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Sol–gel processing of titanium-containing thin coatings

Part II *XPS Studies*

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Through X-ray photoelectron spectroscopy, chemical composition and the valency state of elements modified by SnO_2, Fe_2O_3 and SiO_2 titanium-based coatings has been studied. It has been established that metal alkoxides and salts used as precursors after a certain thermal treatment of the layer are transformed into the respective oxide stable state. At depth in the coatings, oxides of Ti(IV) and Sn(IV) are unstable and exhibit stoichiometrical disturbances. The phenomenon is discussed in relation to argon-ion sputtering conditions, the inhibition of the diffusion of sodium ions from the glass substrate, and the residual carbon from organic radicals. It has been proved that sol–gel processing, using $(C_4H_9O)_4$ Ti as precursor, may be successfully applied for the synthesis of good, highly reflective oxide coatings of compositions, correlating with those of the starting sol solution.

1. Introduction

It is well known that oxide composition, impurities and homogeneity greatly influence the properties of the coatings themselves. In this respect it is necessary to study the qualitative composition of the coatings on the surface, in longitudinal direction and in the volumetric environment. A prospective method with good results shown in practice in this type of investigation is X-ray photoelectron spectroscopy (XPS) [1]. Brings and Seach [1] summarized results presented on the basis of numerous publications with reference to layer and quantitative XPS and Auger spectroscopic analysis applied in microelectronics, metallurgy, heterogeneous catalysis, corrosion processes and polymers. There are no data cited on sol–gel products initiating from organometallic alkoxides. There are few data in the literature on XPS investigations of quantitative composition and film quality control, obtained through sol–gel processing. For example, Nasu [2] investigated the influence of bridging and non-bridging oxygen in relation to the thermal treatment of the sol–gel materials and the respective glassy substances obtained. Thin layers obtained through sol–gel technology have been investigated for impurities depending on the basic composition and the thermal treatment temperature [3]. On the other hand, it has been reported [4, 5] that XPS is a promising method for establishment of sub-surface and surface chemical composition of glasses subjected to a process of ion implantation and low-temperature plasma surfacial nitrating.

The present study aimed to analyse, in quantitative manner, the chemical composition, valency state of elements, on the surface and at depth, of titanium layers obtained by sol–gel processing, using XPS. On the basis of bonding energy values, i.e. a chemical shift in the photoelectron spectrum of atoms, information is also obtained about the behaviour of the elements on the surface and at depth in the coatings in relation to the initial composition.

2. Experimental procedure

For the investigation, titanate thin layers were chosen; their composition (by synthesis) is presented in Table I. Investigations were carried on mono- TiO_2-containing layers as well as on modified layers. The technological conditions were described in detail elsewhere [6].

For XPS study of the layers obtained, an ESCALAB-2 apparatus (Vacuumgenerators Ltd, UK) was used, working with an AlK_α X-ray source of 1486.6 eV. The experiments carried out at depth in the layers were undertaken after the surface layer was argon-ion-sputtered (energy 8 keV) at a current density of the failing argon-ion beam from 6–100 mA and a treatment time of 0–600 s.

3. Results and discussion

3.1. Definition of the bonding energy and the coordination state of the elements

Fig. 1 shows the photoelectron spectra of a mono-TiO_2 coating, taken at the sample surface and at depth after sputtering for 60 s. In the bonding energy range between 450 and 475 eV from the 2p transition

TABLE I Sol compositions

Code of composition	$Ti(OBu^n)_4$ (mol %)	C_2H_5OH (mol %)	H_2O (mol %)	Second component (mol %)	Coatings in oxide composition (wt %)
001	3.0	97.0	–	–	100 TiO_2
002	3.0	85.0	12.0	–	100 TiO_2
004	4.5	95.0	–	0.5 ($SnCl_4$)	82.54 TiO_2 14.96 SnO_2
006	5.0	93.0	–	2.0 ($Fe(NO_3)_3{\cdot}9H_2O$)	83.70 TiO_2 16.30 Fe_2O_3
103	1.2	50.0	40.0	8.8 ($(C_2H_5O)_4Si$)	84.65 SiO_2 15.35 TiO_2

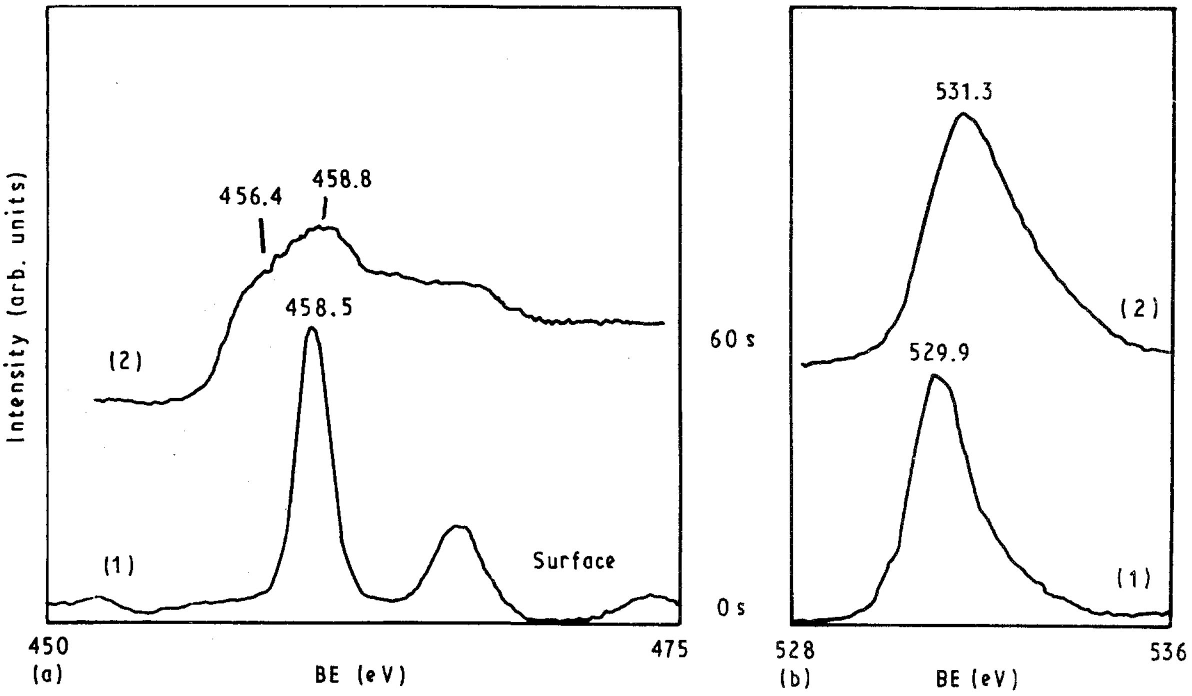

Figure 1 XPS spectra of (a) $Ti(2p_{3/2})$ and (b) O(1s) transitions, (1) surface treatment, and (2) after sputtering for 60 s; coating with code 001 on glass substrate.

spectrum of titanium, peaks corresponding to three values of bonding energy 458.5, 456.4 (diffuse) and 458.8 eV, respectively, were found. After comparison with published charts for bonding energy [1, 7], it was established that the first maximum from the spectrum taken for the surface layer is due to the contribution of Ti(IV) from TiO_2. The second maximum, registered at depth, is reduced and coincides with that for TiO_2 shifted to 458.8 eV. This is also a contribution from titanium with a lowered valency state in the layer, found in a form close to that of TiO [8, 9], indicating that at depth the layer stoichiometry is disturbed and TiO_2 tends towards the TiO state. This has been confirmed by the 1s transition of oxygen. Here the energy peak (531.3 eV) of oxygen located at depth is very close to that corresponding to TiO and is shifted with respect to that corresponding to TiO_2(529.9 eV) [1, 7, 8].

There are two possible causes of the titanium reduction process. The first one may be the sensitivity of Ti(IV) ions towards the bombardment with argon ions where, according to the literature [1, 7], Ti(IV) is easily reduced to Ti(II) as a result of the argon sputtering process. The second cause may be the presence of residual carbon in the layer from organic radicals introduced by molecular precursors. Carbon after burning during the thermal treatment up to 500 °C draws oxygen from the surrounding atmosphere and layer network.

To shed further light on this phenomenon we investigated the refraction index at depth in the layers using elipsometry [10]. Stiochiometrical disturbances at depth would, as one normally predicts, increase the refraction index at that depth because of the reduction taking place. It was established that the refraction index values decrease with depth and very slightly increase with increasing coating thickness. Therefore, further experiments were carried out, first to check the residual carbon, and second, to check the ion diffusion from the glass substrate towards the coating. It was established that, depending on the temperature and the duration of thermal treatment, there were traces in the coatings of residual carbon, incorporated into the layer network. On the basis of the carbon bonding energy values (carbon has 1s transition at 287 eV), the carbon forms no compounds and it may be assumed that probably it is in the form of graphite [11–13]. It has also been established that the titanate coatings show a sodium ion thermo-diffusion process inside the volume from the glass substrate.

Fig. 2 shows the photoelectron spectra of Ti ($2p_{3/2}$; 458.2 eV) and Na (1s; 1072 eV) transitions from a titanium coating on the surface and at depth, after argon-ion sputtering for 300 and 600 s. The spectra show stoichiometrical disturbances of TiO_2 at depth. Sodium ions were confirmed to be present on the surface and also at depth. Depending on the values of the bonding energy of sodium ions, there is no doubt that sodium ions are predominantly present as Na_2O [1, 14, 15]. The sodium content in deep layers decreases and even reaches the zero limit. This is due to the argon-ion bombardment, because sodium is a light element and possesses a high coefficient of sputtering [1] and so its concentration is low. It is obvious that through the method used it is not possible to produce an element diffusion profile on the phase-boundary coating/glass substrate, therefore it is desirable to apply secondary ion mass spectrometry (SIMS) too.

Fig. 3 shows the spectrum of a titanate coating surface of the composition with code 006. From the Ti ($2p_{3/2}$) transition spectra it was established that titanium is in the fourth coordination in the form of titanium dioxide. This is confirmed by the oxygen spectrum [1], with a contribution at 529.8 eV, i. e. a contribution due to oxygen atoms bonded to Ti(IV). At the Fe ($2p_{3/2}$) transition, it is seen that iron is in the third valency state, i.e. oxygen surrounding Fe_2O_3 according to the value of the peak registered at 710.6 eV. From the nitrogen spectrum presented in the same figure, it is clearly seen that there is no residual nitrogen on the surface, due to the contribution from $Fe(NO_3)_3 \cdot 9H_2O$, used as a starting material.

Figs 4 and 5 show the results of the XPS analysis of a titanate coating containing SnO_2. It has been established that on the surface titanium is present as TiO_2. At depth, from the chemical shift of the Ti ($2p_{3/2}$) transition, we may judge that its spectrum is a result from two overlapping peaks at maxima 456.1 and 458.5 eV, respectively, thus indicating reduction process is taking place, with some changes in titanium stoichiometry towards a lower valency state. It has been proved that no chlorine was present at depth, introduced by the sol solution through the stannic(IV) chloride (see Fig. 4). Even so, the quantity of $SnCl_4$ (see Table I) and the duration of thermal treatment are sufficient to stimulate its evaporation. Through SEM analysis and microdistribution investigation of the elements [16], it has been established that gel products contain chlorine only up to 120–180 °C. No chlorine is found in gel of composition code 005, analysed after thermal treatment at 500 and 1000 °C for 10 min. On increasing the amount of the chlorides introduced, an increase of the residual chlorine content was found. This leads to a degradation in the film quality, as also reported by Dislich [17].

Fig. 5 shows the photoelectron spectra of Sn ($3d_{5/2}$) and O (1s) for the same sample. The surface spectrum shows the presence of Sn(IV) as SnO_2. The spectra from deeper layers are reduced in intensity, thus indicating a decrease in the concentration of Sn(IV) and its tendency towards an Sn(II) transition. Bearing in mind that according to the literature [17] no data are available concerning the tendency of tin to reduce its valency state due to the argon-ion sputtering process, we may presume that stoichiometry is in disorder because of processes taking place during the thermal treatment. For example, the burning of organic radicals incorporated in the gel film or the diffusion of mobile sodium ions from the substrate, cause bonding or a shift of the oxygen anions in the glassy network. Naturally the process enables M–O bond shortening and stimulates the reduction of Ti(IV) ans Sn(IV) towards their lower valency state.

Fig. 6 shows the results from the XPS profile analysis of a film containing silicon dioxide. The surface of the film gives peaks of Si(IV) and Ti(IV) as SiO_2 and TiO_2. At depth, the picture is basically unchanged. We presume that oxygen is evenly distributed between

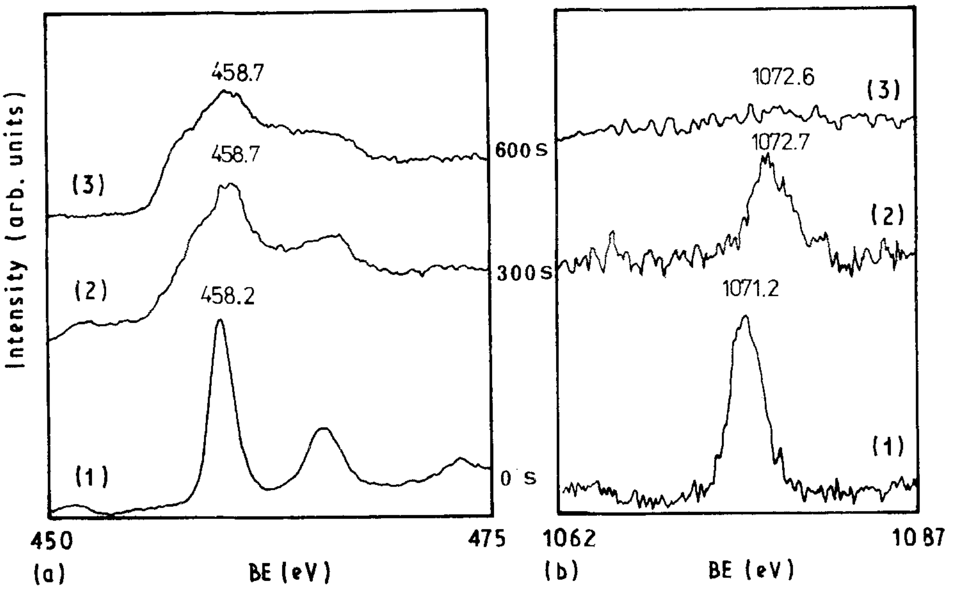

Figure 2 XPS spectra of (a) Ti($2p_{3/2}$) and (b) Na(1s) transitions, (1) surface treatment and (2, 3) at depth, after sputtering for (2) 300 s, and (3) 600 s; thin coating with code of composition 001.

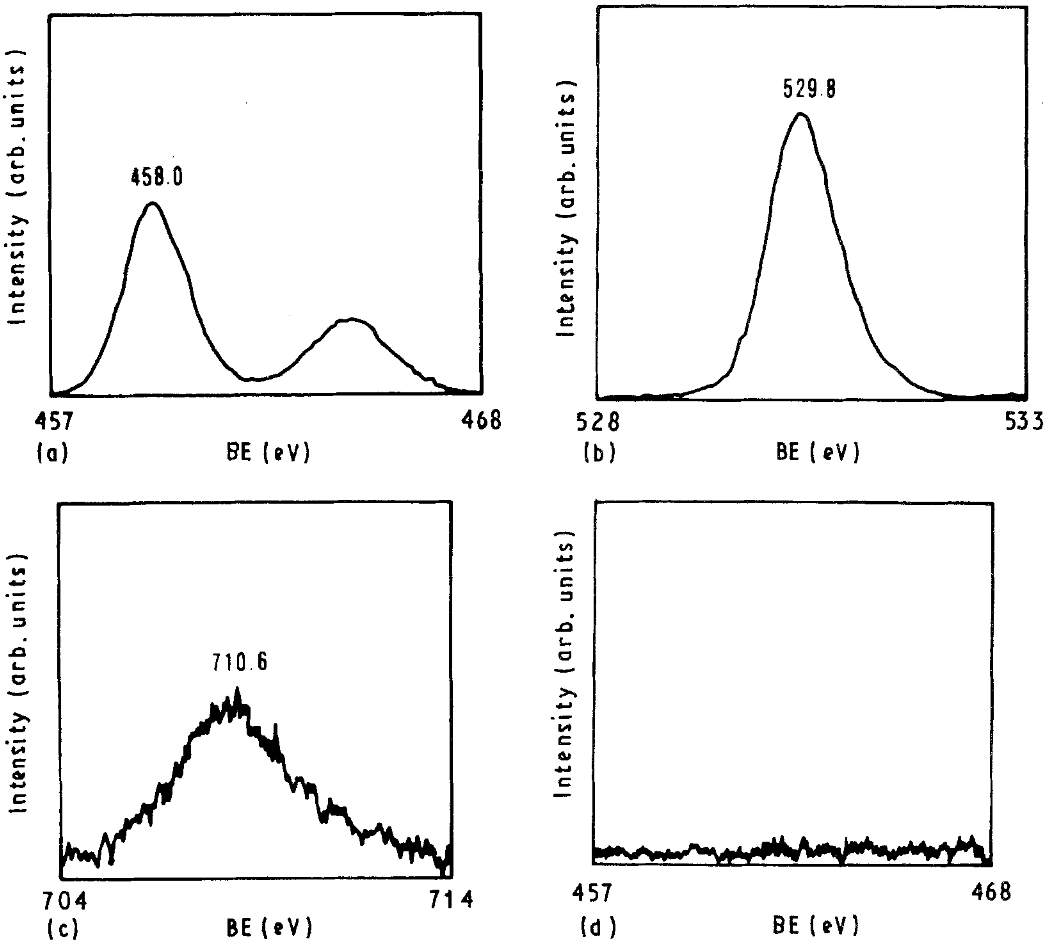

Figure 3 Surface XPS spectra of (a) Ti(2$p_{3/2}$), (b) O(1s), (c) Fe(2p) and (d) N(1s) transitions of a coating with code 006.

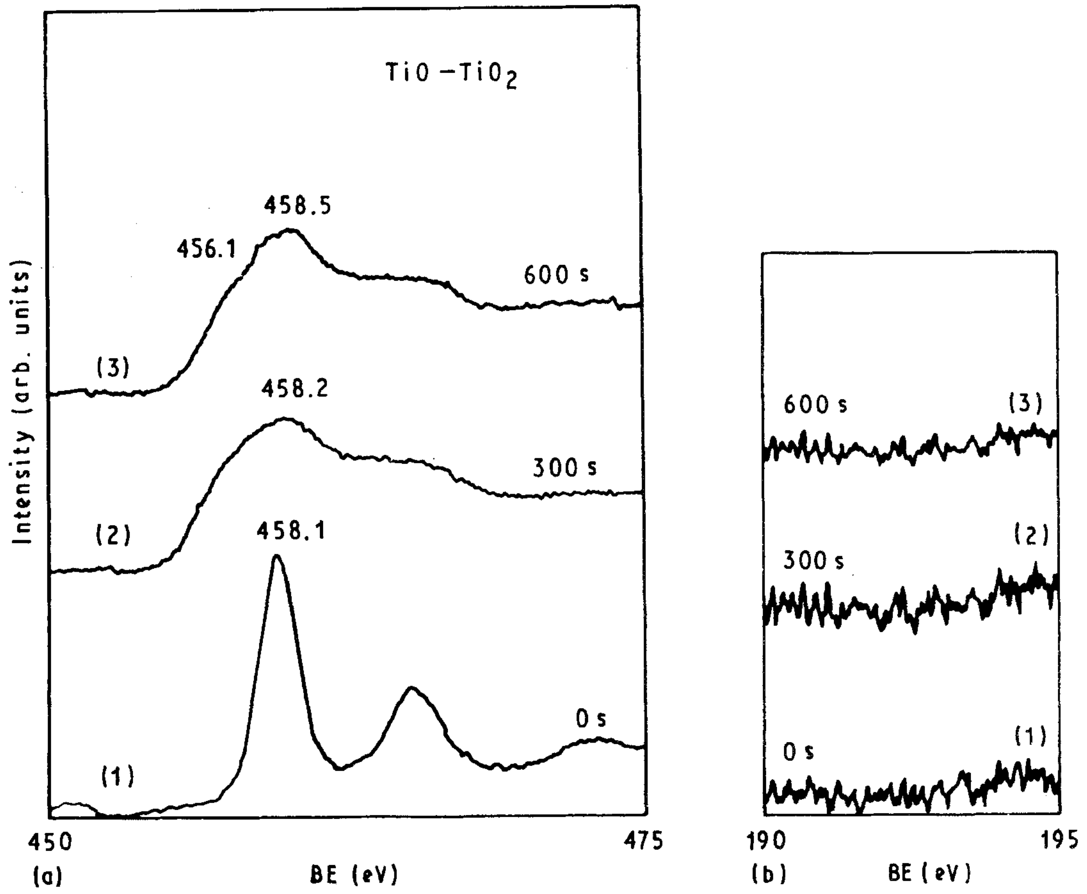

Figure 4 (1) Surface XPS spectra and (2, 3) XPS spectra at depth of (a) Ti(2$p_{3/2}$ and (b) Cl(2p) transitions, respectively; coating with code 004.

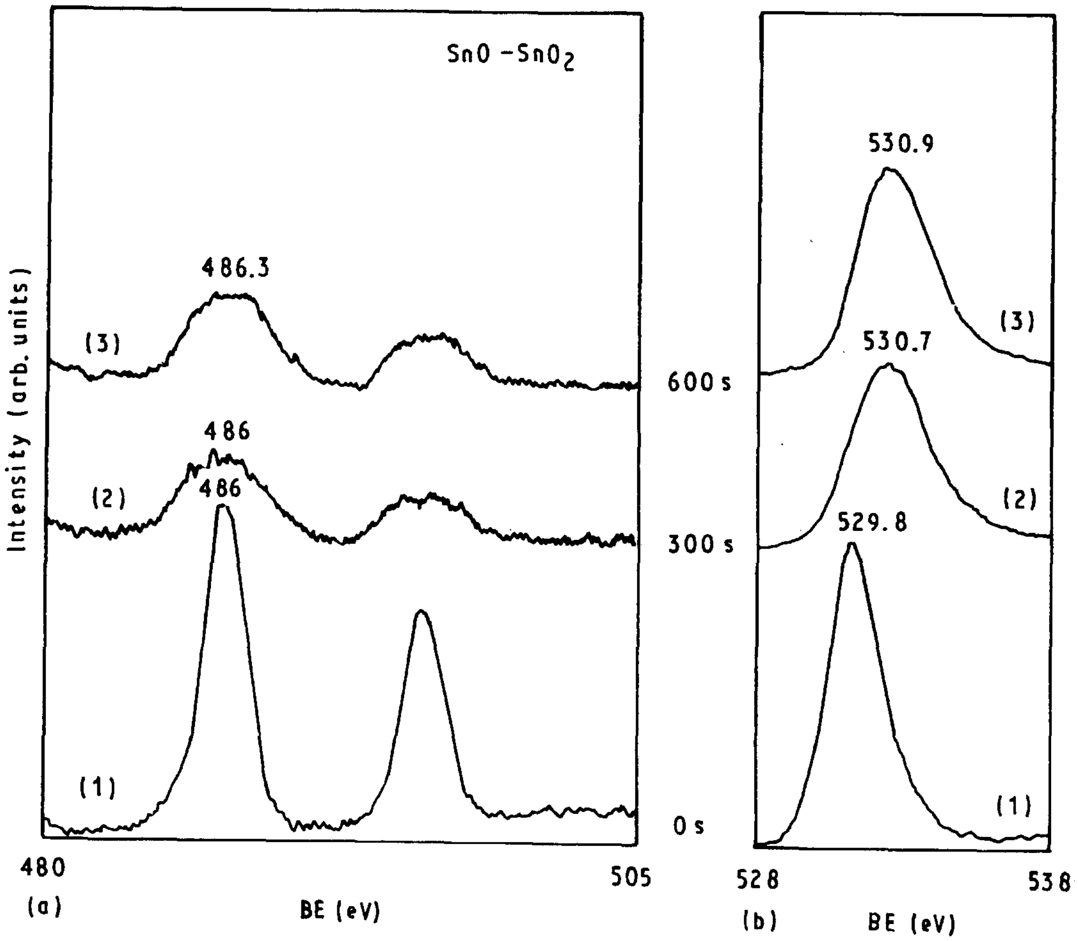

Figure 5 XPS spectra of (a) Sn(3d) and (b) O(1s) transitions, (1) after surface treatment, (2) after 300 s and (3) after 600 s sputtering time, of coating with code 004.

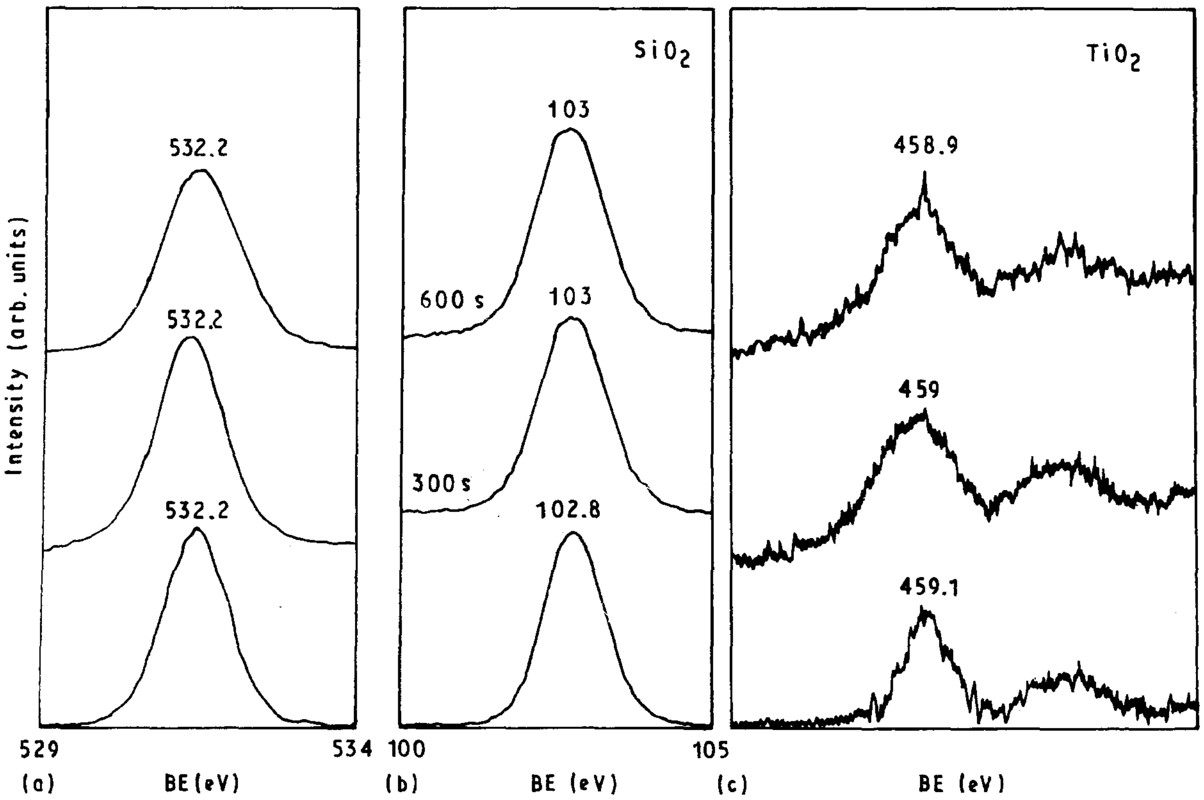

Figure 6 XPS spectra of (a) O(1s), (b) Si(2p) and (c) Ti(2p$_{3/2}$), transitions after 0, 300 and 600 s sputtering time respectively; coating with code 103.

silicon and titanium atoms in the network because of a lack of peaks indicating their lower oxide environment. It is typical for this case that silicon dioxide gives a stabilizing effect and prevents the reduction of titanium. It is obvious that the silicon–titanium–oxygen network of the film exhibits a high stability and perfect homogeneity at depth.

3.2. Quantitative-layer chemical analysis

The composition of the gel film initially obtained from the moment of the dipping process of the glass substrate, up to its final transformation in a solid oxide coating, is perpetually changed during the course of thermal treatment. At first, hydrolysis–condensation reactions take place, and freeing alcoholic groups and introducing hydroxyl groups into the media. As drying begins, alcohol and water included in the gel volume as well as some of the as yet unreacted organometallic components, evaporate. With increasing temperature, the remaining part of the organic radicals burn out or evaporate, while the nitrates and the chlorides, introduced in the starting sol solution, decompose. Drying and burning leading to a densification of the coating are often accompanied by additional structural alterations. For example, the formation of new chemical bonds, the breaking of bonds, sublimation of some easily volatile components, immiscibility or crystallization processes, etc. To a greater extent, the final composition of the coating depends not only on the chemical composition of the sol solution but also on the intensity of hydrolysis and polycondensation processes, as well as on the incorporation of group modifiers or radicals, which are introduced and remain in the space between the polymer chains of the gel-like network.

On the basis of the phenomena described it is clear that all parameters will extensively influence the composition, and the physical and chemical properties of the coating itself. To perform a more adequate interpretation of the film properties [18] it was necessary to check the quantitative composition of the coatings on the surface and at depth. Analysis was carried out using the primary information from the photoelectron peaks, theoretically calculated sections of photoionization, as well as the free-electron motion. The results are presented in Table II.

For the values given in Table II we should remember that chemical composition of the surface layer of the multicomponent sample changes during the argon-ion sputtering process, because of the difference in the sputtering coefficients of the chemical elements. Argon-ion bombardment probably changes, to some extent, the composition of the sample tested, because of two processes: first, an atom transportation process to a depth of 1–20 nm as a function of the sample, and second, the conditions of sputtering and the selectively different extent of sputtering of atoms of one or more surface layers. The problem of changes in composition during the course of sputtering in the XPS study still remains. As is seen from Table II, the sol–gel method enables us to obtain comparative results, even in composition and depth coatings. It was established for titanate coatings, that the thermal diffusion of sodium ions from the substrate towards the layer is an easily accomplished process. On the other hand, the oxygen content in the film depth is high, which shows that the change in stoichiometry of TiO_2 at depth is most probably due to an argon-ion sputtering process rather than to reduction through sodium-ion diffusion.

Fig. 7 presents a depth profile of the elements in titanate coatings containing silicon and tin ash. As is seen, elements are comparatively uniformly distributed in depth. In the coating (code 004) there is a slight increase of titanium content and a slight decrease in the tin concentration. Oxygen is uniformly distributed. A stable distribution of elements is seen in the titanate–silicate coating, indicating that the layer composition is stable and uniform at depth.

4. Conclusions

1. Using XPS analysis, the chemical composition of modified titanate coatings, as well as the valency of the elements in them, has been defined.

2. It was proved that it is possible to synthesize thin oxide coatings through sol–gel processing, with a composition approximately identical to the oxide content in the sol solution.

3. It was established that alkoxides and salts, used as starting materials, after thermal treatment are transformed to the respective oxide state, where the cations retain their valency. The oxides of Ti(IV) and

TABLE II Composition of titanium-containing coatings according to XPS analysis

Code of composition	Ti (at %)	O (at %)	Second component (at %)	Impurities	Sputtering time (s)
001	30.2	63.7	–	6.1 Na[a]	0
006	29.5	59.0	11.40 Fe	N[b] (not found)	0
004	22.8	70.0	7.10 Sn	Cl[b] (not found)	0
	31.9	65.1	3.00 Sn	Cl (not found)	300
	29.1	68.8	2.10 Sn	Cl (not found)	600
103	4.8	62.0	33.20 Si	Traces of C[b]	0
	5.5	61.3	33.10 Si	Traces of C	300
	5.5	61.5	32.80 Si	Traces of C	600

[a] Elements diffused from the glass substrate.

[b] Elements introduced in the sol solution with the starting materials.

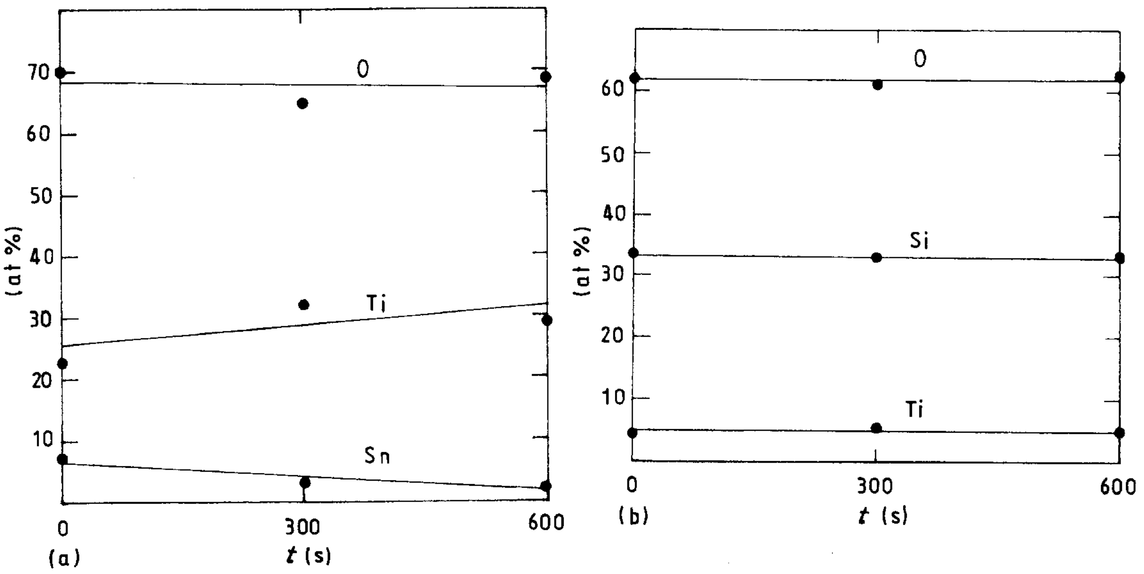

Figure 7 Depth profile of the element concentration of selected layers with code (a) 004 and (b) 103.

Sn(IV) are the only ones exhibiting disturbances in the stoichiometry of the coating at depth, and showing a tendency to lower the oxidation grade. We consider this phenomenon to be related mainly to the technological conditions of dip coatings, as well as with the eventual reduction process by diffused sodium from the glass substrate and of residual carbon from the starting organometallic components.

4. Coating impurities such as chlorine, carbon or nitrogen, introduced in the sol solution with the starting materials, are found in the layers as traces, or are entirely absent after a thermal treatment at 500 °C.

5. It was determined that in most cases the coatings are characterized by a uniform depth–concentration profile of the elements. In other cases the difference in the element sputtering coefficients, the presence of modifiers, and the diffusion of elements from the substrate, influence the homogeneity of the composition of the layers at depth.

References

1. D. BRINGS and M. SEACH (eds), "Practical Surface Analysis by Auger and X-ray photoelectron Spectroscopy" (Wiley, London, New York, 1983) translated into Russian (Mir, Moscow, 1987) pp. 353, 458, 530 and 533.
2. H. NASU, J. NEO and J. MACKENZIE, *J. Non-Cryst. Solids* **99** (1988) 140.
3. H. SHU-FANG, L. KLEIN and R. CARACCIOLO, *ibid.* **120** (1990) 267.
4. H. SCHRODER and R. HASS (eds), "Physics of Thin Films" (Academic Press, New York, 1969) p. 87.
5. H. SCHRODER, in "Proceedings of the Xth International Congress on Glass", Kyoto Japan (1975) p. 8.
6. B. SAMUNEVA, V. KOZHUKHAROV, Ch. TRAPALIS and R. KRANOLD, *J. Mater. Sci.*, in press.
7. V. NEFEDOV, "Rentgeno-elektronnaja Spectroscopija Khimicheskich Soedinenii" (Khimia, Moscow, 1984).
8. C. WAGNER and G. MUILNBERG (eds), "Handbook of X-ray Photoelectron Spectroscopy", (Physical Electronics Division, Perkin-Elmer Corporation, Eden Prairie, MN, 1879).
9. J. SOLOMON and W. BAUN, *Surf. Sci.* **51** (1975) 228.
10. R. AZZAM and N. BASHARA, "Ellipsometry and Polarized Light" (North Holland, Amsterdam, New York, 1977), translated into Russian (Mir, Moskow, 1981) pp. 316, 343.
11. H. DISLICH and A. JACOBSON, FRG Pat. 1494872 (1965).
12. H. DISLICH, *Angew. Chem. Int. Ed. Engl.* **18** (1979) 49.
13. H. DISLICH and E. HUSSMAN, *Thin Solid Films* **77** (1981) 129.
14. S. SAKKA and K. KAMIYA, *J. Non-Cryst. Solids* **48** (1982) 31.
15. S. SAKKA, in "Better Ceramics through Chemistry", edited by C. Brinker, D. Clark and D. Ulrich (Elsevier-North Holland, New York, 1984) p.91.
16. Ch. TRAPALIS, V. KOZHUKHAROV and B. SAMUNEVA, in "Proceedings of the 7th CIMTEC Satellite Symposia - S1", 24–30 June, 1988, Montecatini, Italy, Vol. 67, paper S1 1C-P06.
17. H. DISLICH, in "Glass Science and Technology", Vol. 2, "Coatings on Glass" (Academic Press, 1984) Ch. 8, p. 251.
18. V. KOZHUKHAROV, Ch. TRAPALIS and B. SAMUNEVA, *J. Mater. Sci.* in press.

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