

Characterization of Sol-Gel Thin Films of  
 $\text{TiO}_2\text{-PbO}$ ,  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  and  $\text{TiO}_2\text{-CeO}_2$  Compositions.

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ABSTRACT

Single and multilayer sol-gel thin films of  $\text{TiO}_2\text{-PbO}$ ,  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  and  $\text{TiO}_2\text{-CeO}_2$  composition were deposited on glasses using the dip coating technique. The precursors included  $\text{Ti}(\text{OPr}^i)_4$  chemically modified by acetyl acetone and diluted in  $\text{Pr}^i\text{OH}$  and sols of  $\text{Pb}(\text{OAc})_2$ ,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  diluted in acetic acid. The  $\text{TiO}_2\text{-CeO}_2$  sol was prepared by mixing  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  in ethanol and then adding  $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_4$ . Structure texture and homogeneity of their main constituents was established by XRD, XPS, SIMS and SEM-EDX techniques as a function of heat treatments.

1. INTRODUCTION

The utility of sol-gel methods for producing glass and ceramic materials with high chemical homogeneity at relatively low temperatures is now well recognized. Recently considerable attention has been directed to the use of these methods for the production of thin, thick, single and multilayers coatings as these techniques offer outstanding opportunities, including low cost of precursors, rapid drying, uniform shrinkage and easy elimination of volatiles. The possibility to obtain coatings with microscopic structures which can be tailored by heat treatment from highly porous to fully dense is also an asset for several interesting applications. Furthermore, rather simple and commercially viable processing methods are available to coat substrates of nearly any size and geometry<sup>1</sup>.

We have shown in earlier publications that Sol-Gel coatings of  $\text{TiO}_2\text{-PbO}$ ,

TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>-CeO<sub>2</sub> compositions obtained by dip-coating, have a high optical quality; almost flat spectral transmission and reflection characteristics can be obtained in the visible by adjusting their thickness. These properties suggest their use for the preparation of achromatic beam splitters and neutral-colored solar-energy-reflecting windows<sup>2,3</sup>. We have also demonstrated that thick films of TiO<sub>2</sub>-PbO composition can be successfully used for the realization of passive planar wave guides where up to 4 effective modes have been optically coupled<sup>2,3</sup>. More recently we discovered that TiO<sub>2</sub>-CeO<sub>2</sub> films exhibit reversible electrochemical insertion for Li<sup>+</sup> ions while maintaining high optical transmissivity; these outstanding properties turn these films natural candidates for the realization of transparent counter electrode in all solid state electrochromic transmissive or reflective devices<sup>4,5</sup>.

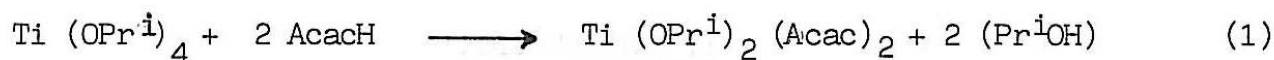
These various applications prompted therefore a more thorough investigation of the film structure, texture, and (2D, 3D) homogeneity of their elemental constituents during the densification process. This paper presents original and recent data obtained with sol-gel of TiO<sub>2</sub>-PbO, TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>-CeO<sub>2</sub> thin films compositions using techniques such as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), scanning electron microscopy (SEM), electron diffraction spectroscopy (SEM-EDX) and X-ray diffraction (XRD).

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Precursor and sol preparations of TiO<sub>2</sub>-PbO composition

The method used to prepare the precursor sols is based on the chemical modification of titanium isopropoxide Ti(OPr<sup>i</sup>)<sub>4</sub> by the rather strong chelating ligand and stabilizing agent acetylacetone AcacH<sup>6,7</sup>.

The preparation of the complex alkoxide is described by the exothermic reaction<sup>9</sup>.



The yellow and homogeneous solution is then mixed for 30 minutes until its temperature lowers to 25°C. A solution of lead acetate Pb(OAc)<sub>2</sub> in acetic acid (concentration 720 g/l) is then added and stirred for 30 minutes. This sol is quite stable and does not present gelation or precipitation for several months. Both precursor sols can be mixed in any proportion. The typical volumes used for films of composition TiO<sub>2</sub>- 0,25 PbO (PbTi<sub>4</sub>O<sub>9</sub>) are given bellow:

Pr <sup>i</sup> OH	Acac H	Ti(OPr <sup>i</sup> ) <sub>4</sub>	Pb acetate sol	pH
40 ml	3 ml	4 ml	1,81 ml	5,7

## 2.2. Precursor and sol preparation of TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub> composition

Similar procedures were also used for the preparation of precursors and sols of TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub> composition. However, the bismuth sol was prepared by mixing Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in acetic acid with a concentration of 665 g/l. The typical volumes used for films of TiO<sub>2</sub>-0,12Bi<sub>2</sub>O<sub>3</sub> composition are given below:

Pr <sup>i</sup> OH	Acac H	Ti(OPr <sup>i</sup> ) <sub>4</sub>	Bi nitrate sol	pH
30 ml	1,8 ml	2,5 ml	1,9 ml	0,86

## 2.3 Precursors and sol preparation of TiO<sub>2</sub>-CeO<sub>2</sub> composition

The starting solution was prepared by dissolving Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> in ethanol, adding then tetraisopropyl orthotitanate Ti(O-iso-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>. The concentration of Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> cannot exceed 0,25 M because of the solubility limit of the salt in ethanol at room temperature. The presence of the cerium-ammonium nitrate stabilizes the solution.

## 2.4. Films preparation and characterization

The thin films have been obtained by dip-coating on common glass substrate except those of TiO<sub>2</sub>-CeO<sub>2</sub> which have been coated on ITO Baltracon substrates. The withdrawal speed was of the order of 4-15 cm/min. After each coating procedure the films were dried and heat treated in air at a specified temperature (up to 500° C) for different period of time (up to 1 h). The whole process was repeated to obtain thicker films.

The films have been characterized by XPS, SIMS, SEM, SEM-EDX and XRD techniques in order to study the evolution of their structure, texture, 2D and in depth profile composition during the densification treatment.

- a) XPS was performed on a PHI model 5900 instrument\* equipped with a hemispherical analyser and unmonochromatized Mg X-ray source. The samples were sputtered depth profiled with Ar ions (2 KV, ~ 7nA). XPS recording was performed with the ion beam off at the pressure lower than 10<sup>-9</sup> Torr. The angle between the surface sample and the analyser was 70°. The chemical analysis was obtained by using the PHI software routines, version 3 modification B. The concentration of each element is given in atomic percent and represents the total atomic concentration regardless the chemical state.
- b) SIMS was performed on a Cameca IMS 3 f instrument\*. A 8 Kev mass analysed cesium ion beam with approximately 500 µm diameter was used for all analyses and depth

profiles. All samples were coated with a thin gold layer and covered with a grid in order to avoid charging effects.

- c) SEM was performed on a Hitachi s-800 instrument\*.
- d) SEM-EDX was performed on a Jeol/Tracor instrument\*\*
- e) XRD was performed on a Rigaku Rotaflex RU200B instrument\*\*\*

## RESULTS AND DISCUSSION

### 3.1. Films of TiO<sub>2</sub>-PbO composition

The basic composition of these films was TiO<sub>2</sub> - 0,25 PbO (PbTi<sub>4</sub>O<sub>9</sub>) equivalent to an atomic concentration of 7,2% Pb, 28,6% Ti and 64,2% O. All the films heat treated in air up to a temperature of 500°C for up to 60 minutes were found amorphous to X-ray. Figure 1 shows SEM micrograph of films heat treated at 190°C and 60 min. They appear uniform except for small amount of dust, possibly precipitations and small inhomogeneities. The coatings fired at 500°C for 60 minutes are practically densified with an overall smooth continuous surface. Figure 2 indicates a micrograph of a layer with pores and possibly precipitates and cracking near the lower edge of the substrate (end of the dip process) were also observed.

XPS analysis was performed on two similar samples. Figure 3 shows three typical survey scans for a TiO<sub>2</sub> - 0,25 PbO film heat treated at 190°C for 60 minutes: a) spectrum recorded at the surface (as received). b) spectrum recorded after 20 minutes Ar sputtering (at ~ 1/6 of the depth). c) spectrum recorded after 125 minutes Ar sputtering near the glass-film interface. All the peaks have been identified and the spectra shows the presence of O, Ti, Pb, C, Na and Ca. A detailed analysis<sup>8</sup> shows that the O and Ti peaks are hardly affected by the sputtering while features appear on the lower binding energies (BE) side of the Pb 4f peaks already after 4 or 8 minutes of sputtering; these features grow into a doublet of equal intensity of the original doublet after 75 minutes of sputtering. After 125 minutes (near the interface) the doublet of lower BE has a higher intensity. This behavior is due to ion-induced chemical damage leading to a reduction of lead. The fact that the Ti 2p peaks are not affected is not clear and will be discussed later.

Figure 4 shows the relative concentration in atomic percent of the elements O, C, Ti, Na, Pb and Ca determined as a function of the sputtering time (depth). The concentration of carbon is still high and goes high deep into the layer but decreases with distance from the film surface. The elimination of the organic group is not yet complete at this temperature and the fact that lead was introduced as an acetate

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Fig 1. SEM micrograph of a one layer ~ 250 nm thick  $\text{TiO}_2 - 0,25 \text{ PbO}$  film heat treated in air at  $190^\circ\text{C}$  during 60 minutes showing inhomogeneities on the surface.



Fig. 2. SEM micrograph of one layer ~ 150 nm thick  $\text{TiO}_2 - 0,25 \text{ PbO}$  film heat treated in air at  $500^\circ\text{C}$  during 60 minutes showing pox marks and possible precipitates.

may be of certain importance (see the results of  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  films for comparison).

The profile of the elements which are likely to stay in the matrix after complete densification (O, Ti, Pb, Na and Ca) is shown in Figure 5. In this figure the carbon contribution has been eliminated and the relative concentration of the remaining elements has been normalized. It is worth nothing that the ratio Pb/Ti (right scale), which originally was 0,25, is not constant through the layer. This is due to a slight enrichment of lead and a depletion of Ti near the surface. However, the overall relative concentration of lead beyond this subsurface is practically equal to the original value (7,2%). Na and Ca may have been introduced during the firing in air but the diffusion from the glass substrate cannot be rule out.

Heat treatment of a similar film at  $500^\circ\text{C}$  during 60 minutes confirms the above results. Figure 6 shows three typical XPS survey scans taken a) at the surface (as

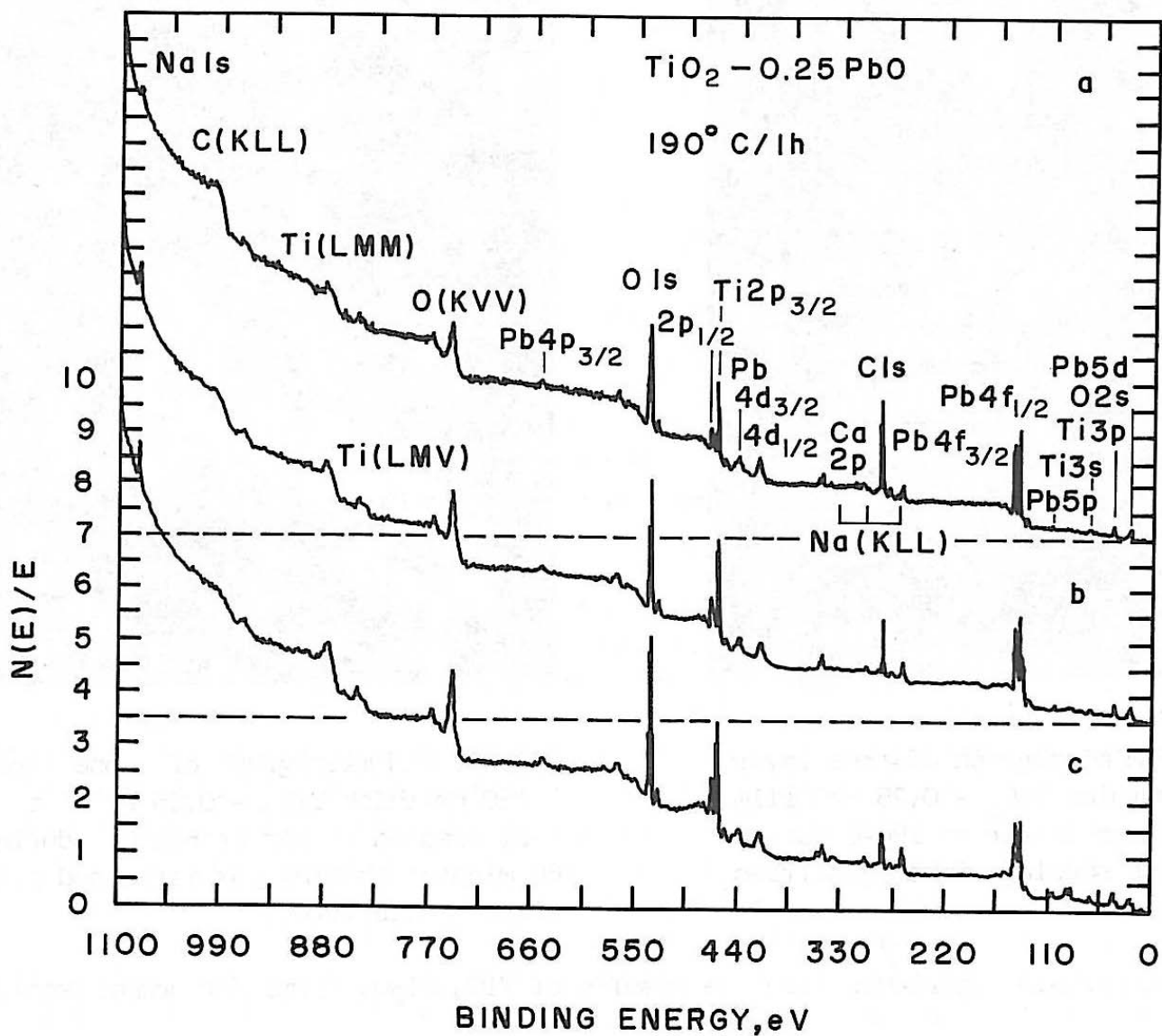


Fig.3. XPS survey of a one layer  $\text{TiO}_2 - 0.25 \text{PbO}$  film heat treated in air at  $190^\circ \text{C}$  during 60 minutes and recorded a) at the surface as received, b) after 20 minutes sputtering ( $\sim 1/6$  of the depth), c) after 125 minutes of sputtering (near the glass-film interface)

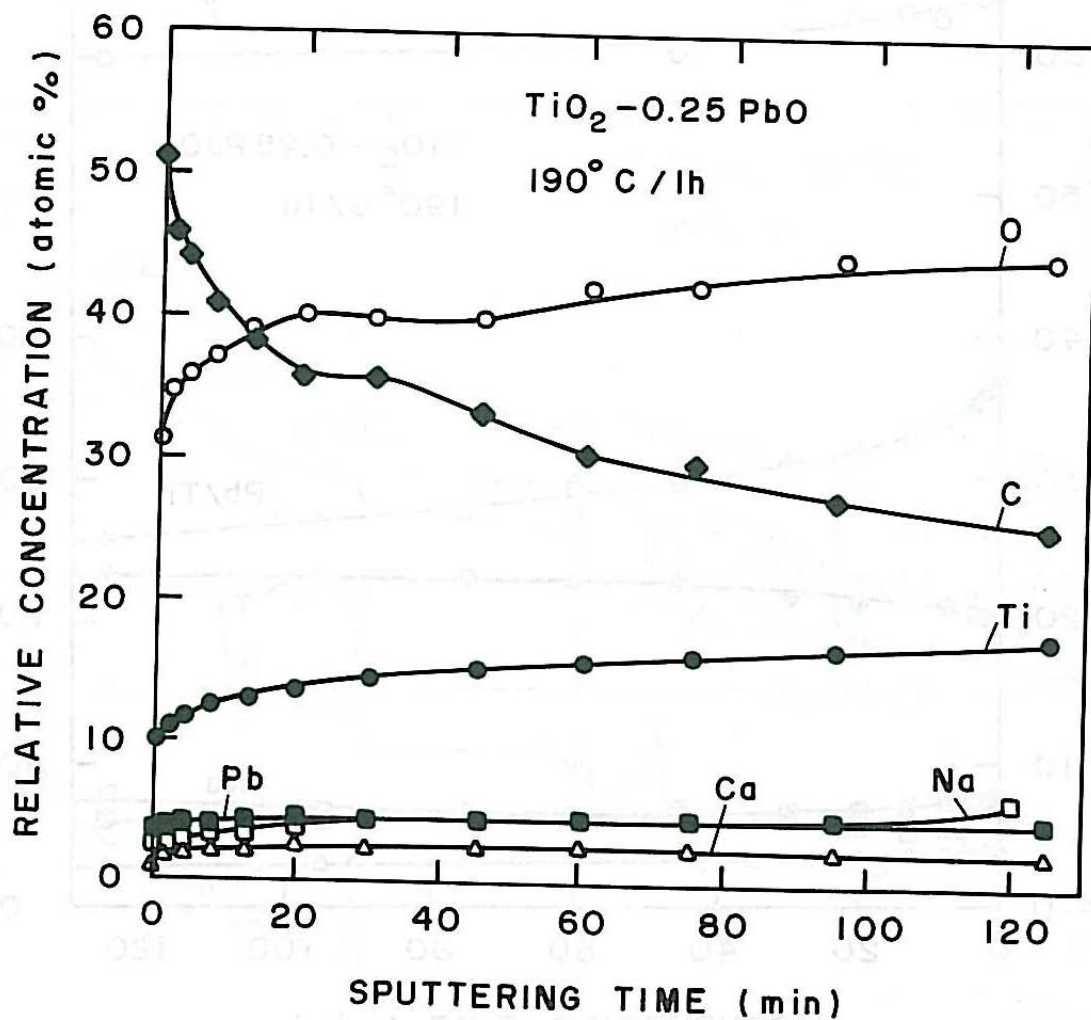


Fig. 4 XPS profile of  $\text{TiO}_2-0,25 \text{ PbO}$  film heat treated in air at  $190^\circ \text{C}$  during 60 minutes.

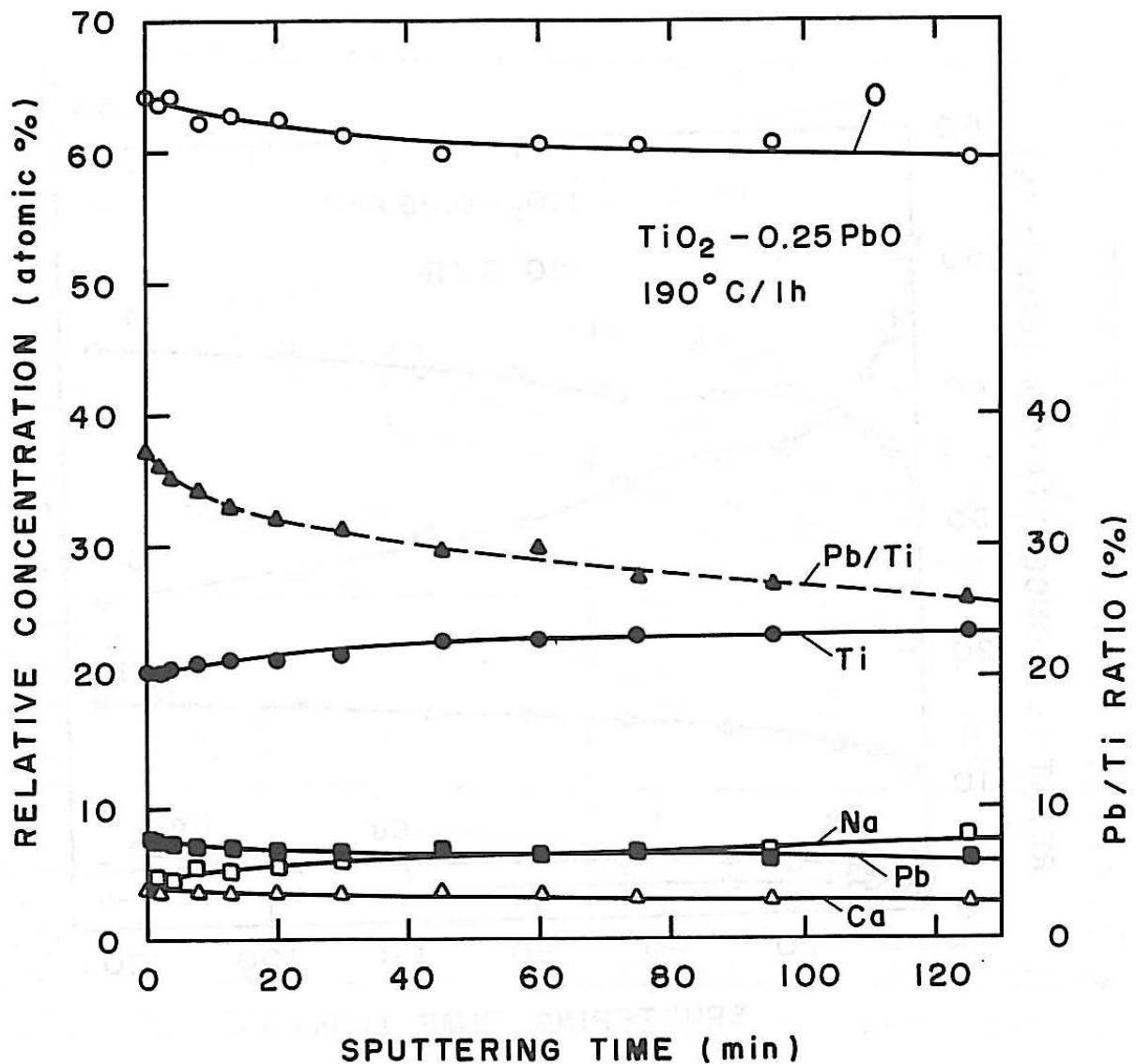


Fig. 5 Same as figure 4 after elimination of the carbon contribution and recormalization of the atomic concentration (left scale). The depth profile of the ratio Pb/Ti is also shown (right scale).

received) b) after 20 minutes of sputtering (~ 1/3 of the depth) c) after 80 minutes of sputtering (beginning of the glass-film interface).

A detailed analysis<sup>8</sup> shows that sputtering has little effect on the O 1s peak; however a small shoulder appears at lower BE when the interface is reached due probably to oxygen in the glass substrate. On the other hand the sputtering has now a stronger effect on the Pb 4f peaks; a low BE doublet already appears after 3 minutes sputtering indicating lower oxidation states and its intensity grows rapidly as we penetrate into the layer and becomes even higher than the original doublet. The



high BE doublet tends to decrease and becomes finally a shoulder near the interface. Ti 2p doublet peaks are now also affected by the sputtering. A shoulder starts to develop already after 5 minutes and is present throughout the layer indicating the transformation of  $Ti^{4+}$  to lower oxidation states. The carbon peak is only present in the upper 3 nm and practically disappears after 5 minutes sputtering. Ca concentration has also dropped below the detection limit. The profile of the elements is

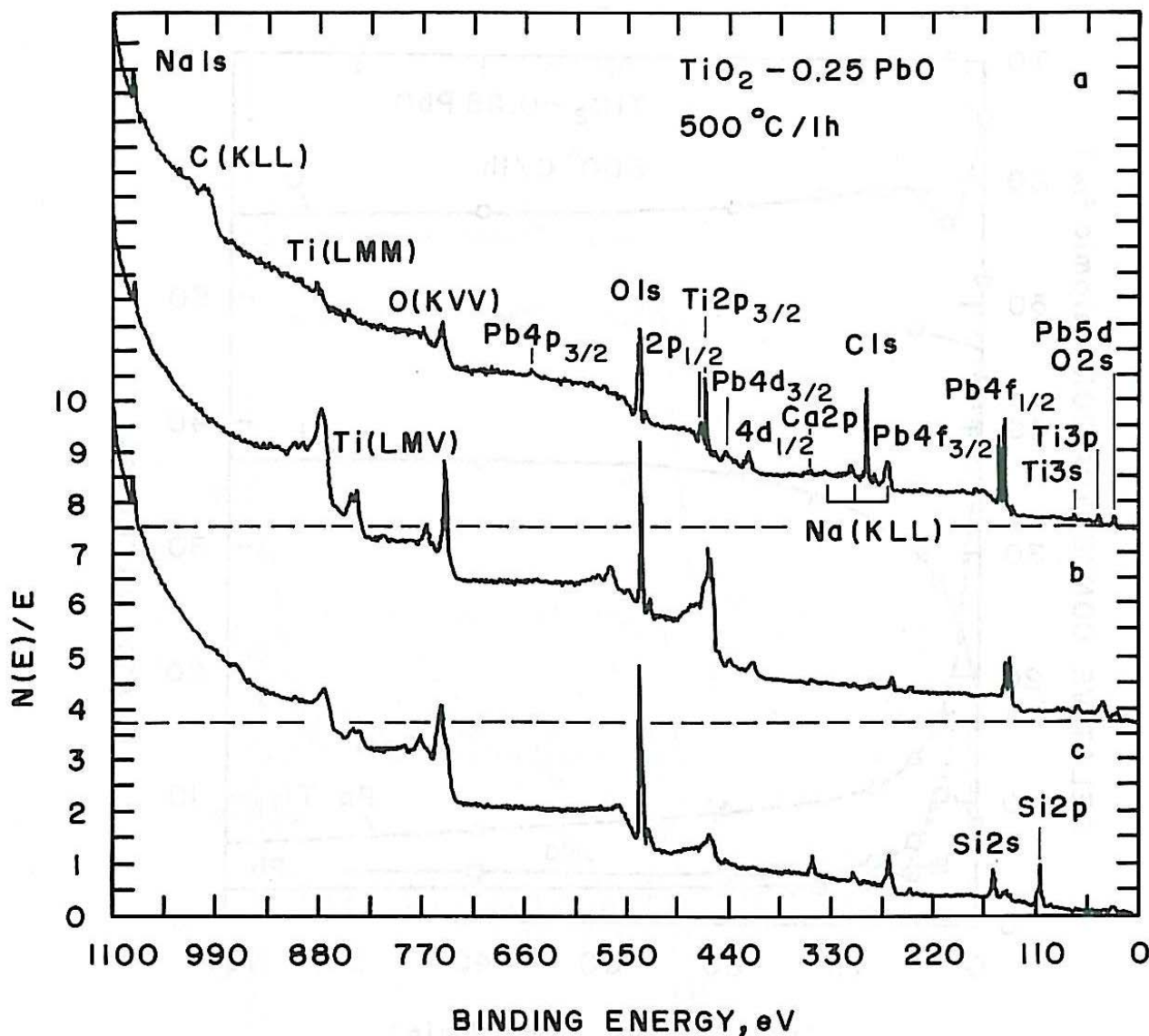


Fig.6 XPS survey of a one layer  $TiO_2-0,25 PbO$  film heat treated in air at  $500^{\circ}C$  during 60 minutes and recorded a) at the surface (as received), b) after 20 minutes of sputtering ( $\sim 1/3$  of the depth), c) after 80 minutes of sputtering (beginning of the glass-film interface).

shown in Figure 7. The ordinate gives the relative concentration of O, Ti, Pb and Na only. The carbon contribution has been eliminated and its profile, shown in the figure as a dotted line is only given for information.

The most important result of this figure is the depth variation of the ratio Pb/Ti (originally equal to 0,25). This ratio is high near the surface because of the segregation of Pb and the strong depletion of Ti; it rapidly decreases below

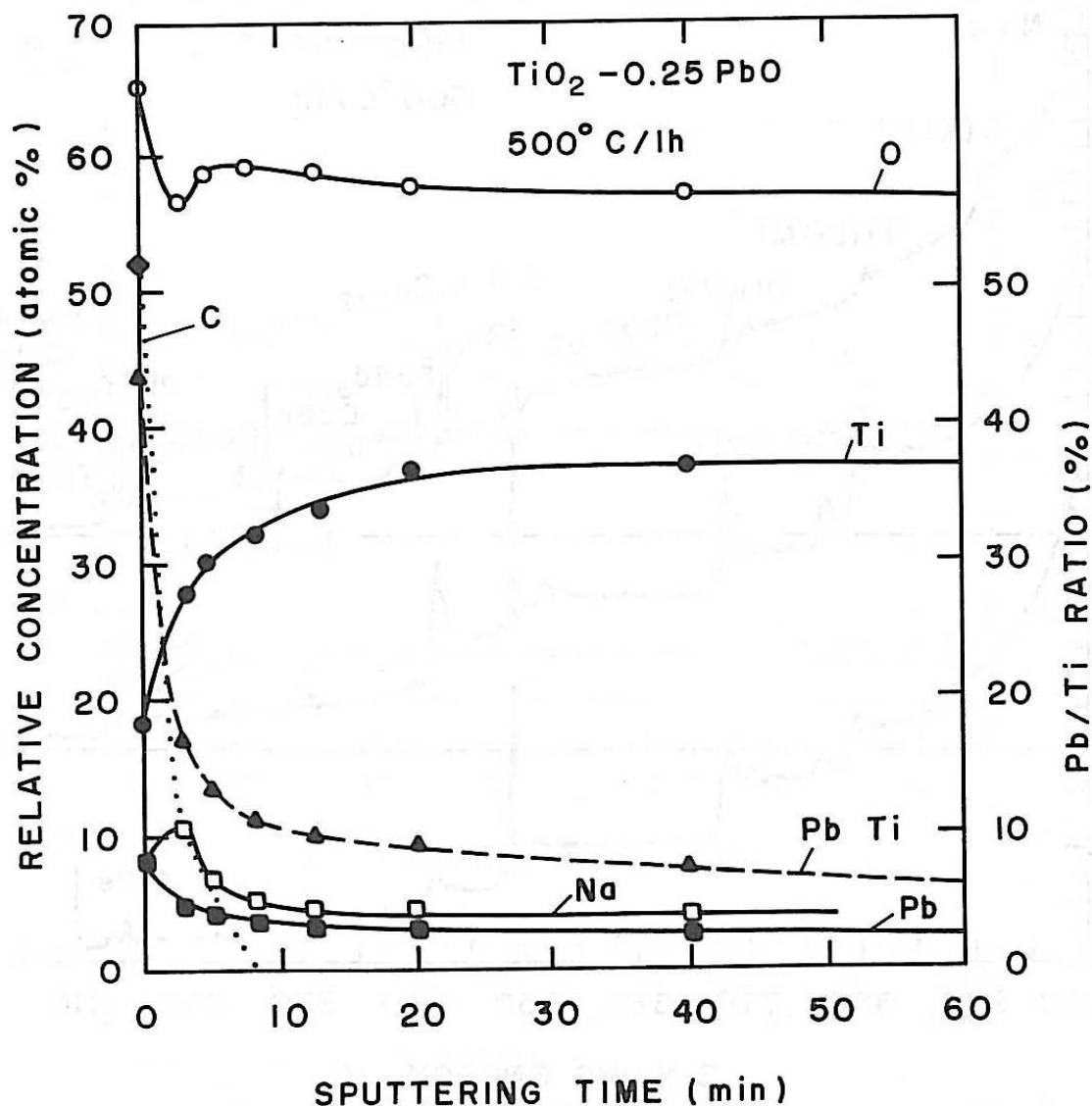


Fig. 7 XPS profile of a one layer  $\text{TiO}_2 - 0,25 \text{ PbO}$  film heat treated in air at  $500^\circ\text{C}$  during 60 minutes. The C contribution (shown as a dotted line) has been eliminated and the left ordinate scale refers to the relative concentration of O, Ti, Pb, Na only. The ratio Pb/Ti is also shown (right scale)

the original values, because the lead concentration beyond the subsurface is low (3% instead of 7,2%).

These results indicate that lead (or lead oxide) volatilizes easily even at this low temperature (500°C). It may be therefore difficult to obtain in film form compound materials of technical interest with definite stoichiometry in the

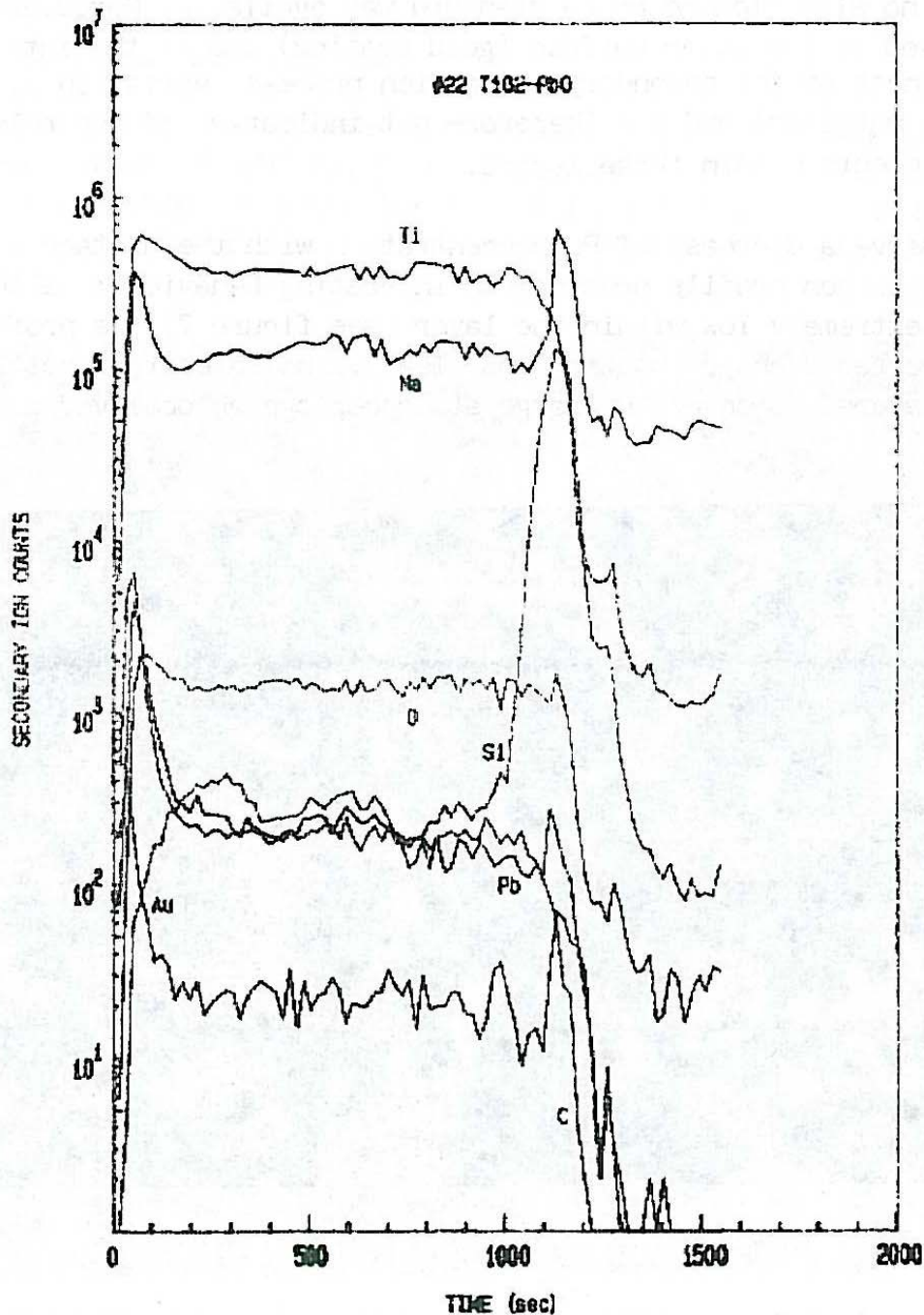


Fig. 8 SIMS profiles on a 3 layers TiO<sub>2</sub>-0.25 PbO film heat treated at 500°C during 15 minutes after each dip.

TiO<sub>2</sub>-PbO system using the sol-gel process. This (expected) behavior confirms recent XRD results<sup>10,11</sup> on the observation of significant phase formation of lower lead content such as PbTi<sub>3</sub>O<sub>4</sub> in sol-gel prepared PbTiO<sub>3</sub> after 570°C firing.

SIMS profiles obtained with a 3 layers TiO<sub>2</sub>-0,25 PbO coating heat treated, after each dip, at 500°C during 15 minutes are shown in figure 8 and confirmed the XPS results. We must however recall that comparison of the ordinate (count values) of each element has no significance as no standard was available. Moreover the sharp variations observed at the outer surface (gold coating) and at the interface glass-film are consequences of the secondary ionization process (variation of the sensibility in different matrices) and are therefore not indicative of the relative concentration of the elements within these layers.

We clearly observe a decrease of Pb concentration with the distance from the film surface. The carbon profile presents an interesting behaviour: although its concentration is extremely low within the layer (see figure 7) its profile is similar to three inverted U shape function and clearly indicates the position of the three deposited layers. Moreover the large atmospheric peak observed on the surface

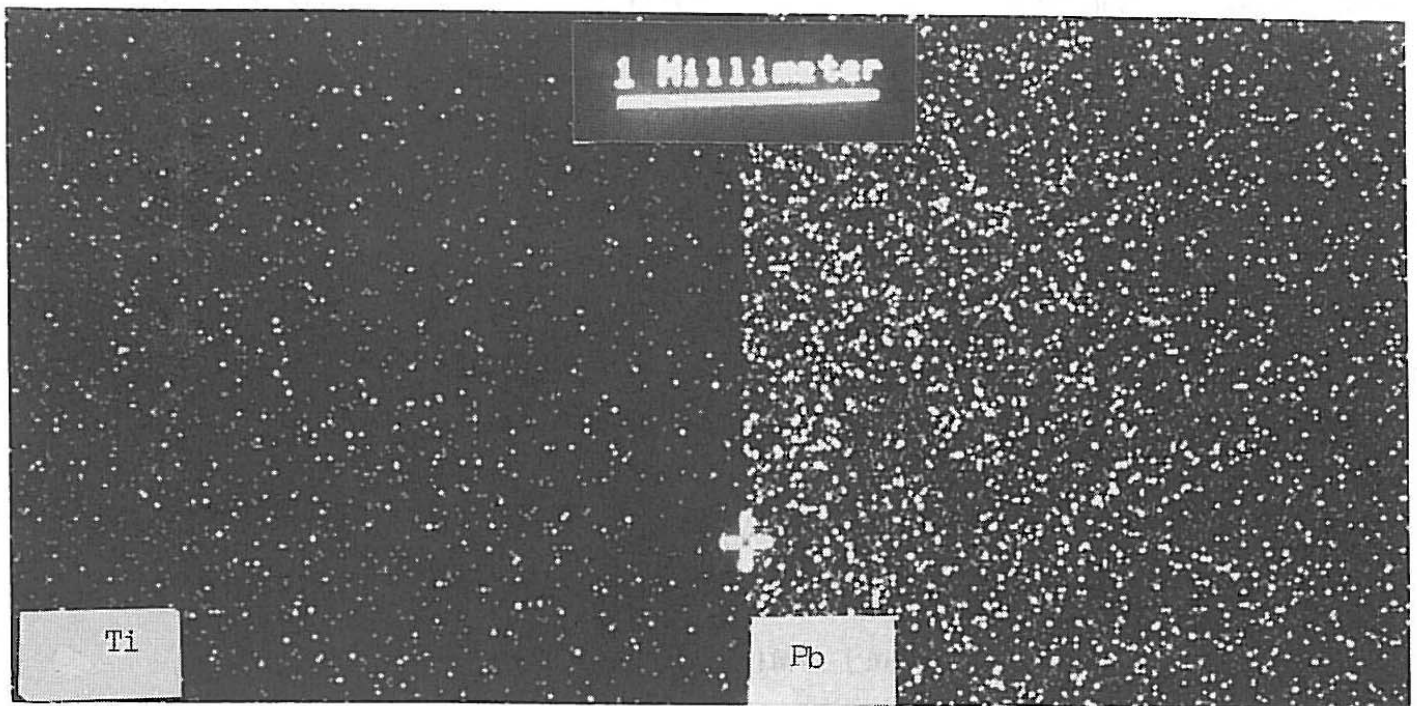


Fig. 9 2-D repartition of Ti and Pb measured by SEM-EDX with a TiO<sub>2</sub> - 0,25 PbO sample fixed at 500°C during 60 minutes.

layer by XPS and which we would expect at each layer interface (around  $t = 450$  s and 750 s respectively) are not present.

Finally figure 9 shows that the 2-D repartition of Ti and Pb measured by SEM-EDX with a  $\text{TiO}_2\text{-}0,25 \text{ PbO}$  sample fired at  $500^\circ\text{C}$  is quite homogeneous and uniform. Similar results have been obtained for the other elements up to very high magnification of 56000x.

### 3.2. Films of $\text{TiO}_2\text{-Bi}_2\text{O}_3$ composition

The basic composition of these films was  $\text{TiO}_2\text{-}0,125\text{Bi}_2\text{O}_3(\text{Ti}_4\text{BiO}_{9,5})$  giving an atomic concentration of 6,9% Bi, 27,6% Ti, 65,5% O. All the films heat treated in air up to a temperature of  $500^\circ\text{C}$  for the period of time up to 60 minutes were found amorphous to X-ray. The films heat treated at  $190^\circ\text{C}$  for 60 minutes have a very good surface quality (Fig.10). The surface of samples heat treated at  $480^\circ\text{C}$  presents however

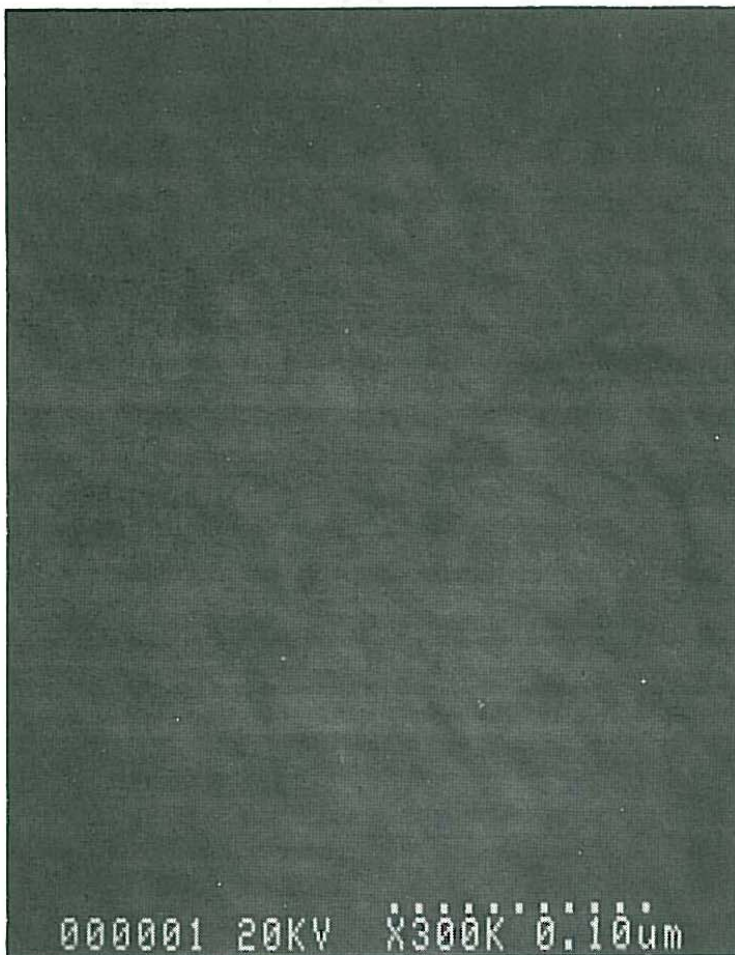


Fig. 10 SEM micrograph of a one layer  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  film heat treated at  $190^\circ\text{C}$  during 60 minutes.



Fig. 11 SEM micrograph of a one layer  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  film heat treated at  $480^\circ\text{C}$  during 60 min showing inhomogeneities and precipitates on the surface.

some inhomogeneities with cracks near the edge of the film (Figure 11).

XPS analysis was performed on two similar samples. Figure 12 shows three typical survey scans obtained with a film heat treated at 190°C during 60 minutes. :a) at the surface (as received). b) after 32 minutes Ar sputtering (~ 1/6 of the depth) c) after 180 minutes Ar sputtering at the beginning of the interface. All the peaks have been identified and the recorded spectra show the presence of O, Ti, Bi, C, Na and Si (in the interface). Detailed analysis<sup>8</sup> shows that the sputtering does not

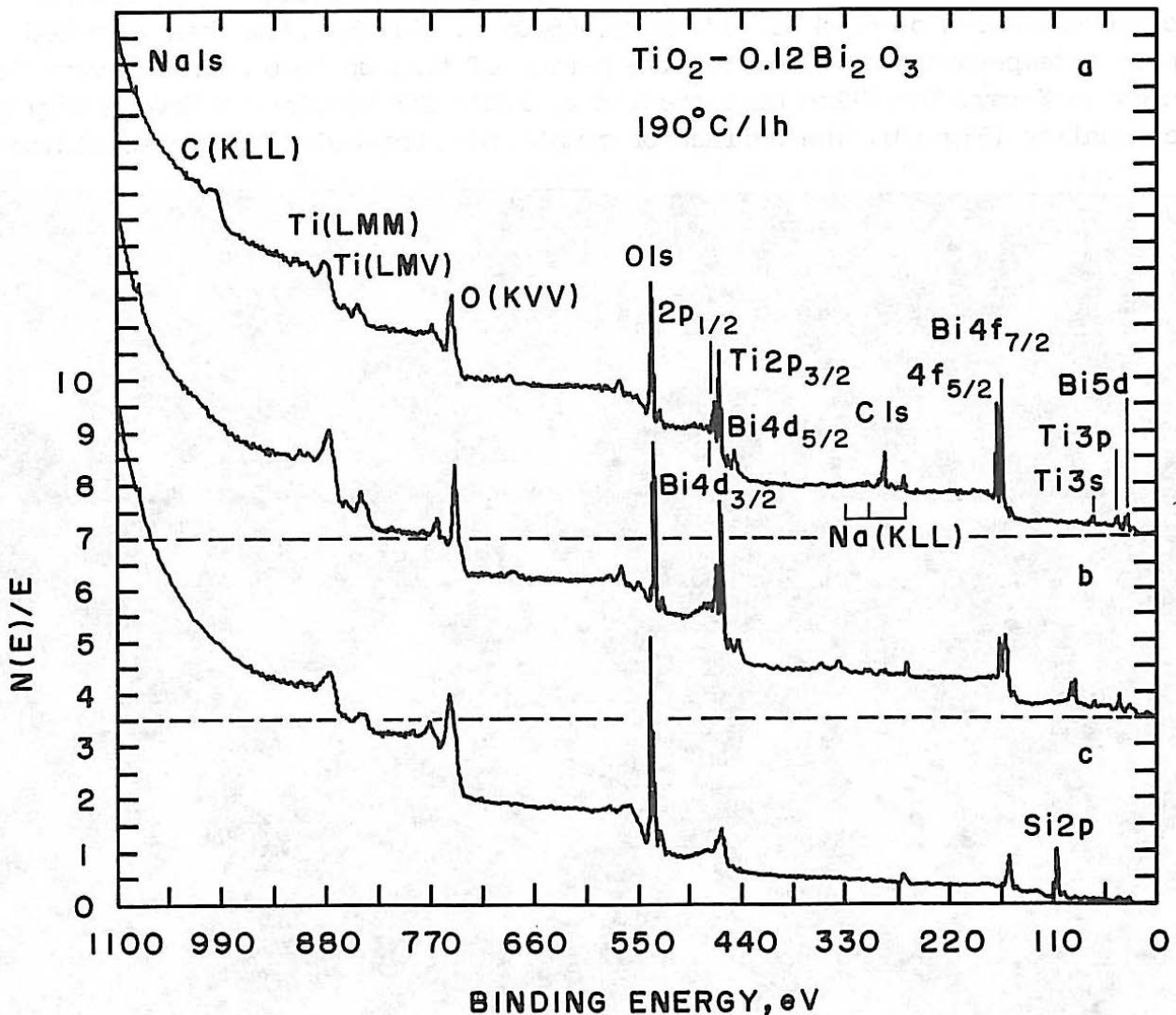


Fig. 12 XPS survey scans of a one layer  $\text{TiO}_2 - \text{Bi}_2\text{O}_3$  film heat treated in air at 190°C during 60 minutes and recorded a) at the surface (as received), b) after 32 minutes Ar sputtering (~ 1/6 of the depth), c) after 180 minutes sputtering (beginning of the glass-layer interface).

affect the O 1s peak. However contrary to the  $\text{TiO}_2\text{-PbO}$  composition, the Ti 2p doublet is affected: by the ions and reduced Ti features are observed after 40 min sputtering. The Bi 4f doublet is also strongly affected; a shoulder appears already after two minutes sputtering indicating that bismuth has been reduced. As we proceed two doublets are observed and after 40 minutes sputtering the reduced form is the dominant one. Na and C are only observed in the first half of the layer.

Figure 13 shows the relative concentration of the observed elements determined as a function of the sputtering time (depth). Contrary to what has been observed with the  $\text{TiO}_2\text{-PbO}$  composition, C and Na appear only in the subsurface of the film together

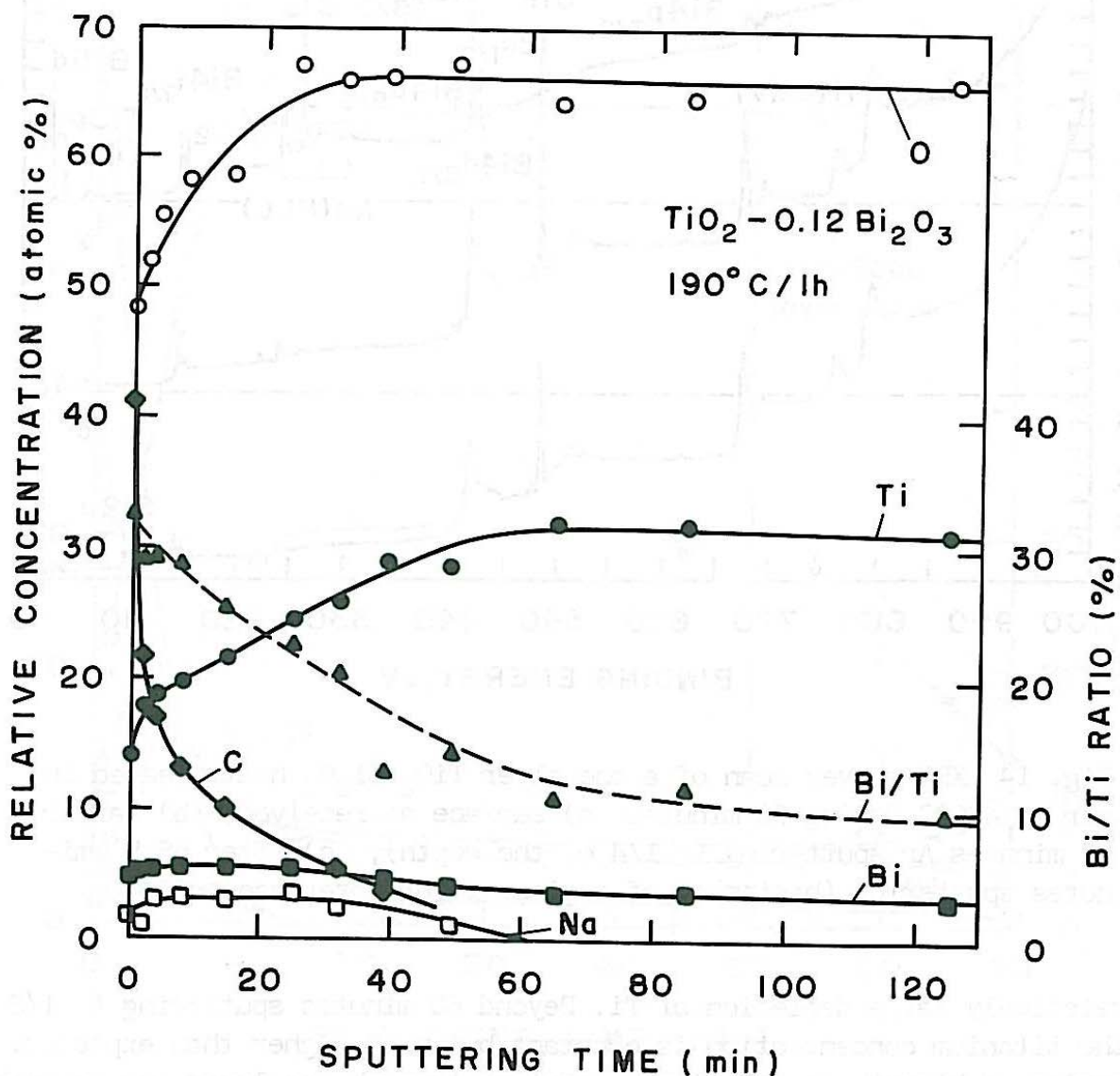


Fig. 13 XPS profiles of a one layer  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  film heat treated in air at  $190^\circ\text{C}$  during 60 minutes.

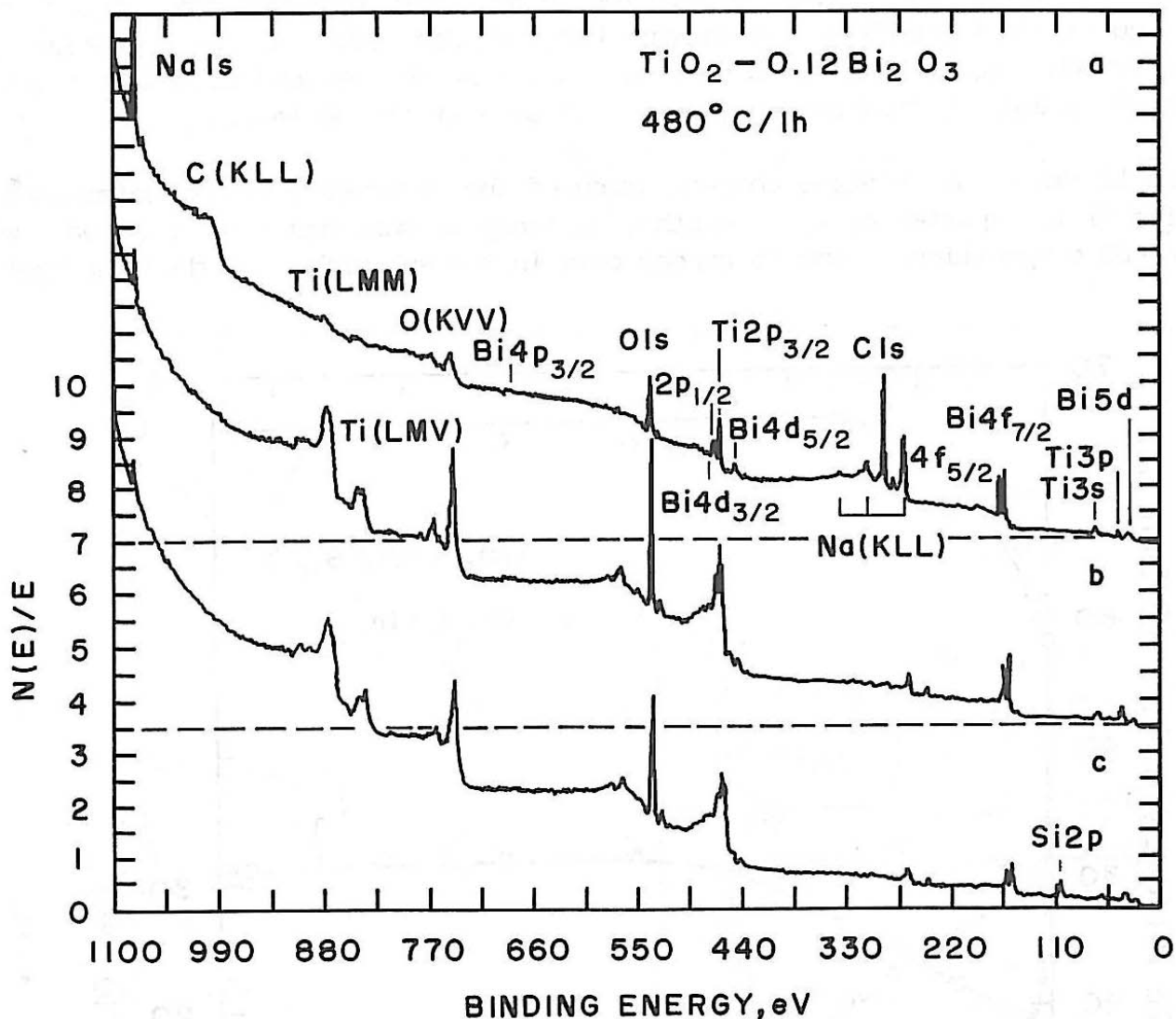


Fig. 14 XPS survey scan of a one alyer  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  heat treated in air at 480°C during 60 minutes a) surface as received, b) after 12 minutes Ar sputtering (~ 1/4 of the depth), c) after 65,5 minutes sputtering (beginning of a glass-layer interface).

with a relatively large depletion of Ti. Beyond 60 minutes sputtering (~ 1/3 of the depth) the titanium concentration is constant but much higher than expected. The concentration of bismuth is relatively constant through the layer but is much lower than expected (4% instead of 6,9%). Both effects strongly affect the Bi/Ti ratio profile which is not constant through the layer and much lower than expected (originally 0,25).The reason for the low incorporation of Bi is not clear as we do not have data on dried sample at room temperature without heat treatment. However as we shall see below, Bi like Pb (or their oxides) volatilizes during the heat treatment and



this effect is already well pronounced for bismuth at 190°C.

Figure 14 shows three typical XPS scans of a similar sample heat treated at 480°C during 60 minutes and recorded a) at the surface (as received), b) after 12,5 Ar sputtering (~ 1/4 of the depth), c) after 65,5 minutes sputtering (in the interface glass-layer). The behavior of the O 1s peak is similar to what has been observed in the TiO<sub>2</sub>-PbO compositions. The peak is not affected throughout the layer but a small shoulder appears toward higher BE when the interface is reached. This

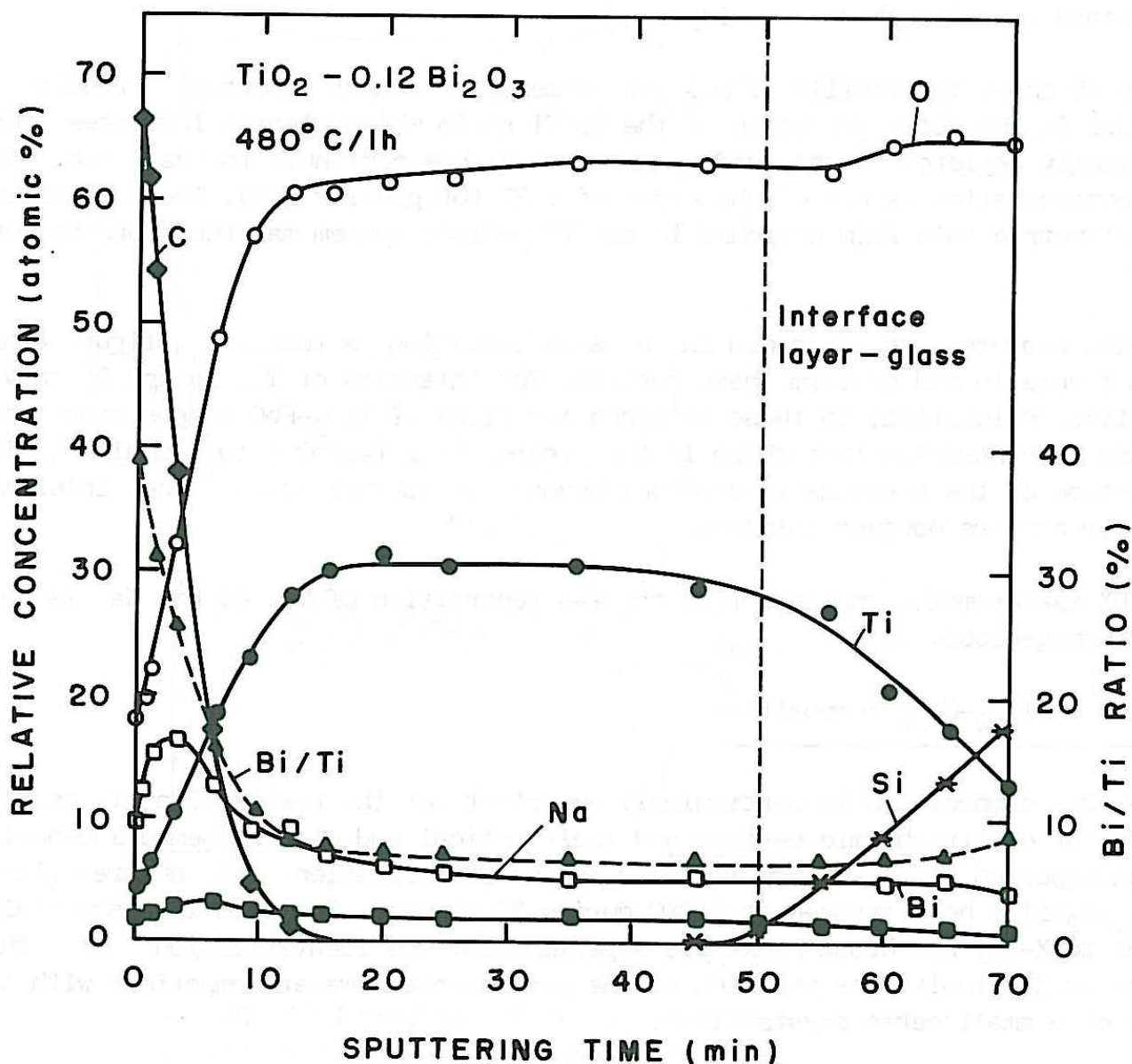


Fig. 15 XPS profiles of a one layer TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub> film heat treated in air at 480°C during 60 minutes (left scale). The ratio Bi/Ti is shown as a broken line (right scale).

feature is attributed to oxygen in the glass substrate.

The results on Ti are also similar. We observe a broadening of the 2 p peaks and the appearance of a shoulder. A new doublet was never observed. The Bi behaviour is interesting. A shoulder at lower BE values of the 4 f doublet is already seen at the surface. It indicates the presence of a lower oxidation state even without sputtering. Sputtering enhances this feature. After 3,5 minutes sputtering the high and low BE doublet are of almost equal intensity and after 6,5 minutes the lower BE doublet become dominant. At the interface we observe Si 2 p and Si 2s as a shoulder of the Bi 4 f 7/2 peak. C is only observed at the surface while a low concentration of Na appears now throughout the layer.

Figure 15 shows the profile of all the elements. The most important result of this figure is the depth variation of the Bi/Ti ratio which clearly indicates that Ti is strongly depleted at the surface and that Bi has continued to evaporate. Its overall concentration is now of the order of ~ 2% (originally 6,9%). The preparation of stoichiometric thin film compound in the  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  system may therefore be very difficult.

The SIMS measurements performed in the same condition as that of figure 8 are shown in figure 16 and confirm these results. The intensity of Ti, Na and O curves are practically identical to those obtained for films of  $\text{TiO}_2\text{-PbO}$  composition but the carbon concentration (not shown in the figure) is a factor 2 to 5 smaller. The concentration of the elements is constant beyond the subsurface. The interface glass-layer appears however thinner.

SEM-EDX measurements indicate that the 2-d repartition of Ti, O, Bi, Na is uniform and homogeneous.

### 3.3. Films of $\text{TiO}_2\text{-CeO}_2$ composition

$\text{TiO}_2\text{-CeO}_2$  composition is particularly important for the realization of counter electrode for electrochromic devices and their optical and electrochemical behaviour have been reported<sup>4,5,6</sup>. Figure 17 shows XRD characterization of a three layer  $\text{Ce}_{0,5}\text{Ti}_{0,5}\text{O}_2$  film heat treated at 520°C during 30 minutes. The film is essentially amorphous to X-ray but broad peaks are superimposed. The identification of this structure is difficult; the position of the peaks seems however compatible with the presence of a small ceria crystallites.

Figure 18 shows SIMS profiles for Ti, Ce, Na, O,  $\text{Sn}^{118}$  and In for a two layer  $\text{Ti}_{0,5}\text{Ce}_{0,5}\text{O}_2$  film deposited on an ITO coating and heat treated at 420°C during 15 minutes. Comparing the intensity of the curves with those obtained previously under identical experimental conditions we see that the oxygen level is identical and that the titanium counts are smaller indicating that cerium has substituted these ions in

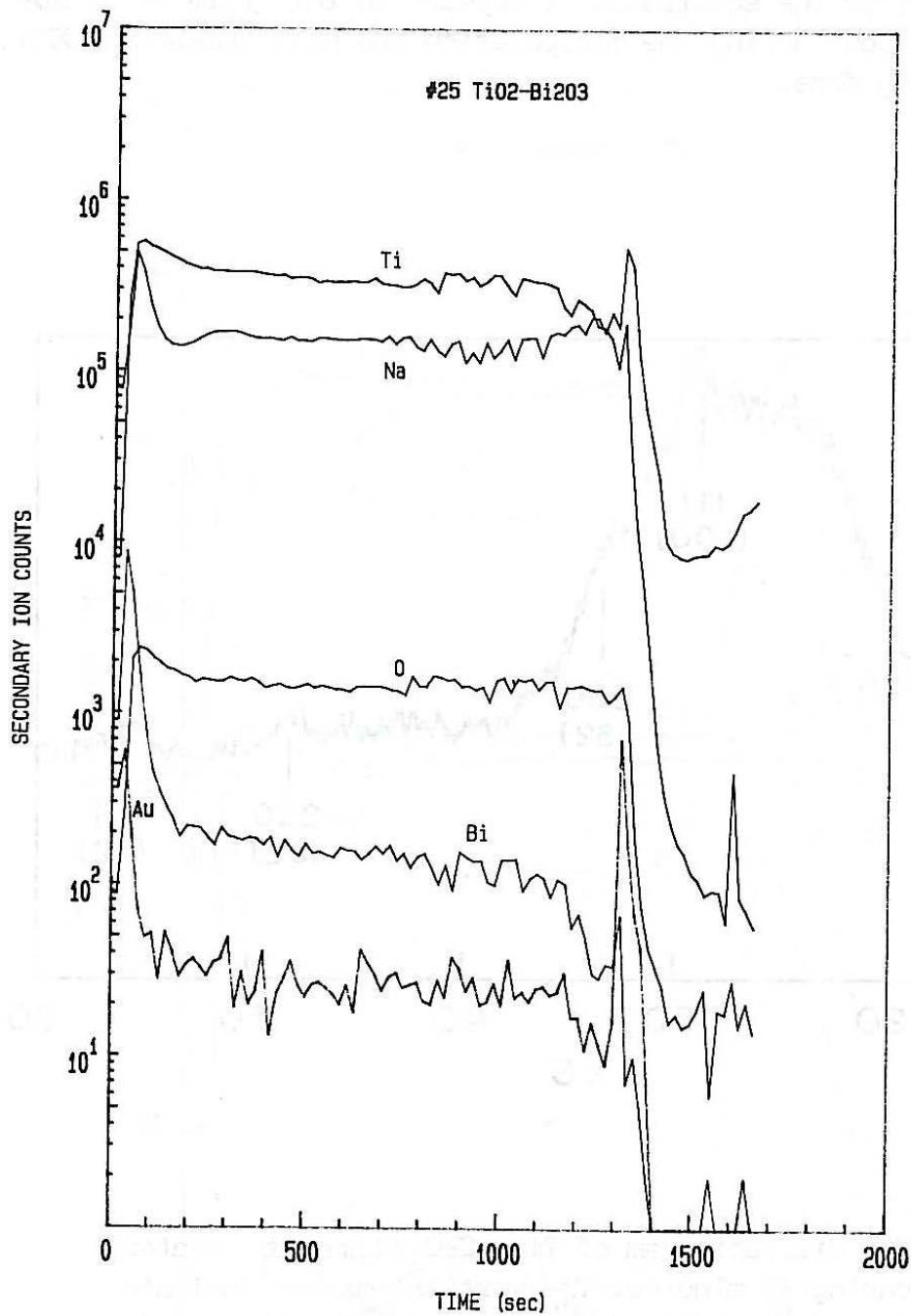


Fig. 16 SIMS profiles of a 3 layer  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  film heat treated in air at  $480^\circ\text{C}$  during 60 minutes.

higher amount than bismuth and lead and probably has not suffered volatilization effect. Sodium counts are a factor four lower indicating that the ITO barrier has impeded its diffusion from the substrate. It appears in this film as an atmospheric contamination brought about during the manipulation and heat treatment. XPS measurements have not yet being done.

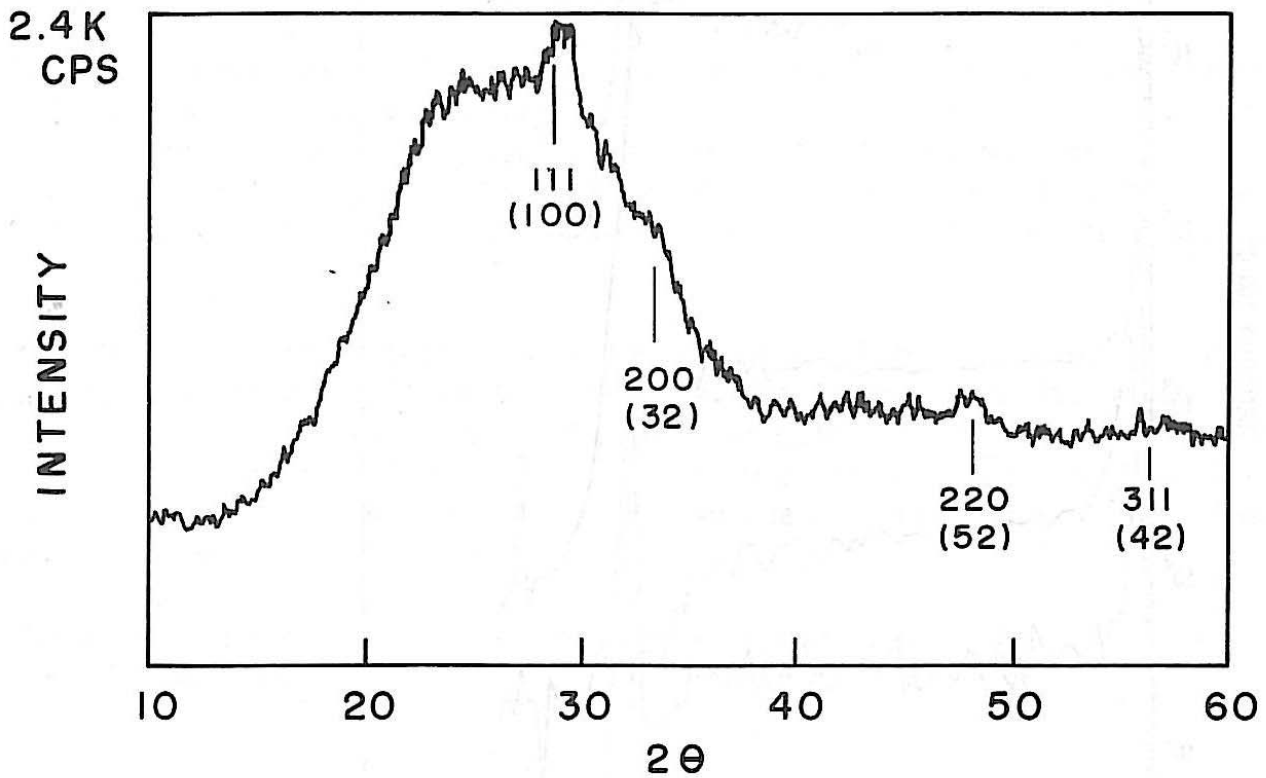


Fig. 17 XRD diffractogram of  $\text{TiO}_2\text{-CeO}_2$  film heat treated at  $520^\circ\text{C}$  during 30 minutes. The vertical marks indicate the position of the first four lines of crystalline  $\text{CeO}_2$  as well as their hkl and relative intensity values.

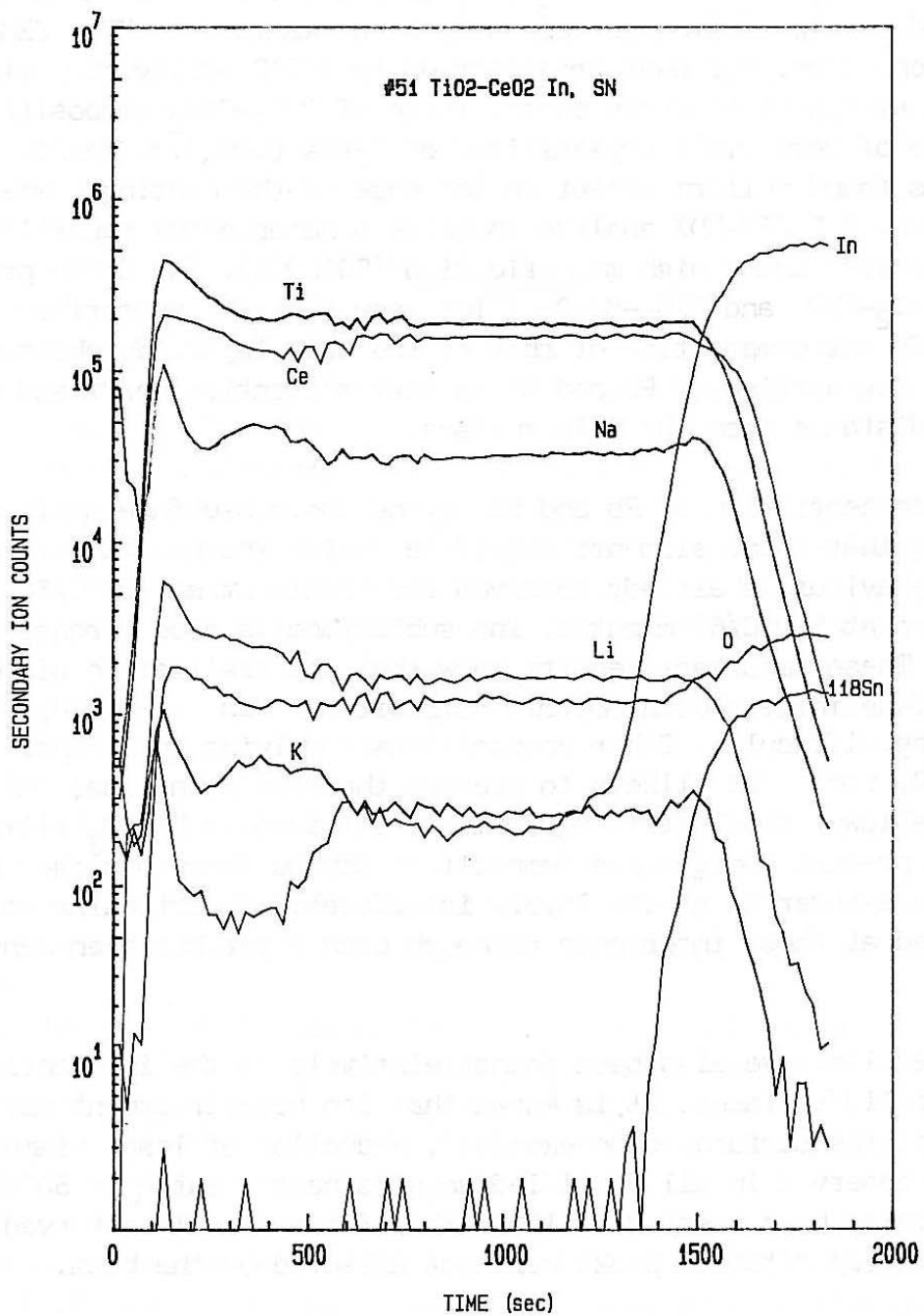


Fig. 18 SIMS profiles of Ti, Ce, Na, O, In and  $^{118}\text{Sn}$  of a 2 layer  $\text{Ti}_{0.5}\text{Ce}_{0.5}\text{O}_2$  film deposited on ITO coated glass substrate and heat treated at  $420^\circ\text{C}$  during 15 minutes.

#### 4. CONCLUSIONS

The structure, texture and 2 d and depth profile chemical composition of thin films of  $\text{TiO}_2\text{-PbO}$ ,  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  and  $\text{TiO}_2\text{-CeO}_2$  compositions prepared by sol-gel methods and deposited by dip coating process have been examined by XRD, SEM, DEM-EDX, XPS and SIMS techniques. For heat treatment up to  $500^\circ\text{C}$  during 60 minutes the films were found amorphous to X-ray except those of  $\text{TiO}_2\text{-CeO}_2$  composition which show the presence of very small crystallites of Ceria ( $\text{CeO}_2$ ). Their texture observed by SEM was found uniform except on the edge of the coatings where cracks and pores appeared. 2 D SEM-EDX analyse indicate a homogeneous repartition of all the main elements even under high magnification (560000x). The depth profiles measured by XPS in  $\text{TiO}_2\text{-PbO}$  and  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  films show that the subsurface ( $\sim 10$  to  $15$  nm) has a different composition of that of the bulk layer. We observe a depletion of Ti and a segregation of Pb and Bi so that the ratios Pb/Ti and Bi/Ti decrease with the distance from the film surface.

Moreover the concentration of Pb and Bi beyond the subsurface is lower than expected indicating that these elements evaporate during the heat treatment of densification. This behaviour is already observed for treatment at  $200^\circ\text{C}/60$  minutes but is more pronounced at  $500^\circ\text{C}/60$  minutes. The subsurface is also strongly contaminated by carbon. These important results show that the realization of multicomponent thin film of definite stoichiometric composition in the  $\text{TiO}_2\text{-PbO}$  and  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  may be difficult. Other compositions involving low vapor pressure oxide like BaO, etc are likely to present the same phenomena; this may explain in part the low ferroelectric performance obtained on  $\text{BaTiO}_3$  films<sup>12,13</sup>. Multilayer films present homogeneous composition beyond the subsurface and no subsurface effects are observed at the layers interfaces. In particular no atmospheric carbon is detected at these interfaces although each layer has been densified separately.

Interesting results have also been found relatively to the interaction of Ar ion beam with these solid surfaces. It is known that ion beam treatment may change the chemical nature of the surface to be examined. Reduction of lead, bismuth and titanium have been observed in all densified samples heat treated at  $500^\circ\text{C}$ . In partly densified samples heat treated at  $190^\circ\text{C}$  the effect is only observed for lead and bismuth but the 2p titanium peaks were not affected by the beam.

It is accepted that the ion-induced chemical damage is due to preferential sputtering of the oxygen from the oxide matrix and atomic rearrangement. Models based on a Sigmund's classification of sputtering events and sputtering yield equation have been developed by Malherbe<sup>14</sup> using a collisional approach in which both mass and bonding effects of the binary components are incorporated and by Kelly<sup>15</sup> using a thermal approach in which chemical binding is presumed to be the dominant factor. A more detailed analysis of these porous and densified samples<sup>8</sup> may therefore bring valuable indications on the viability of these models.

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