

Research Article

Effect of TCO/ $\mu\text{c-Si:H}$ Interface Modification on Hydrogenated Microcrystalline Silicon Thin-Film Solar Cells

Shin-Wei Liang, Cheng-Hang Hsu, and Chuang-Chuang Tsai

*Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University,
1001 University Road, Hsinchu 300, Taiwan*

Correspondence should be addressed to Shin-Wei Liang; singwayshepherd@gmail.com

Received 19 July 2013; Accepted 21 November 2013

Academic Editor: Francesco Bonaccorso

Copyright © 2013 Shin-Wei Liang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The effects of H_2 plasma exposure on optical, electrical, and structural properties of fluorine-doped tin oxide (FTO) and AZO/FTO substrates have been investigated. With increasing the time of H_2 -plasma exposure, the hydrogen radical and ions penetrated through the FTO surface to form more suboxides such as SnO and metallic Sn , which was confirmed by the XPS analysis. The Sn reduction on the FTO surface can be effectively eliminated by capping the FTO with a very thin layer of sputtered aluminum-doped zinc oxide (AZO), as confirmed by the XPS analysis. By using the AZO/FTO as front TCO with the subsequent annealing, the p-i-n $\mu\text{c-Si:H}$ cell exhibited a significantly enhanced J_{SC} from 15.97 to 19.40 mA/cm^2 and an increased conversion efficiency from 5.69% to 7.09%. This significant enhancement was ascribed to the effective elimination of the Sn reduction on the FTO surface by the thin AZO layer during the Si-based thin-film deposition with hydrogen-rich plasma exposure. Moreover, the subsequent annealing of the sputtered AZO could lead to less defects as well as a better interface of AZO/FTO.

1. Introduction

Hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) is a promising material for high efficiency thin-film solar cells due to its advantages of reduced light-induced degradation and a lower bandgap, which lead to a higher photocurrent compared to hydrogenated amorphous silicon [1–6]. However, the superstrate p-i-n $\mu\text{c-Si:H}$ solar cells are usually prepared by exposing the textured transparent conductive oxide (TCO) substrate to strongly hydrogen-diluted silane plasma. This can lead to the interactions of TCO with hydrogen plasma which results in chemical reduction of TCO surface. Schade et al. reported that the optical transmission of tin oxide was reduced by the formation of an oxygen-depleted surface layer due to the chemical reduction of the oxide by the hydrogen plasma [7]. This surface of chemical reduction containing Sn and SnO not only affected the optical properties of the film but also may act as the source for Sn diffusion into the subsequent deposited film upon the tin oxide. Several groups have also studied the chemical reduction of a tin oxide surface due to hydrogen or argon plasma exposure [8–12]. To eliminate or alleviate the chemical reduction of

the TCO surface, other group has replaced indium tin oxide (ITO) or fluorine-doped tin oxide (FTO) with a layer of textured aluminum-doped zinc oxide (AZO), which is more resistant to plasma damage [13, 14]. However, thicker layers of sputtered AZO are not so desirable, with their flattened surface, which tend to show reduced haze and poor light trapping. In this study, we introduced a very thin AZO coating (3–5 nm) onto the textured FTO glass to maintain the light trapping and preserve the quality of the TCO/ $\mu\text{c-Si:H}$ interface for $\mu\text{c-Si:H}$ single-junction solar cells.

2. Experimental Details

A commercial textured FTO ($\text{SnO}_2\text{:F}$) glass was used as a substrate for a superstrate (glass/FTO/p-i-n) $\mu\text{c-Si:H}$ single-junction solar cells. A very thin layer of AZO (3–5 nm) was capped on the top of the textured FTO film by a radio frequency magnetron sputtering system, using a commercial AZO target with 4 inches in diameter at the power of 100 W. The target-substrate distance was 15 cm, and the substrate temperature was room temperature. Subsequent annealing of the FTO or AZO/FTO (FTO capped with a very thin

AZO) films was done in O_2 or N_2 environment at $200^\circ C$ for up to 4 hours. The $1.2\ \mu m$ -thick μc -Si:H single-junction solar cells were prepared by a 27.12 MHz PECVD system with NF_3 *in situ* plasma cleaning and a load-lock system. The doped and undoped μc -Si:H thin films were deposited by introducing SiH_4 , B_2H_6 , PH_3 , and CO_2 with high H_2 dilution.

To investigate the property change of FTO and AZO/FTO films after H_2 plasma exposure, the H_2 plasma was generated by the 27.12 MHz PECVD system with H_2 flow rate of 800 sccm, a pressure of 500 Pa, and a power density of $0.33\ W/cm^2$. These were the same deposition parameters of μc -Si:H p-layer except the introduction of SiH_4 and B_2H_6 . The optical and electrical properties of the FTO or AZO/FTO films were measured by a UV-Vis-IR spectroscopy and a Hall measurement, respectively. To further identify the plasma-induced changes on the FTO surface, an X-ray photoelectron spectroscopy (XPS) was performed on both treated and untreated samples, and the morphology was studied by a scanning electron microscopy (SEM). All XPS spectra were obtained in a fixed analyzer transmission mode, with 280 and 55 eV pass energies for survey spectra and high resolution spectra, respectively. AM 1.5 G solar simulator and external quantum efficiency (EQE) were employed for the device characterization. The cell area was defined by the metal electrode which was $0.25\ cm^2$.

3. Results and Discussion

To simulate the condition of the μc -Si:H p-layer deposition on the FTO films, we exposed the FTO substrate in the H_2 -plasma for 72 seconds, which was the same conditions as the μc -Si:H p-layer except the SiH_4 and B_2H_6 . To examine the durability of FTO substrate after H_2 -plasma exposure, a very thin layer of AZO (3–5 nm) was capped on the top of the textured FTO film for comparison with the only FTO substrate, due to the better chemical resistance of AZO against H_2 -plasma exposure.

Figure 1 shows the effect of H_2 -plasma treatment duration on optical transmission for FTO and AZO capped FTO (AZO/FTO) films. As the time of H_2 -plasma exposure increased from 0 to 900 seconds, the total transmission of FTO samples decreased from 81.41% to 46.71% at the wavelength of 550 nm, and the diffuse transmission exhibited the same trend. The decrease in transmission should be ascribed to the increased reflection and absorption of the increasing metallic Sn and the suboxide, SnO, with the increasing penetration depth of hydrogen ions. Chantarat et al. also mentioned that the optical bandgap became narrower due to the upward valence band and the downward conduction band since the both excess Sn and SnO may create crystal disorder and trap electron carriers [15]. Moreover, the AZO/FTO after 72-second H_2 -plasma exposure showed comparable transmission compared to the FTO without H_2 -plasma exposure, which should be due to the suppression of tin reduction by the thin AZO. This indicated that a very thin layer of AZO can significantly mitigate the deterioration of optical transmission after H_2 -plasma exposure.

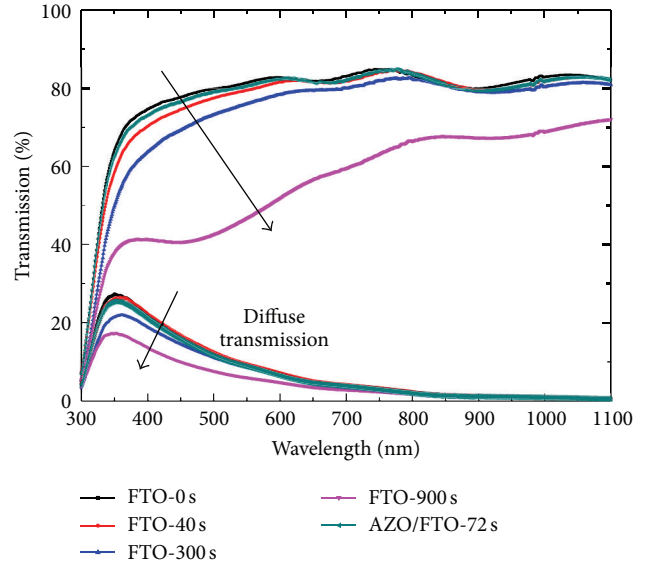


FIGURE 1: Effect of H_2 -plasma treatment time on optical transmission of FTO and AZO/FTO films.

We further investigated the effect of chemical reduction on electrical properties of FTO and AZO/FTO films after H_2 -plasma exposure. Although the combination of the surface layer after H_2 -plasma exposure and the underlying FTO was inhomogeneous, the dependence of the sheet resistance on the time of H_2 -plasma exposure can still be obtained by the Hall measurement. As the time of H_2 -plasma exposure increased from 0 to 900 seconds, the sheet resistance increased from 6.76 to 10.00 Ω/sq . With the increasing exposure time, the hydrogen radical and ions penetrated through the FTO surface to form more suboxides such as SnO and Sn, which was revealed by the XPS. The decrease in the sheet resistance was ascribed to the formation of less conductive suboxides as SnO [9]. Moreover, after the same time of 72-second H_2 -plasma exposure, the FTO substrate showed a sheet resistance of 8.52 Ω/sq and the AZO/FTO substrate showed a sheet resistance of 7.75 Ω/sq , which should be ascribed to the restraint on tin reduction by the thin AZO. Based on the mention above, the thin layer of AZO can alleviate the deterioration of sheet resistance and optical transmission after H_2 -plasma exposure.

Figure 2 displays the plane-view SEM images of the textured FTO films with or without H_2 plasma exposure. The sharp microstructures on the FTO films before H_2 plasma exposure were approximately 100–500 nm in grain size. After the H_2 -plasma exposure for 72 seconds, the surface morphology exhibited many small particles (20–30 nm in grain size) on the original FTO. As the time of H_2 -plasma exposure increased to 900 seconds, the original FTO microstructures were damaged heavily and the size of small particles increased to 50 nm. These small particles may be ascribed to the reduction of the $SnO_2:F$ (FTO) surface which became SnO and metallic Sn with increasing the duration of plasma exposure [9]. The study also reported that the thickness of the surface layer of chemical reduction was found

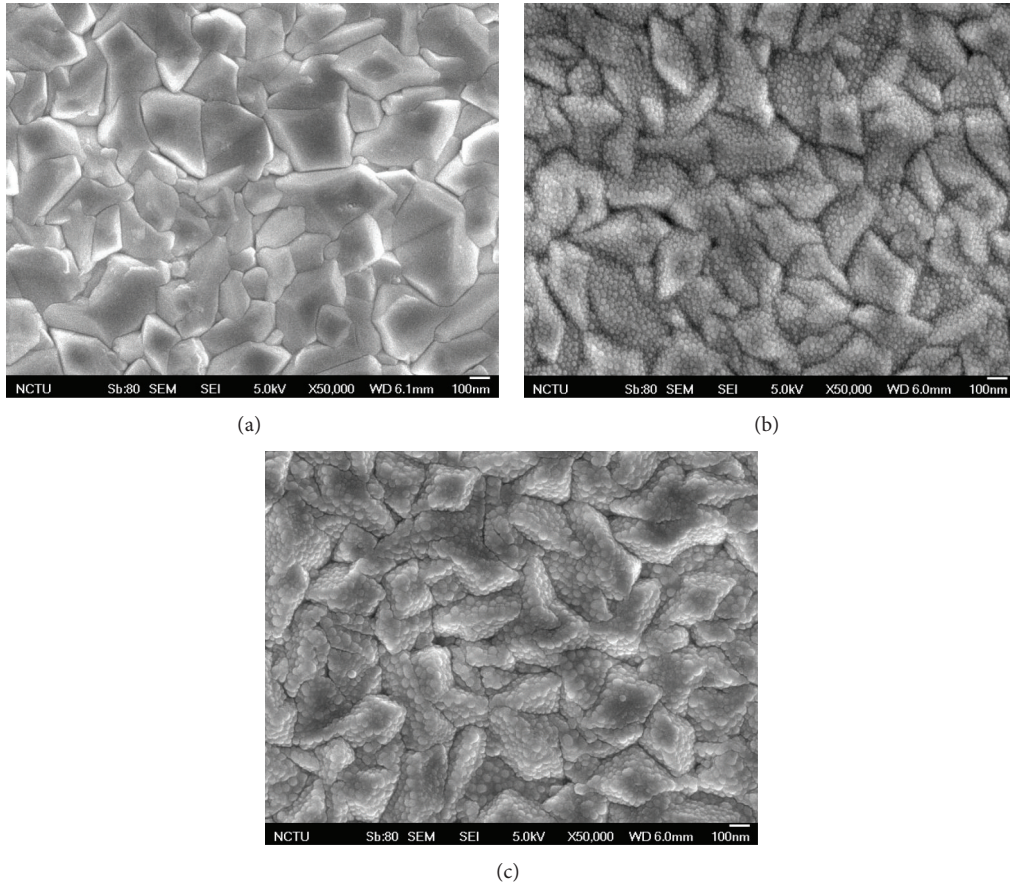


FIGURE 2: Plane-view SEM images of the textured FTO films (a) without H_2 plasma exposure, or with the H_2 plasma exposure for (b) 72 seconds and (c) 900 seconds.

to be 100 and 150 nm after H_2 -plasma (0.25 W/cm^2 , 13 Pa) exposure for 900 and 1800 seconds, respectively. In contrast, the surface damage and chemical reduction in our study would be more severe due to the higher power density and higher pressure (0.33 W/cm^2 , 500 Pa).

The combination of the optical, electrical, and structural results showed the FTO films were deteriorated after H_2 -plasma exposure, which may be originated from the chemical reduction to form the metallic Sn or suboxides of SnO . To further identify the plasma-induced changes on the SnO_2 surface, the survey spectra and high resolution spectra of XPS were obtained. The measured signals including oxygen and carbon (a surface contaminant) were not shown for brevity. The Sn $3d_{5/2}$ peaks of high resolution spectra as a function of H_2 plasma exposure for FTO and AZO/FTO films were shown in Figure 3. A single Sn peak of the FTO without H_2 -plasma exposure was observed at 487.0 eV. As the time of H_2 -plasma exposure increased from 0 to 900 seconds, the main peak shifted to lower binding energy. Schade et al. reported that the core level peak of SnO_2 is 487.0 eV, the main SnO peak is 486.7 eV, and the peak at 484.6 eV is due to elemental Sn [7]. These results confirmed that FTO film was reduced to the suboxide as SnO and metallic Sn with the increasing H_2 -plasma exposure duration. However, the AZO/FTO after 72-second H_2 -plasma exposure showed similar main peak at

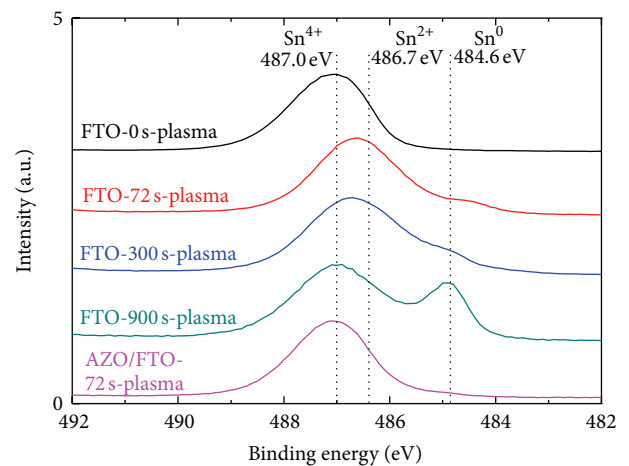


FIGURE 3: Sn $3d_{5/2}$ signal of XPS spectrum as a function of H_2 plasma exposure time for FTO and AZO/FTO films.

487.0 eV compared to the FTO without H_2 -plasma exposure. This demonstrated that a layer of AZO can effectively protect the FTO films from chemical reduction during H_2 -plasma exposure.

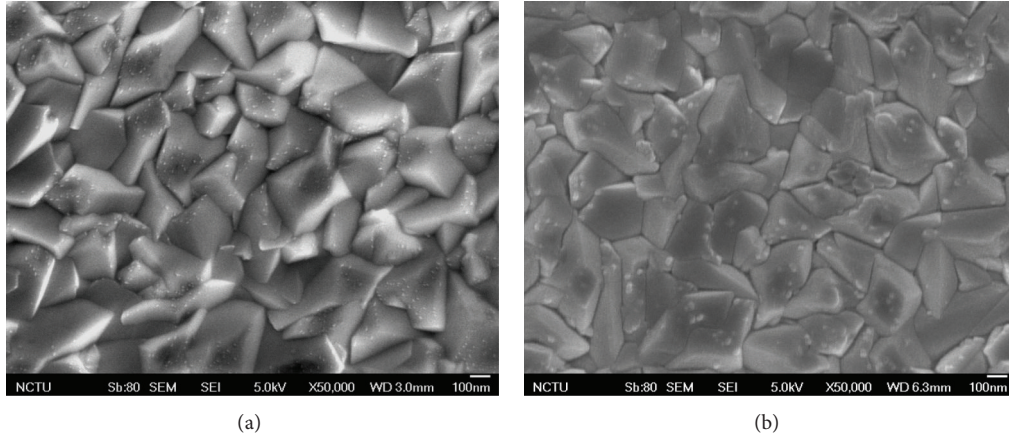


FIGURE 4: Plane-view SEM images of the 5 nm AZO capped FTO films (a) without and (b) with 72-second H_2 -plasma exposure.

The plane-view SEM images of the surface morphology of 5 nm AZO layer capped FTO films with and without 72-second H_2 -plasma exposure are shown in Figure 4. Before 72-second H_2 -plasma exposure, the thin AZO layer covered well on the original FTO texture, as shown in Figure 4(a). Compared to the FTO films undergoing 72-second H_2 -plasma exposure (shown in Figure 2(b)), the amount of the small particles on the original FTO microstructure arising from chemical reduction was significantly lowered by capping the 5 nm-thick AZO, which is shown in Figure 4(b). Combined with the XPS results, this confirmed that 5 nm-thick AZO layer can prevent the FTO surface from the reduction of tin oxide and ion bombardment during H_2 -plasma exposure. However, due to the less conductive nature of AZO material, the AZO film should be kept as thin as possible to retain the optoelectrical properties, while maintaining chemical reduction resistance. In this study, we have found that an optimized thickness of 5 nm-thick AZO film was obtained for the resistance to the hydrogen plasma as well as the cell performance. Based on the above results, the AZO/FTO structure with subsequent annealing in O_2 or N_2 environment at $200^\circ C$ was employed for the fabrication of μc -Si:H solar cells.

Figure 5 provides the J-V characteristics of $1.2 \mu m$ -thick μc -Si:H single-junction cells using the FTO or AZO/FTO as front TCO with subsequent annealing in N_2 or O_2 environment. The p-i-n μc -Si:H cell using only FTO exhibited a lower short circuit current density (J_{SC}) of 15.97 mA/cm^2 and a poor conversion efficiency of 5.69%. By using the unannealed AZO/FTO as front TCO, the J_{SC} increased to 17.42 mA/cm^2 . This was attributed to more optical transmission through the AZO/FTO substrate into the absorber due to the elimination of Sn reduction, which was confirmed by the results of optical transmission, as shown in Figure 1. However, the low efficiency and FF implied that the interface of TCO or TCO itself may need subsequent annealing for sputtered AZO. By using the AZO/FTO as front TCO with the subsequent annealing at $200^\circ C$ in O_2 environment for 0.5 hour, the p-i-n μc -Si:H cell exhibited a surprisingly enhanced J_{SC} from 15.97 to 19.40 mA/cm^2 , and the increased conversion efficiency

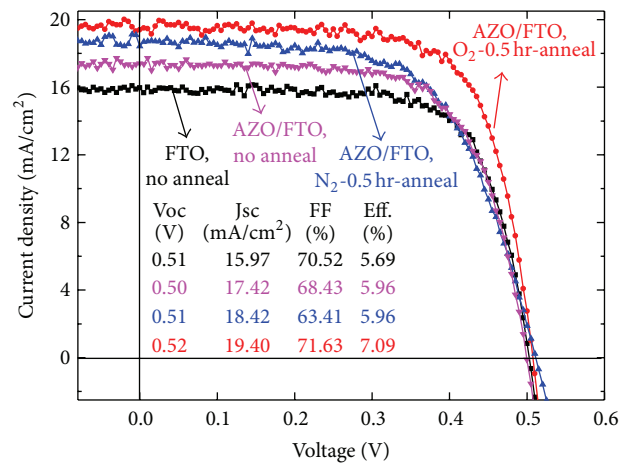


FIGURE 5: J-V characteristics of $1.2 \mu m$ -thick μc -Si:H single-junction cells using the FTO or AZO/FTO with subsequent annealing in N_2 or O_2 environment as front TCO.

from 5.69% to 7.09%. This significant enhancement was ascribed to the effective elimination of the Sn reduction on the FTO surface by the thin AZO layer during the Si-based thin-film deposition with hydrogen-rich plasma exposure. Moreover, the subsequent annealing of sputtered AZO could diminish the sputtering damage, leading to less defects and better interface of AZO/FTO. These results also corresponded to the quantum efficiency measurement, as demonstrated in Figure 6.

Figure 6 reveals the quantum efficiency (QE) of $1.2 \mu m$ -thick p-i-n μc -Si:H cells using the FTO or AZO/FTO as front TCO with subsequent annealing in N_2 or O_2 environment. Compared to the μc -Si:H cell using only FTO, the quantum efficiency of the μc -Si:H cell using AZO/FTO without annealing increased over wide wavelength range due to the suppression of the Sn reduction. The 0.5 hour annealing treatment of AZO/FTO in N_2 environment exhibited higher quantum efficiency than that of the AZO/FTO without annealing. The major QE enhancement at the wavelength

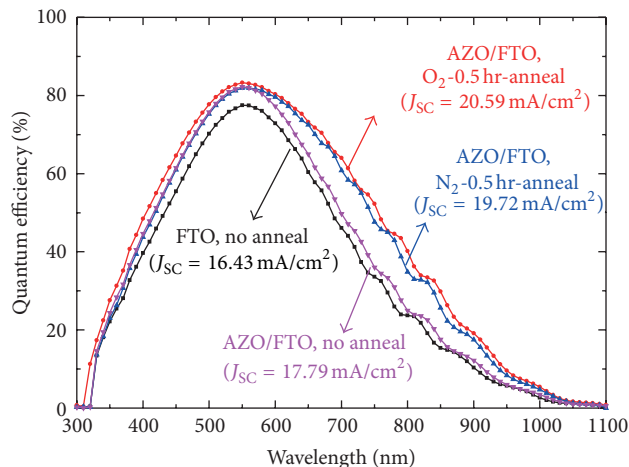


FIGURE 6: Quantum efficiency of 1.2 μm -thick p-i-n $\mu\text{c-Si:H}$ single-junction cells using the FTO or AZO/FTO as front TCO with subsequent annealing in N_2 or O_2 environment.

from 550 to 1100 nm may originate from the increased transmission after annealing in N_2 environment due to the reduction in the density of grain boundaries [16]. Besides, it is observed that the AZO/FTO after annealing in O_2 environment showed even higher quantum efficiency across whole measured wavelength than that in N_2 environment, which might be ascribed to the higher transmission after annealing in O_2 environment due to the decreased bulk defects and a small increase in bandgap [17]. By employing the AZO/FTO with O_2 annealing treatment for 0.5 hour, the $\mu\text{c-Si:H}$ solar cell exhibited a relative enhancement of the QE of more than 25% compared to the FTO configuration without annealing.

4. Conclusion

The effects of H_2 plasma exposure on optical, electrical, and structural properties of FTO and AZO/FTO substrates have been investigated. With increasing the time of H_2 -plasma exposure, the hydrogen radical and ions penetrated through the FTO surface of chemical reduction to form more suboxides such as SnO and metallic Sn , which was confirmed by the XPS analysis. The Sn reduction on the FTO surface can be effectively eliminated by capping the FTO with a very thin layer of sputtered AZO (3–5 nm), as confirmed by the XPS analysis. By using the AZO/FTO as front TCO with the subsequent annealing, the p-i-n $\mu\text{c-Si:H}$ cell exhibited a significantly enhanced J_{SC} from 15.97 to 19.40 mA/cm^2 and an increased conversion efficiency from 5.69% to 7.09%. This significant enhancement was ascribed to the effective elimination of the Sn reduction on the FTO surface by the thin AZO layer during the Si-based thin-film deposition with hydrogen-rich plasma exposure. Moreover, the subsequent annealing of the sputtered AZO could lead to less defects as well as a better interface of AZO/FTO. The quantum efficiency of the AZO/FTO configuration cell

exhibited a relative enhancement of more than 25% compared to the FTO configuration without annealing.

Conflict of Interests

The authors do not have any conflict of interests with the content of the paper.

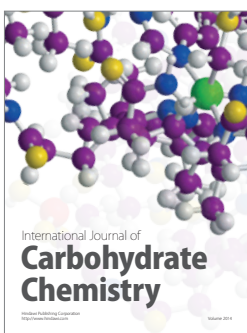
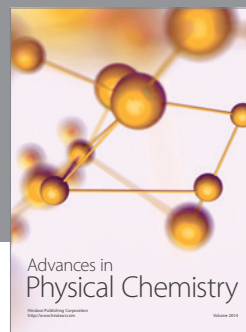
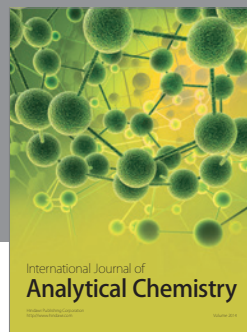
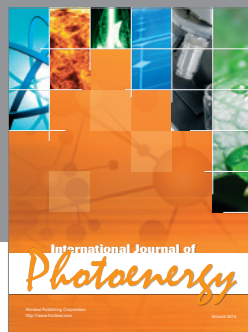
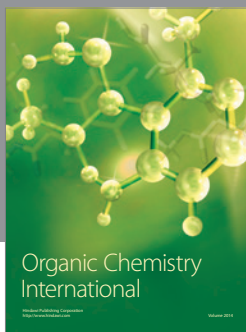
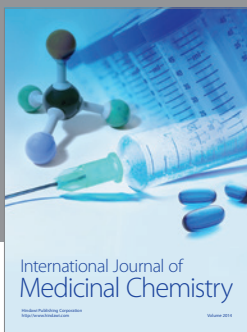
Acknowledgment

This work was supported by the National Science Council of Taiwan under Grant number 102-3113-P-008-001.

References

- [1] J. Meier, R. Flückiger, H. Keppner, and A. Shah, "Complete microcrystalline p-i-n solar cell—crystalline or amorphous cell behavior," *Applied Physics Letters*, vol. 65, no. 7, pp. 860–862, 1994.
- [2] A. Shah, E. Vallat-Sauvain, P. Torres et al., "Intrinsic microcrystalline silicon ($\mu\text{c-Si:H}$) deposited by VHF-GD (very high frequency-glow discharge): a new material for photovoltaics and optoelectronics," *Materials Science and Engineering B*, vol. 69-70, pp. 219–226, 2000.
- [3] M. Kondo, "Microcrystalline materials and cells deposited by RF glow discharge," *Solar Energy Materials and Solar Cells*, vol. 78, no. 1–4, pp. 543–566, 2003.
- [4] A. V. Shah, J. Meier, E. Vallat-Sauvain et al., "Material and solar cell research in microcrystalline silicon," *Solar Energy Materials and Solar Cells*, vol. 78, no. 1–4, pp. 469–491, 2003.
- [5] J. Kočka, "Relation of defects and grain boundaries to transport and photo-transport: solved and unsolved problems in microcrystalline silicon," *Journal of Non-Crystalline Solids*, vol. 358, pp. 1946–1953, 2012.
- [6] R. B. Bergmann, T. J. Rinke, R. M. Hausner, M. Grauvogl, M. Vetter, and J. H. Werner, "Thin film solar cells on glass by transfer of monocrystalline Si films," *International Journal of Photoenergy*, vol. 1, no. 2, pp. 89–93, 1999.
- [7] H. Schade, Z. E. Smith, J. H. Thomas III, and A. Catalano, "Hydrogen plasma interactions with tin oxide surfaces," *Thin Solid Films*, vol. 117, no. 2, pp. 149–155, 1984.
- [8] J. H. Thomas III, "X-ray photoelectron spectroscopy study of hydrogen plasma interactions with a tin oxide surface," *Applied Physics Letters*, vol. 42, no. 9, pp. 794–796, 1983.
- [9] S. Major, M. C. Bhatnagar, S. Kumar, and K. L. Chopra, "The degradation of fluorine doped tin oxide films in a hydrogen plasma," *Journal of Vacuum Science and Technology A*, vol. 6, pp. 2415–2420, 1988.
- [10] T. Minami, H. Sato, H. Nanto, and S. Takata, "Heat treatment in hydrogen gas and plasma for transparent conducting oxide films such as ZnO , SnO_2 , and indium tin oxide," *Thin Solid Films*, vol. 176, no. 2, pp. 277–282, 1989.
- [11] J.-M. Themlin, M. Chtaïb, L. Henrard, P. Lambin, J. Darville, and J.-M. Gilles, "Characterization of tin oxides by x-ray-photoemission spectroscopy," *Physical Review B*, vol. 46, no. 4, pp. 2460–2466, 1992.
- [12] L. Raniero, I. Ferreira, A. Pimentel et al., "Role of hydrogen plasma on electrical and optical properties of ZGO, ITO and IZO transparent and conductive coatings," *Thin Solid Films*, vol. 511-512, pp. 295–298, 2006.

- [13] H. C. Weller, R. H. Mauch, and G. H. Bauer, "Studies on the interface between novel type ZnO and p-a-SiC:H in 1.5 eV a-SiGe:H pin diodes in comparison to SnO_x and ITO," *Solar Energy Materials and Solar Cells*, vol. 27, no. 3, pp. 217–231, 1992.
- [14] H. N. Wanka, G. Bilger, and M. B. Schubert, "CO₂ plasma treatment of tin oxides," *Applied Surface Science*, vol. 93, no. 4, pp. 339–348, 1996.
- [15] N. Chantarat, S.-H. Hsu, C.-C. Lin, M.-C. Chiang, and S.-Y. Chen, "Mechanism of an AZO-coated FTO film in improving the hydrogen plasma durability of transparent conducting oxide thin films for amorphous-silicon based tandem solar cells," *Journal of Materials Chemistry*, vol. 22, no. 16, pp. 8005–8012, 2012.
- [16] A. Mahmood, N. Ahmed, Q. Raza et al., "Effect of thermal annealing on the structural and optical properties of ZnO thin films deposited by the reactive e-beam evaporation technique," *Physica Scripta*, vol. 82, no. 6, Article ID 065801, 2010.
- [17] O. Hamad, G. Braunstein, H. Patil, and N. Dhere, "Effect of thermal treatment in oxygen, nitrogen, and air atmospheres on the electrical transport properties of zinc oxide thin films," *Thin Solid Films*, vol. 489, no. 1-2, pp. 303–309, 2005.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

