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Full Length Article

Vectorial method used to monitor an evolving system: Titanium oxide thin films under UV illumination

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ABSTRACT

Under *in situ* UV illumination, some materials present evolution of their opto-electronic properties that can be monitored by spectroscopy. We present here a mathematical method which can be applied to spectroscopic measurements when an evolving set of data is recorded: the vectorial method. The investigations and quantifications are performed by Infrared spectroscopy and XPS on organic-inorganic thin films prepared by sol-gel. The inorganic part of these hybrid thin films contains Ti oxide-network based whereas the organic part is composed of N,N-dimethylformamide and its hydrolysis products. Under UV illumination, those films exhibit intermediate bandgap behavior due to the photoreduction of Ti(IV) in Ti (III). The role of the solvent in the thin film is underlined during the process of photoreduction together with an understanding of the condensation of the Ti oxide-based network, as these evolutions are critical for the opto-electronic properties of those thin films.

1. Introduction

Over the last decade, a new generation of solar cell was intensively described in the literature. This third generation aims at overpassing the Shockley-Queisser theoretical limit of efficiency conversion which is 31% for a single junction solar cell [1]. Several solutions were proposed such as quantum dot solar cells, tandem solar cells, up and down conversion solar cells and intermediate band solar cells. The later concept was first described by Luque and Marti [2] and consists in introducing an intermediate level in the bandgap of the absorber material. Thanks to this intermediate band, the absorption range becomes wider, due to new absorption processes (valence band-intermediate band and intermediate band-conduction band). Several investigations were performed to identify materials presenting this feature. Among those materials, one hybrid sol-gel, based on titanium oxide, presents some interesting characteristics and was already described in the literature [3–6]. Under UV illumination, an intermediate band appears inside the band gap, in a reversible way, related to the reduction of Ti(IV) to Ti(III), the different Ti oxidation degrees present in the film. Photons with energy at least equal to the band-gap leads to the generation of a hole-electron pair. Since the bottom of Ti oxide conduction band mainly consists in 3d orbitals of the cation, the photogenerated electron stabilizes one of the T_{2g} orbital. This feature is associated with the appearance of a level below the conduction band [7]. However, this is associated to modifications in the organic and inorganic parts of the sol-gel. To evaluate this impact, we decided to follow the progress of the changes via two spectroscopic experiments on hybrid thin films prepared from aged-sols. First, the evolution of the organic part was measured via Infrared analysis under *in situ* UV illumination. Secondly, a similar experiment was run (*in situ* UV illumination) in XPS, in order to understand how the inorganic part of the Ti-oxide network is impacted by the intermediate band appearance. In order to go further in the analytical process we undertook an innovative method of treatment: the vectorial method. This mathematical method was first described in 2015, by Baltrusaitis et al. [8] and then successfully applied to graphite supported copper nanoparticles [9]. Thanks to this method, it is possible to obtain information without any *a priori* prerequisite in a set of evolving data and to mathematically create spectra which were not experimentally reachable. The principle is to extract mathematical vectors with a physical meaning that can reproduce a whole set of data, through linear combinations of the mathematical vectors. The latter have to be identified in a full set of vectors from a weighted difference between two experimental spectra denoted S_i and S_f (Fig. 1) presenting an evolution (S_i and S_f stand for initial and final spectra). Actually, among those vectors, for defined weighted factors α and β, it is possible to find two vectors such as A and B in Fig. 1

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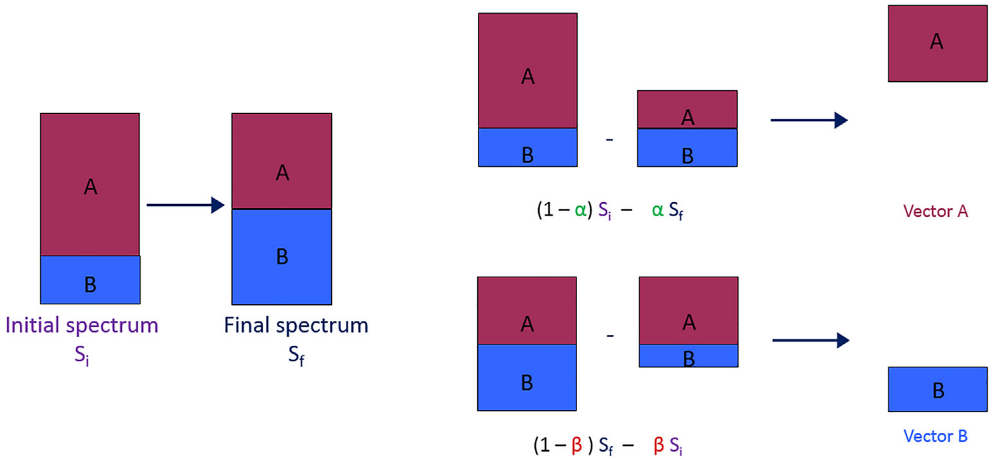

Fig. 1. Schematic view of the vectorial method processing.

which, once linearly combined together, will account for all the experimental set of data. Picking the different vectors requires logic. Indeed, vectors should present coherent spectroscopic evolutions (only positive bands or peaks) and information (existing bands or peaks).

This paper deals with the vectorial method applied to hybrid organic-inorganic films evolving under UV illumination to quantify changes in the inorganic and organic parts of thin films. The vectorial method was so far applied to XPS data only, however, here, we report that it can also successfully be applied to Infrared spectroscopy.

2. Material and methods

2.1. Synthesis

The mechanism of titanium oxide sol and gel (hereafter denoted TiDMF) formation was already detailed in previous studies [3,5]. In a typical experiment, the hybrid organic-inorganic sol is prepared by adding 12 mL of N,N-dimethylformamide (DMF, Carlo Erba, synthesis grade) drop by drop to 5 mL of ice-cooled $TiOCl_2.1.4HCl.7H_2O$ (4.85 mol L^{-1} in titanium, Millennium Chemicals) solution to reach a concentration of 1.42 mol L^{-1}. The reaction mixture is then heated at 70 °C for 20 hours until a viscous and transparent aged-sol is obtained. The advancement of the reaction is monitored by Raman diffusion, until 3.4 DMF per Titanium were hydrolyzed as dimethylammonium chloride (DMACl) and methanoic acid (HCOOH). This equilibrium value originates from the composition of the titanium oxychloride. The aged-sol is then redispersed in the solvent to reduce the viscosity (typically 2 mL of aged-sol in 6 mL of DMF) in order to manage the thickness of the films.

2.2. Films preparation

Films were prepared by spin coating on reflective p-doped silicon for Infra-Red analysis in diffuse reflection mode and UV transparent glass substrates for *in situ* XPS analysis to allow illumination from the bottom side (cf XPS experimental description). After ultrasonication for 5 min with deionized water (removal of dust), ethanol (removal of grease) and isopropanol (pre-treatment for UV-ozone) respectively, substrates are treated under UV-ozone for 10 min to improve wettability of TiDMF aged-sol. Thicknesses of 1 μm were reached by spin coating TiDMF sol, by using the following program: 2 min 3000 rpm and 2 min 4000 rpm. Thicknesses were controlled using a profilometer Dektak 8 (Bruker Nano).

2.3. Infrared analysis

Infrared measurements were performed on a Fourier Transform spectrometer Bruker Vertex 70, using a Praying Mantis diffuse reflection setup to collect diffuse reflectance spectra. Moreover, to control the environment around the samples, they were set in a Harrick HVC accessory under different atmospheres (ambient, dry and secondary vacuum of 5×10^{-4} Pa), for an equilibrium time of 30 min minimum. The chamber was equipped with three optical windows: two infrared transparent windows to allow collecting the Infrared excitation and the Infrared reflectance signals and the third visible transparent silica window to allow *in situ* continuous UV illumination (led emitting at 365 nm). Infrared spectral measurements were recorded every five minutes for the first 30 min, then every 10 min. We recorded the infrared spectra of samples without any mixing with another non-infrared-absorbent matrix allowing us to avoid any surface modifications. A DTHS detector and a KBr beam splitter in the Michelson interferometer were used for both spectral ranges NIR (8000–4000 cm^{-1}) and MIR (4000–400 cm^{-1}). For each sample, at least 20 scans with a spectral resolution of 4 cm^{-1} were recorded. The sample spectra obtained by this technique are presented in this work as the result of the subtraction of the original spectrum and that of a reference. The pseudo absorbance is plotted as log (R_{sample}/R_{ref}) where R_{sample} and R_{ref} are respectively the diffuse single-beam reflectance of the sample and the reflectance reference.

2.4. XPS analysis

XPS measurements were performed on a Kratos Axis Ultra and on a Kratos Axis Nova spectrophotometers using a monochromatic Al Kα source 1486.6 eV operating at 150 W, with charge neutralizer. Survey spectra were recorded at a pass energy of 160 eV corresponding to an all over instrument resolution measured on Silver Fermi edge of 1.95 eV and a step of 1 eV from -5 to 1350 eV. High resolution spectra of O 1 s, Ti 2p, N 1 s, C 1 s, and Cl 2p core levels were recorded with an all over instrument resolution measured on Silver Fermi of 0.53 eV and a step of 0.1 eV at a pass energy of 40 eV. To perform the *in situ* illumination, samples of TiDMF were placed on a dedicated sample holder with an incorporated UV led (emitting at 375 nm with a 3.2 mW cm^{-2} power density) [6]. The bottom side of the films are illuminated through a UV transparent substrate. Calibrations were performed on Cl 2p3/2 peak (197.9 eV) since it is the only peak which does not present any position evolutions during illumination, with only one chloride chemical environment for all measurements. All spectra were fit-