallel to the sample. An electron beam of 4 keV energy was used for AES. In both cases the outgoing electrons were analyzed by the use of a 180°-hemispherical analyzer in FAT 50 (XPS) and FRR 5 (AES) modes. Auger spectra have been recorded in both dN/dE and integrated modes. A quadrupole mass spectrometer was used to monitor partial pressure of selected gases during annealing procedures.

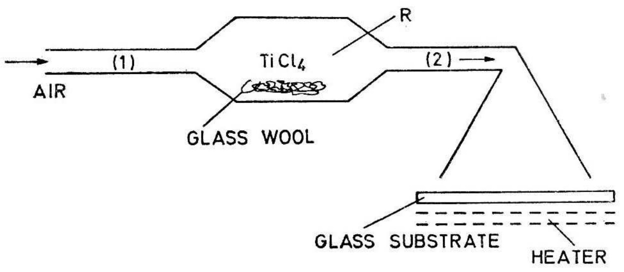

Fig. 1. The layout of the apparatus for CVD of TiO_2 *thin films in normal atmosphere.*

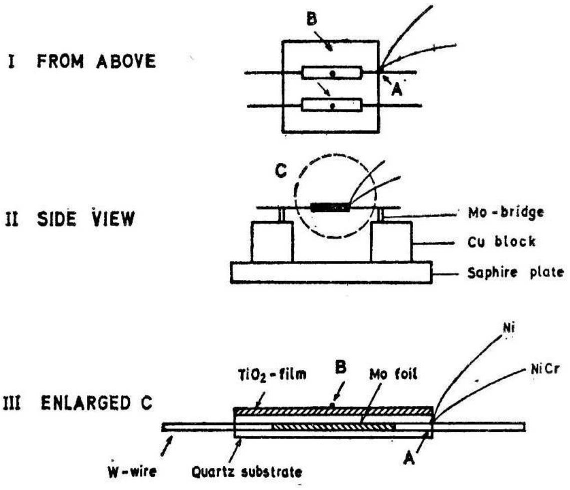

Fig. 2. Schematic representation of the sample holder arangement together with a quartz substrate with integrated Mo-heaters. *The A and B denote the points where the sample temperature is controlled by the* Ni/NiCr *thermocouple (A) and the pyrometer (B). The* Mo-heaters *are connected to the* W-wires *which in turn are via two* Mo-bridges *connected to two mutually insulated* Cu-blocks *which are electrically attached to the power-supply.*

The samples were heated resistively, a method which appeared to be tricky for the quartz substrate. Figure 2 shows the basic arrangement of the quartz plate with incorporated heaters (Mo foils) and a sample holder of the spectrometer. Quartz plate (B) of an area of 1 × 1.5 cm and a thickness of 0.2 cm, was polished with alumina powder of the final finess of 0.06 μm grade. Temperature was measured with Ni-NiCr thermocouple spotwelded at the entering point of one of the Mo foils (point A, Fig. 2) into the substrate and, as well, with a pyrometer controlling at the point just above the center of the Mo foil (point B, Fig. 2) and at the point of the thermocouple. The accuracy of measurements was ± 10 K and the temperatures in text are given for the center of the sample. However, a temperature gradient across the sample of approximately 30 K was always present as a consequence of both the sample and the heaters geometry.

In the case of the Au and Mo substrates the accuracy of the sample temperature measurement was better as the thermocouple was directly attached to the Au or Mo foil. Area of the gold and molibdenum foils was 1×0.3 cm^2, and thickness 5×10^{-3} cm. Mo foil was 15 min. baked out at 1300 K in an inert atmosphere and both, Mo and Au, foils were chemically cleaned prior to CVD procedure.

3. Results and discussion

Our previous Raman measurements$^{3)}$ had shown a change of stoichiometry for the thermal treatment of TiO_2 in non-oxidizing atmosphere of H_2. We had proposed the mechanism of loosing O_2 by forming molecules of water which, as it is well known, desorbs at substrate temperature ≈ 500 K$^{12)}$. As the thermal treatment in vacuum also affects stoichiometry of TiO_2 thin films, as reported in some cases$^{13)}$, we wanted to check thermal stability of our samples under the same conditions. Our samples were 300 nm thick, thus being different from the few monolayers samples of reported experiments. We have performed XPS and AES experiments on "as received" TiO_2 thin films on SiO_2, Au, Mo substrates, in vacuum of 10^{-6} Pa in the themperature range 295 K to 1200 K.

Figure 3 shows a typical large-scan Auger electron spectrum of "as received" TiO_2 film on Mo after 24 hours staying in high-vacuum environment. One observes the signals of carbon (C KLL at 271 eV), titanium (Ti LMM at 418 eV, 6 additional peaks from 330 - 451 eV) and oxygen (O KLL at 512 eV)$^{17)}$. The spectrum is typical also for the films grown on Au and quartz. In just a few cases, traces of chlorine were detected at 180 eV.

The representative XP spectrum shows, as judged from the position and the shape of the peaks representing Ti 2p levels (Fig. 4) that the surfaces of the samples of TiO_2 thin films as received, indeed have a composition of the TiO_2. The XPS results are presented in Table 1. Due to the presence of significant amount of impurities, it was not possible to obtain a reliable information on the stoichiometry of the TiO_2 films from the measured peak areas. Therefore, the O/Ti ratio was estimated according to the method proposed by Sayers et al.$^{12)}$ who correlated measured O 1s–Ti2$p_{3/2}$ binding energy difference with the stoichiometry of the TiO_2 films.

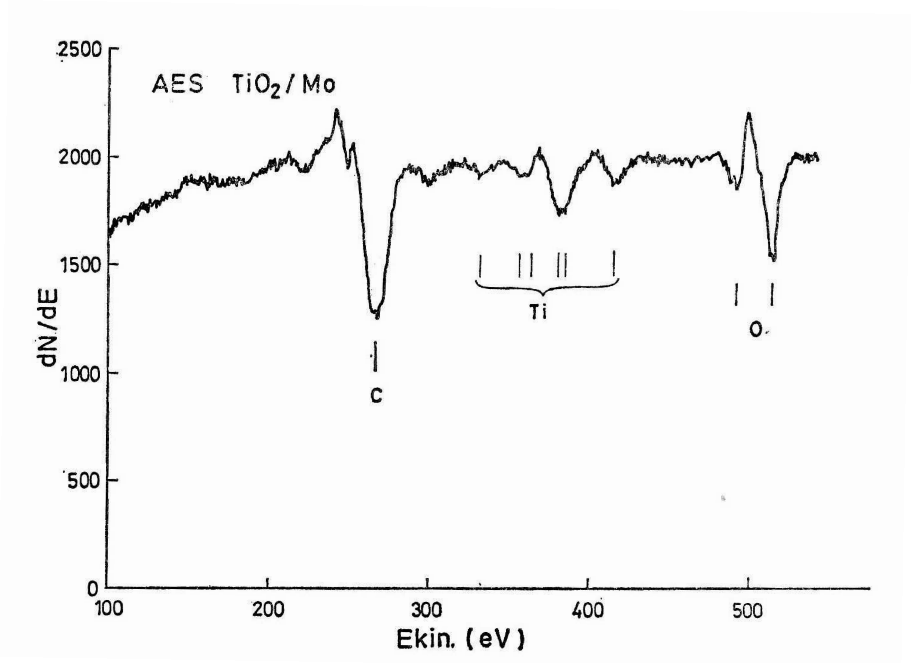

Fig. 3. Auger electron spectrum of "as received" TiO_2 *film on* Mo *substrate.*

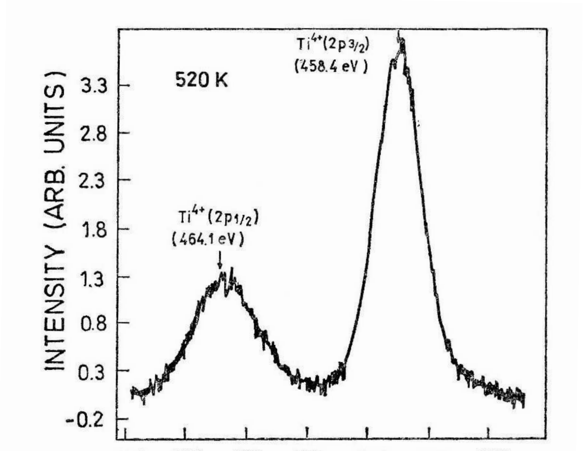

Fig. 4. X-ray (MgKα) *photoelectron spectrum of* Ti 2p *levels of the* TiO_2 *film deposited on the quartz substrate. The spectrum was taken after 15* min. *annealing at 520* K. *Very similar spectra were obtained for all samples and at all annealing temperatures.*

TABLE 1.

Substrate	ΔE_B (eV) O 1s – Ti 2p$_{1/2}$	O/Ti from ΔE_B	C_c (%)
Quartz	72.2	1.8 ± 0.1	50
Au	71.5	2.0 ± 0.1	57
Mo	71.5	2.0 ± 0.1	77

Binding energy difference between Ti 2p$_{3/2}$ *and* O 1s *levels in* TiO_2*; Ratio* O/Ti *according to* ΔE_B *from the work of Sayers et al.*$^{12)}$*; Carbon concentration at the surface of* TiO_2 *thin films. XPS empirically derived sensitivity factors*$^{14)}$ *for* C 1s *atomic level.*

From the data in Table 1 it is obvious that the sample surface slabs are polluted with quite a lot of carbon. In order to learn about chemical nature of the carbon containing contaminants, we analyzed the XPS C 1s level spectra. Figure 5 shows a C 1s spectrum of the film on Mo; it does not differ significantly from other samples. The spectrum is taken from the "as received" sample after staying for one day in high vacuum; very similar lineshapes were obtained after annealing experiments (this is discussed later in the text). The analysis included background subtraction by the Shirley method and fitting procedure with three curves, each of which was represented with four parameters: intensity, peak position, full width at half maximum (FWHM) and a Gaussian-Lorentzian convolution. The highest binding energy peak (the lowest intensity) was set free of all parameters, while the other two peaks had FWHM fixed at 1.5 eV$^{18)}$. The assignation of the synthetic three peaks in Fig. 5 may only be approximate: according to generally accepted tables

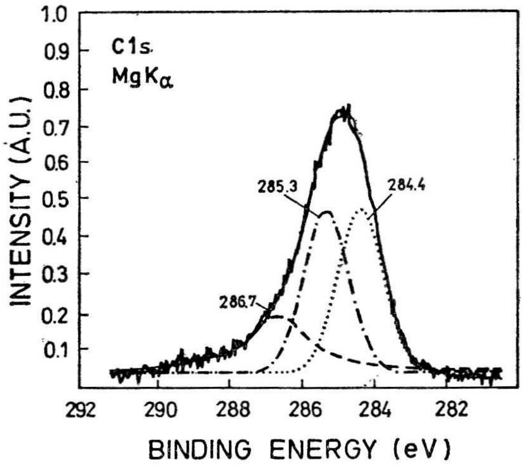

*Fig. 5. X-ray (*MgKα*) photoelectron spectrum of* C 1s *taken from "as received"* TiO_2 *sample. For details see the text.*

of chemical shifts[18)], the peak at 284.4 eV could be ascribed to elemental carbon, most probably in a form of graphite; the peaks at 285.3 (high intensity) and 286.7 eV (low intensity but broad) correspond to various types of organic impurities. This finding should not be surprising taking into account that the samples had been, during preparation and before insertion into vacuum chamber, permanently exposed to atmospheric conditions. It should be noted here that no high oxygenated carbon compounds (peak positions above 290 eV) and no TiC (peak position at 281 eV) may be seen in the spectrum in Fig. 5.

Although the concentration of carbon is high in all samples, it varies largely between them. This may indicate an influence of the substrate to the pollution of the TiO_2 thin films during the process of preparation. The highest concentration of C impurity was found in Mo substrate. This is not surprising since carbon is one of the main impurities in this class of metals. Our assumption here is that heating of the Mo substrate (≈ 650 K) during the CVD process promotes diffusion of carbon from the substrate into the growing thin film producing thus more carbon in the film than in the case of the quartz substrate whose influence in this matter should be negligible. We have tested several, different, by CVD method obtained, TiO_2 films deposited on different quartz and Mo substrates and have obtained the same results. This finding suggests that a substrate may add to the pollution of the TiO_2 samples. Concentration of carbon at different annealing temperatures is presented in Table 2 for the case of the quartz substrate. It shows a rather high value of 50% at the room temperature while at 760 K noticably decreases. It reaches the lowest value at the highest annealing temperature of 1200 K.

Since the chemical state of titanium was determined (by using Sayers et al.[12)] relation) to be Ti^{4+}, it was possible to fit the measured O 1s spectra assuming two peaks of which one corresponds to the TiO_2 film. Figure 6 shows the O 1s peak of the film on the quartz substrate. The spectrum was fitted with two peaks (at 531.5 and 529.6 eV). The peak at the lower binding energy corresponds to TiO_2 oxygen while the other one could be ascribed to hydroxyl groups, according to Levin et al.[13)]. These spectral features persist to the very high temperatures, higher than 800 K, which is also shown in Fig. 6b.

The possible changes in the oxidation state during thermal treatments in vacuum, may be detected using XPS spectra by monitoring binding energy difference between O 1s and Ti $2p_{3/2}$ levels[12)]. According to literature[12,15)], several varieties of titanium and titanium oxides show changes in this energy difference of the order of magnitude of a few eV, maximum 7 eV for some Ti hydrides. According to Sayers et al.[12)] there is a linear dependence between ΔE_B and the ratio O/Ti for TiO, TiO_2 and Ti_2O_3 oxides. We have used this data as a calibration curve for our measured values for ΔE_B at different temperatures.

These values for the TiO_2 on the quartz substrate are presented in Table 2, showing almost constant value of approximately 72 eV. As we introduce these values in a graph representing $\Delta E_B = f(\mathrm{O/Ti})$ as obtained by Sayers et al.[12)], it is possible to obtain values for O/Ti ratio for our thin film samples at different high temperatures during thermal treatment. These values are given in Table 2. Our values for Ti/O ratio are almost constant (very close to 2) for the whole temper-

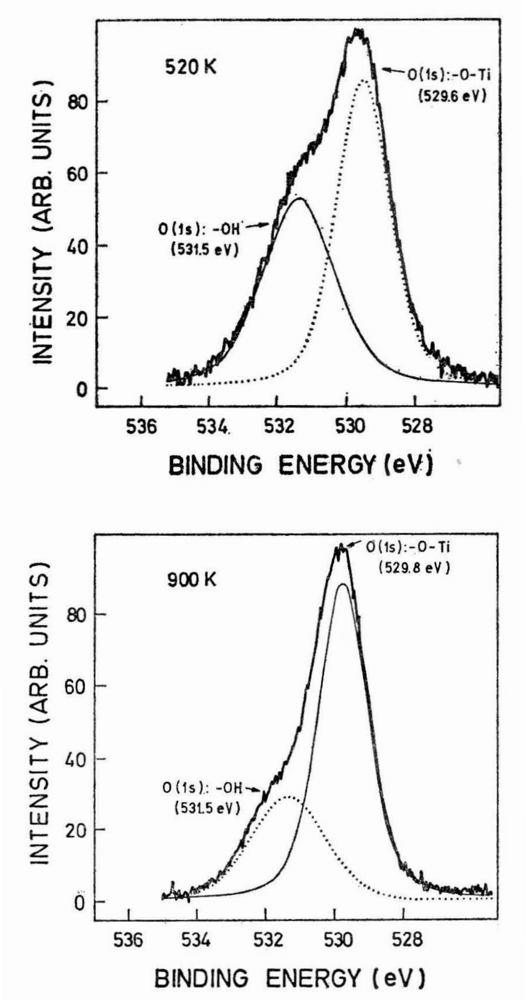

Fig. 6. O 1s *XPS (*Mg Kα*) spectrum of the* TiO_2*, thin film on the quartz substrate after annealing at 520 (a) and 900* K *(b).*

ature range, approaching at the highest temperatures the characteristic value for stoichiometric TiO_2. This leads to conclusion that our thermal treatments do not change stoichiometry in the TiO_2 samples on quartz, even at the temperatures as high as 1200 °C.

The same information is also obtained from the spin-orbit splitting ΔE of ths 2p electrons of titanium. This energy difference: $\Delta E_{2p} = E(2p_{1/2}) - E(2p_{3/2})$ increases slightly with the oxidation state in Ti series[13)]. Also, in the case of the 2p1/2 and 2p3/2 bands of Ti oxides, the full width at half maximum of these peaks decreases appreciably in the d^0 configuration of the metal as in TiO_2. For both,

TABLE 2.

T_{anneal} (K)	ΔE_B (eV) O 1s – Ti 2p$_{1/2}$	O/Ti from ΔE_B	C_c (%)
295	72.2	1.8 ± 0.1	50
520	72.1	1.8 ± 0.1	44
760	72.0	1.9 ± 0.1	23
900	71.8	1.9 ± 0.1	11
1080	71.8	1.9 ± 0.1	15
1200	71.8	1.9 ± 0.1	3

Binding energy difference between Ti 2p$_{3/2}$ *and* O 1s *levels in* TiO_2 *deposited on the quartz substrate.* O/Ti *ratio according to* ΔE_B *from data of Sayers et al.*[12)]*; Carbon concentration at the surface of* TiO_2 *thin film: the data are derived from corrected*[14)] C 1s *XPS peak areas.*

the ΔE_{2p} and the FWHM values for the Ti 2p, we find almost constant value in the whole temperature range. The fourth value relevant for the determination of possible non-stoichiometry induced by a thermal treatment is the shift of Ti 2p binding energy. It is known[15)] that lowering of binding energy is connected with decreasing of oxidation state in Ti oxides. By comparing measured peak positions with those given by Rao et al.[15)], we have determined that there is no change in stoichiometry as a function of annealing temperature.

Taking into account the analysis presented in Fig. 6, one may estimate the O/Ti ratio due solely to the TiO_2 films and use it to determine a possible change in their stoichiometry. After the deconvolution of the oxygen peaks (Fig. 6), we have removed the O 1s contribution originating from OH species prior to the computation of the O/Ti ratios. Throughout the whole temperature range, from room temperature to 1200 K, this ratio remained practically constant, indicating constant stoichiometry of our thin film samples on the quartz substrate during the thermal annealing in vacuum of 10^{-6} Pa.

The results of thermal annealing in vacuum of TiO_2 thin films deposited on Mo substrate are presented in Table 3. The O/Ti ratio is constant throughout the whole temperature range thus supporting the results obtained for the samples on the quartz substrate. The concentration of carbon is higher than in the samples on the quartz substrate. It is showing a large drop above 970 K. TDS data for the H_2 and CO_2 in this experiment show large increase of partial pressures of these gases above 800 K and 900 K, respectively.

By comparing the constant stoichiometry of TiO_2 thin films with the concentration of carbon (Tables 2 and 3) at temperatures higher than 770 K and taking into account the parallel process of loosing O 1s intensity at the higher binding energy side, compare spectra in Fig. 6 (different hydroxyl group intensities[16)], we could propose mechanism of loosing C and OH as:

$$2OH \rightarrow 2H_2 + 2\,O \quad (800\ K) \tag{2}$$

$$C + 2O \rightarrow CO_2 \quad (900\ K) \tag{3}$$

Overall reaction:

$$2OH + C \rightarrow H_2 + CO_2 \tag{4}$$

TABLE 3.

T_{anneal} (K)	ΔE_B (eV) O 1s – Ti $2p_{1/2}$	O/Ti from ΔE_B	C_c (%)
295	71.5	2.0 ± 0.1	77
540	71.5	2.0 ± 0.1	72
660	71.5	2.0 ± 0.1	71
600	71.5	2.0 ± 0.1	67
970	71.8	1.9 ± 0.1	65
1050	71.4	2.0 ± 0.1	12

Binding energy difference between Ti $2p_{3/2}$ *and O 1s levels in* TiO_2 *deposited on the molybdenum substrate.* O/Ti *ratio according to* ΔE_B *from data of Sayers et al.*12)*; Carbon concentration at the surface of* TiO_2 *thin film: the data are derived from corrected*14) C 1s *XPS peak areas.*

During annealings at temperatures above 770 K we have, by means of TDS, detected significant desorption of H_2 and $C0_2$. The total pressure in the vacuum chamber has risen to 2×10^{-4} Pa. Though a major part of this increase may be attributed to the desorption caused by heating of the sample holder, both the composition and the behaviour of the partial pressures of selected gases (CO, CO_2, H_2O, H_2, O_2) support the above written relations.

TABLE 4.

T_{anneal} (K)	I_{Ti}	I_O	I_C	O/Ti	C_c (%)
295	24	90	703	3.7	78
540	108	294	853	2.7	68
660	97	304	932	3.1	70
800	65	173	585	2.7	71
970	113	240	711	2.1	67
1050	135	310	616	2.3	58

AES data for the TiO_2 *thin film on molybdenum substrate: corrected*17) *peak to peak intensities are given for the most prominent peaks of* Ti, O *and* C.

Table 4 presents AES results for the peak to peak intensities of the most prominent Ti (387 eV), O(512eV) and C(271eV) peaks, O/Ti ratios and concentration of carbon. The given intensities are obtained by correcting measured intensities with corresponding sensitivity factors[17).

The O/Ti ratio varies at values significantly higher than 2 up to the annealing temperature of 970 K. Above this temperature the process of CO_2 formation according to the relation (4) is reducing the content of oxygen in the surface layer. This can be connected with the concentration of C, which in the case of AES measurements stays high to the very high temperatures, opposite to XPS findings. This discrepancy can be explained by the fact that AES and XPS detect carbon atoms from different surface depths due to the largely different kinetic energies of C KLL and XPS C 1s electrons. The mean free path of the C KLL electron (kinetic energy ≈ 270 eV) is shorter than that of the C 1s electron (kinetic energy ≈ 980 eV). Therefore, it may be concluded that XPS probes carbon deeper than the topmost layer. The higher the annealing temperature, the faster carbon diffusion and surface segregation takes place. At the same time, increased temperature stimulates reactions (2) – (4) which remove carbon from the surface. Eventually, due to this cleaning procedure, the bulk of the sample is gradually getting free of carbon. The difference between AES and XPS data at the highest annealing temperature indicates that C indeed segregates to the film surface during annealing, making significant concentration gradient between the topmost and deeper layers. This finding leads us to conclusion that significant amount of observed carbon originates from the film bulk. This is in accordance with our previously mentioned[2,4,5,6,8) bulk sensitive measurements of this system. AES results obtained from the TiO_2 on gold substrate show stoichiometric value for O/Ti ratio and concentration of carbon comparable to that one on the quartz.

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TERMIČKA STABILNOST TANKIH SLOJEVA TiO_2 DOBIVENIH KEMIJSKIM TALOŽENJEM IZ PARE. XPS I AES KARAKTERIZACIJA

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Proučavana je termička stabilnost tankih, polikristaličnih slojeva TiO_2 dobivenih jednostavnim kemijskim taloženjem iz pare na podloge iz kvarca, molibdena i zlata. Korištene su metode XPS i AES na uzorcima prije i poslije termičkog napuštanja u rasponu temperatura od 298 do 1200 K. Našli smo ugljik, vodu i O-H skupine kao nečistoće na površinama slojeva. Diskutirani su utjecaji termičkog napuštanja i nečistoća na stehiometriju slojeva.