Spin – coating of SnO₂ thin films

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Abstract. The functional characteristics of thin film planar solar cells are very sensitive to the presence of pores, voids or holes. Thus deposition of compact, dense and uniform layers is essential in that technology. These issues are especially important in organometallic perovskite solar cells where the active layers are in the nano metric scale. In this emerging technology the reduction of cost-efficiency ratio is a serious barrier for commercialization. In this work we have investigated different parameters of the process of deposition of SnO₂ thin films by spin coatings which influence its compactness and impenetrability. Influences of the thermal treatments on the properties of the films were investigated by UV – vis spectrometry, X-ray diffractometry (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy AFM), X-Ray Photo-electron spectroscopy (XPS) and Spectral Elipsometry (SE). Finally the coverage ability of the SnO₂ films was checked by Cyclic Voltammetry (CV) in aqueous redox solution.

1. Introduction

Organometallic perovskite photovoltaics rival chalcopyrites and silicon based devices and appears to be most promising technology for planar thin film solar cells on flexible substrates. Currently, the record efficiency for perovskite solar cells jumped over 23% [1, 2] and there is still some gain to achieve by further optimization of materials properties [2], processing or interface engineering [3]. The most popular electron selective layer (ESL) in these devices is the meso-porous TiO₂ owing to its good photoelectric properties [4]. However, the electron mobility of TiO₂ is far below the mobility of commonly used hole – transport layers (HTL) resulting in accumulation of charge at the interface and decrease of efficiency [5]. Recently, a more prospective candidate to replace TiO₂ was presented, SnO₂ having higher electron mobility and better match to the energy levels of organometallic perovskite, yielding solar cells with efficiencies of up to 21 % [6, 7].

In the present work we report the application of the spin coating method for deposition of dense, voids – free SnO₂ thin films and investigation of its properties in order to apply it as electron selective layer in organometallic perovskite solar cells (PSC).
2. Experimental
Solutions of SnCl₄·5H₂O (Acros organics) in concentrations 0.05 or 0.2 M in Isopropyl alcohol – (IPA Macron®) were used for spin coating of the films onto quartz substrates, polished monocrystalline Silicon wafers or glass substrates, covered by conductive TiO₂/Pt/TiO₂ sandwich layer. Working volume was 40 μl, dispensed onto the rotating sample with a size of 15mm x 20 mm for 30 s at rotation speed 3500 min⁻¹. The reaction of formation of the desired films is:

\[
\text{SnCl}_4\cdot5\text{H}_2\text{O} \rightarrow \text{SnO}_2 + 4\text{HCl}↑ + 3\text{H}_2\text{O}↑
\]  

(1)

XPS analyses were performed on a Kratos AXIS Supra spectrometer with an un-monochromatic Al X-ray source under the vacuum better than 10⁻⁶ Pa at 90 degree take-off angle. All the spectra have been charge-corrected by taking C1s peak (Binding Energy (BE) = 285.0 eV) as reference. Film thickness, spectral distribution of the refractive index and the extinction coefficient were measured on an automatic spectroscopic ellipsometer - M2000D, Woollam (Santa Barbara, CA). Diffractometer Rigacu Ultima IV with Cu Kα radiation (λ = 1.5418 Å) at 40 kV accelerating voltage was used in steps 0.01° for 2 s in an angular range 10 to 80° 2θ. Atomic Force Microscopy (AFM) was performed by “Easyscan 2” (Nanosurf®) TAP 190 – Al G. Optical spectroscopy was carried out on UV – VIS – NIR spectrometer JASCO – V 670 in the range 190 - 1500 nm. Cyclic voltammetry (CV) analysis was done in a three electrode configuration in dark. The SnO₂ working electrode was positioned in the back side of the cell squeezed against round window (diameter 4.5 mm) to define equal and constant active surface. Pair of platinum wires were used as electrodes - counter and reference (redox), respectively. The redox electrolyte was 1mM K₃Fe(CN)₆+ 1mM K₄Fe(CN)₆ in aqueous 0.5 M KCl, intensively purged with nitrogen to remove dissolved oxygen. The potentials are referred versus redox potential of the solution, estimated as E_{redox} = 0.280 V (vs AgCl/3M KCl).

3. Results and discussion

3.1. Deposition
The as deposited films were dried at 100 °C for 1 hour and afterwards have been annealed at temperatures 120 °C, 140 °C, 160 °C and 180 °C. To form thick layers the deposition was repeated several times followed in every case of drying and annealing in related temperature. Thickness measurements of the layers were carried out by ellipsometric measurements. Figure 1 presents the final thickness of the layers depending on the number of spin coated films. In the limits of the error it is seen that every succeeding film adds about 5 nm to the common structure.

![Figure 1](image.png)

Figure 1. Dependence of layers’ thickness on number of deposited films, annealed at 140 °C for 1 hour.

3.1.1 XPS analysis
XPS analysis data of an SnO₂ film deposited from solution of 0.05 M Sn⁴⁺ in IPA and annealed at
140 °C in air are presented on figure 2. XPS survey scan in figure 2a represent detected emission signals from tin, oxygen, carbon and trace amounts of chlorine and platinum respectively from the surface of the SnO2 sample. The presence of minor quantity of Pt obviously originates from the substrate.

Figure 2. XPS analysis of SnO2 thin film, annealed at 140 °C: a – survey; b – Sn 3d5/2 core level; c – O 1s core level.

Figure 2b shows the Sn 3d5/2 core level peak which is symmetric and centered at Binding Energy (BE) 487.1 eV corresponding to Sn4+ ionic state bounded by oxygen as a SnO2 compound in the investigated samples [8, 9, 10]. Figure 2c represents the O1s core level spectrum which is asymmetric. The spectrum was deconvoluted using Lorentzian-Gaussian (pseudo-Voigt function) fitting analysis. In the O1s core level spectrum, the peak at BE of 530.1 eV is ascribed to Me-O [11, 12], the peak at BE of 531.1 eV is ascribed to the oxygen deficient region i.e. oxygen vacancies (Vo) [11, 12] and the peak at BE of 531.8 eV is ascribed to the surface hydroxyl groups, which are connected to the surface contaminations [11].

3.2. Structural properties

Figure 3 shows the XRD patterns of SnO2 films with different thickness, deposited on polished Si monocrystalline substrates and annealed at 120 °C for 1 hour.

Figure 3. a - XRD patterns of thin films SnO2, annealed at temperature 120 °C with different thickness: 1 – 5 nm; 2 – 10 nm; 3 – 15 nm; 4 – 20 nm. b - Pattern between 32 ÷ 34 degrees 2θ for distinction of reflexes of Si (200) and SnO2 (101).

Besides the reflexes of the substrate Si (111), Si (200) and Si (220) peaks indexed as planes (002), (220) for tetragonal SnO2 are seen [13]. Detailed analysis of the patterns revealed twinning of the reflex at 33 ° angle 2θ. First of them, at 33.04 °, could be attributed to the substrate Si (200) [14,15,16] and the second one, at 33.12 ° should be attributed to the (101) plane reflex from SnO2. The results are close to the observations reported in [17] for similar SnO2 thin films.
3.3. Optical properties

![Graph showing total transmittance spectra of bare quartz substrate and 2, 3, and 4 SnO<sub>2</sub> thin films sequence deposited onto the same quartz substrate and annealed at 180 °C. The inset shows corresponding bandgap determination on a Tauc plot.]

Figure 4. Total transmittance spectra of bare quartz substrate and 2, 3, and 4 SnO<sub>2</sub> thin films sequence deposited onto the same quartz substrate and annealed at 180 °C. The inset shows corresponding bandgap determination on a Tauc plot.

Figure 4 presents total transmittance spectra from bare quartz substrate and quartz substrate covered with 2, 3, and 4 SnO<sub>2</sub> thin films annealed at 180 °C. We deposited SnO<sub>2</sub> thin film onto quartz substrate due to needs of transparency in the SnO<sub>2</sub> absorption edge region. Presented deposited SnO<sub>2</sub> thin film demonstrated a high optical transparency, with an average transmittance around 90 % in the visible range (400–800 nm), which indicates their applicability in transparent electronics. The absence of interference fringes on the spectrum of the film shows that it is extremely thin. The corresponding optical direct bandgap energy of all deposited SnO<sub>2</sub> thin film was calculated after taken into consideration the reflectivity, absorption coefficient, and film thickness applying expression (2) on a Tauc plot:

\[
(\alpha h\nu)^2 = A(h\nu - E_g)^{1/n}
\]

where \(h\nu\) is the photon energy, \(A\) is a constant called critical absorption, \(n = 0.5\) for direct transition and \(E_g\) is the optical band gap. The values of \(E_g\) for deposited SnO<sub>2</sub> films were obtained by plotting \((\alpha h\nu)^2\) against the photon energy \((h\nu)\) and extrapolating the linear part of the curve to zero on the energy axis as shown in the inset of figure 4. The band gaps of SnO<sub>2</sub> films annealed at 180 °C were determined to be from 3.8 to 4.4 eV which is in agreement with previously reported results [17]. Gradually increasing of the optical band gap is attributable to the quantum size effect, as reported previously in several different systems [18, 19].

3.4. Spectral ellipsometry

Figure 5 shows the spectral distribution of refractive index \(n\) and extinction coefficient \(k\) obtained by spectral ellipsometry analysis of spin coated SnO<sub>2</sub> thin films on glass substrates.
Figure 5. Dispersion Refractive index (n) and extinction coefficient (k) of SnO$_2$ thin films, deposited by spin coating on TiO$_2$/Pt/TiO$_2$ covered glass substrates.

As can be seen for curves of extinction – Figure 5 the region for strong absorption from the curves of extinction coefficient is before 300 nm which is in agreement with the data for optical absorbance in figure 4.

3.5. Atomic force microscopy

Figure 6 presents the AFM image of an SnO$_2$ thin film sample, deposited with solution 0.05 M SnCl$_4$·5H$_2$O in IPA and annealed at 160 ºC for 1 hour. Measured root mean square (RMS) of the surface roughness is 3.9 nm. There are no voids or cracks on the layers and these values characterize the spin coated SnO$_2$ thin films as flat and uniform.

Figure 6. Atomic force microscopy images of SnO$_2$ layers, deposited from solution 0.05 M SnCl$_4$·5H$_2$O in IPA and annealed at 160 ºC for 1 hour.

3.6. Electrical properties

Thin compact SnO$_2$ layers are used in perovskite solar cells to extract electrons from the absorber and prevent recombination with the holes. Characterization of these properties of the spin coated SnO$_2$ thin films was evaluated with Cyclic Voltammetry (CV) measurements in model redox solution of 1mM K$_4$Fe(CN)$_6$ + 1mM K$_3$Fe(CN)$_6$ in 0.5 M KCl, with redox potential $E_{\text{redox}} = 0.2803$ V (vs AgCl/3M KCl) electrolyte, deaerated by bubbling N$_2$. Figure 7 presents the CV curves for redox solution, measured by Pt electrode, background current, measured on conductive substrate electrode – a, CV curve of an SnO$_2$ layer deposited by 0.2 M solution and dried at 100 ºC – b and CV curve of the SnO$_2$ layer, dried and annealed at 140 ºC - c.
Figure 7. Cyclic voltammograms of samples SnO₂ annealed at 140 °C for 1 hour in 1mM K₄Fe(CN)₆ + 1mM K₃Fe(CN)₆ in 0.5 M KCl solution; a – current on the substrate; b – current on the film SnO₂ dried at 100 °C for 1 hour; c – current on the film SnO₂ dried and annealed at 140°C for 1 hour.

As can be seen the current for the redox couple [Fe(CN)₆]⁴⁻ / [Fe(CN)₆]³⁻ on the metal Pt electrode is highest in the interval near redox potential. The current amplitude on the conductive substrate layer TiO₂/Pt/TiO₂ - a decreases in wide potentials range, between -1000 mV ÷ 750 mV (vs. E_redox). The same electrode, covered by spin coated SnO₂ film, dried at 100 °C for 1 hour shows lower current in the same conditions, whereas for sample c – thin film SnO₂ annealed at 140 °C current amplitude decreased sharply in order of magnitude.

4. Conclusions
By spin coating, we deposited flat and uniform void- and crack-free SnO₂ films (Eg 3.8-4.4 eV depending on the thickness) with RMS square mean roughness 3.9 nm after annealing at 140 – 160 °C according to AFM. XPS analysis has shown characteristic signals for Sn⁴⁺ and oxygen in the form of O²⁻. The XRD patterns presented a tetragonal fine structure of SnO₂. For determination of the phase of tetragonal SnO₂ was used reflex near 33 ° 2θ, having in mind the complexity for XRD analysis of reflexes from thin films on mono-crystalline silicon in this vicinity of angles 2θ [14]. In our case the reflex is well defined away of those for (200) plane of Si followed of the pair of reflexes from (220) and (002) planes of SnO₂. The electron selective ability of SnO₂ thin films were assessed by Cycling Voltammetry measurements and were shown that layers deposited from 0.2 M SnCl₂.5H₂O in IPA and annealed at 140 – 160 °C presented noticeable current far away in the cathodic area and negligible anodic current.

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