Ropy Foam-Like TiO2 Film Grown by Water-Based Process for Electron-Conduction Layer of Perovskite Solar Cells

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Ropy foam-like TiO_2 film grown by water-based process for electron-conduction layer of perovskite solar cells

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ABSTRACT

Self-assembled TiO_2 foam-like films, were grown by the water based **S**treaming **P**rocess for **E**lectrodeless **E**lectrochemical **D**eposition (SPEED). The morphology of the ~1 μm thick films consists of a tangled ropy structure with individual strands of ~200 nm diameter and open pores of 0.1 to 3 micron dimensions. Such films are advantageous for proposed perovskite solar cell comprising $CH_3NH_3PbI_3$ absorber with additional inorganic films as contact and conduction layers, all deposited by SPEED. Lateral film resistivity is in the range 20 – 200 kΩ-cm, increasing with growth temperature, while sheet resistance is in the range 2 – 20 x 10^8 Ω/Sq. X-ray diffraction confirms presence of TiO_2 crystals of orthorhombic class (Brookite). UV-vis spectroscopy shows high transmission below the expected 3.2 eV TiO_2 bandgap. Transmittance increases with growth temperature.

INTRODUCTION

Performance of perovskite Solar Cells (PSC) has advanced rapidly [1-6]. Perovskites are compounds of the form ABO_3. Solar cells based on spin-coated mesoporous TiO_2 scaffold, $CH_3NH_3PbI_3$ perovskite absorber layer, and a 2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9′-bifluorene (spiro-OMeTAD) hole transport layer have been reported with power-conversion efficiency as high as 15%, and with 20% considered achievable. However mesoporous TiO_2 as a conducting layer has demonstrated poor quality and poor electron conduction [7]. We present here a robust foam-like TiO_2 film grown by a water-based process that can be a superior alternative. Similarly, the organic spiro-OMeTAD used previously as hole conductor has poor hole transport. Instead, durable films of CuS with excellent hole transport grown by our same aqueous process might be substituted [8,9]. With these films, the photovoltaic cell comprising "glass / SnO_2:F / TiO_2 / $CH_3NH_3PbI_3$ / CuS / Mo" can be prepared (Fig. 1, left), where electron-hole pairs are generated in the perovskite by 300-800 nm wavelength light. Photo-generated electrons are injected into the embedded TiO_2 wires that transport these electrons to the transparent-conducting SnO_2:F electrode [10]. Photo-generated holes are injected into the inorganic CuS hole layer with transport to the Mo electrode. Since the TiO_2 lies above the perovskite absorber layer, it must have high transparency in the visible range while maintaining sufficiently high electron conductivity.

Our aqueous process is called **S**treaming **P**rocess for **E**lectrodeless **E**lectrochemical **D**eposition, or SPEED. This method deposits self-assembled nanocrystalline inorganic thin films over large areas without vacuum. Water-soluble compounds with complexing agents grow films by heterogeneous reaction on the substrate, with little wasteful homogeneous reaction. Hydrophilic substrates bind hydroxyl ions (OH^-), which are attachment sites for nucleation with density exceeding 10^{12} cm^{-3}. The substrate is heated to provide at least the reaction activation energy.

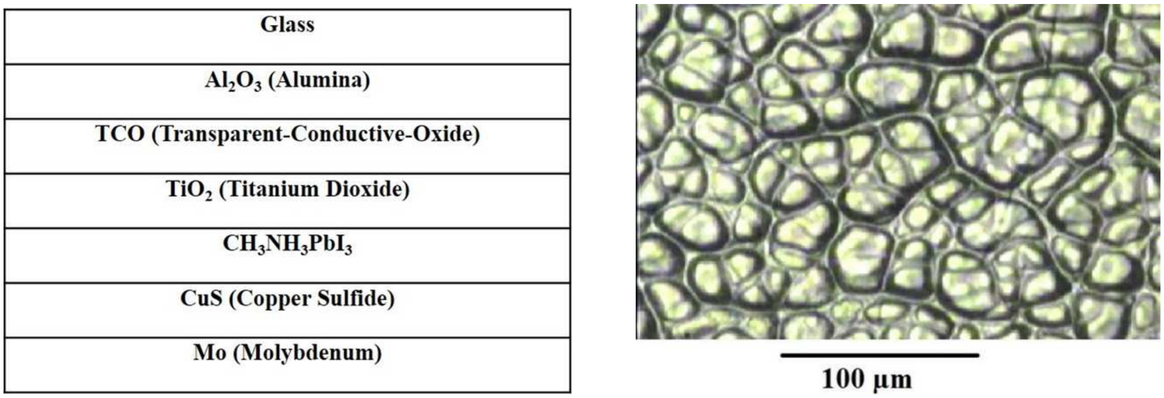

Figure 1. (left) Schematic of proposed Perovskite Solar Cell layer structure (right) Optical microscope image of SPEED-grown TiO_2 thin film.

TiO_2 exists in nature as the minerals Rutile (tetragonal), Anatase (tetragonal) and Brookite (orthorhombic). Typical properties of TiO_2 comprise high electrical resistance, high mechanical durability [11], rigidity [12], high permittivity, excellent visible transmittance, and high chemical stability [13]. These features have led to an extremely wide range of commercial applications, including ultra-thin capacitors, MOSFETs, optical coatings, optical waveguides, polarizers, protective coatings, corrosion-barriers, solar cell photo-anode, humidity and oxygen sensors. In powder form, TiO_2 is used as a white pigment in paint, plastic, inks, paper, cosmetics, washing powder, toothpaste, sunscreen, foodstuffs, pharmaceuticals, photographic plates, and catalysts. TiO_2 films have been deposited by many different techniques, including hydrolysis and pyrolysis [14], pneumatic spraying [15], ultrasonic spraying [16], dip coating [17], plasma enhanced chemical vapor deposition [18], atmospheric pressure chemical vapor deposition [19], metal organic chemical vaper deposition [20], ultra high vacuum chemical vapor deposition [21], low pressure chemical vapor deposition [22], evaporation [23], spin on methods [24], sputtering [25], ion assisted deposition (iad) [26], plasma adonization [27], reactive ion plating [23], laser ablation [29], filtering arc deposition [12], atomic layer epitaxy [30], and screen printing [31]. There are many different parameters that affect the crystalline phase of deposited TiO_2 thin films, including deposition method, deposition temperature, annealing temperature, deposition rate, deposition pressure, precursor type, reaction atmosphere, impurities, and substrate type.

EXPERIMENT DETAILS

Borofloat glass substrates were cleaned using a heavy-duty degreaser, acetone, and de-ionized water. Then, the substrate was mounted on a heater set to the growth temperature between 270 and 400 ℃ with ~10 ℃ uncertainty. The SPEED version used here is vapor phase SPEED (VPSPEED). The water-based precursor is nebulized into 10 to 20 µm droplets, which are sprayed onto the substrate. Growth rate exceeds 200 nm per minute. Reaction byproducts are decomposed and volatilized. A computer controls the position of the spray nozzle on a 2-axis CNC machining table. Five spray cycles were made for each sample. Annealing was performed for 10 minutes in a tube furnace preheated to 450 C.

Scanning electron microscopy (SEM, Zeiss ULTRA-55) with Energy Dispersive Spectroscopy (EDS) was performed at the UCF Materials Characterization Facility (MCF). For cross-sectional SEM imaging, samples were cut and their edges polished. Asymmetric out-of-plane X-ray Diffraction (XRD) was measured using PANalytical Empyrean. The incidence angle with respect to the sample plane was 1 degree. The X-ray wavelength was Cu K-Alpha 1, 0.1540598 nm. Optical microscopy was performed using a Nikon Labophot Microscope. In-plane resistivity was measured using a 4-point probe. Resistivity normal to the plane was determined by measuring the I-V curve via a 1 cm^2 evaporated Ni contact. A Cary 500i spectrophotometer was used to measure film transmittance spectra using bare substrates in the reference channel.

RESULTS

Fig. 1 (right) presents an optical microscope image of a multilayer film comprising Na Glass substrate, SnO_2:F transparent conducting oxide [10], TiO_2:Ni, and Ni. This sample was annealed at 270 C. The image reveals significant porosity with a length scale of 10s of microns. In films grown at higher temperature, this microstructure was less pronounced.

Fig. 2 presents top-view and cross sectional SEM images of the TiO_2 film. In top view, the films have a ropy texture, with large surface area. The cross-section reveals the film thickness to be ~1 µm. Energy Dispersive Spectroscopy (EDS) confirms the presence of Ti, O, and Ni in the film. There is 16% as much Ni as Ti in the film, which agrees with the mix in the precursor.

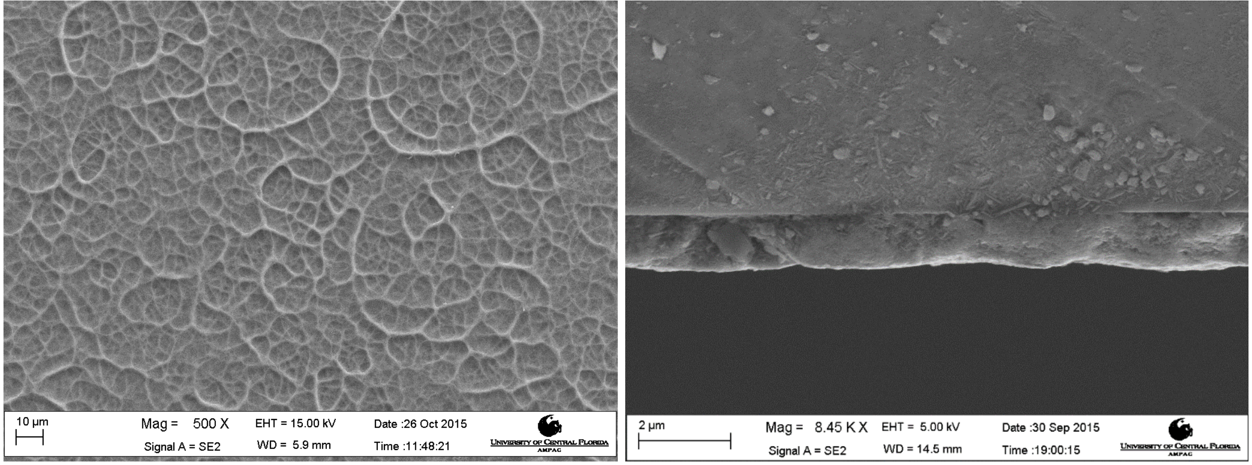

Figure 2. SEM images for TiO_2:Ni film. (left) top view. (right) cross section.

Fig. 3 (left) presents example XRD data for one of the films. The growth temperature was 300 C and sample was not annealed. XRD spectra were collected for all samples, and their XRD patterns were found to be independent of growth temperature and annealing. The spectra were compared with reference spectra for Anatase, Rutile and Brookite (shown) from International Centre for Diffraction Data (ICDD) PDF2 Release 2014. The phase was identified as Brookite (orthorhombic).

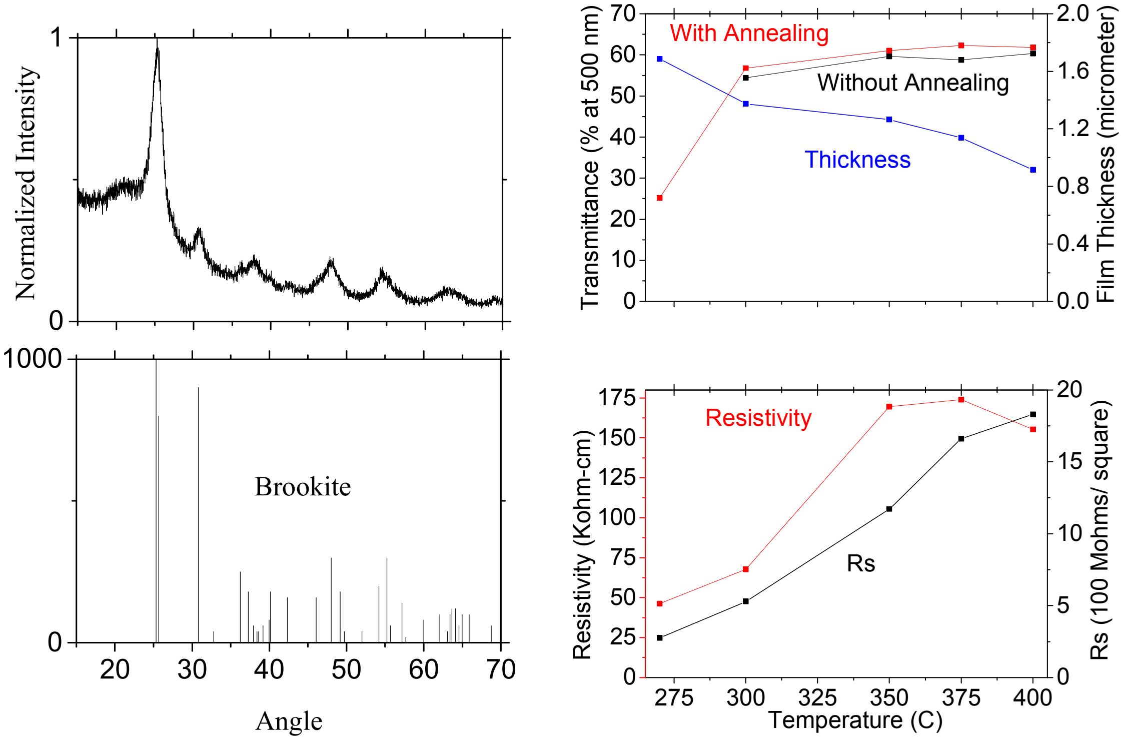

Figure 3. (left) Typical XRD spectrum of SPEED-grown with Brookite phase reference data. (right) Resistivity, sheet resistance, film thickness, and optical transmittance at 500 nm wavelength versus growth temperature.

Fig. 3 (right, top) presents a plot of film thickness (from SEM cross sections) as a function of growth temperature. Post-growth annealing caused no significant difference in the film thickness, so results for annealed and unannealed samples are averaged. For the same 5 spray cycles, the thickness decreases by a factor of ~2 on increasing growth temperature from 270 to 400 C.

Fig. 4 (right, bottom) presents the measured in-plane resistivity and sheet resistance as a function of growth temperature. The two curves are not exactly proportional because of differences in film thicknesses for different samples. The resistivity increases with growth temperature and covers the range 40 - 200 kΩ-cm. In plane conduction less important for solar cell function than vertical transport, since photo-electrons must pass vertically through the TiO_2 layer to reach the FTO transparent conducting top contact. If the resistivity to vertical transport is the same as the horizontal, we would expect a resistance for 1 cm^2 cross section and 1 micron thickness to be in the range 4 – 20 Ω. However, the vertical resistance through a Ni pad of this area was found to be 4500 Ω, presumably due to high contact resistance.

The optical transmittance spectra of the films all have the same rapid drop at wavelengths below 388 nm, which corresponds to fundamental absorption above the 3.2 eV TiO_2 bandgap. Transmittance increases with growth temperature as shown in Fig. 3 (right, top), which may be reasonably attributed to a combination of the correlated thickness decrease and R_S increase.

SUMMARY

We reported physical, electrical, and optical properties of nano-crystalline orthorhombic TiO_2 thin films of micron thickness grown by an aqueous spray deposition method. The proposed perovskite solar cell presented is a type of considerable current interest, which can benefit from our TiO_2 layer as electron collector, and which can be entirely fabricated by our aqueous process. Work to complete and test such a cell is ongoing.

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