Flexible fluorine-doped tin oxide based composite electrodes for photovoltaic applications

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ABSTRACT

Fluorine-doped tin oxide (FTO) thin films have been deposited by spray pyrolysis on flexible substrate showing both promising electro-optical and mechanical properties. In parallel, FTO layers have also been grown under the same conditions on three-dimensional substrate made of glass on which spin coated zinc oxide nanoparticles were deposited in order to fabricate diffuse FTO thin films. At an optimal nanoparticle surface density, the FTO layer exhibits a haze factor averaging 72% over the visible range owing to cauliflower-like structres as revealed by secondary electron microscopy. The electro-optical properties were not found to degrade significantly as compared with growth on a bare glass substrate. A sheet resistance of 10.5 Ω/sq combined with an average total transmittance of 76% in the visible range, substrate included, were obtained. The aim of this study is to eventually fabricate flexible diffuse transparent electrodes for photovoltaic applications.

Keywords: transparent conductor, spray pyrolysis, flexible substrate, haze factor, tin oxide

1 INTRODUCTION

Transparent Conductive Oxide (TCO) thin films combining high electrical conductivity and optical transparency are an integral part of many optoelectronic devices and in particular, thin film solar cells where they are used as a front electrode. Their electro-optical properties play a decisive role for the device efficiency. In the case of solar cells, increasing the optical path length of incoming light via light trapping or diffuse scattering, plays an important role for the device performances [1][2]. Such a scheme can be achieved by high haze factor fluorine-doped tin oxide (FTO) electrodes as shown in Ref. [3] using nanopatterning or in Ref. [4] using wet chemical etching. The amount of light scattered can be evaluated by calculating the haze factor which is defined as the diffuse transmittance over the total transmittance. Furthermore, these electrodes (hazy or not) are usually made on glass which makes the resulting device non flexible. Yet, the need for flexible electronics is growing stronger. Therefore, flexible TCO thin films are attracting significant interest since they are light weight, low cost and amendable to high throughput manufacturing. Hence, this study is motivated by the need for fabricating high quality flexible and rigid high haze factor front electrodes for solar cell applications. The originality of the work is that such electrodes are obtained without using techniques such as nanopatterning, wet chemical etching or vacuum deposition techniques.

2 EXPERIMENTAL

FTO thin films were deposited by ultrasonic spray pyrolysis directly under atmospheric pressure on polyimide (PI) DuPont© Kapton® polyimide flexible substrates and glass substrates (Corning C1737). These samples will be referred to FTO/PI. The FTO growth was performed at 400°C from a precursor solution with the following concentrations: 0.16 M tin chloride pentahydrate 98% (Sigma-Aldrich) and 0.04 M ammonium fluoride 98% (Sigma-Aldrich) dissolved in methanol. As for the high haze factor electrode, an additional step was undertaken to fabricate a nanostructured three-dimensional substrate: zinc oxide (ZnO) nanoparticles (NPs) (Sigma-Aldrich) of 100 nm diameter at most were spin coated on a Corning 1737 glass acting as a three-dimensional substrate. ZnO NPs were suspended in isopropyl alcohol with a concentration set to 1 wt.%. The volume of the solution used for deposition was varied (from 0.1 to 0.6 mL) in order to change the NP surface density. Then, FTO layers were deposited on top using the same experimental conditions mentioned above except the growth temperature which was set to 420°C. These specimens will be referred to FTO/ZnO NPs. A control sample initially consiting of a bare glass substrate was systematically used as a benchmark. The morphology of the resulting structures was investigated by scanning electron microscopy (SEM) imaging recorded with an FEI Quanta 250 Plus equipment. The root mean square roughness of the different layers was derived by using an atomic force microscope (AFM) (Veeco - Dimension 3100). The electro-optical properties were studied with a four-point probe and Perkin-Elmer Lambda 950 spectrophotometer fitted with an integrating sphere. At last, mechanical property data were collected using a homemade automated bench.

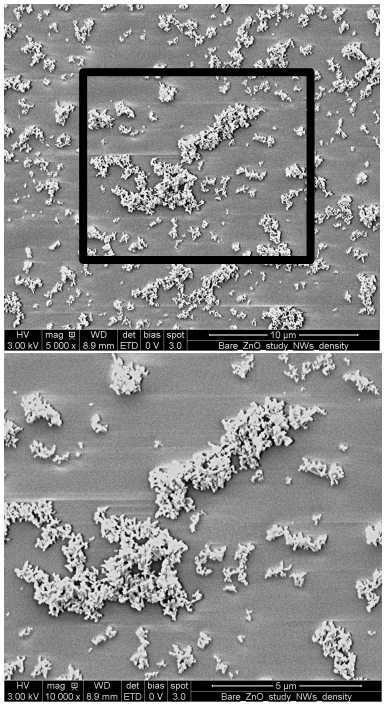

Figure 1: SEM micrographs of spin coated ZnO NPs (0.4 mL, 1 wt.%) on a Corning glass substrate (top). A higher magnification micrograph from the area delimited by the black rectangle is also shown (bottom).

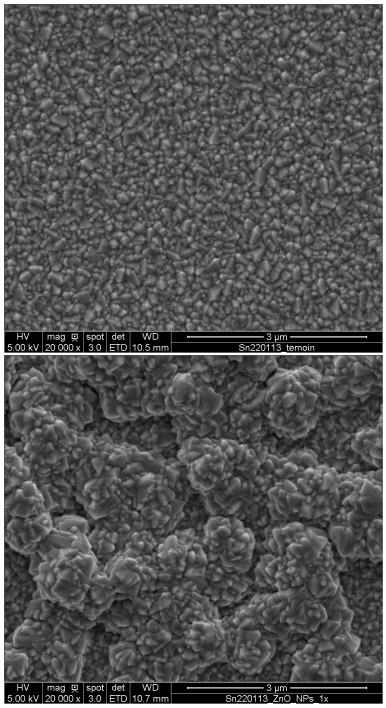

Figure 2: SEM micrographs of the control FTO thin film on a bare glass substrate (top) and the FTO coated ZnO NPs (0.4 mL, 1 wt.%) on a glass substrate (bottom).

3 RESULTS AND DISCUSSIONS

3.1 Structural properties of FTO/PI

FTO films were grown on PI substrates by spray pyrolsyis and exhibited polycrystalline cassiterite structure. They become more textured as the film thickness increases as also observed on glass in Ref. [5]. The texture coefficient determined by the Harris method [5] was indeed observed to increase from 0.5 to 1 as the film thickness changed from 215 to 480 nm. This was associated with an increase in the root mean square (RMS) surface roughness from 10.5 to 19.2 nm as measured by AFM [6]. The value of the surface roughness is to be taken into account when fabricating diffuse thin films for both device integration and interpretation of light scattering.

3.2 Structural properties of FTO/ZnO NPs

In order to test our process, different volumes of ZnO NPs were spin coated on glass substrates to effectively get a three-dimensional substrate: 0.1, 0.4 and 0.6 mL. Fig. 1 shows the surface morphology obtained after spin coating 0.4 mL of solution.

The ZnO NPS tend to form small (a few hundreds of nanometres) to large aggregates of a few microns introducing a wide variety structure sizes and shapes. Since the FTO coating involves a high temperature stage of 420°C for about 30 min, it was verified that no morphological change (such as further aggregation) occurs after annealing in air for 30 minutes at 420°C. This was the case on glass substrate and we believe this would be similar on polymer materials as well due to their similar thermal conductivity and roughness.

After deposition of ZnO NPs, the surface morphology of the FTO thin film changed dramatically from a rather smooth pyramid-like (Fig. 1, top) surface morphology to a much rougher one involving the very surface morphology but over cauliflower-like structures as observed in Fig. 1 (bottom). Such structures have already been evidenced by Hongsingthong et al. [7] but with ZnO grown on textured etched glass.

This observed diversity in terms of size and shape of the structures accounts for the large haze factor demonstrated by this type of electrode over the visible and the near infrared range. This can also be appreciated by cross-sectional SEM imaging as illustrated in Fig. 3.

The FTO layer is about 300 nm thick and is very conformal. The resulting RMS roughness increases up to 135 nm as compared with the one of the control glass on bare glass (16 nm).

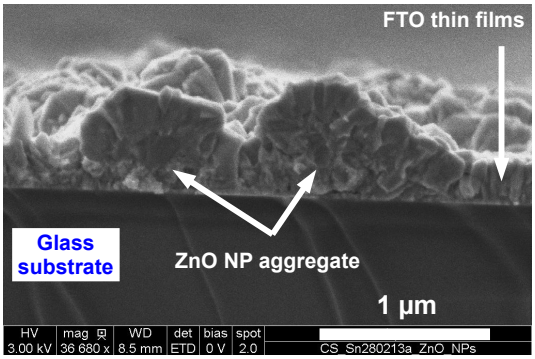

Figure 3: Cross sectional SEM micrographs of a FTO/ZnO NPs (0.4 mL, 1 wt.%) on a Corning glass substrate.

3.3 Electro-optical properties of FTO/PI

The obtained FTO electro-optical properties on the flexible substrate are found already compatible with some electronic applications. In a previous study [6], the best compromise in terms of physical properties was found for the FTO films deposited on PI at 400°C for a film thickness of 215 nm; the latter exhibited a low electrical resistivity of 7.7×10^{-4} Ω cm combined with a total transmittance up to 80% for wavelength larger than 780 nm.

3.4 Electro-optical properties of FTO/ZnO NPs

In parallel, ZnO NPs nanostructured glass substrate with various ZnO NP surface densities were fabricated. Transmittance spectra were collected before and after the FTO coating (see Fig. 4). A FTO layer grown on a bare glass substrate is also given for reference purpose only.

In this study, the haze factor of ZnO NPs dispersed on glass is ranging from to 7.5 to 26.1 at 550 nm. But after coating them with a 300 nm FTO layer, this very same factor is correspondingly increased by a factor of 8 to 3 at 550 nm. Even if this point requires further study, we believe that the different pyramid-like structures orientated in multiple directions over the cauliflower-like structures might play a role.

Moreover, after FTO coating, the total transmittance in the visible range is only slighlty degraded for the 0.1 and 0.4 mL spin coated ZnO NP solutions while the haze factor is greatly enhanced (from a few percent to over 60%) as compared with the FTO deposited on bare glass (control sample). Interestingly as well, the sheet resistance varied very little between the control sample and the high haze factor thin film incorporating ZnO NPs. Only for the highest surface coverage of ZnO NPs (corresponding to the use of 0.6 mL of solution)

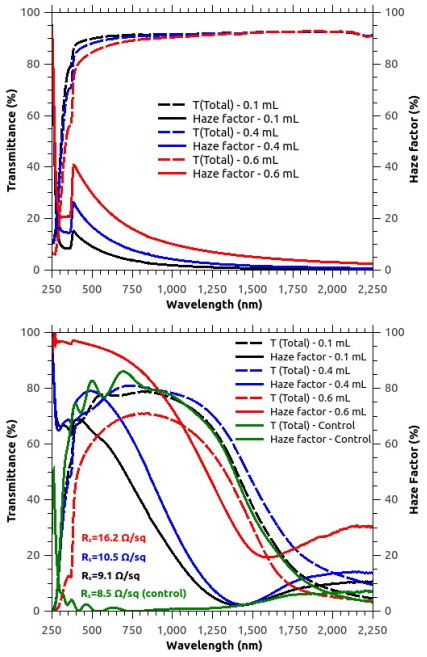

Figure 4: Total transmittance spectra of 0.1, 0.4 and 0.6 mL (1 wt.%) spin coated ZnO NP solutions (top) and the corresponding spectra of FTO/ZnO NP specimens (bottom). The contribution of the substrate is included in each case.

did the total transmittance decrease by about 10% in the visible range while the sheet resistance nearly doubled. Table 1 gives a summary of the results obtained.

The light scattering ability of a TCO is determined by the feature sizes and shapes of the TCO surface. In each samples, higher haze is observed at the shorter wavelengths. This indicates that the short-wavelength light scatters more efficiently since the wavelength of the light in the layers becomes comparable to the surface roughness as well to the average grain size estimated to be 100 nm based on the SEM micrographs for all the films grown in this study since the growth parameters were kept constant. Based on Table 1, the specimen consisting of 0.4 mL of spin coated ZnO NP solution subsequently coated with FTO is considered to be the optimal one regarding the structural and electro-optical properties.

3.5 Mechanical properties of FTO/PI

The stability of the thin film electrode properties under mechanical bending tests was assessed by measuring the electrical resistance as defined by $R(n)/R_0$ versus the number of bending cycles via an automated mechanical bench. R_0 is the initial resistance and R(n) is the electrical resistance measured after n bending cycles. The radius of curvature was set to 3.5 mm. For a film thickness of 330 nm, thick film demonstrates a

Table 1: Structural and electro-optical properties of standard and diffuse FTO transparent electrodes prepared in this study. The FTO layers is about 300 nm thick in each case. "Volume" refers to the volume of spin coated ZnO NP solution, R_s to the sheet resistance, HF to the haze factor and T(550 nm) to the total transmittance taken at 550 nm.

Volume (mL)	R_s (Ω/sq)	HF (550 nm) (%)	T(550 nm) (%)	RMS roughness (nm)
0.1	9.1	61.7	77.6	116
0.4	**10.5**	**77.7**	**74.2**	**135**
0.6	16.2	94.8	62.9	189
Control specimen	8.5	1.2	78.2	16

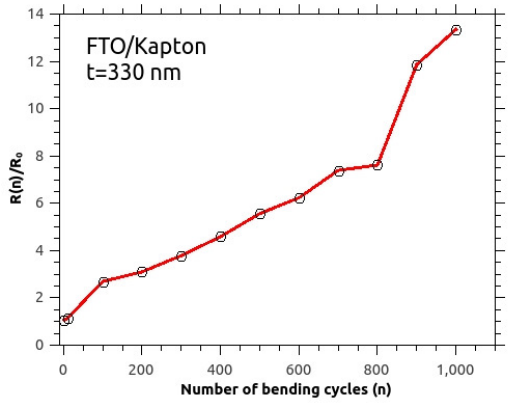

Figure 5: $R(n)/R_0$ versus the number of bending cycles (n) for a 330 nm thick FTO/PI. The growth temperature was kept constant at 400°C.

good resistance to fatigue (see Fig. 5) given the small chosen radius of curvature while exhibiting the following physical properties: ρ=5.6x10^{-4} Ω cm and a total transmittance at 780 nm of 73.6% [6]. Enhancing the haze factor for this type of electrode might be extremely beneficial for fabricating high efficiency flexible DSSCs even for total transmittance values in this range.

3.6 Device integration of the FTO/ZnO NP electrodes

The optimal fabricated electrodes (0.4 mL spin coated ZnO NP solution) were included in operating Dye-sensitized solar cells (DSSCs). As a result, the conversion efficiency of the DSSCs was enhanced from 4.3% to 6.5%. Let us note here that this improvement is the results from the measurements of 8 different DSSCs. A similar results has been achieved by C-H. Tsai et al. [8] using textured FTO electrodes in DSSCs. Meanwhile, the maximum power has been increased from 1.09 to 1.66 mW/cm^2.

4 CONCLUSIONS AND PERSPECTIVES

In this contribution, we are proposed an original approach to fabricate flexible and diffuse transparent electrodes for photovoltaic applications. Spin coated ZnO NPs on glass were subsequently coated by an FTO layer grown by spray pyrolysis. This enabled the fabrication of transparent electrode with a haze factor averaging 72% while keeping an average total transmittance of 76% over the visible range. The electrical properties were found to be minimally affected except at very high ZnO NP densities. We are expecting high haze factor transparent electrodes to play a major role in the years to come for second and third generation solar cells.

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