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Determination of sodium migration in sol–gel deposited titania films on soda-lime glass with r.f. glow discharge optical emission spectroscopy

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ABSTRACT

Transparent TiO_2 films were produced via sol–gel spin and dip-coating techniques. Soda-lime glass (SLG) and SiO_2 precoated glass were used as substrates. The thin films were characterized by X-ray diffraction (XRD), X-ray reflectometry (XRR), optical profilometer and glow discharge optical emission spectroscopy (GD-OES). Na migration was detected in the amorphous TiO_2 films which are deposited on SLG substrates. In order to prevent sodium migration a barrier layer was introduced between TiO_2 film and glass. The beneficial role of this barrier layer on alkali migration is verified and the mechanism of prevention of migration is proposed relying on the results of GD-OES depth profile measurements.

1. Introduction

Titanium dioxide (TiO_2), in the anatase form, is very well known for its photocatalytic activity and used in a wide range of applications [1]. However, during the heat treatment step of the sol–gel produced titania films, migration of sodium from the soda-lime glass into the TiO_2 layer causes the formation of large band-gap brookite and sodium titanates instead of anatase which demolishes the photocatalytic efficiency [2].

Pt doped TiO_2 thin films on glass substrates were studied by Takahashi et al. [3]. In order to produce TiO_2 films, they have preheated the glass substrate to 700 °C and sprayed the sol. They have reported that the structure of the anatase film showed dependence on film thickness. Films with a thickness more than 50 nm showed a crystalline structure.

Yu et al. [4] also investigated the effect of film thickness on the grain size and photocatalytic activity. They prevented Na migration by increasing the thickness of TiO_2 layer.

Paz and Heller [5] studied sodium migration in titania films formed on SLS with XPS. Their results show that when TiO_2 film was coated on soda-lime glass, Na migration length not only exceeded the film thickness but also Na segregated at the surface of the TiO_2 film. They observed that when thicker films were made by applying two layers of TiO_2, the atomic fraction of sodium at the surface was only slightly smaller than in films made by applying a single layer. By boiling of the soda-lime glass in sulfuric acid for 30 min (referred as hydrogen glass) prior to coating TiO_2, Na migration was markedly prevented. They hypothesize that calcinations of the proton-exchanged "hydrogen glass" surface of soda-lime glass with a polymeric TiO_2 precursor produces a thin and effective sodium migration barrier.

Davies et al. [6] studied on the effect of a SiO_2 migration barrier on the migration of sodium from soda-lime glass into a fluorine doped tin oxide film. They have used SIMS depth profiling in order to detect Na migration from glass into the film. They have reported that a silica layer with a thickness of 10 ± 3 nm reduces Na concentrations in the tin oxide by two orders of magnitude, relative to that in films without the migration barrier.

Hattori et al. [7] studied on photoreactivity of sol–gel TiO_2 films produced on soda-lime glass which was precoated with a SiO_2:F layer. They have reported that the aim of doping F was the improvement of crystallinity of anatase. Their RBS measurements showed that Na migration was completely prevented by the presence of a SiO_2:F barrier layer.

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This study aims to investigate the extent of sodium migration into sol–gel produced and calcined titania films depending on film thickness and the presence of a silica interlayer with GD-OES technique. In our knowledge, until now, the detection of alkali migration is not studied with GD-OES technique. GD-OES is a mature technique for the characterization of solid samples; since it does not require any complex sample preparation. The technique has been widely used for bulk, surface and depth profile analysis of metals, oxides and semiconductor materials [8]. Radiofrequency GD-OES can perform direct elemental analysis of glasses [9]. Although the sputtering rates for glass are greatly reduced compared with conductive materials (~2 nm s^{-1} compared with 50–150 nm s^{-1} for metals), r.f. GD-OES offers good spatial depth resolution (nm) and elemental sensitivity for several applications.

2. Experimental

Titanium-based sol was prepared by stirring titanium isopropoxide, de-ionized water, propanol-2 and nitric acid (with a molar ratio of Ti $(OC_3H_7)_4$:H_2O 1:2). The sol was spin coated on soda-lime glass substrates with a speed of 1000, 2000 and 3000 rpm. Some of the samples were also coated with a sol–gel SiO_2 layer for preventing sodium migration. Titanium-based sol was dip coated on SiO_2 precoated SLS glass with different withdrawal rates in order to change film thicknesses.

The samples were fired at 500 °C for 1 h. The crystal structure of the films were determined with a Philips PW 3710 grazing incidence X-ray diffractometer using the following parameters: radiation, Cu Kα; scan range, 10–90°; scan rate, 0.02°/s; grazing incidence, 0.5°. The thicknesses of SiO_2 films were measured with Veeco Wyko NT1100 optical profilometer. The thicknesses of titanium-based films were determined with XRR method within a scan range of 0.8–2° and a scan speed of 0.005°/s. A JY 5000RF r.f GD-OES instrument (Jobin Yvon Horiba) was used for elemental depth profile analysis. The instrument was equipped with a standard 2 mm glow discharge source. The pulsed r.f. operation mode is used for the acquisition of qualitative depth profiles. The optimum sputtering conditions were determined as 480 Pa Ar pressure and 100 W power. Spectral emission lines were measured simultaneously with an acquisition rate of one point per 0.1 s.

3. Results and discussion

The thicknesses of the TiO_2 films which were produced with three different speeds on glass substrates by sol–gel spin coating technique were determined as 42, 52 and 75 nm with XRR technique (Fig. 1a). All of the coatings exhibited an X-ray amorphous behavior after firing at 500 °C for 1 h (Fig. 1b).

In order to reveal the extent of alkali migration into these films GD-OES analysis with depth profiling is utilized. Fig. 2 shows the qualitative depth profile of titania on soda-lime glass with a film thickness of 75 nm for only Na, Ti and Ca. The results clearly showed that Na and Ca diffused from glass-film interface up to the surface in all of the titania films. The amorphous structure observed can be attributed to the migration of Na ions from the glass substrate as reported by Paz and Heller [5]. Their results also showed that sodium could diffuse although the nascent TiO_2 film in an amount sufficient to prevent crystallization. However, these results did not support the conclusion of Takahashi et al. [3] who had reported thickness dependence for anatase formation. In our case, even with films thicker than 50 nm sodium migration and amorphous structure was observed. The GD-OES results obtained in this study showed that not only sodium but also calcium migrated althrough the titania films during the firing stage of the films.

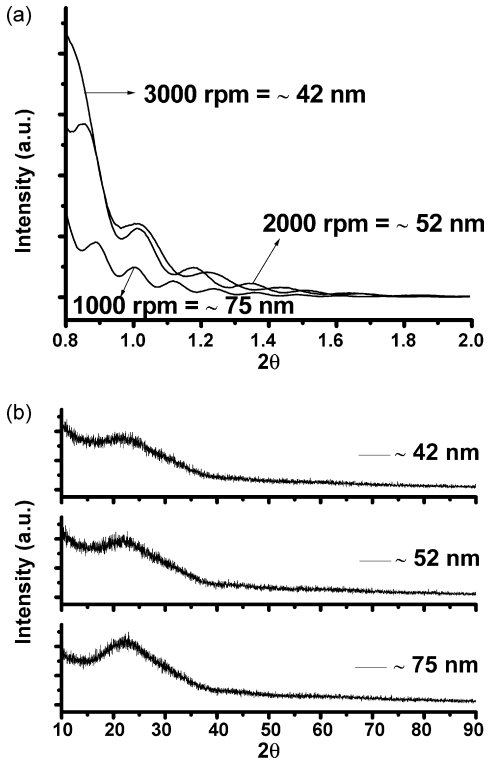

Fig. 1. (a) XRR spectra and (b) X-ray diffraction patterns of TiO_2 coatings deposited on SLG substrates by spin coating technique.

In order to have the desired anatase structure for the photocatalytically active surfaces after firing, migration of elements which promotes the amorphous structure must be prevented. In this study, a SiO_2 barrier layer was introduced between glass and TiO_2 layer as previously [10–12] suggested and the extent of Na and Ca migration within these types of structures is investigated for the first time by GD-OES depth profiling.

The glass samples after coating with silica gel were fired at 500 °C for 1 h. The thickness of SiO_2 films was determined as 100 nm (approximately) from the GD-OES craters by optical profiler (Fig. 3a and b).

The thicknesses of TiO_2 coatings deposited on SiO_2 precoated glass substrates by dip-coating technique were determined by XRR technique. The thicknesses were 30, 67, 110 nm for withdrawing rates of 1, 2.5 and 5 mm/s, respectively (Fig. 4a). The XRD patterns of all the films revealed the presence of crystalline anatase phase of

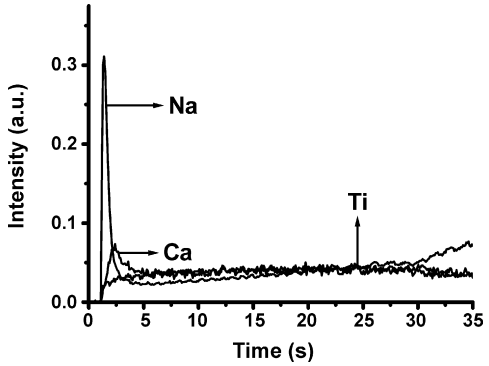

Fig. 2. Qualitative depth profile of amorphous TiO_2 film on soda-lime glass for 1000 rpm speed between 0 and 35 s for only Na, Ti and Ca.