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# Contact resistance of indium tin oxide and fluorine-doped indium oxide films grown by ultrasonic spray pyrolysis to diffusion layers in silicon solar cells

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ABSTRACT

A simple method is described for estimating the contact resistance between a transparent conducting oxide film and a diffusion layer in a silicon solar cell. We have investigated the effect of film growth temperature on the contact resistance between $n^{++}$-Si and $p^{++}$-Si layers and $In_2O_3$:Sn (ITO) and $In_2O_3$:F (IFO) films grown by ultrasonic spray pyrolysis. The effect of growth temperature on the properties of the $SiO_x$ layer in IFO/$SiO_x$/$n^{++}$-Si structures has been studied by Fourier transform infrared absorption spectroscopy. The process for IFO deposition on $n^{++}$-Si layers has been modified in order to reduce the IFO/$SiO_x$/$n^{++}$-Si contact resistance. The use of modified IFO has reduced the series resistance of an ITO/($p^{++}nn^{++}$)Cz-Si/IFO bifacial solar cell for low-concentration applications by 0.13 Ω cm$^2$, from 0.39 to 0.26 Ω cm$^2$; extended its operating range of concentration ratios by a factor of 1.5, from 1–3.5 × to 1–5.3 ×; and improved its efficiency in the operating range from 17.6–17.9 to 17.7–18.2%.



## 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 [1], in particular in displays, light emitting diodes, and some types of solar cells, mainly in thin-film devices. At the same time, TCO films have only been used in the manufacture of crystalline silicon (c-Si) solar cells by Sanyo Electric [2]. Researchers at this company have recently obtained a record high efficiency (24.7% [3]) with $In_2O_3$:Sn (ITO)/a-Si/c-Si heterostructures, thereby demonstrating that TCO films have immense potential for use in solar cells. Note that the success of the HIT structure is primarily due to the high level of c-Si surface passivation with undoped a-Si film.

Note also that the first attempts to apply TCO films in solar cells were made as early as about 40 years ago. In the late 1970s, considerable research effort focused on solar cells based on TCO/$SiO_x$/c-Si heterojunctions [4–8], which have recently attracted increased interest [9–14]. Solar cells have been demonstrated with an efficiency of 6.8% for ZnO:Al (AZO)/$SiO_x$/p-Si heterojunctions [11], 8.5% for ZnO:In (IZO)/$SiO_x$/n-Si [7], 14.1% for $SnO_2$/$SiO_x$/n-Si [8], 16.2% for ITO/$SiO_x$/n-Si [9], and 17.8% for $In_2O_3$:F (IFO)/$SiO_x$/p-Si [14]. In those studies, most attention was paid to the ability to increase the open-circuit voltage $V_{oc}$ of solar cells by raising the potential barrier height in the heterojunction and optimizing the properties of the intermediate layer ($SiO_x$).

In the early 1980s, TCO films were proposed as antireflection coatings and, at the same time, as transparent electrodes in p–n junction silicon solar cells [15,16]. This approach allows one to overcome problems arising from the use of a high-efficiency, high-sheet-resistance (> 100 Ω/sq), homogeneous emitter, in particular, those related to the shunting of the emitter, the high metal/Si contact resistance, and the high spreading resistance of the emitter between the contacts [17–24]. In recent years, this issue has been receiving increasing attention [25-37]. Table 1 presents some of the results obtained to date. Note that the highest efficiency and the highest open-circuit voltage are offered by solar cells that have not an ITO but an IFO film on their $n^{++}$-Si emitter.

Analysis of the literature demonstrates that studies aimed at optimizing the properties of TCO films for use in silicon solar cells were typically concerned with their parameters such as resistivity, optical transmission, and TCO/Si heterojunction barrier height. There has been less work on the passivation level of the emitter surface [33,34,38]. Moreover, the contact resistance between TCO films and diffused emitters in silicon solar cells has not yet been studied in sufficient detail.

In this paper, we describe a simple method for estimating the contact resistance between a TCO film and a heavily doped diffusion layer in silicon. The method was used to determine the TCO/$n^{++}$-Si

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**Table 1**
Parameters of solar cells with TCO antireflection coatings: short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), series resistance ($R_s$), and conversion efficiency ($\eta$). $n^{++}$-Si and $p^{++}$-Si stand for heavily doped n- and p-type silicon layers, respectively.

| Year, reference | Solar cell structure | Method[a] | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (mV) | FF (%) | $R_s$, (Ω cm$^2$) | $\eta$ (%) |
|---|---|---|---|---|---|---|---|
| 1985, Chaoui [16] | ITO/($n^{++}pp^{++}$)Cz-Si/Al | SP[b] | 33.7 | 565 | 74.0 | – | **14.1** |
| 2005, Untila [25] | IFO/($n^{++}pp^{++}$)Cz-Si/ITO | USP[c] | 36.6 | 619 | 76.2 | – | **17.3** |
| 2005, Untila [25] | ITO/($p^{++}nn^{++}$)Cz-Si/IFO | USP | 36.2 | 623 | 78.3 | – | **17.7** |
| 2008, Batzner [26] | ITO/($n^{++}pp^{++}$)Cz-Si/Ni/Cu | MS[d] | 32.8 | 605 | 76.7 | 0.89 | **15.2** |
| 2010, Verma [27] | AZO/($n^{++}pp^{++}$)Cz-Si/Ti/Ag | Sol-gel | 12.1 | 573 | – | – | – |
| 2012, Kim [28] | 3D-ITO/($n^{++}pp^{++}$)Cz-Si/Al | MS | 29.6 | 604 | 79.8 | – | **14.3** |
| 2012, Kim [29] | ITO/($n^{++}pp^{++}$)Cz-Si/Al | MS | 32.7 | 583 | 74.0 | 0.17 | **14.1** |
| 2012, Ryu [30] | ITO/($n^{++}pp^{++}$)Cz-Si/Al | MS | 36.2 | 600 | 78.3 | – | **16.9** |
| 2012, Untila [31] | ITO/($p^{++}nn^{++}$)Cz-Si/IFO | SP | 35.1 | 611 | 76.7 | 0.43 | **16.5** |
| 2013, Kim [32] | ITO/($n^{++}pp^{++}$)Cz-Si/Al | MS | 36.8 | 604 | 74.8 | 1.4 | **16.7** |
| 2013, Khan [33] | AZO/($n^{++}pp^{++}$)Cz-Si/AZO | Sol-gel | 26.5 | 594 | 71.2 | 3.81 | **11.2** |
| 2014, Kim [34] | ITO/$SiO_x$/($n^{++}pp^{++}$)Cz-Si/Al | MS[e] | 33.3 | 618 | 83.0[e] | – | **17.1** |
| 2014, Le [35] | ITO/($n^{++}pp^{++}$)Cz-Si/Al | MS | 35.2 | 604 | 82.5 | – | **17.6** |
| 2014, Untila [36] | IFO/($n^{++}pp^{++}$)Cz-Si/ITO | USP | 37.3 | 630 | 78.6 | 0.23 | **18.6** |
| 2014, Untila [37] | ITO/($p^{++}nn^{++}$)Cz-Si/IFO | USP | 35.3 | 635 | 78.6 | 0.37 | **17.6** |

[a] TCO film growth method.
[b] SP—spray pyrolysis.
[c] USP—ultrasonic spray pyrolysis.
[d] MS—magnetron sputtering.
[e] Result was extracted from the Suns–$V_{oc}$ measurement.

and TCO/$p^{++}$-Si contact resistances for ITO and IFO films grown by ultrasonic spray pyrolysis (USP) at various growth temperatures. Electrical, optical properties and composition of ITO and IFO films have been reported elsewhere [14,39–41].

The next step of this study was to optimize IFO film growth on the $n^{++}$-Si emitter in order to reduce the IFO/emitter contact resistance. The use of optimized IFO in the fabrication of an ITO/($p^{++}nn^{++}$)Cz-Si/IFO bifacial solar cell for low-concentration systems allowed its series resistance to be reduced by 0.13 Ω cm$^2$: from 0.39 to 0.26 Ω cm$^2$.

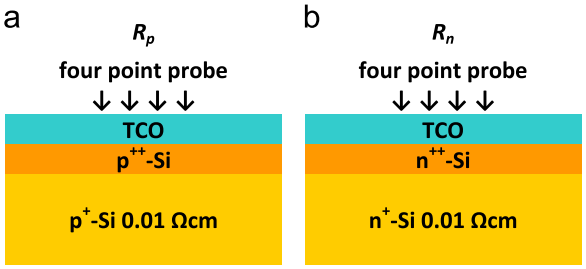


**Fig. 1.** Schematics of the (a) TCO/($p^{++}p^{+}$)Cz-Si and (b) TCO/($n^{++}n^{+}$)Cz-Si test structures. Their sheet resistances, $R_p$ and $R_n$, respectively, were measured from the TCO side.

## 2. Experimental

All of the silicon structures used in this study were manufactured at Solar Wind Ltd. (Krasnodar, Russia) from (1 0 0)-oriented Czochralski silicon (Cz-Si) wafers using standard equipment and standard industrial solar cell fabrication processes [42]. The wafers were textured with pyramids by a standard etching procedure in an alkali solution containing isopropanol. The heavily doped layers, denoted as $p^{++}$-Si and $n^{++}$-Si, were produced by boron and phosphorus diffusions, respectively, from spun-on glass sources. Such diffusion layers, with a sheet resistance of ~60–80 Ω/sq and near-surface carrier concentration of ~$10^{20}$ cm$^{-3}$, are typically used in solar cells [43]. The diffusion layer fabrication process was described in detail elsewhere [42]. After the diffusion process, the wafers were cut into squares 25 × 25 mm$^2$ in dimensions.

### 2.1. Test structures

($p^{++}p^{+}$)Cz-Si and ($n^{++}n^{+}$)Cz-Si test structures (Fig. 1) were produced from p- and n-type low-resistivity (~0.01 Ω cm) silicon wafers ~625 μ thick, which will be denoted for clarity as $p^{+}$-Si and $n^{+}$-Si, respectively. Note that the wafers had a sheet resistance $R_{Si}$ as low as ~0.16 Ω/sq.

TCO (IFO and ITO) films ~85 nm thick were grown on the surface of the silicon structures by USP: pyrolysis of film-forming solution (FFS) aerosols generated by an Al'bedo IN7 ultrasonicator at a working frequency of 2.64 MHz. The experimental setup used was described previously [40]. The aerosol was delivered from the atomization chamber to the deposition chamber by a carrier gas at a flow rate of 0.8 L/min, unless otherwise indicated. As a carrier gas, we used an Ar+5% $O_2$ mixture for IFO film growth and oxygen or argon for ITO growth. For convenience, the ITO films grown in an oxygen atmosphere will be referred to as ITO-Ox, and those grown in argon, as ITO-Ar. The aerosol was sprayed onto a substrate placed on a massive plate heated to a desired temperature. The temperature of the plate, $T_D$, was measured by a thermocouple. The film growth time was 3 min, unless otherwise indicated.

Prior to TCO deposition, the structures were treated for 10 min in an ammonia–peroxide mixture ($H_2O$:$H_2O_2$:$NH_4OH$=5:1:1, 75–80 °C) and for 30 s in 4% HF. Note that our ITO and IFO films possess very high chemical stability: to dissolve the films, they should be held in concentrated HF for more than 20 min. Moreover, the sheet resistance of the films is not influenced by the ammonia–peroxide treatment.

The IFO film was grown using 0.2 M $InCl_3$+0.05 M $NH_4F$+0.1 M $H_2O$ in methanol as an FFS. The ITO film was grown using a 0.1 M $InCl_3$+0.003 M $SnCl_4$+7 M $H_2O$ solution in methanol. After the TCO deposition, the edges of the structure were removed by cleaving with a diamond scribe in order to eliminate edge shunting.

In a number of experiments, the structures were annealed. To this end, they were placed in the deposition chamber, preheated to 375 °C, and nebulized methanol was delivered to the chamber by a carrier gas (Ar).

The sheet resistance was measured by the four probe method using a Jandel Engineering RM 3000 test unit:

$R_n$, the sheet resistance of the TCO/($n^{++}n^{+}$)Cz-Si structure measured from the TCO side;