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Using the acetylacetonates of zinc and aluminium for the Metalorganic Chemical Vapour Deposition of aluminium doped zinc oxide films

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ABSTRACT

Metalorganic Chemical Vapour Deposition is a promising method for the growth of thin aluminium doped zinc oxide films (ZnO:Al), a material with potential application as transparent conducting oxide (TCO), e.g. for the use as front electrode in solar cells. For the low-cost deposition, the choice of the precursors is extremely important. Here we present the deposition of quite homogeneous films from the acetylacetonates of zinc and aluminium that are rather cheap, commercially available and easy to handle. A user-made CVD-reactor activating the deposition process by the light of halogen lamps was used for film deposition. Well-ordered films with an aluminium content between 0 and 8% were grown on borosilicate glass and Si(100). On both types of substrate, the films are crystalline and show a preferred orientation along the (002)-direction. The 0.3 to 0.5 μm thick films are highly transparent in the visible region. The best films show a low electric resistivity between 2.4 and 8 mΩ cm.

1. Introduction

Zinc oxide (ZnO) is a transparent low-cost and non-toxic material with various interesting properties e.g. a wide direct band gap (3.37 eV) and a large binding energy (60 meV [1,2]. Due to the similarity of its optical and electronic properties to those of gallium nitride it is discussed as a possible alternative to GaN-based applications, including the use in blue or UV-LED devices. In contrast to the preparation of GaN, the precursors for the preparation of ZnO are easy to handle and less toxic. Doping the ZnO with group III elements such as gallium [3], boron [4], and aluminium [5] results in an improved electrical conductivity without degrading the optical transmission in the visible spectral range. Therefore, M-doped ZnO (M=Ga, B, Al) is discussed as a transparent conducting oxide (TCO) with potential applications as e.g. front electrodes in solar cells devices [6,7], or electrical gas sensors [8]. Furthermore, ZnO doping is achieved by replacing Zn^{2+} atom with atoms of elements of higher valence such as Pb^{4+}, Sn^{4+}, In^{3+}, and Al^{3+}. It is worthy to mention that among the entire group III, Al is a cheap, abundant, non-toxic material and can be an ideal candidate for dope ZnO [9]. Due to its potentially cheaper production, ZnO:M (M=Al, Ga, B) are possible alternative materials for indium-tin-oxide (ITO) which is usually used in such devices.

Keeping the potential market of these applications in mind, it is obvious that the development of low-cost and

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powerful deposition techniques is important. Until now, several strategies have been followed to deposit thin zinc oxide films, including wet chemical methods like sol–gel deposition [10] and spray pyrolysis [11]. Also physical vapour deposition, such as rf-magnetron sputtering [12] and molecular beam epitaxy (MBE), or chemical vapour deposition (CVD) have been used. A brief review of the latter technique is given in Ref. [13]. Among these techniques, metal-organic chemical vapour deposition (MOCVD) is a powerful method for the preparation of high quality films with high deposition rates. It was used in the present study.

It is obvious that for the development of a low-cost deposition process, the choice of the precursor is most important. For the MOCVD growth of zinc oxide, different precursors have been reported in the literature: often diethyl zinc (DEZ) [14,15]and dimethyl zinc (DMZ) [16] are used, resulting in the growth of highly pure ZnO films. Less attention has been paid to the growth of ZnO-films from zinc acetate [17] and zinc acetylacetonate ($Zn(acac)_2$) [18–20], because it is reported that these precursors tend to produce carbon contaminations. It is suspected that these contaminations influence the electric and optical properties of the grown films negatively. However, zinc acetate and $Zn(acac)_2$ have the advantages of being commercially available and thus being rather cheap. Further, they are chemically stable in atmospheric air, non-toxic and easy to handle. This favours their use in an industrial coating process.

Because of these reasons, we have studied the growth of zinc oxide films from zinc acetylacetonate in more detail. Aluminium acetylacetonate ($Al(acac)_3$) was used as an aluminium source for the preparation of Al-doped ZnO films. Undoped ZnO and Al-doped ZnO films were deposited on silicon and borosilicate glass substrates by a photo assisted rapid thermal metal organic chemical vapour deposition (RT-MOCVD) technique, where the deposition process is activated by the radiation of halogen lamps. On the one hand, our investigations were focused on the control of the deposition parameters, such as pressure, deposition temperature, and dopant (Al) concentration. On the other hand, electrical and optical properties, which are most important for the above mentioned applications, were extensively studied.

Finally, it should be mentioned that to the best of our knowledge, no previous work was done on the deposition of doped zinc oxide from acetylacetonates of zinc and aluminium using a similar deposition process.

2. Experimental

2.1. Film deposition

The experimental set-up used for film deposition is shown in Fig. 1. For further details see Refs. [21,22]. It is composed of a stainless steel cylindrical chamber of 200 mm height with two nozzles. The deposition nozzle has a 4 mm diameter hole and is positioned at an angle of 30° from the horizontal surface of the substrate holder. It's function is to introduce the reactants. The second nozzle is used to protect the window. A flow of inert gas (N_2) is introduced through this nozzle in order to avoid the deposition on the window during the deposition process.

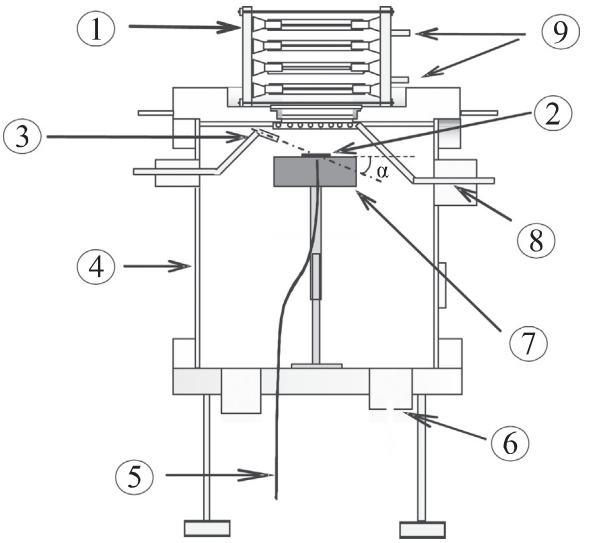

Fig. 1. Sketch of the used CVD-reactor: (1) Lamps, (2) substrate, (3) Nozzle, (4) CVD chamber, (5) Themocouple, (6) Exhaust, (7) Substrate holder, (8) Window protection nozzle, (9) N_2 flow entrance for cooling the lamps.

The temperature of the substrate was monitored and controlled by using a K-type thermocouple inserted in the substrate holder and attached to the backside of the substrate. The substrate was heated with 10 halogen lamps and maintained at the desired temperature using a controller. For all experiments, the total pressure within the chamber was fixed at 200 mbar. During deposition of the un-doped zinc oxide films, zinc acetylacetonate ($Zn(acac)_2$) was evaporated in a fluidized bed evaporator at a temperature of 110 °C (not shown in Fig. 1). The vapour was transported to the chamber with a flow Φ_{Zn,N_2} of 500 standard cubic centimetre (sccm) nitrogen as carrier gas, entering through a cylindrical nozzle of 4 mm diameter. Before reaching the orifice, 100 sccm oxygen was added for supporting the oxidation. Additional 200 sccm N_2 (Φ_{N_2}) was added in order to increase the gas velocity. Finally, the gas mixture at the orifice consists of nitrogen, $Zn(acac)_2$, and oxygen in excess. This gas mixture was then blown onto the substrate under an angle $\Theta = 30°$ relative to the surface, as shown in Fig. 1. The distance between the orifice and the substrate was approximately 70 mm.

For the deposition of the Al-doped ZnO films, $Al(acac)_3$ was evaporated in a separate fluidized bed evaporator and transported to the chamber with a carrier gas flow of nitrogen Φ_{Al,N_2} which was varying for different Al-concentrations between 0 and 80 sccm. Before reaching the orifice, it was added to the above mentioned Zn $(acac)_2$-vapour/N_2/O_2-mixture while the additional nitrogen flow Φ_{N_2} was decreased by the amount of Φ_{Al,N_2}. Thus, the total flow of the gas mixture was constant for all experiments.

The substrates were either pieces of clean silicon wafers (Si (100)-orientation) type (n) or borosilicate glasses, both sized (1 cm × 1 cm). Prior to deposition, these substrates were ultrasonically cleaned in ethanol for 20 min, rinsed in deionized water, and dried thereafter.