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Atomic Layer Deposition of zinc oxide for solar cell applications

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ABSTRACT

Atomic Layer Deposition (ALD) is a vapor phase thin film deposition technique, performed at low substrate temperatures, which enables the deposition of extremely uniform thin films. This technique is scalable up to very large substrates, making it very interesting for industrial applications. On the other hand, ZnO, both undoped and aluminum doped is commonly used as a transparent electrode in solar cells based on Cu(In,Ga)Se_2 (CIGS), and is usually deposited by Physical Vapor Deposition techniques. In this paper, we investigate the potential of ALD for the deposition of ZnO windows for solar cell applications. Thin films of a few hundreds of nanometers were grown by ALD, both undoped and doped with aluminum. They were studied by X-ray diffraction, electrical transport measurements, Atomic Force Microscopy and transmittance experiments.

1. Introduction

Cu(In,Ga)Se_2 (CIGS) based solar cells are among the most promising photovoltaic devices when taking into account both efficiencies and cost per watt. A typical CIGS solar cell uses both undoped zinc oxide (ZnO) and highly conducting, doped ZnO as transparent windows. Although the role of undoped ZnO is not yet fully understood, it seems that it improves efficiency by filling pinholes in the buffer

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layer and improving series resistance [1]. Highly conductive ZnO is usually obtained by aluminum doping of ZnO, in order to obtain transparent electrodes that will efficiently collect the photo-generated carriers. Resistivities below 10^{-3} Ω cm are routinely obtained by Physical Vapor Deposition (PVD) methods [2], but there may be a technological difficulty to obtain high film uniformities on very large surfaces, for production purposes. Atomic Layer Deposition (ALD) is a vapor thin film deposition technique where the precursors are sequentially introduced in the growth chamber, in a periodical manner, in order to saturate the surface [3]. Chemical reaction with the previously introduced precursor occurs, leading to the formation of the desired film and extreme uniformities may be achieved over areas that can be scaled to industrial standards easily. Following the usual deposition process for solar cells, ZnO layers are stacked over CIGS and CdS layers, and deposition temperature has to be limited to avoid interdiffusion in the cell, which is detrimental to its efficiency [4]. ALD growth can be realized at low substrate temperature, making it a perfectly suited technique for the solar cell technology. The objective of this paper is to study the applicability of this technique to the deposition of both intrinsic (non intentionally doped) ZnO (i-ZnO) and Aluminum doped ZnO (AZO) for solar cell applications.

2. Experiments

All the samples were grown on soda lime glass (SLG) substrates, previously cleaned in organic solvents.

Diethyl zinc (DEZ) and Trimethylaluminum was purchased from Sigma Aldrich. A custom made ALD reactor was used for the synthesis of ZnO and doped ZnO films. ALD was performed using sequential exposures of DEZ (TMA) and H_2O separated by a purge of nitrogen with a flow rate of 100 sccm. The deposition regime for ZnO and Al_2O_3 consisted of 0.1 s pulse of DEZ (TMA), 30 s of exposure to DEZ (TMA), 40 s of purge with nitrogen. The temperature was varied between 100 and 130 °C. The growth rates of ZnO and Al_2O_3 were 2 Å and 1.8 Å per cycle respectively as it has been determined elsewhere [5,6].

All the samples are detailed in Table 1. Transmittance experiments were performed on ZnO thin films using a 100 W halogen lamp and a monochromator with a 2400 grooves/mm grating. An Hamamatsu R928 photomultiplier, biased at 900 V was used as detector. X-ray diffraction data was taken using a Bruker D8 discover diffractometer equipped with a 60 mm Göbel mirror, focusing the Cu Kα lines (λ = 1.54184 Å), in the $\theta/2\theta$ configuration. Electrical measurements (Hall effect, four probes resistivity) were made using an Ecopia HMS 3000 equipment, with a magnetic field of 0.56 T. Roughness of the samples was probed by Atomic Force Microscopy (AFM) with a SMENA NTMDT system. The measurements were carried out in tapping mode, with a silicon cantilever having a typical tip radius lower than 10 nm. Constant thicknesses of the films were checked by profilometry, using a DEKTAK 3 system.

Table 1
Samples growth conditions, thicknesses and electrical properties. n.m. indicates that the corresponding electrical properties were not measurable, the sample being insulating.

Sample	Cycles of ZnO	Cycles of Al_2O_3	Number of repetition	Thickness nm	Tg °C	Al doping %	n cm^{-3}	μ (cm^2/V s)	ρ (Ω cm)
1	1000	–	–	200	130	None	2.2×10^{18}	1.9	1.54
2	1000	–	–	200	100	None	1.1×10^{18}	2.2	2.54
3	750	–	–	150	100	None	9.5×10^{17}	4	1.65
4	25	3	4	200	100	10%	1.2×10^{19}	2.8	0.19
5	100	1	10	200	100	1%	1.7×10^{19}	3.0	0.12
6	750	–	–	150	100	None	3×10^{18}	4.7	0.45
7	500	–	–	100	100	None	n.m.	n.m.	n.m.
8	250	–	–	50	100	None	n.m.	n.m.	n.m.
9	50	3	16	160	100	5%	4.3×10^{19}	2	7.4×10^{-2}
10	50	3	20	200	130	5%	8.5×10^{19}	4	1.8×10^{-2}