Annealing of ZnO and SnO_2 transparent conductive oxides

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Abstract

Transparent Conductive Oxide (TCO) are used in different field [1], especially as antireflective layers on the surface of solar cells [2,3].But in the solar cells process, annealing steps are often used , i.e ; the front metallic contacts of solar cells are obtained by serigraphy at high temperature (800 – 830°C). In this case what happen in TCOs used as antireflective layers ?. In this work we present the comparison of changes in physical properties of two TCOs: tin oxide SnO2 and zinc oxide ZnO when they are annealed at low and high temperatures. These films are deposited by the Atmospheric Pressure Chemical Vapour Deposition APCVD technique. Tin oxide is deposited from tin dichloride (SnCl2, $2H_2O$) precursor and zinc oxide is obtained by the use of zinc acetylacetonate $Zn(C_5H_7O_2)2$. The electrical and optical properties of tin oxide and zinc oxide are determined by the four points probes method and spectrophotometry measurement. The values of the resistivity of tin oxide and zinc oxide are 10^{-4} Ω.cm and 10^{-3} Ω.cm respectively. These films present an optical transmission higher than 80%. The scanning electronic microscopy images show that the films have a polycrystalline aspect. A post annealing of these TCOs at 450°C improves their electrical properties, while an annealing at higher temperature damage them.

Key words: Thin films, tin oxide, zinc oxide, APCVD, Annealing

Introduction:

Tin oxide and zinc oxide are transparent conductive oxide. These materials present an optical transmission of about 80%.Their band gaps are large, comprised between 3,2 and 4.6 eV [4]. They are used in microelectronics as thin films in gas sensor and mainly at the surface of solar cells as antireflective layers [4]. In this paper we present the physical properties of tin oxide and zinc oxide obtained by the same technique: atmospheric pressure chemical vapour deposition APCVD. The influence of annealing at high and at low temperature will also be studied.

Experiment

APCVD (figure 1) is a chemical process which consists on heating a precursor under oxygen flow. The vapours of the precursor react with oxygen and are carried on the surface substrate. The precursor used to deposit tin oxide thin films is the hydrated tin dichloride ($SnCl_2$, $2H_2O$) those vapour react with oxygen gas at the surface of the substrate. The deposition temperature is fixed at 490°C.

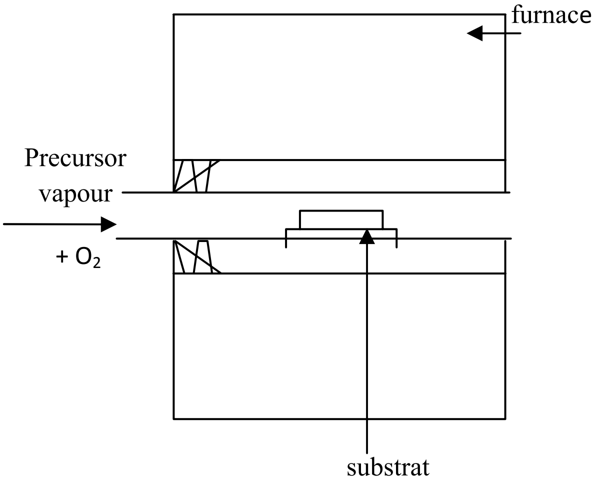

Figure 1: Atmospheric Pressure Chemical Vapour Deposition system

Zinc oxide is deposited by APCVD from zinc acetylacetonate $Zn(C_5H_7O_2)2$. The vapours of this precursor react with oxygen gas inside the tubular furnace which is fixed at the temperature of 450°C. To understand the effect of low and high temperatures on the characteristics of SnO_2 and ZnO thin films, we have annealed the thin layers at 450°C and at 800°C. The sheet resistance of the films is measured by the four probes method. The spectrophometry is used for characterising the transmittance spectra. The surface morphology of tin and zin oxides is obtained by scanning electronic microscopy. Hall measurement is used to determine the hall mobility of the films. The thicknesses of the films are measured by using profilometry.

Our experiment results are introduced in the PC1D simulation software to simulate the photovoltaic parameters of the silicon solar cells that have tin oxide or zinc oxide antireflective layer. The silicon solar cells that we have proposed to simulation are presented in figure 2.

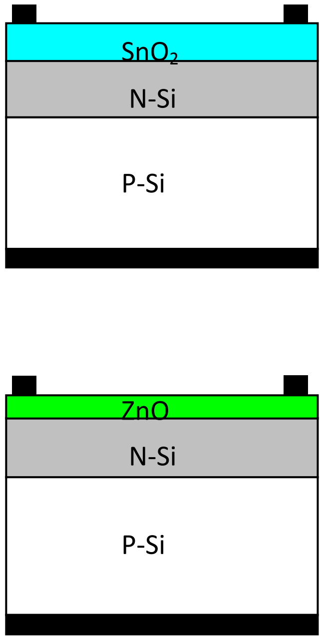

Figure 2: solar cells proposed to simulate by PC1D

Results

The optical transmittances (figure 3) of the films in the range of wavelengths from 350 to 1200 nm are presented in the figure 3. The zinc oxide remains transparent in the near infrared while tin oxide films become opaque beyond 1100 nm.

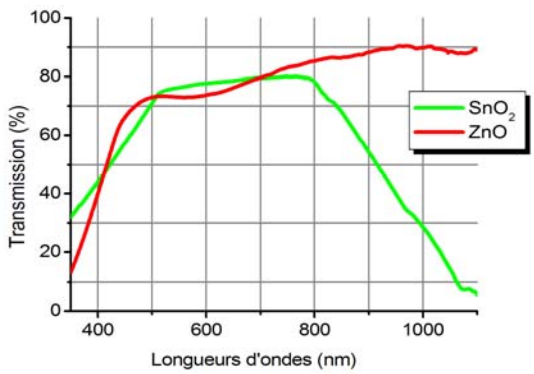

Figure 3: Transmittance of ZnO and SnO_2 thin films

The electrical properties of tin and zinc oxides are different. The tin oxide layers have a resistivity of about 10^{-4} Ω.cm and hall mobility of 15 cm²/(V.s) while the zinc oxide films present a resistivity of 10^{-3} Ω.cm and a hall mobility of 100 cm²/(V.s). Tin oxide thin films are less resistive than zinc oxide layers. This difference is certainly due to the uniformity of the films (figure 5).

The results obtained by PC1D simulation show that the using of the tin oxide as an antireflective layer on the surface of homojunction solar cell increase the photovoltaic efficiency by 2% and by 1% for those that have the ZnO antireflective layer compared to the homojunction solar cell without antireflective layer.

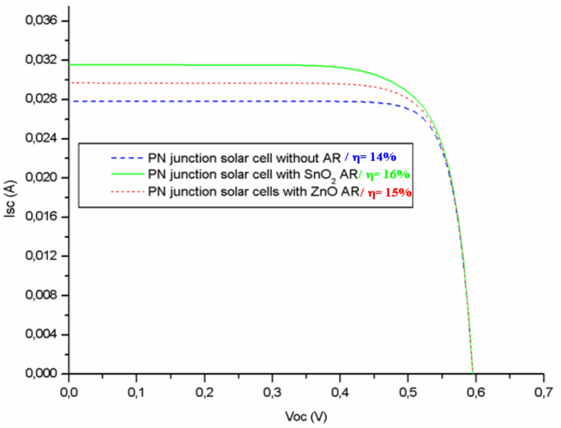

Figure 4: I=f(V) characteristics of PN homojunction silicon solar cells, without antireflective layer, with SnO_2 antireflective layer and with ZnO antireflective layer.

The annealing of the zinc oxide and tin oxide films at high temperatures causes a damage of the surface of the films as shown in figure 5 (a_3) and (b_3). While annealing at 450°C improves the quality of these TCOs.

The initial sheet resistance of ZnO films is equal to 100 Ω/□. It decreases after an annealing at 450 ° C and become 70 Ω/□. But it increases and reaches the value of 200 Ω/□ for the films annealed at 800 ° C. The same variation of sheet resistance is obtained for the heat treatments of SnO_2 films. The initial sheet resistance value of 70 Ω/□ decreases until 55 Ω/□ when the films are heated at 450 ° C. Annealing at 800 ° C gives an increase in R_{SHEET} that reaches the value of 105 Ω/□.

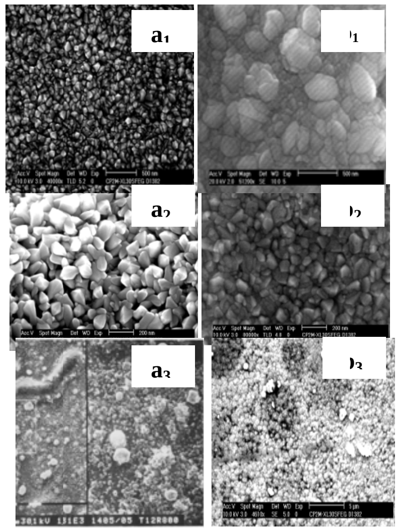

Figure 5: SEM images of SnO_2 (a) and ZnO (b) films before heat treatment (1) and after annealing at 450°C (2) and at 800°C (3).

Conclusion:

The films of SnO_2 and ZnO obtained by APCVD have good electrical and optical properties. The heat treatment at high temperature (800°C) of these films damages the surface of these materials. But an annealing at 450°C improves the electrical properties of these TCOs.

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