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Structural Studies of Titanium Oxide Multilayers

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Multilayers of titanium oxide on conductive glasses (silica, covered with indium/tin and tin oxides) were obtained by different methods (from suspension, by sol–gel, by vacuum sputtering). X-ray diffraction and positron annihilation depth-resolved characterization of these samples are presented. The data allow us to determine optimal deposition parameters, in order to obtain the anatase phase, important in practical applications in photoelectrochemical cells.

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1. Introduction

Titanium oxide multilayers are used in photochromic devices [1], photochemical applications [2], photoelectrochemical cells [3], and in semiconductor devices as isolating gate material [4]. Both the thickness of TiO_2 layers and the exact phase (amorphous, low-temperature anatase or high-temperature rutile) are important in these applications.

In particular, TiO_2 nanocrystalline anatase, covered with monolayers of organic pigments allows us to achieve as high as 10% quantum yield in photoelectrochemical solar cells [5]. In such devices, TiO_2 is deposited on a glass substrate which is covered with transparent, conductive oxides, like tin-indium oxide (ITO). Recently, additional thin metallic layers separating ITO and TiO_2 are used [6].

In this paper, we report structural studies of TiO_2 layers deposited by different methods on glass and on glasses covered with conducting oxides. In the extended work [7], we have described different methods of deposition: (1) sol–gel,

(2) dc magnetron sputtering, and (3) deposition from suspensions of nanocrystalline TiO_2. This latter method, although giving nanocrystalline morphology of the TiO_2 surface, did not produce uniform layers. Sodium glasses, sodium glasses covered with tin/indium oxides, and alumina–silicate glasses covered with tin/indium oxides were used as substrates. Layers were studied by scanning electron microscopy, photoabsorption in UV and VIS range. Compositional analysis has been carried on by electron-induced X-ray emission, positron annihilation spectroscopy, and X-ray diffraction techniques. Complex multilayers were used as photocathodes in photoelectrochemical cells.

The optimal mode of preparing these mutlilayers, in order to achieve both high quantum yield of photoemission and assure a high efficiency of the charge transfer to underlying conducting layer, remains an open question. To our knowledge, the possible presence of charge trapping defects between layers has not been studied yet.

2. Samples

The main method used was the sol–gel deposition. A starting solution to obtain TiO_2 films was prepared by mixing titanium butoxide with ethanol (EtOH) in a molar ratio 1:5 and acetyloacetone (AcAc) as the complexing agent. The films were deposited by a spin-off coating technique. The resulting gel layers were dried and then heated at a chosen temperature (from 300°C to 700°C, as specified) for 1 hour in air (with a 5 hour temperature rise ramp) in order to obtain smooth homogeneous films. By repeating the above procedure we obtained double and triple layers; the thickness of a single deposition was about 150 nm.

As substrates sodium–silica glass (a typical composition is 72.6% SiO_2, 15.2% Na_2O, 0.8% B_2O_3, 1.7% Al_2O_3, 4.6% CaO, 3.6% MgO) and alumina–silica glass (55.0% SiO_2, 7.0% B_2O_3, 10.4% Al_2O_3, 21% CaO, 1.0% Na_2O) of 1.1 mm thickness were used. These glasses, already covered with ITO layers (150–300 Å for Na–Si glasses, 1200–1600 Å for Al–Si glasses) were obtained from Sigma-Aldrich. In Na–Si glasses a barrier coating of SiO_2 200–300 Å thick is placed between the glass and the ITO layer.

In the case of TiO_2 films, obtained by dc magnetron sputtering, the sodium silicate glass substrates without ITO layer were used. The sputtering was performed from metallic Ti target in a mixed Ar/O_2 atmosphere with O_2 contents of about 24–38%. The substrates were located at about 8 cm above the target. Deposition times were 60 and 120 minutes, with 140 W magnetron power applied.

3. Techniques

Structural phase analysis was performed by X-ray diffraction (XRD) technique using a PANalytical X'Pert PRO diffractometer. Conventional X-ray tube with Cu anode, operated at 45 kV and 40 mA, was used as an X-ray source.

The use of a variable-energy positron beam allows us to study depth-resolved profiles of the material down to a few micrometer deep layers [8]. A slow positron beam with an energy variable between 50 eV and 25 keV was obtained by moderating positrons from a 30 mCi ^{22}NaCl radioactive source in a 1 μm thick single-crystal tungsten foil. Details about apparatus and the measurement techniques are reported in Ref. [9].

The shape of the 511 keV annihilation line has been characterized by the S-parameter, calculated as the ratio of the counts in the central area of the peak $|511.0 - E_\gamma| \leq 0.85$ (in keV) and the total area of the peak $|511.0 - E_\gamma| \leq 4.25$ (in keV). It has been normalized to the S-value in a defect-free, high-purity silicon (the positron lifetime measured in such a sample was 220 ps).

The Doppler shape parameter was measured as a function of the positron implantation energy. The implantation depth (in Å) can be obtained from positron energy using the formula: $d = (400/\rho)E^{1.6}$ with E being the beam energy and ρ — the layer density. However, exact densities of the layers are not known. The densities for bulk materials would be 3.84 g/cm^3 for anatase, 4.26 g/cm^3 for rutile, 6.95 g/cm^3 for SnO_2, 7.18 g/cm^3 for In_2O_3. In reference to Fig. 4a, the positron mean range at 7.5 keV implantation energy would be 1400 Å for the density of 7 g/cm^3; in reference to Fig. 4b, for the density of 4 g/cm^3 the implantation energy of 2.75 keV corresponds to the depth of 500 nm. In order to determine the thickness of the layers and the positron diffusion length, VEPFIT numerical packet [10] was used.

4. Results

In Fig. 1 X-ray diffraction measurements of ITO substrate on Si–Al glass and of TiO_2 layers annealed at three temperatures are shown. The sample annealed at 300°C does not show the presence of anatase, indicating an amorphous phase of TiO_2. A similar amorphous phase is observed in samples deposited by vacuum deposition, see Fig. 2a. Both the sample annealed at 500°C and surprisingly that annealed at 700°C show the presence of anatase. However, in the latter sample a spur signal, probably due to some interlayer mixed phase arises (see Fig. 1d). The anatase phase is present also in samples deposited on SnO_2 layers, see Fig. 3a.

Positron measurements substrates, see Fig. 4a, allow us to determine the values of the S-parameter for the two glasses: it amounts to 0.515 for sodium–silica glass and about 0.48 for alumina–silica glass. In the case of the Al–Si glass, it is also possible to determine the S-parameter for the ITO layer — 0.47; in the case of Na–Si glass, the layer is too thin to be measured with positrons. The diffusion length for positrons in ITO layer is quite small — about 4 nm; the depth of ITO layer as obtained from VEPFIT deconvolutions is 140 nm in all samples.

In the case of Al–Si substrate, in positron data, we observe three well-distinct layers: all three samples (see Fig. 4b), the S-parameter converges to a similar bulk

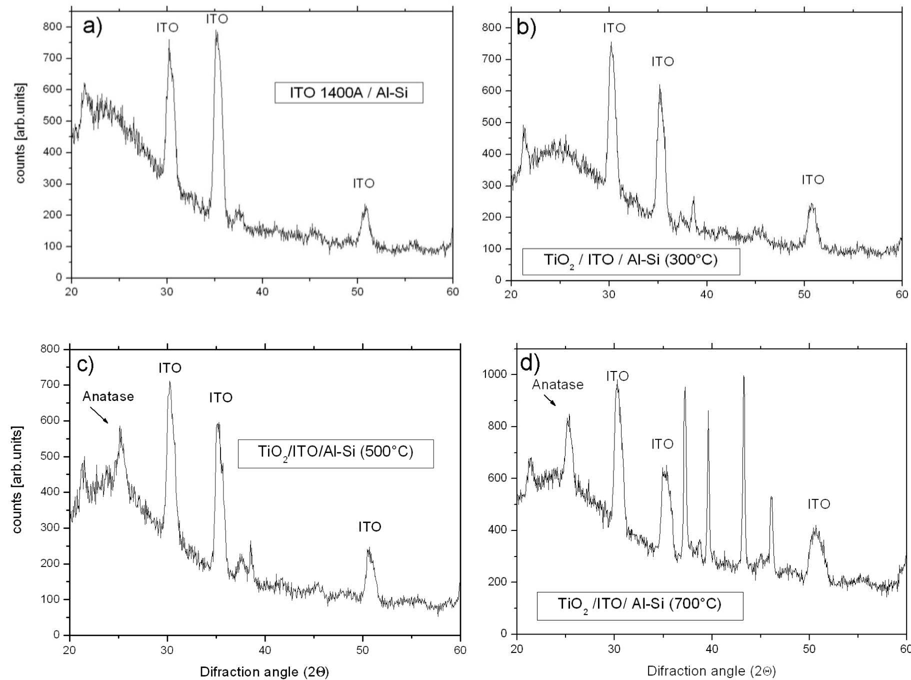

Fig. 1. XRD analysis of TiO_2 (300 nm) / ITO (140 nm) layers on alumina–silica glasses. Peaks due to the anatase phase are well visible for sample annealed at 500°C (c) and 700°C (d) but not for the sample annealed at 300°C (b). XRD of sample annealed at 700°C (d) shows additional, no-identified peaks, probably due to the mixing between the substrate glass and the ITO layer. XRD spectrum of solely ITO layer without TiO_2 is shown for comparison (a).

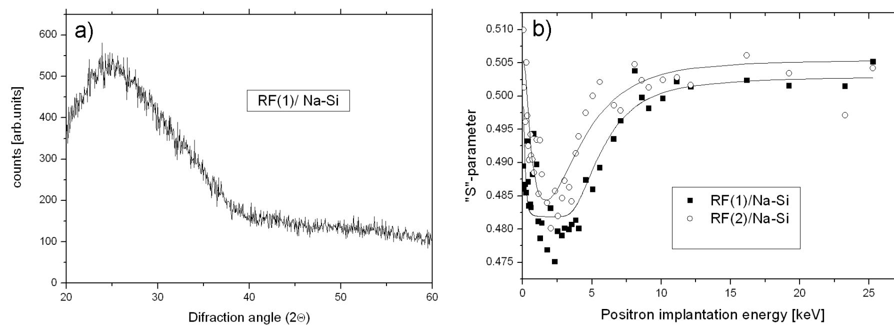

Fig. 2. X-ray diffraction (a) and positron-annihilation S-parameter (b) by TiO_2 samples deposited on Na–Si glass (without conducting oxide layer) by dc magnetron sputtering (the expected thickness of the layer is about 200 nm for sample no. 2 and 500 nm for sample no. 1).

S-value, characteristic of the Al–Si glass. Minima in S curves in Fig. 4b for the samples heated at 300°C and 700°C are shifted to higher energies than that of 500°C sample, indicating a thinner layer and/or lower density of TiO_2 phase in the latter sample. On the other hand, the minimum for the 700°C-sample is deeper, close to the value of pure ITO, and indicating *lowered* diffusion of positrons between TiO_2 and ITO layers.

The S values for TiO_2 layers for samples in Fig. 4b fall from 0.495 in 300°C sample to 0.458 in 500°C and 0.467 in 700°C sample. This continuous lowering of the S-parameter would indicate a continuous change of the structure, towards a more compact one (from amorphous to anatase and rutile). The positron dif-

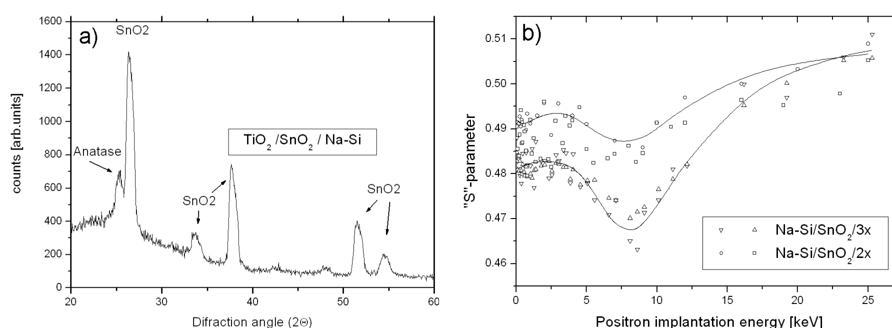

Fig. 3. X-ray diffraction (a) and positron-annihilation S-parameter (b) by sol–gel technique on SnO_2-coated sodium–silica glasses (a triple layer in (a) and a double and a triple layer of TiO_2 in (b)).

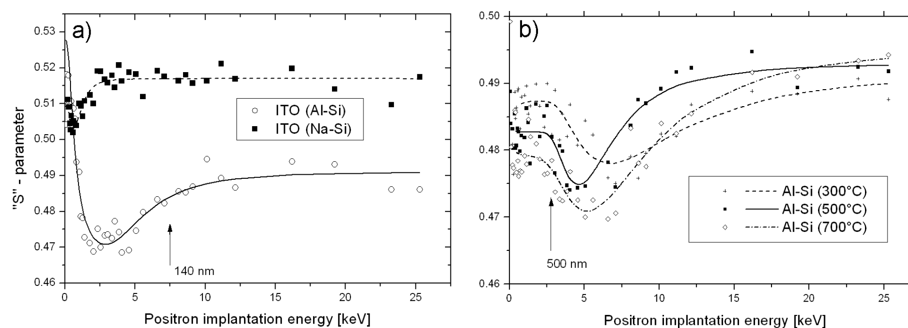

Fig. 4. Positron-annihilation S-parameter dependence on positron implantation energy for samples deposited by sol–gel technique on Sigma-Aldrich ITO-coated glasses. (a) S-parameter for "as-received glasses" — allowing to determine characteristic S for the glass substrate and ITO layer. (b) Double TiO_2 layers on alumina-silicate glasses, annealed at different temperatures. The arrow in (a) corresponds to the mean range of positrons of 140 nm, as calculated for the layer density of 7 g/cm^3; in (b) — to the depth of 500 nm, as calculated for 4 g/cm^3.

fusion length in TiO_2 layers is high, 140 nm for the 300°C sample and about 45 nm in 500°C and 700°C samples. This high diffusion length explains the high effectiveness of charge transfer from TiO_2 to ITO, indispensable for photovoltaic processes.

Layers deposited on SnO_2 show similar S-parameters to those deposited on ITO (cf. Fig. 3b). Layers deposited by sputtering of Ti in O_2 atmosphere are different, as seen by positrons, from all other samples, showing a high value of S-parameter on surface. This would indicate the presence of numerous trapping centers.

In conclusion, both the presence and different types of TiO_2 phases can be traced by positron-depth resolved annihilation and XRD techniques. Well--defined layers, of anatase on ITO, not intermixed with substrate, give the best photoelctrochemical performance [7].

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