Available online at www.sciencedirect.com

ScienceDirect

Solar Energy 127 (2016) 184–197

SOLAR ENERGY

www.elsevier.com/locate/solener

Bifacial 8.3%/5.4% front/rear efficiency ZnO:Al/n-Si heterojunction solar cell produced by spray pyrolysis

G.G. Untila *, T.N. Kost, A.B. Chebotareva

Lomonosov Moscow State University, Skobeltsyn Institute of Nuclear Physics, 119991 Moscow, Russian Federation

Received 23 November 2015; received in revised form 12 January 2016; accepted 20 January 2016

Communicated by: Associate Editor Takhir M. Razykov

Abstract

Using an as-deposited Al-doped ZnO (AZO) film synthesized by ultrasonic spray pyrolysis directly onto crystalline silicon (c-Si), we demonstrate a bifacial AZO/n-Si heterojunction solar cell (HJSC) with high efficiency of 8.3%/5.4% under front/rear illumination. To optimize fabrication process, the influence of substrate temperature T_D (in the range 310–460 °C), annealing, and film thickness d on the film and AZO/c-Si junction properties were studied systematically. SEM, ellipsometry, EDX spectroscopy, transmission, reflection, and external quantum efficiency spectra, resistivity ρ, Hall, Suns–V_{oc}, and light I–V measurements were used for the analysis. Annealed junctions, AZO/n-Si and AZO/p-Si, as well as AZO/p-Si junction with as-deposited films showed small open-circuit voltage V_{oc} (<300 mV). The highest V_{oc} (~480 mV) showed AZO/n-Si junction with as-deposited film grown at 410 °C. We employed as-deposited AZO films grown at 410 °C in AZO/(nn$^+$)Cz-Si/In$_2$O$_3$:F bifacial heterojunction solar cells, which differed only in the AZO film thickness. Increasing d from 260 to 910 nm resulted in the following: (1) the photocurrent did not changed; (2) ρ and R_{sh} of the film, V_{oc} and the series resistance of the HJSCs decreased; (3) the fill factor FF and efficiency η increased (for front illumination, FF: from 29.1 to 57.3%, η: from 3.3 to 8.3%, respectively). At rear illumination, the best cell showed the efficiency of 5.4%. At 1-sun front illumination and 20–50–100% 1-sun rear illumination, such a cell will generate energy approaching that produced by a monofacial solar cell of 9.1–10.3–12.1% efficiency.

Keywords: Heterojunction solar cells; Silicon; Al-doped zinc oxide; Ultrasonic spray pyrolysis; Electrical properties; Optical properties

1. Introduction

Offering a unique combination of high electrical conductivity and high optical transmission in the visible range, transparent conducting oxide (TCO) films have found wide practical application, in particular in flat panel displays, light emitting diodes, thin-film transistors, electrochromic devices, sensors, as well as in most types of solar cells, such as: organic, dye sensitized, and perovskite solar cells, solar cells based on cadmium telluride and copper indium diselenide (Cu(In,Ga)Se$_2$) compound semiconductors, amorphous, microcrystalline, and crystalline silicon (c-Si) (Liu et al., 2010; Avrutin et al., 2011; Razykov et al.,2011; Untila and Zaks, 2011; Qiu et al., 2013).

The first attempts to apply TCO films in c-Si solar cells were made as early as about 40 years ago. In the late 1970s, considerable research effort were focused on TCO/SiO$_x$/c-Si heterojunction solar cells (HJSCs) (DuBow et al., 1976; Franz et al., 1977; Shewchun et al., 1980; Maruska et al., 1983), which have recently attracted increased interest (Untila et al., 2013a; Bivour et al., 2015; Bullock et al.,

---

* Corresponding author. Tel.: +7 (495)932 88 02.
E-mail address: guntila@mics.msu.su (G.G. Untila).

http://dx.doi.org/10.1016/j.solener.2016.01.028
0038-092X/

2015; Gerling et al., 2016; Kobayashi et al., 1995a, 1993; Battaglia et al., 2014; Bethge et al., 2013; Lupan et al., 2009; Fang et al., 2014; Ibrahim and Ashour, 2006; Djessas et al., 2014; Baik and Cho, 1999; Pietruszka et al., 2014; Hsu et al., 2012; Ben Ayadi et al., 2014; Chebotareva et al., 2015). Whereas theoretical predictions claim a possible solar to electricity conversion efficiency of 19–21% for such cells (Shewchun et al., 1980; Hussain et al., 2015) experimental efficiencies are lower. Table 1 presents some of the best results obtained to date. It is seen that the efficiency of HJSCs with an indium oxide-based film, In_2O_3:Sn (ITO) or In_2O_3:F (IFO), is higher than that offered by solar cells that have ZnO-based films. Note that ITO films dominate on the market because of the best compromise between low electrical resistivity and high transparency (Gordon, 2000). However, due to the expected scarcity of indium (Razykov et al., 2011), efforts are underway to develop ZnO-based thin films (such as ZnO:Al (AZO), ZnO:Ga (GZO), and ZnO:In (IZO)) as an alternative for ITO as the transparent electrode in solar cells.

The physical properties of ZnO-based films are generally dependent on deposition techniques and conditions. Many deposition techniques have been developed in order to obtain transparent and conductive ZnO-based thin films, including magnetron sputtering (MS), (Djessas et al., 2014; Ben Ayadi et al., 2014) pulsed laser deposition (PLD) (Fang et al., 2014; Hsu et al., 2012), atomic layer deposition (ALD) (Bethge et al., 2013; Pietruszka et al., 2014), chemical vapor deposition (Hu and Gordon, 1992), sol–gel process (Baik and Cho, 1999), successive chemical solution deposition (SCSD) (Lupan et al., 2009), and spray pyrolysis (SP) (Bivour et al., 2015; Kobayashi et al., 1995a; Ibrahim and Ashour, 2006), etc. Among these techniques, SP method is the most promising method for the cost reduction of cell fabrication because of the simplicity of the apparatus and fast deposition rate. Using SP method, Kobayashi et al. 20 years ago achieved the efficiency of 6.9% for IZO/n-Si HJSC (Table 1). This result was the highest for 18 years. Recently, in 2013, Bethge et al. obtained conversion efficiency of 8.05% for AZO/La_2O_3/p-Si HJSC fabricated by ALD method. However, further efficiency improvements are mandatory to render HJSCs economically viable. For this purpose, different approaches are under study. For example, it was proposed to deposit an ITO film on top of ZnO film (Kobayashi et al., 1995a; Ben Ayadi et al., 2014). The shortcoming of this approach is that it uses a large amount of indium. Besides, various metal oxides were probed as an interfacial layer between TCO film and silicon substrate, namely Al_2O_3, ZrO_2, Y_2O_3, La_2O_3, and MoO_3 thin films (Battaglia et al., 2014; Bethge et al., 2013).

In this work, we demonstrate a bifacial AZO/n-Si HJSC produced by ultrasonic spray pyrolysis (USP) method (an advanced version of the SP) reaching an efficiency of 8.3%/5.4% under front/rear illumination. The influence of growth temperature, annealing, and film thickness on the film and AZO/c-Si junction properties were studied systematically. To our surprise, we did not find in the literature any attempts to obtain an AZO/n-Si HJSC by spray pyrolysis.

2. Experimental

2.1. Samples

We fabricated the following test samples: AZO on glass for Hall and optical measurements, as well as AZO/(nn^+)

Table 1
Parameters of HJSCs with indium oxide based and zinc oxide based TCOs: short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and conversion efficiency (η).

Reference	Solar cell structure	Method[a]	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)
Untila et al., 2013a	IFO/p-Si	USP	37.7	618	76.3	**17.8**
Bivour et al., 2015	ITO/WO_x/FZ-n-Si	MS	~33.5	~660	~80.0	**~17.7**
Bullock et al., 2015	ITO/MoO_x/SiO_x/n-FZ-Si	MS	35.0	637	75.0	**16.7**
Gerling et al., 2016	ITO/V_2O_x/n-Si	MS	34.4	606	75.3	**15.7**
Kobayashi et al., 1993	ITO/n-Si	SP	39.0	540	71.2	**15.0**
Battaglia et al., 2014	ITO/MoO_x/n-Si	MS	37.8	580	65.0	**14.3**
Shewchun et al., 1980	ITO/p-Si	IBS[b]	32.2	581	74.5	**14.0**
Bethge et al., 2013	AZO/La_2O_3/p-Si	ALD	21.4	527	71.3	**8.05**
Kobayashi et al., 1995a	IZO/n-Si	SP	30.1	410	56.0	**6.9**
Lupan et al., 2009	AZO/p-Si	SCSD	28.0	335	72.1	**6.8**
Fang et al., 2014	IZO/n-Si	PLD	35.6[c]	380	49.7	**6.7**
Ibrahim and Ashour, 2006	AZO/p-Si	SP	10.0[d]	520	63.0	**6.6**
Djessas et al., 2014	IZO/p-Si	MS	25.0	480	50.0	**6.0**
Baik and Cho, 1999	AZO/n-Si	Sol–Gel	23.5	372	60.6	**5.3**
Pietruszka et al., 2014	AZO/ZnO/p-Si	ALD	34.0	270	50.0	**5.0**
Hsu et al., 2012	AZOY/n-Si	PLD	31.5	240	51.0	**3.9**
Kobayashi et al., 1995a	ITO/IZO/n-Si	SP	32.0	410	65.0	**8.5**
Ben Ayadi et al., 2014	ITO/AZO/p-Si	MS	21.0	475	50.0	**5.0**

[a] TCO film growth method.
[b] IBS – ion-beam sputtering.
[c] Result was derived by us using the *EQE* spectrum given in the article.
[d] Result was obtained under 500 W/m^2 illumination.