Solution processed TiO₂/BiFeO₃/poly(3-hexylthiophene) solar cells

Vedat Keskin^a, Arunava Gupta^{b,c,d}, and Greg Szulczewski^{*,b,d}

^aSamsun Ondokuz Mayis University

Civil Aviation College

Ballica, Turkey

and

^bCenter for Materials for Information Technology

^cDepartment of Chemical and Biological Engineering

^dDepartment of Chemistry

The University of Alabama

Tuscaloosa, AL 35487

Abstract

We report the fabrication of solar cells by spin-coating and annealing sol-gel layers of TiO₂ and BiFeO₃ on indium oxide coated glass substrates. A layer of poly(3-hexylthiophene) was spin coated onto the inorganic layers to form hybrid organic-inorganic solar cells. X-ray powder diffraction revealed the BiFeO₃ layers are polycrystalline with rhombohedral texture and average crystallite size about 20 nm. Scanning electron microscopy images showed the films are granular and microporous. Irradiation with visible light resulted in a photocurrent of 0.05 mA cm⁻² and an open circuit voltage of -0.46 V.

*Electronic email: gjs@ua.edu

Key words: ferroelectrics, sol-gel preparation, solar energy materials, polymers

Introduction

Over the past few years there have been major advances in the solution-processing of hybrid organic-inorganic solar cells.[1] The discovery that organometal-halides with a perovskite structure that can be solution processed has lead to remarkable increases in power conversion efficiency.[2-5] These studies have motivated others to revisit the potential of inorganic perovskites as photovoltaic materials.[6-14] Since the perovskites are ferroelectric, internal electric fields due to the electric polarization may help dissociate excitons. Among the family of metal-oxide perovskites, BiFeO_3 is an archetypical example of a room-temperature multiferroic material.[15] Bismuth ferrite is a direct band gap (~ 2.6 eV) semiconductor with a large electrical polarization and weak ferromagnetism at room temperature.[15] BiFeO_3 thin films can be prepared by sputtering,[11,19-20] chemical vapor deposition,[9,12] molecular beam epitaxy[21] and pulsed laser deposition.[7,18] These methods involve high vacuum systems and are not amenable to low-cost fabrication. In contrast, sol-gel methods can produce films by annealing spin-coated sol-gel solutions.[24-28] However, the ease of processing the material comes with a trade-off in chemical and physical properties. In general, the films made from sol-gel processing have more defects (i.e. usually oxygen vacancies) and lower saturation magnetization and electric polarization.

Prior work on the photovoltaic effects in BiFeO_3 depends on the quality of the sample and whether the material is a thin film or bulk single crystal. In the case of the bulk photovoltaic effect, unlike traditional semiconductors that require p-n junctions to generate photocurrents, ferroelectrics can produce an open circuit voltage (V_{oc}) much larger than the optical band gap.[7,9,12] First principle calculations of the bulk photovoltaic effect in BiFeO_3 have reconciled some experimental measurements using the “shift current” model.[31] For practical photovoltaic applications, thin films are required. In this regard, Yang *et al.* observed above band gap voltages in thin films of BiFeO_3 grown by metal-organic chemical vapor deposition.[16] They proposed that

electrostatic potentials develop at domain walls, which sum over all the walls between the electrode separation to yield the above bandgap V_{oc} . Similarly, Bhatnagar *et al.* observed $V_{oc} \sim 50$ V in 100 nm thin films grown by pulsed laser deposition on (110) $TbScO_3$ substrates.[7] By using a combination of temperature-dependent and polarization dependent photocurrent measurements, the authors concluded that the large V_{oc} was due to enhanced conductivity of domain walls. However, it appears that a large V_{oc} has not been observed in sol-gel prepared thin films or a parallel-plate device geometry. Here we report a procedure to fabricate solar cells using solution-processing techniques based on a $BiFeO_3$ absorber layer. Our general strategy was to use TiO_2 as an electron collection electrode (hole blocking layer), $BiFeO_3$ as the light absorbing material, and poly(3-hexylthiophene) as a hole-transport layer (electron blocking layer).

Material and methods

Indium tin oxide (ITO) coated glass substrates were cut into $15 \times 15 \text{ mm}^2$ slides, and cleaned by sonication with soap in water, ultrapure water, acetone and ethanol (10-15 minutes for each step). Lastly, the substrates were cleaned in a UV-ozone source for 30 min. A “dense” TiO_2 layer was deposited on the ITO substrate to increase the surface energy. A solution was formed from a 3:10 weight ratio of titanium(IV) isopropoxide (98+%, Acros Organics) and isopropanol (ACS reagent, $\geq 99.5\%$). The “dense” TiO_2 layer was deposited on top of the cleaned ITO substrates by spin coating the solution at 3000 rpm for 30 seconds, followed by consecutive heating for 2 minutes at 180°C , 2 minutes at 300°C and 1 hour at 500°C . Next, the solution to deposit a “porous” layer of TiO_2 was prepared by adding 0.3 mg of polyvinylpyrrolidone to 3.5 ml of ethanol, adding 0.5 mL of acetic acid and 1 mL of titanium(IV) isopropoxide. The “porous” TiO_2 layer was spin-coated and annealed by the same method for the dense TiO_2 layer. The $BiFeO_3$ layer was spin coated from a sol-gel reaction solution prepared by adding $Bi(NO_3)_3 \cdot 5H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ in 1.1:1 molar ratio to 12 ml of ethylene glycol. A 10% excess of Bi was used to compensate for the loss of Bi during the thermal annealing

process. The resulting mixture was stirred at 80°C for 1 hour to obtain the sol, then left to dry overnight at the same temperature in an oven. The concentration of the precursor solution was adjusting by adding 1mg of the sol-gel to 10 ml of ethanol, which was stirred and sonicated for 30 minutes before spin coating. The thin film was spin coated from the precursor solution at 3000 rpm for 10 to 15s. Immediately the spin-coated film was dried at 150 °C for 1 min and repeated 10 times. The temperature was increased to about 275 °C, when color of the film darkened the temperature was dropped to 150 °C. Previous thermal gravimetric analysis has shown that the organic residues are pyrolyzed by 275 °C and no more weight loss occurs up to 750 °C. [24] This sequence was repeated to control the thickness of the BiFeO₃ layer. Finally, the film was annealed at 450 °C for 30 min in air. The layer thicknesses were determined with a Dektak XT profilometer. The BFO film was approximately 600 nm thick after 10 cycles of the spin coating process. A poly(3-hexylthiophene), or P3HT, solution (Alfa-Aesar) was spin coated on top of the perovskite at 3000 rpms for 30 seconds and annealed at 120 °C for 20 minutes. Aluminum (100 nm) was deposited under high vacuum by thermal evaporation through a shadow mask to produce 2 mm x 2 mm top contacts.

The samples were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS). The XRD measurements were done on a Bruker D2 Phaser desktop diffractometer with a Cu K α x-rays. The SEM images were taken on a JEOL 7000 operating at 20 kV. The XPS measurements were done with a Kratos Axis 165 with a monochromatic Al K α x-ray. No charging was observed and the binding energy scale was set so that the adventitious C(1s) peak was 285.0 eV. XPS measurements were performed with spectrometer pass energy set to 40 eV for the high energy scans and 160 eV for the survey scan. A monochromatic Al K α x-ray source was operated at 150 W. Current density-voltage (*J-V*) measurements were acquired using a Keithley SourceMeter (model 2400) as the voltage and current source under ambient laboratory conditions. The light source was a 150 W Xe lamp

(Newport). A long pass filter (FGL400, Thor labs) was placed after the lamp so that only visible light was incident upon the solar cells. Optical absorption spectra were measured on a Varian (model Cary 50) spectrophotometer in transmission mode.

Results and Discussion

The surface morphology of the BiFeO_3 layer was characterized with a field emission scanning electron microscope. The SEM images revealed that the BiFeO_3 layers were granular (Fig. 1a). A low magnification image (see Fig. 1b) shows that there were no macroscopic cracks in the film.

FIG.1. SEM images of a BiFeO_3 film. The image at the left and right was taken at 1600 X and 330X magnification, respectively.

X-ray diffraction reveals the TiO_2 and BiFeO_3 layers are polycrystalline. There is a small amount of a secondary phase in the film that is assigned to $\text{Bi}_2\text{Fe}_4\text{O}_9$ (JCPDS #25-0090). It is very difficult to avoid the formation of $\text{Bi}_2\text{Fe}_4\text{O}_9$ in the synthesis of BiFeO_3 . [30]

Using the Scherrer equation and the measured FWHM of the (100) reflection, the average BiFeO_3 crystallite size is estimated to be about 20 nm. The presence of the (014) and (110) peaks indicate the rhombohedral phase. [28] The peak at 25.5° is characteristic of the (101) plane of TiO_2 in the anatase phase. All the other peaks are from the ITO film.

FIG 2. Representative XRD spectrum of the inorganic thin films (glass/ITO/TiO₂/BFO).

FIG. 3 Survey x-ray photoelectron spectrum of the BiFeO₃ layer.

Figure 3 shows the XPS spectra of a sol-gel processed BiFeO₃ film. Only the peaks due to Bi, Fe and O are found in the spectrum. No nitrogen from the nitrate anion was observed. The most intense Bi peaks are the Bi(4f_{7/2}) and Bi(4f_{5/2}) with binding energies of 159.5 and 164.8 eV, respectively. These binding energies are in agreement with published values for Bi³⁺. [31] The main Fe peaks are the Fe(2p_{3/2}) and Fe(2p_{1/2}) with binding energies of 711.1 and 724.6 eV, respectively. These binding energies are consistent with Fe³⁺ cations. [31] Figure 4 shows the electronic absorption film of the BFO layer, which is consistent with other published results. [22,23]

FIG. 4. Optical absorption spectrum of a BFO film.

FIG. 5. Current density versus voltage curves in the light (red) and dark (black).

Figure 5 shows the J-V curves that illustrate the photovoltaic effect. In the dark, the J-V curve indicated diode behavior. The open circuit voltage was about -0.46 volts. Upon irradiation the open circuit voltage was nearly unchanged, but the maximum current density increased to 0.05 mA cm⁻². Although the absolute power conversion efficiency is low (~0.01 %), it is comparable with previously published values for BiFeO₃ layers grown by pulsed laser deposition.[32] One source of the low power conversion efficiency is presence of oxygen vacancies in the BiFeO₃ layer, which serve as n-type donors and act as recombination centers. Second, choice of Al as the top contact on the P3HT layer may not produce the largest open-circuit voltage. For example, Reesha-Jayan and Manthiram have shown that a Cu layer on P3HT produced as higher V_{oc} than Ag or Au electrodes.[33] Nonetheless, Al is known to form an abrupt contact to the P3HT

layer.[34,35] The role of the small amount of $\text{Bi}_2\text{Fe}_4\text{O}_9$ in the film is very difficult ascertain because it was present in all the films we made. There have been a few reports on the photocatalytic properties of $\text{Bi}_2\text{Fe}_4\text{O}_9$ microcrystals. [36-39] Optical absorption spectra of the microcrystals reveal two peaks in the visible region: one near 500 nm and another 700 nm. Since we do not observe the peak at 700 nm (see Fig. 4) we can conclude that the $\text{Bi}_2\text{Fe}_4\text{O}_9$ does not contribute significantly to the production of carriers. On-going studies are aimed at optimizing the thickness of each layer, changing the top electrode material and annealing temperature/time to improve the overall power conversion efficiency.

Conclusions

In summary, ITO/ TiO_2 / BiFeO_3 /P3HT/Al solar cells were fabricated by a low-cost solution deposition method. The BiFeO_3 was grown at low temperature (275°C) and produces a polycrystalline film with average crystallite size about 20 nm. Irradiation of the cells with visible light resulted in a photocurrent of 0.05 mA cm⁻² and open circuit voltage of -0.46 volts.

Acknowledgements

The authors acknowledge the U. S. National Science Foundation for partial support of this work through grants No. CHE-1012850 and the Ondokuz Mayıs University Research Fund (PHY.SHYO.1922.13.001) The authors thank Ed Ellingsworth, Kim Anderson and Archana Panikar for technical assistance; the Central Analytical Facility at The University of Alabama for use of the Kratos XPS spectrometer and JEOL SEM; and Dr. Shanlin Pan for use of his solar cell testing apparatus.

References

- [1] M. Gratzel, R. A. J. Janssen, D. B. Mitzi, and E. H. Sargent, *Nature (London)* **488**, 304 (2012).
- [2] A. Yella, L.-P. Heiniger, P. Gao, M. K. Nazeeruddin, and M. Gratzel, *Nano Lett.* **14**, 2591 (2014).
- [3] G. E. Epersom, M. Burlakov, P. Docampo, A. Goriely, and H. J. Snaith, *Adv. Funct. Mater.* **24**, 151 (2014).
- [4] B. Conings, L. Beten, C. de Dobbelaere, J. D' Haen, J. Manca, and H.-G. Boyen *Adv. Mater.* **26**, 2041 (2013).
- [5] I. Grinberg, D. V. West, M. Torres, G. Gou, D. M. Stein, L. Wu, et al., *Nature (London)* **503**, 509 (2013).
- [6] Y. Yuan, Z. Xiao, B. Yang, and J. Huang, *J. Mater. Chem. A* **2**, 6027 (2014).
- [7] A. Bhatnagar, A. R. Chaudhuri, Y. H. Kim, D. Hesse, and M. Alexe, *Nature Comm.* **4**, 2835 (2013)
- [8] R. Moubah, O. Rousseau, D. Colson, A. Artemenko, M. Maglione, and M. Viret, *Adv. Funct. Mater.* **22**, 4814 (2012).
- [9] J. Seidel, D. Fu, S.-Y. Yang, E. Alarcón-Lladó, J. Wu, R. Ramesh, and J. W. Ager III, *Phys. Rev. Lett.* **107**, 126805 (2011).
- [10] M. Alexe and D. Hesse, *Nature Comm.* **2**, 256 (2011).
- [11] W. Ji, K. Yao, and Y. C. Liang, *Phys. Rev. B* **84**, 094115 (2011).
- [12] S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C.-H. Yang, M. D. Rossell, et al., *Nature Nanotech.* **5**, 143 (2010).
- [13] W. Ji, K. Yao, and Y. C. Liang, *Adv. Mater.* **22**, 1763 (2010).
- [14] T. Choi, S. Lee, Y. Choi, V. Kiryuhkin, and S.-W. Cheong, *Science* **324**, 63 (2009).
- [15] G. Catalan and J. F. Scott, *Adv. Mater.* **21**, 2463 (2009).
- [16] S. Y. Yang, L. W. Martin, S. J. Byrnes, T. E. Conry, S. R. Basu, D. Paran, et al., *Appl. Phys. Lett.* **95**, 062909 (2009).

- [17] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, et al., *Science* **299**, 1719 (2003).
- [18] A. Anshul, A. Kumar, B. K. Gupta, R. K. Kotnala, J. F. Scott, and R. S. Katiyar, *Appl. Phys. Lett.* **102**, 222901 (2013).
- [19] B. Liu, Z. Peng, J. Ma, J. Wang, Q. Zhao, and Y. Wang, *Phys. Status Solidi A* **4**, 819 (2013).
- [20] H. W. Chang, F T. Yuan, P. C. Chen, C. R. Wang, C. S. Tu, and S. U. Jen, *J. Alloys Compounds* **574**, 4012 (2013).
- [21] J. F. Ihlefeld, N. J. Podraza, Z. K. Liu, R. C. Rai, X. Xu, T. Heeg *et al.* *Appl. Phys. Lett.* **92**, 142908 (2008.)
- [22] S. R. Basu, L. W. Martin, Y. H. Chu, M. Gajek, R. Ramesh, R. C. Rai, et al., *Appl. Phys. Lett.* **92**, 091905 (2008).
- [23] A. J. Hauser, J. Zhang, L. Mier, R. A. Ricciardo, P. M. Woodward, T.L. Gustafson, et al. *Appl. Phys. Lett.* **92**, 222901 (2008).
- [24] Z. Lin, W. Cai, W. Jiang, C. Fu, C. Li, and Y. Song, *Ceramics International* **39**, 8729 (2013).
- [25] Y. Guo, B. Guo, W. Dong, H. Li, and H. Liu, *Nanotechnology* **24**, 275201 (2013).
- [26] Y. Sun, Y. Zhou, H. Liu, Z. Xia, M. Lup, K. Wan, et al., *J. Sol-Gel Sci. Technol.* **66**, 429 (2013).
- [27] Q. Man, W. Sun, F. Yang, C. Qiu, Y. Zhao, and G. Hu, *J. Mater. Sci. Mat. Electron* **25**, 1269 (2014).
- [28] W. Dong, Y. Guo, B. Guo, H. Liu, H. Li, and H. Liu, *Material Letters* **88**, 140 (2012).
- [29] S. M. Young, F. Zheng, and A. M. Rappe, *Phys. Rev. Lett.* **109**, 236601 (2012).
- [30] K. Feng, L.-C. Wang, J. Lu, Y. Wu, and B.-G. Shen, *CrystEngComm* **15**, 4900 (2013).
- [31] A. T. Kozakov, A. G. Kochur, K. A. Googlev, A. V. Nikolsky, I. P. Raevski, V. G.

- Smotrakov, et al, J. Electron Spec. Rel. Phenom. **184**, 16 (2011).
- [32] Z. Liu and F. Yan, J. Am. Ceram. Soc. **95**, 1944 (2012).
- [33] B. Reeja-Jayan and A. Manthiram, ACS Appl. Mater. Interfaces **3**, 1492 (2011).
- [34] P. Dannetun, M. Boman, S. Stafström, W. R. Salaneck, R. Lazzaroni, C. Fredriksson, et al, J. Chem. Phys. **99**, 664 (1993).
- [35] N. Rujisamphan, F. Deng, R. E. Murray, C. Ni, and S. I. Shah, Solar Energy Materials & Solar Cells **109**, 56 (2013).
- [36] Q.-J. Ruan and W.-D. Zhang, J. Phys. Chem. C **113**, 4168 (2009).
- [37] Q. Zhang, W. Gong, J. Wang, X. Ning, Z. Wang, X. Zhao, et al, J. Phys. Chem C **115**, 25241 (2011)
- [38] Y. Li, Y. Zhang, W. Ye, J. Yu, C. Lu, and L. Xia, New J. Chem. **36**, 1297 (2012).
- [39] Y. Zhang, Y. Guo, H. Duan, H. Li, L. Yang, P. Wang et al, RSC Adv. **4**, 28209 (2014).