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Effect of TiO₂ Mesoporous Layer and Surface Treatments in Determining Efficiencies in Antimony Sulfide-(Sb₂S₃) Sensitized Solar Cells

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We have fabricated antimony sulfide (Sb₂S₃) sensitized nano-structured solar cells prepared by chemical bath deposition. By incorporating a surface treatment on the antimony sulfide films, an improvement in solar cell performance is observed. The influence of the TiO₂ photoanode structure on solar cell efficiencies is also studied by varying the TiO₂ nanoparticle size. Although smaller nanoparticle size provides a much larger effective surface area for sensitizer attachment, the smaller pore size lead to an over-aggregation of Sb₂S₃ particles on the surface pores. Devices fabricated on particles of size ~100 nm exhibited an efficiency of 2.3%.

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Dye sensitized solar cells also known as Grätzel cells,^{1,2} work on the principle of sensitization, which involves decoupling of the light absorption and charge transport within the solar cell. These cells are attractive due to its low cost, good manufacturability and impressive efficiencies of up to 11.1%.³ However, due to potential problems like degradation of dye and leakage issues associated with corrosive iodine/iodide electrolyte, much extensive work has been done on solid state equivalents of the sensitized solar cell. This has involved the replacement of the iodine/iodide redox with inorganic and organic hole transporting materials like copper (I) thiocyanate (CuSCN),⁴ poly(3-hexylthiophene) (P3HT)⁵ and Spiro-OMeTAD.^{6,7} The reduced thickness of these solid state equivalents due to the difficulty of pore filling within the TiO₂ network^{8,9} and interfacial recombination^{10,11} are limitations to solar cell performance.

As a replacement for the dye, semiconductors such as sulfides, selenides and tellurides are promising materials as absorbers due to their high absorption coefficient and chemical stability. Many semiconductor materials have been studied, including PbS,¹² CdS,¹³ CdSe,^{14–16} CdTe,¹⁷ In₂S₃,¹⁸ and Cu_{2–x}S.¹⁹ Recently, crystalline antimony sulfide (Sb₂S₃), a low bandgap material of 1.7 eV–1.9 eV with a high absorption coefficient ($1.8 \times 10^5 \text{ cm}^{-1}$ at 450 nm) was successfully demonstrated by Moon et al.,²⁰ Itzhaik et al.²¹ and Jeong et al.²² deposited by chemical bath deposition²³ as a sensitizer for a mesoporous TiO₂ network. Although a power conversion efficiency of up to 5.1% has been demonstrated, the parameters which determine the efficiency have not been clearly studied.

Here, we report the fabrication of Sb₂S₃ based solar cells and study some of the factors that modulate the efficiency in these devices. We have studied the effect of surface area and porosity of the TiO₂ mesoporous layer and have also introduced a surface treatment to improve efficiencies. We present physical characteristics of the antimony sulfide films as well as device data to explain the relationship between the TiO₂ morphology and solar cell performance.

Experimental

Fabrication of TiO₂ electrodes.— A compact TiO₂ layer (~80–100 nm) on glass (Pilkington, $15 \Omega \text{ sq}^{-1}$) was used as a blocking layer to prevent contact between P3HT and FTO. Blocking layers used in this study were prepared by ebeam deposition of Ti and then oxidation in air flow. Subsequently, a porous TiO₂ layer (~2 μm) was screen-printed onto the dense TiO₂ layer from either a homemade TiO₂ nanoparticles paste (MKNano, 50 nm Anatase TiO₂) or a commercially available TiO₂ paste (Solaronix R/SP) as described. These

TiO₂ films were treated with 20 mM TiCl₄ for 12 hrs in dark at room temperature and then rinsed copiously with de-ionized water before sintering under oxygen flow at 500°C for 30 min. A barrier layer of In(OH)_xS_y (In-OH-S) was deposited using the procedures reported elsewhere.²⁴ Briefly, the TiO₂ electrodes are immersed in a solution of 25 mM InCl₃, 0.1 M thioacetamide and 0.1 M acetic acid for one hour at 65°C, followed by rinsing in de-ionized water. Thereafter, Sb₂S₃ film was coated onto the TiO₂/In(OH)_xS_y substrates using procedures as described by Messina et al.¹¹

Synthesis and surface modification of antimony sulfide films.— 650 mg of antimony chloride (SbCl₃) was dissolved initially in 2.5 mL acetone followed by the addition of 25 mL of 1 M sodium thiosulphate (Na₂S₂O₃) solution and sufficient water to make the volume to 100 mL. The deposition times of the antimony sulfide were varied while the temperature of deposition was maintained at 4°C. All Sb₂S₃ coated substrates were annealed in 330°C under argon atmosphere for 30 min in a furnace. The as-deposited antimony sulfide is orange-colored and turns dark brown when annealed. A post-treatment was introduced on the antimony sulfide films. TiO₂/Sb₂S₃ substrates were firstly heated at 200°C for 10 min and then surface etched with diluted HCl (40 mM in de-ionized water) for 30 min. Substrates were again immersed in decylphosphonic acid (DPA) for another 30 min.

Application of hole-transporting material.— The P3HT solution (15 mg/mL in 1,2-dichlorobenzene) was spin-coated onto TiO₂/Sb₂S₃ with 2500 rpm for 90 s. To improve the contact between P3HT and Au, a poly(3-(4-ethylenedioxythiophene) doped with poly(4-stylenesulfonate) (PEDOT:PSS; Clevis P VP Al 4083) diluted with two volumes of methanol was introduced onto the TiO₂/Sb₂S₃/P3HT layer by spin-coating at 2000 rpm for 30 s. The TiO₂/Sb₂S₃/P3HT/PEDOT:PSS layer was then annealed at 90°C for 30 min in a vacuum oven. Finally a ~80–100 nm thick layer of gold was deposited on the polymer surfaces at high vacuum (10^{-6} Pa) with a device area of 0.2 cm².

Characterization.— The morphology and composition of antimony sulfide (Sb₂S₃) films were systematically evaluated with a field emission scanning electron microscope (JEOL HSM-7600F) equipped with an Energy Dispersive X-Ray Detector. Crystal structures of the films were investigated by thin film X-ray diffraction (XRD) using Bruker D8 Advance. In addition, the UV-visible absorption spectra were measured using a Shimadzu UV-3600 UV-VIS NIR spectrophotometer and layer thicknesses were characterized using an Alpha-Step IQ Surface Profiler. The porosity and surface area measurements were performed using Nova 3200 surface and pore analyzer. For the device characterization, solar cells are illuminated with

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Figure 1. (a) X-Ray diffraction pattern of antimony sulfide films when annealed at 330°C for 30 min; Blue squares indicate Sb_2S_3 peaks, Red dots indicate Sb_2O_3 peaks (b) Absorbance spectrum of annealed antimony sulfide films. Inset shows a plot of $(\alpha h\nu)^2$ against E where bandgap is extracted and an image of a $\text{Sb}_2\text{S}_3/\text{TiO}_2$ electrodes.

a solar simulator. The light to power conversion efficiencies (PCE) was recorded using a voltage-current source meter (Agilent 4155C Semiconductor Parameter Analyzer) under a solar simulator illumination (San-Ei Electronics, XEC-301S, AAA rated) of air mass 1.5 (100 mWcm^{-2}). The IPCE was measured using 150 W Newport-Oriel Xenon light source, Cornerstone 260 1/4M monochromator, optical chopper set at 60 Hz and Merlin radiometry system. All the fabrication processes and performance measurement were carried out in an inert glove box atmosphere.

Results and Discussion

Synthesis and Characterization of Crystalline Antimony Sulfide Film.— Fig. 1 shows the X-Ray diffraction pattern of an annealed antimony sulfide film which showed sharp peaks at 2θ of 15.8° , 17.6° and 25.2° , corresponding to the crystalline Sb_2S_3 (stibnite) phase with orientation (020), (120) and (130) respectively. The as-deposited antimony sulfide film is amorphous, with no characteristic peaks which is in agreement with previous reports.¹¹ The annealed film was also examined against the oxide phase, Sb_2O_3 (Senarmonite) and traces of antimony oxide were observed. Fig. 1b shows the optical absorption spectra of an Sb_2S_3 film. Bandgap was obtained from a plot of $(\alpha h\nu)^2$ against E by extrapolating to 0. The as-deposited antimony sulfide film has a bandgap of $\sim 2.7 \text{ eV}$ – 2.8 eV . A lower bandgap for the annealed film (1.8 eV versus 2.7 eV) for antimony sulfide films is attributed to improvement in crystallinity.²⁵ Fig. 2 shows the element mapping of Sb_2S_3 coating on TiO_2 nanoparticles. The denser titanium (Ti)

are imaged at the center, which correlates to the TiO_2 nanoparticles. When coated with a thin film of antimony sulfide, a less dense coating from elements of sulfur (S) and antimony (Sb) are imaged at the outer shell.

Device performance.— We have first studied the effect of deposition time (and hence thickness) of Sb_2S_3 on the performance of solar cells. For these studies, we utilized a TiO_2 photoanode fabricated by screen printing a homemade paste consisting of MKNano 50 nm anatase TiO_2 particles. The thickness of antimony sulfide is varied by varying CBD deposition times from 1 h to 3 h. Fig. 3a shows the J - V characteristics of the Sb_2S_3 -sensitized cells with varying absorber deposition time. Upon increasing CBD deposition times from 1 h to 3 h, it is observed that there is an increase in the current density, J_{sc} from 0.94 mA/cm^2 to 4.78 mA/cm^2 , which contributes to a large increase in power conversion efficiency. In contrast, the V_{oc} and FF largely remains the same. The significant increase in J_{sc} with increasing deposition times is attributed to the enhanced absorption (light harvesting) and thus increased charge generation and injection with a thicker antimony sulfide coating in semiconductor-sensitized nanoporous solar cells. The 3 hour growth time corresponds to a film thickness of 270 nm for films grown on planar glass slides (not shown). A Sb_2S_3 thickness of 300 nm will ensure 90% absorption of 550 nm wavelength, indicating that the deposited film is of sufficient thickness for optical absorption.^{26,27} We have also explored longer deposition times, but they displayed lower performance, attributable to recombination in the Sb_2S_3 thin film.²² Grain size is evaluated using Scherrer's relation on the XRD patterns illustrated in Fig. 3d. The grain size of 1 h, 2 h and 3 h deposited Sb_2S_3 films are ~ 19 – 20 nm which did not show significant changes, hence indicating that the grain size effect (1 h–3 h deposition) in the solar cell performance is not pronounced. The corresponding IPCE spectrum for 3 h- Sb_2S_3 device is shown in Fig. 3b. Typically, the IPCE exhibited peak values of approximately 45% between excitation wavelengths of 400 nm–500 nm, with an onset at about 750 nm. Table I summarized the solar cell performance

Figure 2. TEM image of TiO_2 nanoparticles coated with Sb_2S_3 and elemental mapping of Ti, S, Sb atoms.

Table I. Photovoltaic parameters of devices with different Sb_2S_3 thickness and surface treatment.

Sb_2S_3 Surface- treatment	Device	CBD Time [hrs]	J_{sc} [mA/cm^2]	V_{oc} [V]	FF [%]	PCE [%]
No	—	1	− 0.94	0.31	0.39	0.11
No	—	2	− 2.15	0.42	0.40	0.36
No	Control	3	− 4.78	0.43	0.36	0.74
Yes	Oxide	3	− 1.89	0.42	0.40	0.31
Yes	HCl-treated	3	− 6.52	0.46	0.38	1.15

Figure 3. (a) Current density-voltage (*J-V*) curves for devices fabricated with varying Sb₂S₃ deposition timings (1 h, 2 h and 3 h) (b) shows the IPCE of a 3 h-Sb₂S₃ CBD deposited device (c) *J-V* characteristics of control device, after thermal oxidation and acid etching (d) X-Ray diffraction patterns of 1 h, 2 h and 3 h deposited Sb₂S₃ films.

for devices fabricated with varying CBD deposition times of 1 h, 2 h and 3 h.

A surface treatment consisting of a thermal oxidation and subsequent HCl etching of the antimony sulfide layer was introduced subsequent to the chemical bath deposition. A schematic of the processing steps for surface treatment is provided in Fig. 4. Table I shows the photovoltaic performance of solar cells with and without antimony sulfide surface treatment. A 3 h Sb₂S₃/TiO₂ device (without surface modification) showed an efficiency of 0.74%. After thermal oxidation, it was evident that the presence of oxide (Sb₂O₃) reduces the PCE, mainly due to the decrease in J_{sc} (from -4.78 mA/cm² to 1.89 mA/cm²) shown in Fig. 3c. This is indicative of the resistive behavior of the Sb₂O₃ layer, which retards the charge injection from Sb₂S₃ to TiO₂ nanoparticles. With the HCl treatment, the J_{sc} and V_{oc} improved to a large extent. One possible explanation behind

the improved solar cell performance could be that during etching process, the over-aggregated Sb₂S₃ particles, covering the pores of the mesoporous layer, have been oxidized and etched. As a result, the pore openings were cleared which led to better pore infiltration leading to enhanced charge transport between TiO₂/Sb₂S₃/P3HT interfaces.

We have also fabricated devices with larger-sized TiO₂ nanoparticles (~100 nm TiO₂) for comparison. The solar cell efficiency improved to 2.3% efficiency with J_{sc} of 10.84 mA/cm² for ~100 nm nanoparticles. The previously described surface treatments were also employed in the fabrication of the second set of devices. Table II shows the photovoltaic performance of solar cells for 50 nm and 100 nm TiO₂ particle photoanode structure. *J-V* characteristics of devices fabricated with TiO₂ films of different nanoparticle size are shown in Fig. 5a. This illustrates the sensitivity of Sb₂S₃ sensitized solar cells to the underlying TiO₂ photoanode. Fig. 5b shows the external quantum efficiency (EQE) of ~100 nm nanoparticles sized

Figure 4. Schematic of a surface modification consisting of a 2-steps treatment (i) Thermal oxidation (ii) HCl treatment.

Table II. Solar cell performance for devices with different TiO₂ nanoparticle size.

Sb ₂ S ₃ Surface-treatment	TiO ₂ nanoparticle paste [nm]	J _{sc} [mA/cm ²]	V _{oc} [V]	FF [%]	PCE [%]
No	50	4.78	0.43	36	0.74
Yes	50	6.52	0.46	38	1.15
No	100	11.21	0.45	44	2.20
Yes	100	10.84	0.49	44	2.32

Figure 5. (a) *J-V* characteristics of devices fabricated with Sb₂S₃/TiO₂ (100 nm) and Sb₂S₃/TiO₂ (50 nm) electrodes after surface modification (b) EQE of devices fabricated with Sb₂S₃/TiO₂ (100 nm) and Sb₂S₃/TiO₂ (50 nm) electrodes after surface modification.

device where peak values is $\sim 65\%$ between excitation wavelengths of 400 nm–500 nm.

In order to understand the differences between the two different kinds of photoanode, the porosity and surface area of the TiO₂ films were characterized with BET. From the BET measurements, the paste consisting of 50 nm anatase TiO₂ showed surface area of 128.31 m²/g and pore size of 5.2 nm. The paste consisting of ~ 100 nm showed a surface area 13.36 m²/g and pore size of 120 nm. The high surface area of the 50 nm paste was due to smaller nanoparticles (< 50 nm) observed in the paste. Despite the higher surface area (128.31 m²/g) provided by the smaller size nanoparticles for sensitizer attachment, device efficiency did not improve with the increasing surface area. However, the better solar cell performance comes from device fabricated with paste of a larger porosity. The porosity of the TiO₂ paste can affect the performance of the solar cell at two stages of its fabrication. During the chemical bath deposition process, reactants need to diffuse to the sites within the photoanode to deposit the Sb₂S₃, but can be hindered by the narrow path of diffusion. In addition, the diffusion effects can be aggravated when Sb₂S₃ particles aggregate and clog the surface pores, preventing reactants from accessing the TiO₂ paste completely. For larger-sized nanoparticle film, a larger porosity could probably facilitate access of precursor into TiO₂ pores. In addition to the coverage of Sb₂S₃, another factor that could play a role is the pore filling of the sensitized semiconductor by the hole transporting layer (P3HT). Grant et al. whose work focused on larger bulky polymers for pore filling showed that pore size is important for access of long-chain conjugated polymer sensitizer.²⁸ The larger size nanoparticles (having a larger pore size) could have led to better infiltration of P3HT into TiO₂/Sb₂S₃ electrode, resulting in better charge transfer between Sb₂S₃/P3HT interfaces.

Conclusions

In summary, we have compared the efficiencies of antimony sulfide sensitized solar cells formed on 50 nm TiO₂ and 100 nm TiO₂ particles and have also introduced a surface treatment on antimony sulfide to improve solar cell efficiencies. By incorporating the surface treatment, an efficiency of 2.32% is achieved (100 nm TiO₂). The surface treatment is suggested to have removed the over-aggregated Sb₂S₃, covering the pores of the mesoporous layer, after oxidized and etched. In addition, we also observed that although smaller size nanoparticles provide a higher surface for sensitizer attachment, better performance comes from paste with larger porosity. The effect of surface treatment is observed more effectively in devices made of smaller size nanoparticles (PCE 0.7% to 1.1%) as porosity can affect the solar cell efficiencies at 2 different stages of its fabrication. For smaller nanoparticle size TiO₂ film, reactants need to diffuse to the sites within the photoanode to deposit the Sb₂S₃, but can be hindered

by the narrow path of diffusion. In contrast, the larger size nanoparticles (having a larger pore size) could have led to better infiltration of P3HT into TiO₂/Sb₂S₃ electrode, resulting in better charge transfer between Sb₂S₃/P3HT interfaces. We believe that the present findings can help in providing a better understanding of the various factors that determine efficiencies in this kind of semiconductor sensitized solar cells.

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