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Study of the aluminum doping of zinc oxide films prepared by atomic layer deposition at low temperature

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ABSTRACT

This study presents the effect of purge pulses conditions on the electrical and optical properties of zinc oxide films doped with aluminum and grown by ALD at low temperature (160 °C). Undoped ZnO films showed a clear improvement of the carrier concentration when purges were lengthened, which suggests that this purge lengthening causes a higher defect related doping. It was also showed that this purge lengthening leads to a further increase of the carrier concentration in the case of ZnO:Al films attributed to a better spatial repartition of the Al dopants in the film. The evolution of optical properties was also studied and compared to the electrical properties highlighting free carrier absorption and a Burstein–Moss shift. An abnormal modification of the optical properties was observed when the aluminum content in the film was increased.

1. Introduction

Zinc oxide (ZnO) is widely used for applications in optoelectronics. It is a direct bandgap semiconductor with a bandgap energy of about 3.3 eV. This wide bandgap and a large exciton binding energy (60 meV) make it a very interesting material for blue luminescent devices at room temperature [1]. It can be extrinsically n-type doped by substituting Zn atoms with group III elements like B, Al, Ga, In. High doping levels were achieved with aluminum as well as with boron which give a transparent conducting oxide, made of abundant elements and suitable in different applications such as solar cells or liquid crystal displays.

Aluminum doped zinc oxide thin films have been obtained using different deposition methods such as sol–gel [2], sputtering [3], metal organic chemical vapor deposition [4] or spray pyrolysis [5]. The deposition of ZnO by atomic layer deposition (ALD) has also been widely studied because it allows conformal growth on surfaces with high aspect ratios at low temperature [6].

ALD is a chemical vapor deposition method whose particularity is the sequential substrate exposure (also called pulse) to the different reactants. Reactions take place between the gas phase reactant and the reactant chemisorbed during the previous pulse until surface saturation is reached. Exposures are separated by purge steps avoiding gas phase reactions and ensuring that reactions are surface limited. For a binary compound, a growth cycle is composed of two pulses and the two purges associated. To grow zinc oxide, one of the reactants is a precursor of zinc while the second reactant is an oxygen source.

In ALD, the extrinsic doping of ZnO is basically done by inserting periodically a growth cycle containing the foreign element. This implies that impurities are located in planes, which does not favor a uniform distribution. To minimize its electrical resistivity, one of the main parameters to be changed is the deposition temperature [7–10] as the lowest resistivity of $1.35 \times 10^{-4}\,\Omega\,cm$ has been reached at 240 °C [11]. However, for some applications, the deposition temperature should be lower and other ways to improve the conductivity have to be found. The second parameter that is usually studied is the percentage of dopant cycles inserted [10,12–14]. Authors report that the increase of this parameter enhances the doping level up to a value limited by the high density of dopant concentration per plane [13] or the formation of a second phase [14]. For very high aluminum contents, it was reported that the optical bandgap of the film could reach values as high as 3.7 eV, which cannot be attributed to a Burstein–Moss shift [14].

To enhance further the doping level in the films, different techniques have been used to reduce the dopant concentration per plane during the doping cycles. Copulses of zinc and dopant reactants with a precise control of the partial pressures lead to very uniform films [7,8,15]. Using this technique, a carrier concentration

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as high as 6.64×10^{20} cm^{-3} were reported at a growth temperature of 250 °C [15]. A prior pulse of zinc precursor before the dopant precursor pulse has been used to reduce the density of adsorption sites at a growth temperature of 125 °C [16]. Authors reported a decrease of the resistivity compared to the classical route. The same effect was observed using a pulse of alkyl alcohol at a growth temperature of 200 °C [17].

Usually, purge lengths are chosen to ensure the removal of reaction byproducts and the excess of reactants during cycles and thus to avoid CVD like growth. They can also modify the material properties as they influence diffusion processes and surface reconstruction during the deposition. The influence of purge lengths on the crystallographic orientation [18] and on the growth rate [19] of the material has been studied but only few studies of its influence on the electrical properties of ZnO have been done [20].

The aim of this work is to study the effect of purge durations on the electrical and optical properties of ZnO:Al films grown at temperature as low as 160 °C, which is suitable for applications in solar cells.

2. Experimental

2.1. Atomic layer deposition of films

ZnO:Al thin films were deposited in a SUNALE R-200 ALD reactor (Picosun Oy.) with a modified 15 cm × 15 cm square reaction chamber, on 5 cm × 5 cm borosilicate glass substrates that were placed at the center of the reaction chamber. Sources for zinc, aluminum and oxygen were respectively diethylzinc ($Zn(C_2H_5)_2$ noted DEZ) Optograde from Rohm and Haas, trimethylaluminum ($Al(CH_3)_3$ noted TMA) Optograde from Rohm and Haas and deionized Millipore water. Nitrogen (N_2) from Messer with a purity of 99.9999% was used as both carrier and purging gas. Deposition experiments were performed at a substrate temperature of 160 °C.

A ZnO growth cycle consisted in the following steps: DEZ exposure/N_2 purge/H_2O exposure/N_2 purge = $0.1/t_{purge}/0.1/t_{purge}$ s while an Al_2O_3 growth cycle consisted in: TMA exposure/N_2 purge/H_2O exposure/N_2 purge = $0.1/t_{purge}/0.1/t_{purge}$ s. The values chosen for t_{purge} were {2 s; 4 s; 6 s}.

ZnO:Al films were synthesized by incorporating Al_2O_3 growth cycles in the growth of pure ZnO, leading to the supercycle {N ZnO cycles + 1 Al_2O_3 cycle} where N = {14; 19; 24}. All samples were deposited performing a total of 1400 growth cycles, i.e. 56 supercycles for N = 24, 70 supercycles for N = 19 and 93 supercycles plus 5 ZnO cycles for N = 14.

2.2. Films characterization

The thickness of the films was measured using a VEECO DEKTAK 6M profilometer. Thicknesses were determined after creating steps in the films, by masking film parts with chemically resistant tape and dipping the film in hydrochloric acid (0.1 M in water) at room temperature for 30 s. The uncertainty given for the thickness is a standard deviation of twelve measurements taking into account profilometer uncertainty, sharpness of steps, film roughness and film inhomogeneity.

Transmittance and reflectance spectra were obtained using a PerkinElmer lambda 900 Spectrophotometer with a PELA-1000 integrating sphere.

Electrical measurements were done at room temperature using an ECOPIA HMS-3000 Hall effect measurements system with a permanent magnet of 0.5 T. Two square parts with a surface of 4 cm^2 were cut in each sample to determine its electrical properties. Values of resistivity, carrier concentration and electron mobility chosen were the average of these two measurements.

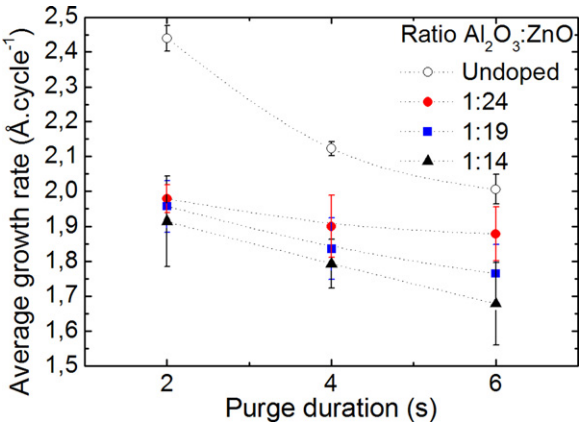

Fig. 1. Evolution of the growth rate as a function of purge durations for the different Al_2O_3:ZnO ratios.

The uncertainty reported is caused by the uncertainty on the film thickness and the variation observed between the measurements.

X-ray diffraction (XRD) studies were performed under Bragg–Brentano conditions with a PANalytical Empyrean diffractometer using Cu Kα radiations.

3. Results

3.1. Growth rate

The evolution of the average growth rate as a function of purge lengths for each Al_2O_3:ZnO cycles ratio is shown in Fig. 1. The average growth rate was determined by dividing the film thickness by the number of cycles (1400). The growth rate decreases as purge length and Al_2O_3:ZnO ratio increase. In the case of undoped films, this decrease is stronger between purges of 2 s and 4 s and weaker between 4 s and 6 s. For doped films, the growth rate decrease is weak and almost linear. The determined growth rate for undoped ZnO ranges from 2.0 Å cycle^{-1} for long purges to 2.4 Å cycle^{-1} for short purges. Those are consistent with reported values (1.8–2.8 Å cycle^{-1} [8,10]) for ZnO films in the ALD process window of ZnO (105–165 °C [8]). The growth rates measured for ZnO:Al films were in the range 1.7–2.0 Å cycle^{-1}, and are also consistent with reported values (1.6–2.0 Å cycle^{-1} [9,10]). Such growth rate evolution that depends on the purge durations has already been observed by Kwon et al. [19].

3.2. Electrical properties

The evolution of the electrical properties of the films as a function of purge durations for the different Al_2O_3:ZnO ratios, is represented in Fig. 2. For both types of films (undoped and doped), the carrier concentration increases as purge lengths increase (Fig. 2 (a)). In the case of doped films the evolution of the carrier concentration is almost linear. However in the case of undoped films, the doping level is one order of magnitude lower than in the doped films but in all cases it increases in the same proportions with the purge durations. We see that the carrier concentration increases as the Al_2O_3:ZnO ratios increases from 1:24 to 1:19. Between the ratios 1:19 and 1:14 the carrier concentration is almost constant. A doping limit was also observed in other reports [10,12–14] and can be caused by a superposition of effective fields [13] or by the formation of a metastable phase $Zn_3Al_2O_6$ [14].

The electron mobility increases slightly with purge lengths for all types of film, but decreases dramatically when the Al_2O_3:ZnO cycle ratio is increased (Fig. 2(b)).