Thin Solid Films 517 (2009) 5881–5887

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Titanium and zirconium hard coatings on glass substrates prepared by the sol–gel method

Paolo Zurlini [a], Andrea Lorenzi [a,b], Ilaria Alfieri [c], Guglielmina Gnappi [a,b], Angelo Montenero [a,b,*], Nicola Senin [d], Roberto Groppetti [e], Paola Fabbri [f,b]

[a] Dipartimento di Chimica G.I.A.F., Università degli Studi di Parma, viale Usberti 17/a, 43100 Parma, Italy
[b] INSTM (Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali), via Giusti 9, 50121 Firenze, Italy
[c] Dipartimento di Scienze Applicate ai Sistemi Complessi, Università Politecnica delle Marche, via Brecce Bianche, 60131 Ancona, Italy
[d] Dipartimento di Ingegneria Industriale, Università degli Studi di Perugia, Via G. Duranti 67, 06125 Perugia, Italy
[e] Dipartimento di Ingegneria Industriale, Università degli Studi di Parma, viale Usberti 181/a, 43100 Parma, Italy
[f] Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università degli Studi di Modena e Reggio Emilia, Via Vignolese, 905 41100 Modena, Italy

ARTICLE INFO

Article history:
Received 17 June 2008
Received in revised form 23 March 2009
Accepted 27 March 2009
Available online 5 April 2009

Keywords:
Sol-gel deposition
Hardness
Surface morphology
Zirconium oxide
Titanium oxide
Boron oxide

ABSTRACT

In this work innovative antiscratch sol–gel coating films deposited on a soda–lime glass substrate are examined. Sol–gel coatings of different composition (TiO_2, TiO_2/B_2O_3, ZrO_2 and ZrO_2/B_2O_3) were prepared starting from Titanium, Zirconium and Boron alkoxides and from boron oxide. Coatings were obtained at room temperature and at atmospheric pressure by dip-coating using common soda lime silicate glass slides as substrates. Densification was carried out at 550 °C for 2 h in air. The morphology of the coatings has been studied by Atomic Force Microscopy, Scanning Electron Microscopy, and with a profilometer. Roughness grows with thickness and with boron addition. The mechanical properties of the films were evaluated by micro scratch at fixed and variable load. The scratch hardness numbers of ZrO_2 and ZrO_2/B_2O_3 coatings reach 6 GPa (glass value = 1.9 GPa), whereas the best value for the critical load is 16.7 N (glass value = 9 N).

1. Introduction

The surface properties of a manufact are often determined mainly by the material and structure of its outermost atomic layers; thus, action on such layers results in great variations of surface functional behaviour. For example, the application of coatings which modify the properties of glassy substrates is an effective method to obtain materials with improved or innovative performance in terms of surface properties.

The employment of antiscratch films is a standard practice when a great resistance to wear is required; this solution is applied in cutting tools, drilling tools and biomedical prostheses. Titanium nitride (TiN) is the most commonly used in these applications, but the technologies for its deposition (physical and chemical vapour deposition) limit the diffusion of TiN and similar materials because of high costs and complexity of the required equipments. When films are considered, a good alternative is offered by the sol–gel method; coatings represent, indeed, one of the most important application of this process, thanks to the possibility to easily create solid films with various compositions, which give specific characteristics to different substrates, working at relatively low temperatures and starting from a liquid solution, with no need of complex equipments.

Sol–gel coatings have been applied to different substrates, such as ceramics, metals, polymers, glasses and alloys [1,2] showing good adherence thru choice of suitable coating composition. Literature reports the use of sol–gel coating to give optical properties like anti-reflecting, non-linear, luminescent or thermochromic.

In a recent study (end of 2006) Yamaguchi et al., [3] reported on the preparation, by sol–gel method, of thin films (100 nm) of Al_2O_3 onto plastic substrates that lower the material reflectance to 1%.

In the field of optical materials, some authors of this paper have published several studies on hybrid organic–inorganic materials showing non-linear properties, where an organic push–pull dye was covalently grafted to a siliconic network, dichroism [4] and photo-refractive gratings [5] were measured. Doping tetraethylorthosilane gels with silver nitrate and other additives, Ritzer et al. [6] have obtained glasses able to change colour with soft temperature treatment and to go back to the former state after heating over 400 °C.

Sol–gel coatings are used to protect the substrate from corrosion [7] or from mechanical stresses [8]; already in 1997 M.A. Villegas et al.,

* Corresponding author. Tel.: +39 0521 905553; fax: +39 0521 905556.
E-mail addresses: gobert501@hotmail.com (P. Zurlini), andrea.lorenzi@unipr.it (A. Lorenzi), ilaria.alfieri@alice.it (I. Alfieri), guglielmina.gnappi@unipr.it (G. Gnappi), angelo.montenero@unipr.it (A. Montenero), nsenin@unipg.it (N. Senin), roberto.groppetti@unipr.it (R. Groppetti), fabbri.paola@unimore.it (P. Fabbri).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.03.211

Table 1
Compositions of the starting sols.

Solution	Precursor	Concentration	H_2O	Solvent	Peptizer concentration
A	$Ti(iOPr)_4$	0.32 M	0.96 M	EtOH	HCl 0.2 M
B	$Zr(nOPr)_4$	0.30 M	0.60 M	iPrOH	CH_3COOH 3 M
C	$B(OEt)_3$	0.32 M	0.96 M	EtOH	HCl 0.2 M

Table 2
Precursor solutions and withdrawal speeds used for depositing thin films samples.

Components	Sample	Precursor	Molar ratio	Solvent	Withdrawal rate
TiO_2	Ti-1 sp4	$Ti(iOPr)_4$	/	EtOH	25 cm/min
TiO_2 /B_2O_3	TiB-1 sp3	$Ti(iOPr)_4 + B_2O_3$ (solid)	Ti:B = 2:1	EtOH	20 cm/min
	TiB-2 sp4				25 cm/min
	TiB-3 sp4	$Ti(iOPr)_4 + B_2O_3$ (solid)	Ti:B = 1:1	EtOH	25 cm/min
	TiB-4 sp3				20 cm/min
	TiB-5 sp4	$Ti(iOPr)_4 + B(OEt)_3$	Ti:B = 2:1	EtOH	25 cm/min
	TiB-6 sp4	$Ti(iOPr)_4 + B(OEt)_3$	Ti:B = 1:1	EtOH	25 cm/min
ZrO_2	Zr-1 sp1	$Zr(nOPr)_4$	/	iPrOH	10 cm/min
	Zr-2 sp2				15 cm/min
	Zr-3 sp3				20 cm/min
	Zr-4 sp4				25 cm/min
ZrO_2 / B_2O_3	ZrB-1 sp2	$Zr(nOPr)_4 + B_2O_3$ (solid)	Zr:B = 2:1	iPrOH	15 cm/min
	ZrB-2 sp3				20 cm/min
	ZrB-3 sp4				25 cm/min

demonstrated the possibility to protect SiC/C substrates from oxidation using a B_2O_3–SiO_2 film: it extends the protection against oxidation from 600 °C to 850 °C, by diminishing the oxidation rate of carbon fibres.

The possibility to dope materials with different cations has been applied in order to give them useful electric properties: Houng et al., [9] have obtained electrical conductivity in ZnO_2 using boron as doping agent, while Qingjiang et al., [10] have used yttrium. By sol–gel processing it is also possible to produce superconducting materials like Yttrium Barium Copper Oxide [11] and perovskites that show ferroelectric behaviour [12].

On account of its versatility, of its ease in industrial scale-up and of its low cost/surface ratio, the sol–gel method is doubtless one of the best ways to deposit films on glass.

In the present work, antiscratch films based on TiO_2, TiO_2/B_2O_3, ZrO_2 and ZrO_2/B_2O_3 were prepared and tested to protect common soda–lime glass. TiO_2 was selected because of its good adhesion to glass and its ability to form homogeneous films, notwithstanding its scratch resistance is similar to that of glass [13]. As to hardness, boron oxide could be a good candidate for antiscratch films, but B_2O_3 is soluble in water and therefore unsuitable for this application. Using the sol–gel process it has been possible to obtain mixed sols and then mixed films insoluble in water and harder than pure TiO_2. Zirconia, instead, is well known for its hardness and chemical resistance, and it has been the spearhead candidate.

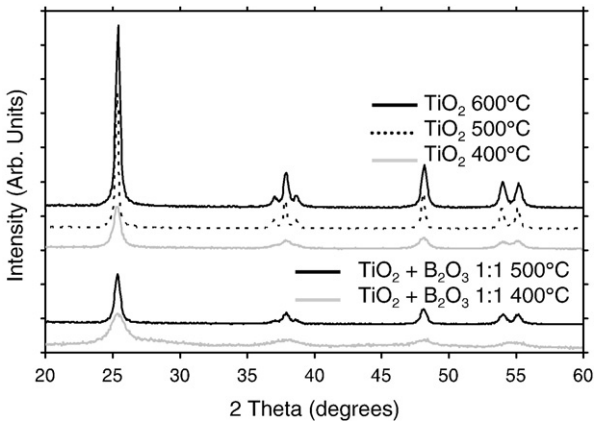

Fig. 1. XRD patterns of powders obtained from the deposition sols based on titanium and titanium–boron oxides treated at different temperatures.

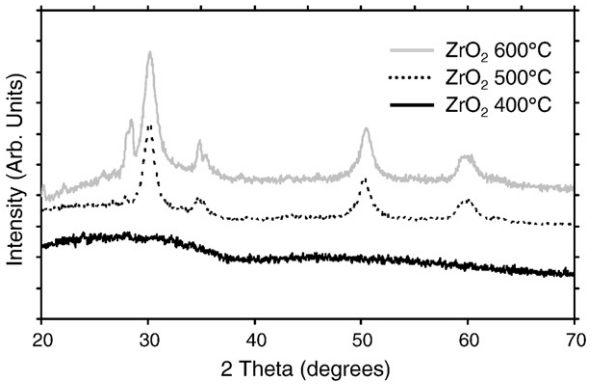

Fig. 2. XRD patterns of powders obtained from the deposition sol based on zirconium oxide treated at different temperatures.

2. Experimental details

Titanium(IV) isopropoxide (Fluka purum), and zirconium(IV) propoxide solution (Fluka 70% wt. in propanol) were used as metal oxides precursors; triethyl borate (Fluka>98%) or boron oxide (Fluka powder>98%) were used as boron sources. Deionised water was used for hydrolysis, hydrochloric acid (J.T. Baker solution 36–38%) and glacial acetic acid (Merck 100%) as peptizer, absolute ethanol (Fluka>99.8%) and isopropanol (Lab-Scan 99.8%) as solvents. Three kinds of sol were prepared: A = TiO_2, B = ZrO_2, C = B_2O_3 (using boron alkoxide). Molar ratios are reported in Table 1.

The preparation of the starting-sols was carried out in dry box because of the high reactivity of titanium and zirconium alkoxides versus water. Mixing these starting-sols, different deposition-sols were prepared (see Table 2).

The films were obtained by an automated dip coating process, using soda–lime glass as substrate. Before deposition, glasses were washed with water and acetone and dried at 80 °C. Four different withdrawal speeds were tested: 10 cm/min (sp1), 15 cm/min (sp2), 20 cm/min (sp3) and 25 cm/min (sp4). Every film was dried at 80 °C for 1 h and then calcined at 550 °C for 2 h (heating rate 100 °C/h). Starting from the sols, bulk powders were also obtained after drying and calcination: the crystalline structure of powders and coatings was analyzed by XRD (X ray diffraction) using a PHILIPS PW1050 with XPERT system THERMO ARL X'TRA with solid state detector (source: Cu kα radiation,

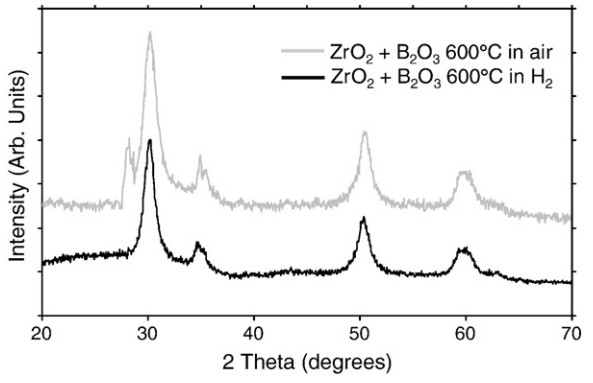

Fig. 3. XRD patterns of powders obtained from the deposition sols based on zirconium–boron oxides treated in different atmosphere.