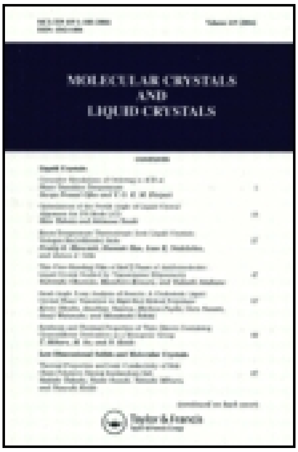
This article was downloaded by: [University of California, San Diego]
On: 07 August 2012, At: 12:15
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Study of the Cesium Carbonate (Cs_2CO_3) Inter Layer Fabricated by Solution Process on P3HT:PCBM Solar Cells

Yongju Park [a] , Seunguk Noh [a] , Donggu Lee [a] , Junyoung Kim [a] & Changhee Lee [a]

[a] School of Electrical Engineering and Computer Science, Inter-University Semiconductor Research Center, Seoul National University, Seoul, Korea

Version of record first published: 16 May 2011

To cite this article: Yongju Park, Seunguk Noh, Donggu Lee, Junyoung Kim & Changhee Lee (2011): Study of the Cesium Carbonate (Cs_2CO_3) Inter Layer Fabricated by Solution Process on P3HT:PCBM Solar Cells, Molecular Crystals and Liquid Crystals, 538:1, 20-27

To link to this article: http://dx.doi.org/10.1080/15421406.2011.563221

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., Vol. 538: pp. 20–27, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.563221

Downloaded by [University of California, San Diego] at 12:15 07 August 2012

Study of the Cesium Carbonate (Cs_2CO_3) Inter Layer Fabricated by Solution Process on P3HT:PCBM Solar Cells

YONGJU PARK, SEUNGUK NOH, DONGGU LEE, JUNYOUNG KIM, AND CHANGHEE LEE

School of Electrical Engineering and Computer Science, Inter-University Semiconductor Research Center, Seoul National University, Seoul, Korea

In this paper, we studied the effect of the electron injection layer, Cesium carbonate (Cs_2CO_3), thickness on the performance of organic solar cell (OSC) based on blends of poly (3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester fullerene derivative (PCBM). The polymer solar cell consists of molybdenum-oxide (MoO_3) as a hole injection layer, P3HT and PCBM bulk hetero junction as an active layer, and Cesium carbonate (Cs_2CO_3) as an electron injection layer. We measured each device by current-voltage measurement and impedance spectroscopy which is widely used for equivalent circuit analysis of solid state structures. The device with the Cs_2CO_3 layer showed about 8–10% higher J_{SC} and about 6–8% higher power conversion efficiency compared with the devices without the Cs_2CO_3 layer.

Keywords Cs_2CO_3; electron injection layer; impedance; polymer solar cell; solution process

Introduction

Polymer solar cells based on solution process have been intensively studied because of their advantages of fabrication of low-cost, flexible, and large-area solar cells [1,2]. The main advantage of polymer solar cells is solution based process such as spin-coating, screen printing, or roll-to-roll coating not only on glass substrate but also on flexible substrates [3,4]. The power conversion efficiencies (PCE) of polymer solar cells are about 4–5% under AM1.5 illumination condition [5], but these efficiencies are much lower than those of inorganic solar cells such as silicon based or compound solar cells [6].

Because of efficiency issues, the potential applications of organic semiconductor in electronic and optoelectronic devices have increased attraction of researcher for

---

Address correspondence to Changhee Lee, Department of Electrical Engineering and Computer Science, Seoul National University, Gwanakro 599, Gwanak-gu, Seoul 151-747, Korea. Tel.: (+82)2-880-9093; Fax: (+82)2-877-6668; E-mail: chlee7@snu.ac.kr

Downloaded by [University of California, San Diego] at 12:15 07 August 2012

the studies of contact (interface) between the organic semiconductor and metallic contact (cathode and anode) [7,8]. In order to increase power conversion efficiency of polymer solar cells, we usually have used Lithium fluoride (LiF) as the electron injection layer by vacuum evaporation [9]. However, they require high temperatures (>500°C) and high vacuum states which increase fabrication costs [10].

In this paper, we report a polymer solar cells based on solution-processable interfacial electron injection layer, Cesium carbonate (Cs_2CO_3), between poly (3-hexylthiophene) (P3HT): phenyl-C60-butyric acid methyl ester (PCBM) and Aluminum electrode. The devices with various thickness of Cs_2CO_3 layer showed about 4~8% higher short circuit current (J_{SC}) and about 5~9% higher power conversion efficiency compared with the device without the Cs_2CO_3 layer. And we also studied the characteristics of organic solar cells using impedance spectroscopy.

Experimental Details

P3HT and PCBM were obtained from Rieke Metals Inc. and American Dye Source Inc., respectively. Cs_2CO_3,(99.995%), Chlorobenzene (C_6H_5Cl, anhydrous, 99.8%), and 2-Ethoxyethanol ($C_2H_5OCH_2CH_2OH$, 99.8%) were purchased from Sigma-Aldrich Chemical Co. Inc.

The organic solar cells were prepared on commercial indium-tin-oxide (ITO) coated substrates. The ITO substrates were subsequently cleaned using isopropyl alcohol, de-ionized water, acetone, methanol in an ultra-sonic bath and dried in vacuum oven at 120°C over 30 minutes. P3HT:PCBM blend solution was prepared with a weight ratio of 1:0.8 in Chlorobenzene. The solution was heated up to 50°C and continuously stirred over 3 h. The Cs_2CO_3 solution dissolved in 2-Ethoxyethanol in the ratio of 0.05, 0.2, 0.6, and 1.0 wt% was prepared.

After that, we deposited 10 nm of molybdenum-oxide (MoO_3) onto the ITO substrate under the high vacuum condition (2×10^{-6} Torr). The P3HT:PCBM solution was spin-coated on MoO_3 layer with a thickness of 120 nm, followed by spin-coating various concentration of Cs_2CO_3 solution (0.05, 0.2, 0.6, and 1.0 wt%), resulting a thickness of 10, 20, 30, and 40 Å. The fabricated films were dried in Ar atmosphere for 2 hours to remove any residual solvent. Then, the Al electrodes (100 nm) were evaporated under high vacuum condition (2×10^{-6} Torr). The samples were heated at 150°C for 30 minutes inside a glove box filled with Ar gas. The overlap for active area between ITO and Al electrode is 4 mm × 5 mm.

The photocurrent-voltage characteristics were measured by a Keithley 2400 source meter in the dark and under illumination from solar simulator (Newport, 91160A). The impedance spectroscopy was measured from 100 Hz to 10 MHz by a HP 4192 impedance analyzer.

Results and Discussions

Figure 1 shows the polymer solar cell structure and its schematic energy levels. The blend of P3HT:PCBM was used as the active layer in the device. MoO_3 layer was adopted in order to lower the energy barrier between ITO and the active layer [11]. And we used the Cs_2CO_3 layer fabricated by spin coating method on P3HT:PCBM films as the electron injection layer.

The morphology of the electron injection layer plays an important role for the interface properties of devices [12]. The electrical properties of the electron injection

Downloaded by [University of California, San Diego] at 12:15 07 August 2012

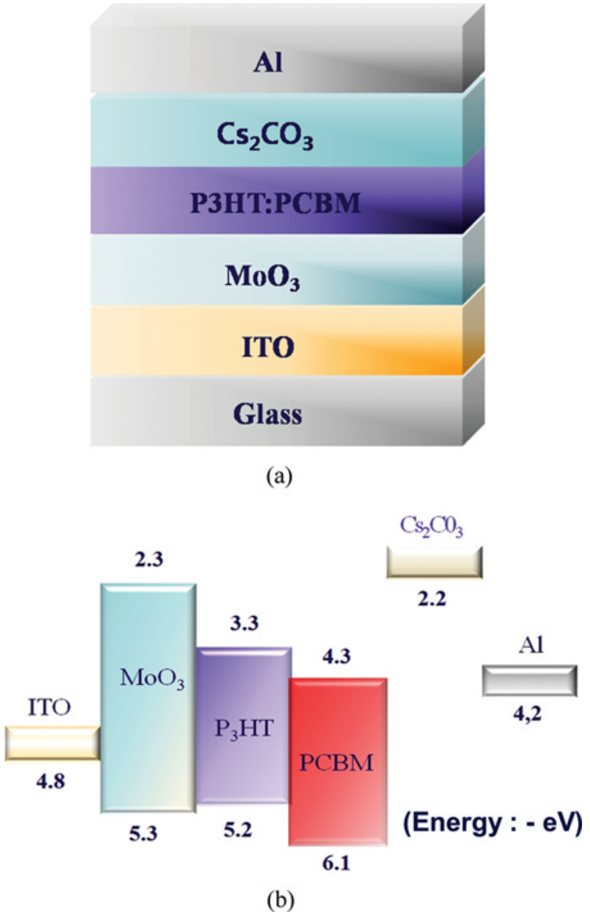


Figure 1. (a) The device structure and (b) schematic energy band diagram of polymer solar cell.

layer also affect the efficiency of charge collection [13,14]. Figure 2 shows the AFM images of the Cs_2CO_3 layer with different thickness. And the surfaces with the root-mean-square roughness values increased from 2.0 nm to 3.2 nm as the thickness of Cs_2CO_3 increased [15].

Figure 3 shows the (a) current density-voltage characteristics under illumination of 100 mW/cm^2 and (b) incident photon to collected electron (IPCE) spectra of polymer solar cells with and without Cs_2CO_3 and LiF as the electron injection layer. So we demonstrated three types of polymer solar cells, ITO/MoO_3/P3HT:PCBM/Al, ITO/MoO_3/P3HT:PCBM/LiF (0.5 nm)/Al, and ITO/MoO_3/P3HT:PCBM/Cs_2CO_3/Al.

And we used Cs_2CO_3 layer with different thickness by changing amount of Cs_2CO_3 dehydrate dissolved in 2-Ethoxyethanol between P3HT:PCBM and Al. The device with Cs_2CO_3 layer showed much improved performances compared to the device without Cs_2CO_3 layer. When we used 20 Å Cs_2CO_3 layer, the device performances exhibited the highest J_{SC} and PCE. The solar cell parameters are

Downloaded by [University of California, San Diego] at 12:15 07 August 2012

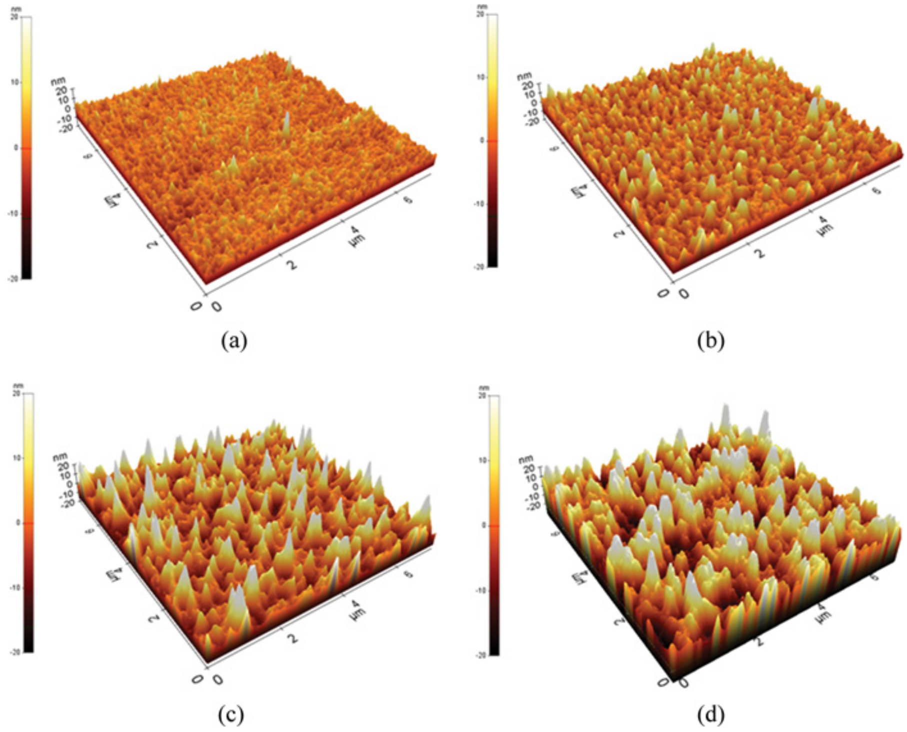


Figure 2. AFM images of Cs_2CO_3 layer with different thickness. Each picture shows Cs_2CO_3 layer with (a) 10 Å, (b) 20 Å, (c) 30 Å, and (d) 40 Å.

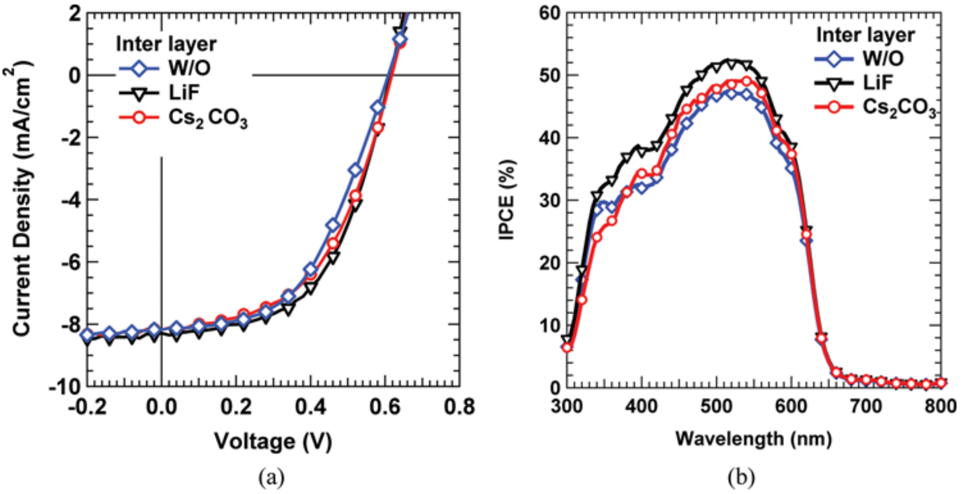


Figure 3. (a) The current density-voltage characteristics under illumination of 100mW/cm^2 and (b) IPCE spectra of polymer solar cells with different structures. We compared three types of polymer solar cells, ITO/MoO_3/P3HT:PCBM/Al, ITO/MoO_3/P3HT:PCBM/LiF (5Å)/Al and ITO/MoO_3/P3HT:PCBM/Cs_2CO_3(20 Å)/ Al.

Downloaded by [University of California, San Diego] at 12:15 07 August 2012

Table 1. The solar cell parameters as a function of Cs_2CO_3 layer thickness and LiF (5Å) as an EIL when we used device structure of ITO/MoO_3/P3HT:PCBM/EIL/Al

EIL Types	Thickness (Å)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
Cs_2CO_3	0	7.98	0.61	50	2.5
	10	8.18	0.62	52	2.64
	20	8.24	0.62	53	2.72
	30	8.23	0.62	50	2.62
	40	8.03	0.62	49	2.52
LiF	5	8.31	0.61	54	2.75

summarized in Table 1 and both J_{SC} and PCE plotted as a function of Cs_2CO_3 layer thickness in Figure 4.

In comparison with LiF, the devices with Cs_2CO_3 layer exhibited similar open circuit voltage (V_{OC}) and J_{SC}, however the PCE and fill factor (FF) of the device was slightly lower. Although the PCE of the devices using Cs_2CO_3 was low a little, it can be deposited with solution based processes such as spin-coating or inkjet printing. It is believed that Cs_2CO_3 layer device offer the possibility of fabricating high performance polymer solar cells using all solution processes.

Polymer solar cells can be modeled as a combination of contact, bulk, and junction resistance (R_C, R_B, R_J), and bulk and junction capacitance (C_B, C_J) [16]. The complete device can be modeled as the two different regions for carrier relaxation. The first region is the active layer region, and the third region is the interface of electron injection layer and the active materials [17]. We applied 0.6 V for impedance analysis because 0.6 V was alike value which device turned on, in order to obtain impedance characteristics [18].

Figure 5(b) shows the Cole-Cole plots of the devices without Cs_2CO_3 layer and with different thickness of Cs_2CO_3 layer at bias of 0.6 V in dark. Device operation

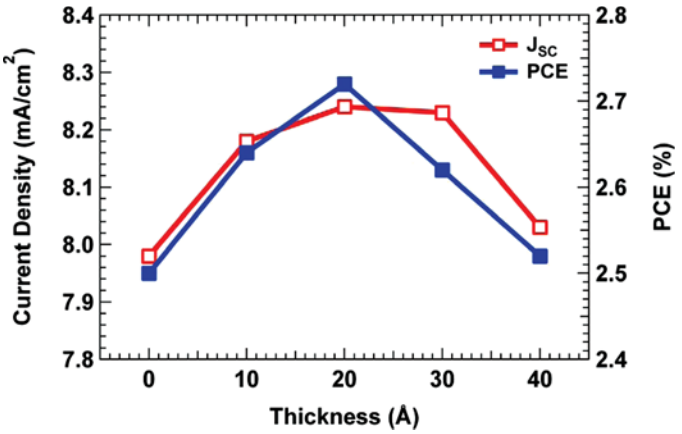
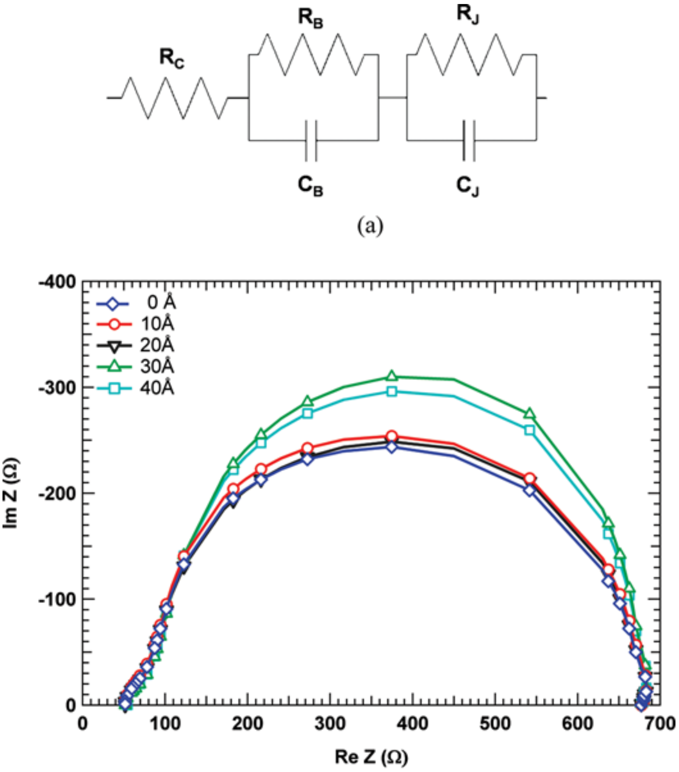


Figure 4. J_{SC} and PCE plotted as a function of Cs_2CO_3 layer thickness.



(a)

(b)

Figure 5. (a) schematic of the combination of resistance and capacitance in parallel of polymer solar cell, (b) The Cole Cole plot of the devices under dark at bias voltages of 0.6 V without buffer layer and with four different thickness of buffer layer.

parameters and the resistance value as a function of Cs_2CO_3 layer thickness in dark at bias of 0.6 V are summarized in Table 2. Because the property of active layer is not influenced by changing the electron injection layer, R_C, R_B, and C_B are not changed a lot with different thickness of Cs_2CO_3 layer. A Cs_2CO_3 formed cluster rather than thin layer which covered whole surface under Cs_2CO_3 layer of 0~20 Å, but R_J

Table 2. Device operation parameters and the resistance value as a function of Cs_2CO_3 layer thickness under dark at bias voltages of 0.6 V

EIL Types	Thickness (Å)	R_C (Ω)	R_B (Ω)	C_B (nF)	R_J (Ω)	C_J (nF)
Cs_2CO_3	0	57.2	67.4	2.2	526.4	46.2
	10	62	68.9	1.8	556.6	49.9
	20	62.4	71.6	1.9	546.0	59.8
	30	65	67.2	3.1	669.6	60.9
	40	62	70.6	3.9	652.6	63.2

Downloaded by [University of California, San Diego] at 12:15 07 August 2012

increased drastically over 30 Å because it formed thin layer covered whole surface [14,20]. Therefore, we obtained the optimized Cs_2CO_3 thickness of electron injection layer as 20 Å.

Conclusion

In summary, we studied the effect of solution-processed Cs_2CO_3 layer as the electron injection layer, and their thickness dependence on the performance of polymer solar cell based on P3HT:PCBM. We measured the photovoltaic characteristics and impedance analysis. The device with the Cs_2CO_3 layer showed higher J_{SC} and power conversion efficiency compared with the devices without the Cs_2CO_3 layer. It is also comparable to the device using LiF as the electron injection layer in terms of J_{SC} and power conversion efficiency. The results and approaches demonstrated in this paper can be applicable to the solution processed optoelectronic devices such as organic light-emitting diodes or organic photo detectors.

Acknowledgment

This work was financially supported by the National Research Foundation (NRF) of Korea through Acceleration Research Program (R0A-2008–000-20108–0) and also supported in part by the Ministry of Education, Science, and Technology (MEST) through the BK21 Program.

References

[1] Yu, G., Gao, J., Hummelen, J. C., Wudl, F., & Heeger, A. J. (1995). *Science*, *270*, 1789.

[2] Brabec, J., Sariciftci, N. S., & Hummelen, J. C. (2001). *Adv. Funct. Mater.*, *11*, 15.

[3] Krebs, F. C. (2009). *Sol. Energy Mater. Sol. Cells*, *93*, 465.

[4] Aernouts, T., Vanlaeke, P., Geens, W., Poortmans, J., Heremans, P., Borghs, S., Mertens, R., Andriessen, R., & Leenders, L. (2004). *Thin Solid Films*, *22*, 451.

[5] Sista, S., Park, M. H., Hong, Z., Wu, Y., Hou, J., Kwan, W. L., Li, G., & Yang, Y. (2010). *Adv. Mater.*, *22*, 380.

[6] Hoppe, H., Sariciftci, N. S., & Meissner, D. (2002). *Mol. Cryst. Liq. Cryst.*, *385*, 113.

[7] Ma, L. P., Liu, J., & Yang, Y. (2002). *Appl. Phys. Lett.*, *80*, 2997.

[8] Twarowski, A. J. (1982). *J. Chem. Phys.*, *77*, 1458.

[9] Günes, S., Neugebauer, H., & Sariciftci, N. S. (2007). *Chem. Rev.*, *107*, 1324.

[10] Farley, N. R. S., Staddon, C. R., Zhao, L., Edmonds, K. W., Gallagher, B. L., & Gregory, D. H. (2004). *J. Mater. Chem.*, *14*, 1087.

[11] Zhao, D. W., Liu, P., Sun, X. W., Tan, S. T., Ke, S., & Kyaw, A. K. K. (2009). *Appl. Phys. Lett.*, *95*, 153304.

[12] Zhang, F. L., Gadisa, A., Inganäs, O., Svensson, M., & Andersson, M. R. (2004). *Appl. Phys. Lett.*, *84*, 3906.

[13] Liu, Q., Duan, L., Li, Y., Qiao, J., Yu, Z., Zhang, D., Wang, L., Dong, G., & Qiu, Y. (2009). *Jpn. J. Appl. Phys.*, *48*, 102302.

[14] Huang, J., Xu, Z., & Yang, Y. (2007). *Adv. Funct. Mater.*, *17*, 1966.

[15] Joshi, A. G., Sahai, S., Gandhi, N., Krishna, Y. G. R., & Haranath, D. (2010). *Appl. Phys. Lett.*, *96*, 123102.

Downloaded by [University of California, San Diego] at 12:15 07 August 2012

[16] Glatthaar, M., Mingirullim, N., Zimmermann, B., Ziegler, T., Kern, R., Niggemann, M., Hinsch, A., & Gombert, A. (2005). *Phys. Stat. Sol. A202*, R125.
[17] Melzer, C., Krasnikov, V. V., & Hadziioannou, G. (2003). *Appl. Phys. Lett.*, *82*, 3101.
[18] Fall, M., Diagne, A. A., Dieng, M. M., Deflorian, F., Rossi, S., Bonora, P. L., Della, C., & Aaron, J.-J. (2005). *Synthetic Metals.*, *155*, 569.
[19] Park, M. H., Li, J.-H., Kumar, A., Li, G., & Yang, Y. (2009). *Adv. Funct. Mater.*, *19*, 1241.
[20] Chen, C. W., Lu, Y. J., Wu, C. C., Wu, E. H., Chu, C. W., & Yang, Y. (2005). *Appl. Phys. Lett.*, *87*, 241.

Downloaded by [University of California, San Diego] at 12:15 07 August 2012