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MULTILAYER SiO_2 AND TiO_2 COATINGS ON GLASSES BY THE SOL–GEL PROCESS

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Glass films of pure SiO_2 and TiO_2 have been prepared on sodalime silica flat slide glasses by the sol–gel process using the dip-coating technique from TEOS and $Ti(OC_3H_7)_4$ solutions. The various parameters such as chemicals concentrations, viscosity, type of catalyst, withdrawal speed and temperature of densification leading to the obtention of good and adherent coatings with definite film thicknesses are reported. The same technique has been used for the deposition of layers of colored films SiO_2–M_xO_y (M = Co, Mn, Nd and Cr). Brilliant yellow coatings have been obtained with TiO_2–CeO_2.

1. Introduction

The coatings of glasses, ceramics and metals with amorphous thin films is probably one of the most important applications of the sol–gel process and there is great technological interest in the preparation of coloured and multilayered dielectric films. Researches and applications for the coating from solution have recently been reviewed by Schroeder [1], Dislich and Hussman [2], Dislich [3], Sakka [4] and Orgaz et al. [5]. The purpose of this work was to prepare transparent and coloured coatings of SiO_2 and TiO_2 on glass substrates by the dip-coating technique and to obtain all the characteristic values of the different parameters and their useful range for which optically and mechanically good coatings of definite thicknesses can be obtained. A further and natural step will be the deposition of multilayers having for example the sequence $TiO_2/[SiO_2/TiO_2]^4$/glass/$[TiO_2/SiO_2]^4$ TiO_2 in order to prepare special antireflective devices.

2. Experimental methods

2.1. Preparation of solutions

The starting solutions for pure SiO_2 coatings were prepared by mixing TEOS and ethanol while tirring and than slowly adding water catalysed with HNO_3. Typical compositions are given in table 1 for a standard 100 ml solution. The stirring of the sols was continued for 2 h. The concentration and the viscosity were adjusted by adding methanol or ethanol and water (figs. 1, 2). The pH of the solutions were kept to values below 1.5 in order to maintain the viscosity practically constant during 10 to 20 days (fig. 1). The SiO_2 doped solutions were prepared by mixing, without stirring, the required amount of TEOS, ethanol, catalysed water and Co, Mn, Cr or Nd nitrates respectively (table 1). After one day the nitrates were completely dissolved and the concentration and the viscosity were adjusted by the addition of methanol and stirring the sols for about 10 min. The pH of the solutions were also kept to a pH value of < 1.5 (table 1).

The starting solutions for coating pure TiO_2 were prepared by dissolving tetraisopropyl orthotitanate $Ti(O\text{–iso-}C_3H_7)_4$ in isopropanol CH_3-$CHOHCH_3$ in a controlled atmosphere having a relative humidity below 40% in order to prevent the strong reaction of the Ti alkoxide with water. The pH of this sol is typically 1.0. A typical composition is given in table 2.

For TiO_2 doped with Ce the sols were prepared by mixing $Ti(O\text{–iso-}C_3H_7)_4$, ethanol and $CeCl_3 \cdot 7H_2O$ (table 2). Such a sol has a pH = 3 and the time of gelification is shorter (fig. 1). Good coatings were obtained with these compositions. The parameters can be slightly varied. However, the doping concentrations are at a maximum limit.

Aeg 702

Table 1
Left side: typical compositions used to prepare 100 ml of standard SiO_2 organometallic sols (without doping). *Right side*: typical values of superficial tension σ viscosity η, lifting velocity U, heat treatment for complete densification and thickness for which good coatings have been obtained

Film	TEOS (ml)	ethanol (ml)	methanol (ml)	H_2O doping (g)	pH	σ (dyn/cm^2)	η (cp)	U (cm/min)	Heat treatment thickness T(°C)	T(min)	(nm)
SiO_2	33	11	44	12 –	~1.5	n.m.	2–4	4–12	~ 500	10–30	100–300
SiO_2:Co	26	9	54	11 6.9 $Co(NO_3)_2{:}6H_2O$	~1.0	27	2–4	4–12	~ 500	10–30	100–300
SiO_2:Mn	26	9	54	11 2.8 $Mn(NO_3)_2.4H_2O$	~1.0	26	2–4	4–12	~ 500	10–30	100–300
SiO_2:Cr	26	9	54	11 4.7 $Cr(NO_3)_3.9H_2O$	~1.0	26	2–4	4–12	~ 500	10–30	100–300
SiO_2:Nd	26	9	54	11 4.5 $Nd(NO_3)$	~1.0	n.m.	2–4	4–12	~ 500	10–30	100–300

Table 2
Left side: typical compositions used to prepare 100 ml of standard TiO_2 organometallic sols (without doping). *Right side*: typical values of superficial tension σ, viscosity η, lifting velocity U, heat treatment for complete densification and thickness for which good coatings have been obtained

Film	$Ti(O\text{–iso-}C_3H_7)_4$	Alcool	Doping	pH	σ (dyne/cm^2)	η (cp)	U (cm/min)	Heat treatment thickness T(°C)	T(min)	(nm)
TiO_2	7.3	92.7 (isopropanol)	–	1.0	23	2–3	2–8	~ 400	10	10– 80
TiO_2:Ce	6:3	93.7 (ethanol)	7.8	~ 3.0	n.m.	2–4	2–8	~ 500	10	50–140

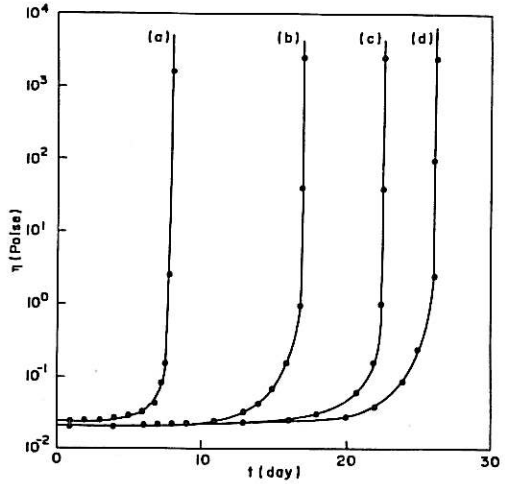

Fig. 1. Viscosity of the various sols measured at 25 °C with a rotating viscosimeter at a shear stress $D_r = 1574\ s^{-1}$ (a) TiO_2:Ce with [Ti]/[Ce] 1:1; (b) SiO_2 [H_2O]/[TEOS] = 4; (c) SiO_2:CoO (Table 1); (d) SiO_2:Mn_2O_3 (table 1).

Lower concentrations with identical viscosity will lead to the obtention of layers with smaller thicknesses. Higher concentrations result in the formation of cracked layers and the films appear non-transparent and usually do not adhere on the substrate.

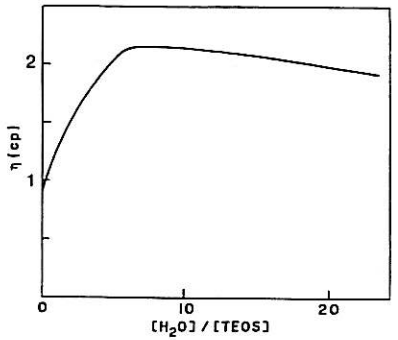

Fig. 2. Initial viscosity of SiO_2 sol as a function of the molar ratio $r = [H_2O]/[TEOS]$ measured at 25 °C with a rotating viscosimeter ($D_r = 1574\ s^{-1}$), pH = 1.13, [ethanol]/[TEOS] = 3.

2.2. Coating technique and heat treatment

The coatings were deposited on commercial microscope slide glasses previously cleaned using the following sequence:

(a) washing with water and detergent;
(b) immersion in sulfochromic solution at 60 °C for 2 h;
(c) washing with bidistilled water;
(d) washing with acetone;
(e) drying in clean air for 1 day.

The slide glasses were dipped into the solution and extracted vertically at different speeds ranging from 2 to 12 cm/min (tables 1 and 2). After the coating a thin scratch was made on it down to the substrate using a sharp blade in order to measure its thickness with a Fizeau interferometer. The heat treatment is specific for each type of film and is given in tables 1 and 2.

For pure SiO_2 the films have to be dried after the coatings for 1 day in air at room temperature before being densifired at ~ 500 °C (heating rate of ~ 20 °C/min). For doped SiO_2 no drying was necessary and the layer could be fired directly at high temperature.

For pure TiO_2 coatings the films have to be dried at room temperature typically for 1 h before the heat treatment at 400 °C (heat rate of 10 °C/min).

For TiO_2: Ce no room temperature drying was necessary and the densification could be carried out directly at ~ 500 °C.

2.3. Characterization of the coatings

The coatings were characterized during their different steps of preparation by a scanning electron microscope (SEM), X-ray diffraction, optical transmission and reflection spectroscopy from 200 nm to 2.3 μm and thickness measurements using a Fizeau interferometer.

3. Experimental results and discussion

In fig. 3 the coating thickness is plotted for porous films of SiO_2 and TiO_2 dried at 60 °C as a function of the withdrawal speed U and the

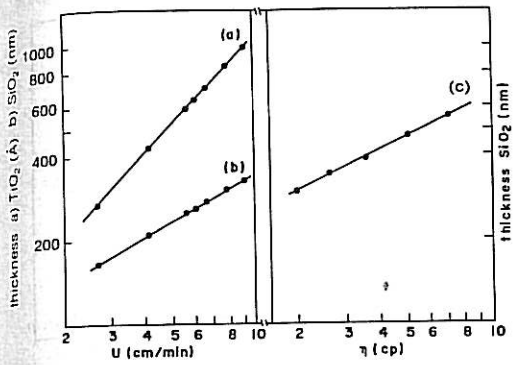

Fig. 3. (a) Thickness variation of porous films dried at 60 °C as a function of the withdrawal speed for TiO_2 ($\eta = 2.1$ cp) and (b) SiO_2 ($\eta = 2.0$ cp) coatings. (c) Thickness variation of porous SiO_2 films dried at 60 °C as a function of the sol viscosity ($u = 7.9$ cm/min).

viscosity of the sol. The SiO_2 film thickness practically follows the Landau–Levich law $t \propto (\eta U/\rho g)^{1/2}$. However the variation of the thickness for TiO_2 is linear with U. For TiO_2 doped with Ce the thickness was found to vary as v^n, the exponent n depending on the molar ratio [Ti]/[Ce] (fig. 4).

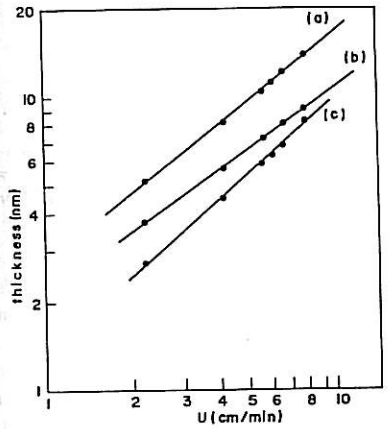

Fig. 4. Thickness variation of a dense film of TiO_2:Ce as a function of the withdrawal speed for molar ratio [Ti]/[Ce]. (a) 3:1; (b) 1:1; (c) 1:2.

3.1. SiO_2: Co

The films showed a homogeneous appearance with a pink colour when not heat treated and a blue colour after densification. Their optical transmission is shown in fig. 5. The optical spectra exhibit a split absorption band at 530, 590 and 640 nm attributed to Co^{2+} ions in a tetrahedral field of oxygen ions (transition $4\Gamma2(F)$–$4\Gamma4(F)$ [6].

3.2. SiO_2: Mn

The porous films are transparent and become brown after the heat treatment. Their optical characteristics (fig. 5) shows a single absorption band at 465 nm which may be due to $Mn^{3+}(d^4)$ in octahedral coordination [7] or Mn^{2+} in tetrahedral symmetry [8].

3.3. SiO_2: Cr

The chromium oxide films present a light green colour. The optical spectra consist of a single band at 370 nm which is associated with Cr^{6+} in tetrahedral symmetry [9]. It is interesting to note that in silica glasses only Cr^{3+} was reported [10].

3.4. SiO_2: Nd

The neodymium oxide films present a violet colour, with large bands at 425 nm and 800 nm

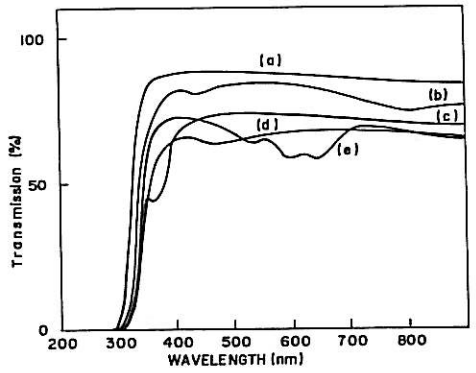

Fig. 5. Optical transmission of (a) uncoated slide glass; (b) SiO_2:Nd; (c) SiO_2:Cr; (d) SiO_2:Mn; (e) SiO_2:Co (see table 1 for parameters).

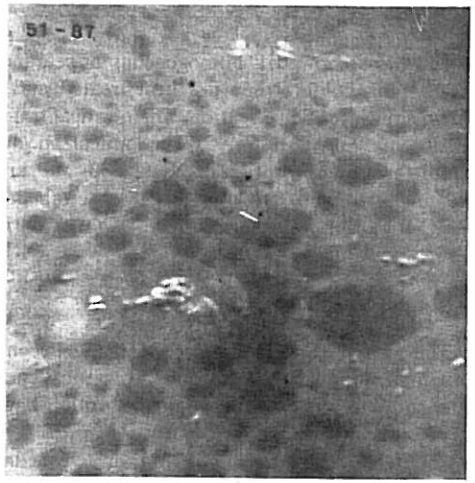

Fig. 6. Scanning electron microscopy of coating SiO_2:Nd film heat treated at 500 °C.

which do not correspond to any lines observed in doped Nd_2O_3 glasses. It is worth noting that contrary to all other coatings which appear homogeneous, the Nd coating presents probably colloidal particles as seen by SEM measurements (fig. 6).

3.5. TiO_2:Ce

Films of TiO_2:Ce present a metallic aspect with bright colors which changes as a function of the film thickness (fig. 7) from brown (c) to blue (d) and yellow (b) when viewed in transmission and from brown (c) to yellow (d) and blue (b) when observed in reflection.

Ce^{4+} and Ce^{3+} do not have absorption in the visible region but it was suggested that cerates of tetravalent titanium may be responsible for the yellow color [11]. SEM measurements do not show any coloidal particles. Further studies are necessary to establish the exact origin of these colors.

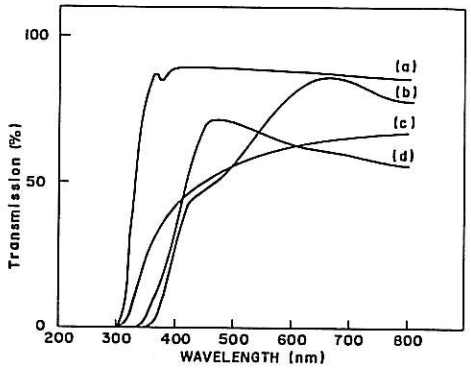

Fig. 7. Optical transmission of dense TiO_2:Ce film. (a) uncoated slide glass; (b) molar ratio [Ti]/[Ce] 3:2 thickness 170 nm; (c) molar ratio [Ti]/[Ce] 1:1 thickness 60 nm; (d) molar ratio [Ti]/[Ce] 1:1 thickness 120 nm.

The results are similar to those obtained by Makishima et al. [12].

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References

[1] H. Schroeder, Phys. Thin Films 87 (1969).
[2] H. Dislich and E. Hussman, Thin Solid Films 77 (1981) 129.
[3] H. Dislich, J. Non-Cryst. Solids 57 (1983) 371.
[4] S. Sakka, Proc. Int. Conf. on Glasses, New Delhi, 1986.
[5] F. Orgaz and R. Rawson, J. Non-Cryst. Solids 82 (1986) 378.
[6] D. Mac Clure, J. Phys. Chem. Solids 3 (1957) 311.
[7] H. Hatmann and H. Schaefer, Z. Naturf 6a (1951) 754.
[8] T. Bates, in: Modern aspects of the vitreous state, Vol. 2, ed. J. Mackenzie (Butterworth, London, 1962).
[9] C. Banford, Phys. Chem. Glasses 3 (1962) 189.
[10] P. Schultz, J. Am. Ceram. Soc. 57 (1974) 309.
[11] C.A. Hampel, Glass Ind. 41 (1960) 82.
[12] A. Makishima, H. Kubo, K. Wada, Y. Kitami and T. Shimohira, J. Am. Ceram. Soc. 69 (1986) 6.