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TCO contacts for high efficiency c-Si solar cells: Influence of different annealing steps on the Si substrates and TCO layers properties

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Abstract

Different Transparent Conductive Oxide (TCO) layers properties are evaluated after annealing steps at temperatures above 200°C, in order to study their potential use in crystalline silicon (c-Si) solar cells fabrication processes. While the conductivity of Indium Tin Oxide (ITO) layers obtained by magnetron sputtering (MS) is almost stable after annealing in air, Aluminum doped Zinc Oxide (AZO) layers deposited by Atomic Layer Deposition (ALD) need a controlled atmosphere to maintain high carrier densities and mobilities. During the annealing processes, contaminating atoms (such as Zn) diffuse into the c-Si bulk and may potentially decrease its quality. Thus, both the contamination of the c-Si bulk and the properties of the AZO layer have been analyzed.

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Keywords: AZO ; ALD ; annealing ; passivated contacts

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1. Introduction

The use of Transparent Conductive Oxide (TCO) layers is becoming mandatory for the fabrication of high efficiency, both sides contacted (BSC) crystalline silicon (c-Si) bifacial solar cells. Low saturation current densities (J_0) may indeed be obtained through different approaches such as "Silicon HeteroJunction" (SHJ) [1], "dopant free"[2], "poly-Si/SiOx" [3,4] or "lightly doped homojunctions"[5], which all lead to high sheet resistances of the electron/hole collecting layers. A TCO layer deposited on top of such junctions is therefore useful to improve both their electrical (lateral and contact resistivity) and optical (front and rear reflectivity) properties. Hydrogenated amorphous silicon (a-Si:H) layers used in the two first approaches cannot withstand annealing temperatures above 250-300°C, which make them hardly compatible with conventional processes used for homojunctions cells. Another drawback of a-Si:H (and also poly-Si to a lesser extent) is its high parasitic absorption which may limit the J_{SC} when used at the front side of BSC cells [3]. TCO layers are extensively studied for "low" temperature processes, compatible with a-Si:H layers, but few studies deal with the behaviour of such layers at higher annealing temperatures. For the "poly-Si/SiO_x" or "lightly doped homojunctions" approaches, a TCO contact may indeed be deposited and/or annealed above 300°C without damaging the junction quality. In those cases, such "high" temperature annealing processes can even improve the contacts, the bulk hydrogenation, the surface passivation or the optical properties of the devices [6–8]. Indium Tin Oxide (ITO) layers obtained by magnetron sputtering (MS) are widespread as TCO's for solar cells fabrication. However using Indium is expensive and this deposition method causes surface damages, resulting in a growing interest towards alternative materials and processes such as Aluminum doped Zinc Oxide (AZO) and Atomic Layer Deposition (ALD)[9]. The aim of this work is to study the influence of different annealing steps on AZO (ALD) layers suitable for high efficiency BSC solar cells fabrication (Fig. 1.). Depending on the annealing conditions (temperature and atmosphere), standard electrical and optical properties of the TCO layers have been evaluated and the influence of the TCO layer on the c-Si bulk has been analysed.



Fig. 1. Schematic diagram of the positioning of the TCO layer developed for passivated contact purposes.

2. Materials and method

Industrial 156×156 mm² n-type pseudo-square Cz wafers were prepared through a wet chemical texturing process. After a cleaning step, AZO layers were deposited by ALD on both sides of the Si wafers (80 nm thick) and on glass substrates (40 nm thick). Annealing steps were carried at varying temperatures from 200°C to 800°C for 5 minutes, in air or controlled atmosphere (vacuum, N_2, Ar-H_2). The sheet resistance (R_{Sheet}) values of the TCO layers were measured using a 4-point probe set-up on the glass samples. Hall effect measurements were used to determine the carrier density and Hall mobility in the TCO layers (glass substrates). Optical spectroscopy was used to measure the transmittance of those layers deposited on glass. After etching the TCO layers 5 minutes in 10%HF solution and a surface cleaning of the silicon wafer in HCl/HNO_3 and then HF/HCl to get rid of the last metal compounds on the surface, ICP-MS (Inductively Coupled Plasma Mass Spectrometry) measurements were carried out to compare the concentration of metal elements in the c-Si bulk before and after the annealing steps. In order to see if the annealing had any influence on the substrate quality, the etched samples were coated with a SiN_x:H layer. The effective carrier lifetime of the c-Si samples was then measured using an Inductively Coupled Photo-Conductance Decay (IC-PCD) technique. The implied open circuit voltage (iV_{OC}) and saturation current density (J_0) were extracted from these measurements to compare the influence of the potential contamination of the Si wafers after the different heat-treatments.

3. Results and discussion

3.1. Interactions of the TCO layers with the c-Si substrates

TCO layers contain atoms which may potentially diffuse into the silicon wafers. To detect that kind of contamination ICP-MS analyses were performed on the c-Si substrates. To highlight the effect of annealing on Al and Zn diffusion, the metal concentrations within the substrate were normalised with respect to the concentrations in the c-Si bulk before annealing (Fig. 2a.). Those results show that zinc and aluminium from the AZO layer thermally diffuse within the silicon substrate. Indeed, increased Al and Zn concentrations in c-Si are observed with the increase of the annealing temperature. The larger Zn concentration increase compared to Al for all temperatures is in good agreement with the higher diffusivity of Zn in silicon [10]. Diffusion of such atoms, could reduce the electrical quality of the c-Si materials [11], especially the bulk carrier lifetime.

In order to evaluate the influence of Al and Zn diffusion on the c-Si bulk, charge carrier lifetime was analysed after the samples had been etched (TCO and Si sub-surface (2 to 5nm etched)) and passivated by SiN_x:H layers. For technical reasons, those samples were annealed in a different oven with the capacity to heat the samples only up to 600°C. Despite the Al and Zn diffusion, iV_{OC} and J_0 values calculated from the IC-PCD measurements are similar to the values expected on n-type Cz silicon wafers for all the annealed wafers (Fig. 2b.). A slight improvement of the iV_{OC} with increasing annealing temperature is even noticeable.

Given those results aluminium and zinc diffusion in the c-Si bulk does not seem to interfere with the carrier recombination properties of the substrate. However, it should be noted that hydrogen might diffuse in the c-Si during the SiN_x:H deposition, thus healing the potential defects created by Al and Zn atoms. This hypothesis is to be verified using other passivating layer (a-Si:H, Al_2O_3) deposition after etching the TCO layer.

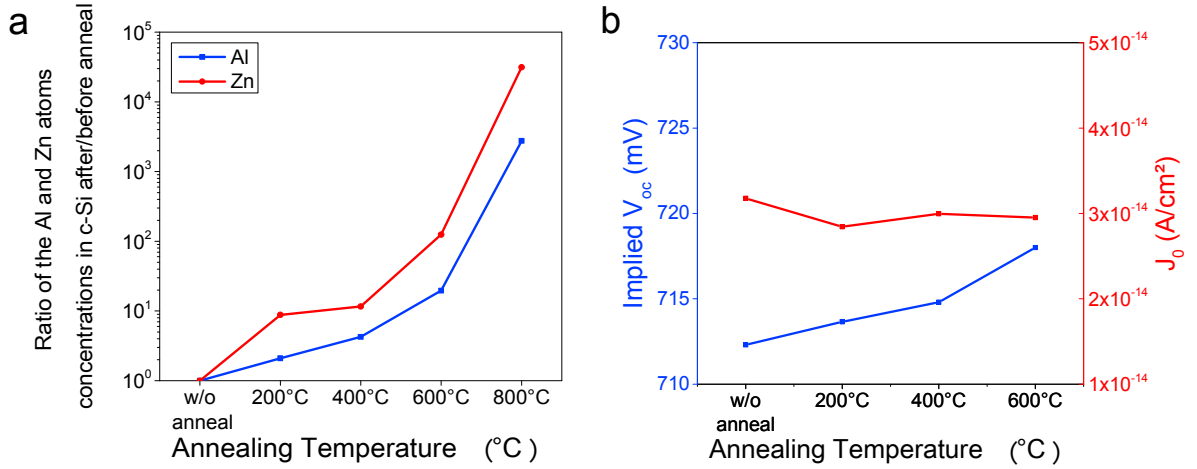


Fig. 1. Variation of Al and Zn concentrations in c-Si bulk after annealing in air at different temperatures (a) and variation of the carrier recombination-linked properties (iV_{OC}, J_0) of annealed wafers after TCO and Si surface etch and SiN_x:H deposition (b)

3.2. Optical and electrical properties of the TCO layers

The properties of AZO (ALD) layers greatly change after thermal treatments - especially in air - with a large decrease of the carrier density and mobility values (Table 1). However in vacuum and under N_2 or Ar-H_2 fluxes, AZO layers appear to be much more stable (Fig. 3.). For temperature above 350°C this trend generally continues, thus AZO layers seem to be sensitive to oxygen adsorption (present in the air) [12]. Measurement at temperature above 350°C are still going on and will be discussed in an upcoming article.

This global trend in sheet resistance variation (Fig. 3.) can be explained thanks to the mobility and the carrier density of the TCO layers (Table 1). Annealing the TCO greatly decreases the carrier density thus limiting the conductivity of AZO, especially for air-annealed samples. Regarding the mobility, its degradation is significant under air, it seems more stable under controlled atmosphere; an increase in mobility can even be seen at 250°C.

However AZO sheet resistance values are still high even right after deposition with Rsheet ≈ 550 Ω/□ for a 40nm AZO layer. Such high resistance of the TCO layer is detrimental for the wanted usage of the TCO layer, thus, either electrical optimisation of AZO is to be further investigated or the AZO layer could be used paired with a sputtered TCO layer showing higher conductivity [9].

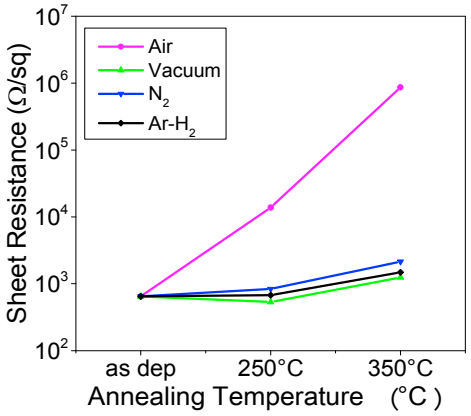


Fig. 3. Variation of the TCO layers sheet resistances with annealing temperatures under different atmospheres

Table 1: Carrier density and mobility of the AZO layer extracted from Hall measurements.

Atmosphere	Carrier density (cm^{-3})		Mobility (cm^2/Vs)	
	250°C	350°C	250°C	350°C
As deposited	$10.3\ 10^{20}$		4.5	
Air	$1.4\ 10^{20}$	$1.5\ 10^{20}$	0.9	0.3
Vacuum	$6.2\ 10^{20}$	$3.2\ 10^{20}$	5.7	4.4
N_2	$4.2\ 10^{20}$	$3.5\ 10^{20}$	6.8	2.8
Ar-H_2	$3.8\ 10^{20}$	$4.2\ 10^{20}$	7.0	3.4

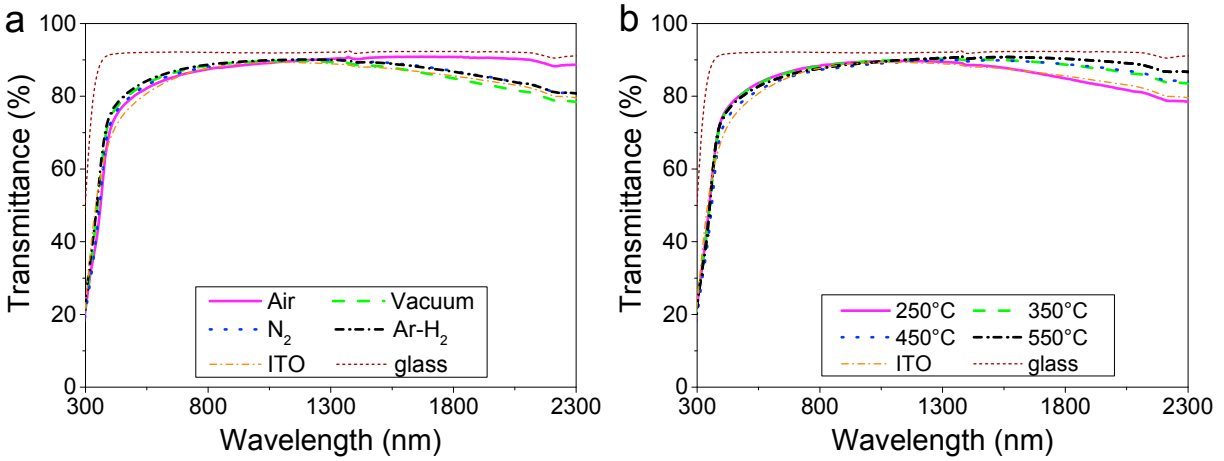


Fig. 4. Transmittance spectra of the AZO layers after annealing at 250°C under different atmospheres (a) and under vacuum at different temperatures (b).

The optical properties of the TCO were analysed using the transmittance spectra. It can be seen in Fig. 4a. that the transmittance at long wavelength (≥ 1300nm) is dependent on the annealing atmosphere. Moreover, the TCO optical properties measured at different temperatures (Fig. 4b) indicate that the layer transparency increases with the temperature. As a result, transparency is directly linked to the annealing conditions. It is well known that the

transmittance in the near IR is directly influenced by the carrier density of the TCO. In any case, a compromise between conductivity and transparency of the TCO has to be found to optimise the device efficiency. Anyhow, to preserve both the TCO electrical and optical properties, it seems that anneal steps have to be made under a controlled atmosphere.

4. Conclusion and perspectives

- Contamination by Al and Zn atoms has been revealed in c-Si substrates coated with AZO after annealing. However, the n-type substrate electronic properties do not seem to be significantly affected par the thermal treatments up to 600°C.
- AZO optical and electrical properties are highly dependent on the annealing atmosphere and temperature. Air annealing was shown to degrade the TCO properties already at low temperature (250°C).
- AZO can be used for passivated contact purposes, though the high temperature post-treatments have to be made under controlled atmosphere to preserve the TCO characteristics.
- To verify if the hydrogen within the SiN_x/H layer heals the defects created by Al and Zn atoms within the Si substrates, other passivation layers such as a-Si:H or Al_2O_3 will be tested.
- Further experiments will be conducted on wafers with shallow junctions to verify that the compatibility of AZO layers with a “High T” solar cell process.

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