Journal of Non-Crystalline Solids 121 (1990) 323–328
North-Holland

Aeg 126

PREPARATION AND CHARACTERIZATION OF THIN FILMS OF TiO_2–PbO AND TiO_2–Bi_2O_3 COMPOSITIONS

E.R. La SERRA, Y. CHARBOUILLOT, P. BAUDRY and M.A. AEGERTER

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560–São Carlos, SP, Brazil

Single and multilayer thin films of $PbTiO_3$, $PbTi_4O_9$ and TiO_2–Bi_2O_3 compositions have been prepared on glass and amorphous silica substrates by using the dip-coating technique. After drying and densification, these films have a high optical quality. They have been characterized by the optical transmission technique and XPS. For certain values of their thickness they present almost flat transmission characteristics in the visible range and can be used as achromatic beam splitter or neutral-colored solar-energy-reflecting windows. Their use as a passive optical waveguide with a propagation of up to 4 modes at $\lambda = 632.8$ nm is also reported.

1. Introduction

The fabrication of high quality thin films and devices has received much attention in recent years. The sol–gel method appears very attractive since it offers potential advantages over traditional techniques. The low processing temperatures may particularly facilitate their use with semiconductor and integrated optical devices. On the other hand the process also allows the fabrication of large surfaces with coatings on either one or both faces of the substrate. In this paper, we present results of the preparation of high optical quality single or multilayer thin films of TiO_2–PbO and TiO_2–Bi_2O_3 compositions obtained by dip-coating.

We first describe in detail the preparation of the precursors, the sols and the experimental conditions required to obtain the films. Then, we show their principal optical characteristics as well as some preliminary XPS results. Finally, we discuss possible applications for the realization of achromatic beam splitters, neutral-colored solar-energy-reflecting glasses and passive optical waveguides.

2. Experimental procedures

TiO_2–PbO and TiO_2–Bi_2O_3 materials have not proved to be important technological systems when prepared via conventional processing procedures. However they are the basic constituents of important electrical ceramics and as thin films may be useful for the development of electronic and optical devices.

2.1. *Precursor and sol preparations of TiO_2–PbO compositions [1]*

The first preparation of a $PbTiO_3$ precursor was made by Gurkovich and Blum [2] through the reaction of lead acetate $Pb(C_2H_3O_2)_2$ dissolved in methoxyethanol $C_3H_8O_2$ with titanium isopropoxide $Ti(OC_3H_7)_4$. The synthesis process was rather complicated and the final product was highly viscous with high moisture sensitivity. Sols were prepared by dissolving this complex in methoxyethanol (1 : 7 ratio volume) introducing the water of hydrolysis as a solution of methoxyethanol and water (2 : 1 ratio) with 0.002 mol HNO_3/mol water added. Gelation occurred in a few minutes and transparent gels were obtained after drying at 34°C for 2–3 weeks. Tetragonal $PbTiO_3$ was reported after firing at 600°C.

The precursor preparation process was later modified by Budd et al. [3,4] who recognized, through gas chromatography, the occurrence of an exchange reaction between the titanium alkoxide and methoxyethanol:

$$Ti(OR')_4 + 4(ROH) \rightarrow Ti(RO)_4 \rightarrow 4R'OH, \quad (1)$$

with $R' \equiv iC_3H_7$ and $R \equiv CH_3OCH_2CH_2$.

The titanium methoxyethoxide prepared in this way at 125°C was then combined with a 2-methoxyethanol solution of dehydrated lead acetate, reacted, and concentrated by repeated vacuum distillations. Sols for gel formation and thin film preparation were prepared by combining an equal volume of the stock solution with a solution of water-catalyst (acid or base)-methoxyethanol. Stable sols were obtained for a $[H_2O]/[PbTiO_3]$ ratio lower than 1.5. For higher ratios gelation occurred in a few minutes with a rate increasing with the water concentration and pH.

We propose an easier method to prepare precursor sols, and particularly useful for obtaining dense material in film form. It is based on the chemical modification of titanium isopropoxide $Ti(OPr^i)_4$ by acetylacetone AcacH, a rather strong chelating ligand and stabilizing agent [5–7]. The preparation of the complex alkoxide is described by the exothermic reaction [8]:

$$Ti(OPr^i)_4 + 2AcacH \rightarrow Ti(OPr^i)_2(acac)_2 + 2(Pr^iOH). \quad (2)$$

The yellow and homogeneous solution is mixed for 30 min until its temperature decreases to 25°C. A solution of lead acetate $Pb(OAc)_2$ in acetic acid (concentration 720 g/l) is then added and stirred for 30 min. This sol does not exhibit gelation or precipitation for at least 6 months. However, its color changes from clear yellow to orange in a few days, indicating either an evolution of the Ti complexation or a change in the particle size. Both precursor sols can be mixed in any proportion to prepare lead-titanate material of other compositions (table 1).

Table 1
Typical composition for the preparation of $PbTiO_3$ and $PbTi_4O_9$ sol

Product	Pr^iOH (ml)	AcacH (ml)	$Ti(OPr^i)_4$ (ml)	Pb acetate solution (ml)	pH
$PbTiO_3$	40	3	4	7.24	4.7
$PbTi_4O_9$	40	3	4	1.81	5.7

Table 2
Typical composition for the preparation of TiO_2–Bi_2O_3 sol

Product	Pr^iOH (ml)	AcacH (ml)	$Ti(OPr^i)_4$ (ml)	Bi nitrate solution (ml)	pH
TiO_2–Bi_2O_3	30	1.8	2.5	1.9	0.86

2.2. *Precursor and sol preparations of TiO_2–Bi_2O_3 composition*

The preparation of the precursors and sols in this system is based on the same ideas and follows a similar procedure. However the bismuth sols were prepared by mixing $Bi(NO_3)_3 \cdot 5H_2O$ in acetic acid with a concentration of 665 g/l. Once again the precursor sol can be mixed in any proportion in order to prepare other compositions. Table 2 shows a typical composition.

2.3. *Film preparation*

Thin films have been obtained by dip-coating either on common glass microscope slides or pure amorphous silica substrates previously cleaned. Usually, both faces of the substrates are coated. The withdrawal speed was typically 4 to 15 cm/min. After each coating procedure, the films were dried and heat treated to 500°C in order to densify them. The thickness of the films, measured with Fabry–Perrot interferometry, were found to be roughly proportional to the withdrawal speed (typically 60 nm for 10 cm/min). The whole process can be repeated if thicker films are desired. Good optical characteristics have been obtained with up to 15 coatings yielding a thickness of about 1 μm.

These films have an index of refraction of about 2.15 and exhibit practically no optical absorption in the visible range. Therefore they are good candidates for reflective coatings. By tailoring their optical thickness, almost flat reflection and transmission properties can be achieved in the visible range.

3. Thin film characterization

The thickness and index of refraction of the films have been determined by best fitting the transmission spectra to theoretical ones calculated using the well known ellipsometric relations.

Figure 1 shows examples of the visible transmission spectrum of a 1 mm thick glass substrate coated on each side by a thin layer of TiO_2–Bi_2O_3 (1 dip) as a function of the heat treatment. The films are practically densified around 450°C and have an index of refraction of 2.12 at 540 nm. The spectrum has an almost flat characteristic in the visible region with a transmission value varying from 53 to 65%. $PbTi_4O_9$ coatings [1] show similar results with however slightly larger optical transmission (see also fig. 3). Their index of refraction is around 2.10.

Preliminary XPS analysis of $PbTiO_3$ and $PbTi_4O_9$ thin films coated on glass substrates are shown in fig. 2 (McPherson ESCA-36 Al Kα 1486.6 eV excitation). The results indicate that all the films have small Na contaminations; the amount of impurity is larger near the substrate (see curves b, c and d) indicating that its presence is probably due to Na diffusion from the substrate into the film during the heat treatment. The spectra show also a small contamination with S, Ca and C. The last impurity is mainly encountered near the surface indicating probably a superficial contamination due to a poor vacuum (10^{-7} Torr); however, an incomplete elimination of the carbon group during the densification process can not be discarded. The average atomic ratio Pb/Ti is 0.65 ± 0.15 for $PbTiO_3$ and 0.33 ± 0.07 for $PbTi_4O_9$. This last value decreases to 0.16 ± 0.04 after 10 kV 17 min Ar sputtering. This indicates that the films are not chemically homogeneous through their thickness and are richer in lead near their external surface.

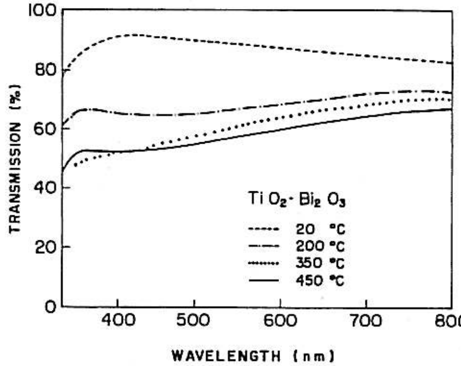

Fig. 1. Transmission spectra of TiO_2–Bi_2O_3 thin film coated on both faces of a glass substrate as a function of the heat treatment.

The energy position of the Ti $2p^{3/2}$ line at 458.5 ± 0.3 eV is consistent with the value 4+; however, the position of the $Pb(4f^{7/2})$ line varies slightly (138.4 to 138.9 eV) and its value is somewhat intermediary between the lines observed for pure PbO and PbO_2. After Ar sputtering (see curve d) both Pb $4f^{7/2}$ and Pb $4f^{5/2}$ start to split showing a possible reduction of Pb into oxide of lower valence.

4. Applications

The good optical quality of these thin films and their ease of fabrication make them interesting candidates for various applications.

4.1. *Preparation of achromatic beam splitters and neutral-colored solar-energy-reflecting windows*

Because of their high refractive index, interesting optical characteristics can be obtained using a single dip-coating procedure either on one or both faces of a glass substrate. By carefully selecting the value $n \cdot t$, almost flat transmission and reflection characteristics can be achieved in the visible spectral region. Figure 3 shows some results obtained with $PbTiO_3$ (t = 72 nm), $PbTi_4O_9$ (t = 55 nm) and TiO_2–Bi_2O_3 (t = 63 nm). Because of the absence of Na diffusion, the coating on pure amorphous silica substrate has a slightly higher index of refraction and gives a lower transmission value. It is worth noting that coating on one side only will reduce the reflection by a factor 2. On the other hand a reduction of the reflection and consequently an increase of the transmission can also be obtained by using mixed SiO_2–TiO_2–PbO

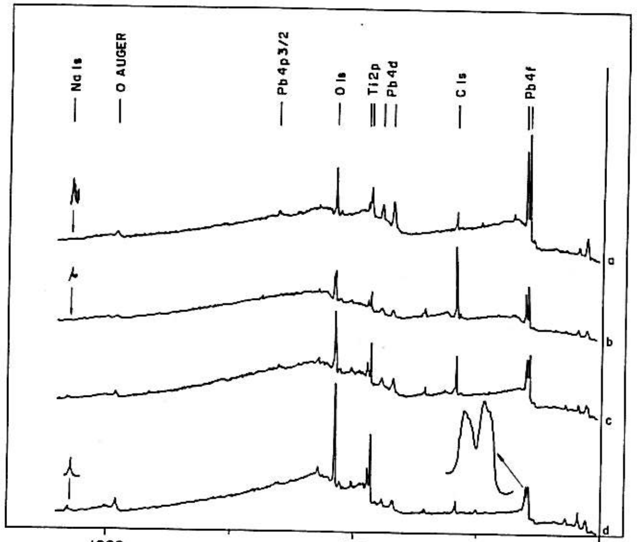

Fig. 2. XPS spectra of TiO_2–PbO dense thin films. The carbon line at 287.8 eV is taken as reference. (a) $PbTiO_3$, $t \approx 70$ nm; (b) $PbTi_4O_9$, $t \approx 55$ nm; (c) Same as (b) after 2 min 10 kv Ar sputtering; (d) Same as (b) after 17 min 10 kv Ar sputtering.

or Bi_2O_3 precursors which gives films with lower indexes of refraction.

Since these films do not have absorption in the visible range, they are good candidates for achromatic beam splitters and neutral-colored

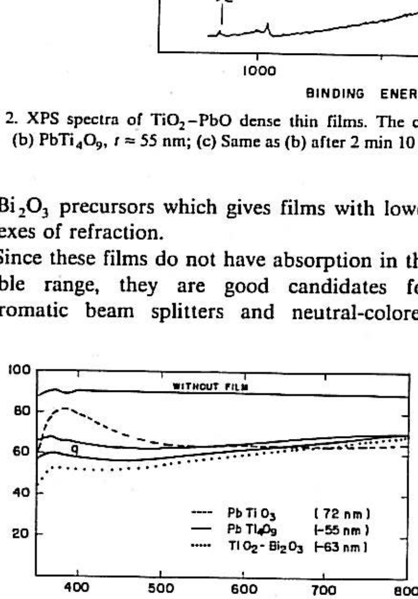

Fig. 3. Transmission spectra of dense films coated on both sides of a glass substrate. – – – –, $PbTiO_3$, $t = 72$ nm, heat treated at 460 °C for 15 min. ———, $PbTi_4O_9$, $t = 55$ nm, $n = 2.10$, heat treated at 460 °C for 15 min. —q—, Same as above coated on amorphous quartz substrate, $t = 51$ nm, $n = 2.19$ heat treated at 460 °C for 15 min. · · · · · ·, TiO_2–Bi_2O_3, $t = 63$ nm, $n = 2.12$, heat treated at 450 °C for 1 h.

solar-energy-reflecting windows. They should present considerable advantages compared with sun shielding glass in which the solar energy is absorbed or stoped in the glass.

The films with lower transmission have optical characteristics similar to the type 416 produced by Schott (unknown composition, thickness and method of preparation).

By choosing an adequate sol composition optical characteristics similar to Schott type 411, 412 and 413 can be easily obtained.

4.2. *Preparation and characterization of passive planar waveguide*

The fabrication of passive optical devices using the sol–gel method is simple and inexpensive. It has great advantages since the method allows the choice of index of refraction and the thickness of the layers. Hermann and Wildmann [9] have shown the feasibility of the method by fabricating planar optical waveguides using SiO_2–TiO_2 Lipicoat

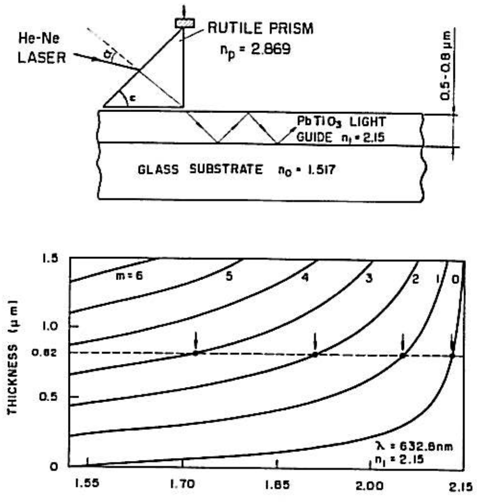

Fig. 4. (Top) Prism coupler method to couple He–Ne laser light beam to a $PbTi_4O_9$ planar waveguide. (Bottom) Dispersion relation for a $PbTi_4O_9$ waveguide ($n_1 = 2.15$ at $\lambda = 623.8$ nm) deposition on a glass substrate ($n_0 = 1.517$) showing the various effective modes of propagation obtained as a function of the film thickness. The dashed line refers to a film 0.82 μm thick (15 layers) measured experimentally (see table 3).

Merck solution. Using a rutile prism coupler, we successfully coupled a He–Ne laser beam to a thin planar $PbTi_4O_9$ film 0.82 μm thick deposited on a common glass substrate. The upper part of fig. 4 shows schematically the experimental set-up and the lower part shows the dispersion relation of the films thickness versus the effective index of refraction, N, for the propagation of TE modes $m = 0$ to $m = 6$ calculated for a thin film of index of refraction $n_1 = 2.15$ [10]:

$$N = n_p \sin\big(\epsilon + \arcsin\big((\sin \alpha)/n_p\big)\big), \qquad (3)$$

where $n_p = 2.869$ and $\epsilon = 42.2°$ are the index of refraction and the angle of the rutile coupling prism, respectively, and α is the angle of incidence of the He–Ne laser light on the prism. Four propagation modes have been observed (TE_0, TE_1, TE_2 and TE_3). The N_m values calculated with the relation (3) are in good agreement, within 1.5%, with those derived from fig. 4.

These results are extremely promising and open a new field of application as the layers were prepared without special substrate cleaning solution, filtration and clean room facilities and confirm the good optical quality of these lead-titanate derived films. It is interesting to note that the theoretical derivation of N_m and the dispersion curves were done by assuming constant values of the index of refraction of the film and substrate with a sharp variation at the interface. The variation of the Pb/Ti atomic ratio observed by XPS in very thin films (fig. 2) probably affects only a very thin layer near the film substrate interface. Thicker films, such as those used for the preparation of a passive waveguide appear much more homogeneous through their thickness. No measurement have been done yet with TiO_2–Bi_2O_3.

Embossing techniques used in integrated optics to fabricate surface-relief gratings and channel waveguides would be another promising possibility. This technique was first developed for hard and resistant SiO_2–TiO_2 sol–gel films (Liquicoat ZLI 1686 Merck) by Lukosz and co-workers [11,12] and more recently by Tohge et al. for SiO_2 films [13]. The technique involves the pressing of a dry film against an aluminized reflective grating or stamper followed by baking at 500 °C. The replica may function as an input or output grating coupler, a Bragg reflector, the pregrooves of an optical memory disk or any other optical device which requires an engraved pattern. Recently, using a microprocessor-controlled dipping arm to withdraw a SiO_2–TiO_2 film from the solution with varying speeds, Hewak and Lit [14], fabricated tapered and lens-like waveguides.

The successful and easy preparation of thin lead titanate films of high optical quality com-

Table 3
Experimental values of α_m and calculated values of N_m (see also fig. 4)

TE_m	α_m (±5′)	N_m (±0.02) (from rel. (3))	N_m (from fig. 4)
TE_0	18°38′	2.15	2.12
TE_1	11°09′	2.07	2.04
TE_2	−0°33′	1.92	1.90
TE_3	14°58′	1.73	1.70

bined with their high refractive index are without any doubt good candidates for future research and applications in this optical field.

5. Conclusion

Thin films have been prepared in the system TiO_2–PbO and TiO_2–Bi_2O_3 using a dip-coating technique.

These films have good optical quality and are easy to prepare. By adjusting their thickness we have obtained almost flat spectral transmission and reflection characteristics in the visible spectral region, suggesting that these films are good candidates for the preparation of achromatic beam splitters and neutral-colored solar-energy-reflecting windows. The chemical and mechanical characteristics have not been yet studied.

Using thicker films we have demonstrated that they can also be used for the realization of passive planar waveguides, with possible applications in the field of integrated optics. Preliminary XPS analysis of TiO_2–PbO films shows, however, that the layers are not as homogeneous as it was thought by measuring their optical characteristics. Contamination with Na, C, Ca, and S has been observed. Ti ions are compatible with a valence 4 but Pb shows a tendency to be intermediary between PbO and PbO_2.

This work was supported by FAPESP, CNPq and FINEP (Brazil). The authors are grateful to Prof. S. Castro, Unicamp (Brazil) for the XPS analysis.

References

[1] M.A. Aegerter, Y. Charbouillot, N. Mohallen, A.A. da Silva and L.H. Godoy, in: Proc. Conf. on the Ultrastructure Processing of Ceramics Glasses and Composites, Tucson, AZ, Feb. 1989, eds. D. Uhlmann and D.R. Ulrich (Wiley, New York) in press.

[2] S.R. Gurkovich and J.B. Blum, in: Ultrastructure Processing of Ceramics, Glasses and Composites, ed. L. Hench and D. Ulrich (Wiley, New York, 1984) p. 152.

[3] K.D. Budd, S.K. Dey and D.A. Payne, Proc. Br. Ceram. Soc. 36 (1985) 107.

[4] K.D. Budd, S.K. Dey and D.A. Payne, in: Better Ceramics Through Chemistry III, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Materials Research Society, Proc. 73, 1986) p. 711.

[5] C. Sanchez, in: Précurseurs Moléculaires de Matériaux Inorganiques. Procédés Sol–Gel, Proceedings CNRS (France) Greco 93 (1987).

[6] C. Sanchez, J. Livage, M. Henry and F. Babonneau, J. Non-Cryst. Solids 100 (1988) 65.

[7] C. Sanchez, F. Babonneau, S. Doeuff and A. Léaustic, in: Ultrastructure Processing of Advanced Ceramics, eds. J.D. Mackenzie and D.R. Ulrich (Wiley, New York, 1988) p. 77.

[8] A. Yamamoto and S. Kambara, J. Am. Chem. Soc. 79 (1957) 4344.

[9] P.P. Hermann and D. Wildmann, IEEE J. Quantum Electron. QE-19 (1983) 1735.

[10] D. Ulrich and R. Torge, Appl. Opt. 12 (1973) 2901.

[11] W. Lukosz and L. Tiefenthaler, Opt. Lett. 8 (1983) 537.

[12] K. Heuberger and W. Lukosz, Appl. Opt. 25 (1986) 1499.

[13] N. Tohge, A. Matsuda, T. Minami, Y. Matsuno, S. Katayama and Y. Ikeda, J. Non-Cryst. Solids 100 (1988) 501.

[14] D.W. Hewak and J.W.Y. Lit, Appl. Opt. 27 (1988) 4562.