



Structural properties of zinc oxide deposited using atmospheric pressure combustion chemical vapour deposition



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ABSTRACT

In this study the deposition of thin zinc oxide (ZnO) films under atmospheric pressure conditions was investigated. The deposition technique applied was combustion chemical vapour deposition (CCVD), at which a propane–air mixture was combusted in a burner. Dissolved zinc nitrate was used as precursor, which was guided as aerosol droplets by the processing gas flow directly into the reaction zone. Fundamental investigations were performed to form undoped ZnO. The structural properties of the films were analysed in dependence of the substrate temperature during the coating process.

The presence of crystalline ZnO structures was proved and differences in film growth and crystallite sizes are revealed. Additionally, the particles generated by the CCVD-flame are characterised. The thin films showed a slight excess of Zn and several states of binding energy could be observed by fitting the core level spectra. Scanning and transmission electron microscopy also indicated ordered structures and additionally different orientations of crystallites were observed.

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1. Introduction

Zinc oxide (ZnO) as a transparent conducting oxide (TCO) is an n-type II–VI semiconductor and has a wide direct band gap of about 3.37 eV [1] at room temperature. There is considerable interest in ZnO because of its high optical transparency, good conductivity for doped ZnO and low production costs. The thin films continue to attract attention because of their wide applications in solar cells [2], varistors [3] and optoelectronic devices, such as window layers or anti-reflective coatings. Further, ZnO can be used in gas sensors because of its chemical sensitivity to different gases [4,5]. Doped ZnO is also a good candidate as a replacement for the commonly used TCO films of indium tin oxide in solar cells or displays.

Normally, ZnO is deposited in a vacuum based process like sputtering or chemical vapour deposition (CVD) operating under low pressure. Conventional CVD uses a reaction chamber, where the components of the film to be deposited are introduced as gas or vapour. In the case of liquids or solids as precursor, they must be heated at these conditions to produce sufficient vapour for acceptable growth rates. An attractive alternative for deposition of ZnO is atmospheric pressure CVD which can be more cost effective and allows continuous production of ZnO coatings on large area substrates. Undoped as well as doped ZnO thin films with specific resistivities ranging from $10^{-4} \Omega \text{ cm}$ to $10^7 \Omega \text{ cm}$ were produced by several atmospheric pressure techniques.

Aerosol assisted chemical vapour deposition (AACVD) [6,7], atmospheric pressure CVD [8], spray pyrolysis [9], various plasma enhanced CVD [10–12], spatial ALD [13] or sol-gel techniques [14,15] are the most common ones. Additionally a number of specialized systems [16–20] have been developed and used for deposition. For preparation of dense and crystalline ZnO films, molecular beam epitaxy and metal organic CVD are preferred [21,22].

The films presented in this study were prepared by combustion CVD (CCVD) using aerosol droplets of a zinc-containing precursor at atmospheric pressure conditions. A zinc compound dissolved in solution was fed directly into the flame by injection through a nozzle into the carrier gas flow. Our aim during these experiments was to deposit zinc oxide films at atmospheric pressure conditions, since this offers the greatest potential for industrial applications. The advantages of this process, compared to other atmospheric processes, are the combination of the following: high dynamic deposition rates depending on the precursor up to 90 nm·m/min, large area coatings realized up to 1.2 m width, low substrate temperature, no additional heating is required, because the energy is provided by the flame and the substrate temperature is easily controlled by its velocity. Combining these with affordable precursor chemicals, readily-available process gases such as propane–air mixtures and economical facility acquirement, this technique is applicable for large area deposition using adhesion promoter, e.g. for powder coating applications or basic optical functional coatings. Compared to chemical and physical deposition techniques using low-pressure conditions, the range of depositable materials is restricted, being especially limited to oxides, but even elements as silver [23] can

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be deposited by CCVD. However in the choice of substrates, its thermal compatibility has to be considered. There is only a very short exposure of the substrates to the flame and therefore the substrate surfaces are barely affected by the heat of the flame. Published literature describing CCVD or its variants [6,7] reports only static systems, where a CCVD burner is used to form thin films on a static substrate in a reaction chamber. In these systems the substrates are exposed to the flame for several minutes and are thus intensely heated up. No large-area coatings can be obtained by these techniques. Thus in our system a burner system coupled with a driving stage is used.

2. Materials and methods

2.1. Film growth by combustion chemical vapour deposition

The flame pyrolysis process is a versatile method for producing thin solid films at atmospheric pressure conditions. Several papers [24–30] report the wide range of possibilities of its application. Exposure to the flame is, for example, an established method used to activate the surface of polymer materials [31,32]. Based on this, a wide range of precursor materials can be used and these can either be supplied as gas, liquid or dissolved solid and introduced into the gas stream as aerosol or directly as gas. Since the precursor is chemically converted, this method is called combustion CVD. The flame provides the necessary energy and also generates highly reactive species such as H^\bullet or OH^\bullet radicals [31, 33]. Additionally, the flame can be divided in several different zones [31], including the reducing zone directly at the burner exit with a length of a few millimetres containing H^\bullet radicals and the oxidising zone with a length of a few centimetres, depending on the burner design, containing several radicals such as O^\bullet , H^\bullet and OH^\bullet . The combustion temperatures in the case of propane rely on the fuel-air feed ratio and are between 1600 °C and 1800 °C [34] for a stoichiometric ratio. Thus, the choice of the flame region is very important in determining the outcome of the thin layer deposition process. Depending on the precursor chemical used, pyrolytic or hydrolytic reactions lead to its decomposition.

The oxidation of hydrocarbons consists of a complex reaction mechanism including several basic reactions. In the case of propane as burning gas, the overall reaction is known to be



In general the reaction of higher order alkanes (C_nH_{2n+2} , $n > 2$) can be simply described within eight steps [29] including the brake of

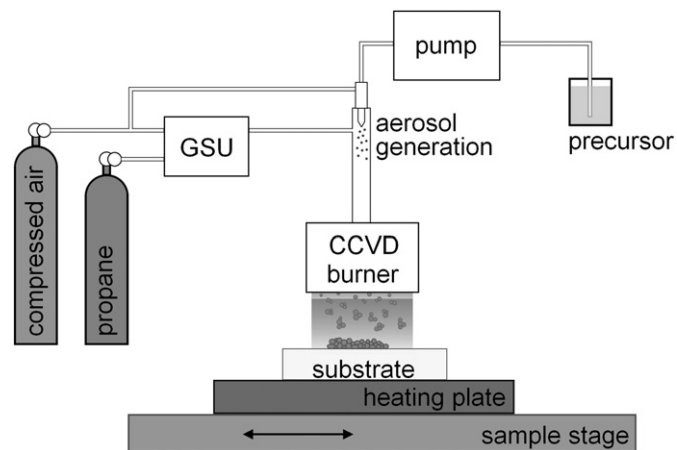


Fig. 1. Schematic illustration of the CCVD set-up used with the main components labelled. The liquid precursor is added to the process gas stream, provided by the gas supply unit (GSU), as aerosol droplets. Additionally the fundamental particle growth process within the flame is shown. The reducing and oxidizing zones of the flame are denoted. The substrates are moved several times below the flame with a specific velocity.

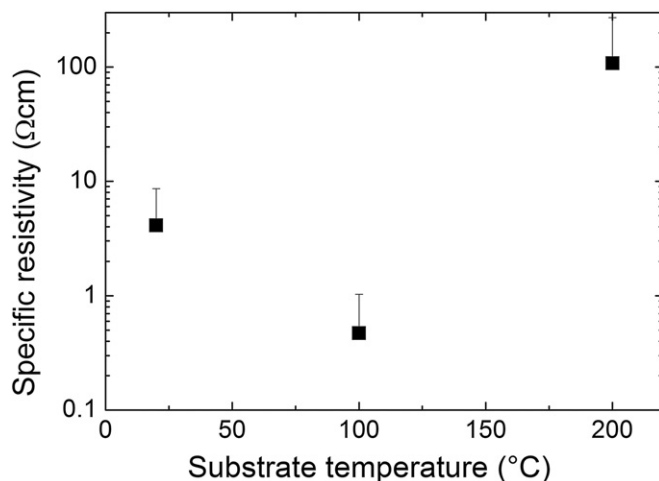
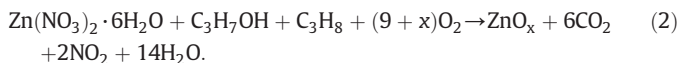


Fig. 2. Dependence of the specific resistivity on the substrate temperature at a low working distance of 4 mm and a substrate velocity of 40 mm/s.

C–C bonds, building of hydrocarbon radicals and its reaction to unsaturated hydrocarbons and hydrogen, oxidation of these unsaturated hydrocarbons as well as formation of carbon monoxide. Further processes and thermodynamic fundamentals are reviewed by Glassman [35] and Warnatz [36]. For a complete combustion of propane the stoichiometric mole-amount of propane to air is calculated to account 1:23.88 using (1) and the volume fraction of oxygen in air (20.94%).

Adding the dissolved precursor chemical zinc nitrate to the chemical reaction of the combustion, it can be written as



Because no additional oxygen gas was introduced, it originates directly from the compressed air. Although a stoichiometric ratio of the combustion is adjusted, it is possible that the oxygen for combusting the precursor solution and propane gas is not sufficient and causes O vacancies in the resulting film [37].

The structural properties of the deposited film are mainly influenced by the facility parameters. One essential factor is the distance between the burner outlets and the surface of the substrate. This distance also influences the substrate temperature in contact with the flame and defines the time interval between the initiation of the chemical reaction to commencement of the film formation. The exit velocity of the gas flow also influences this time of flight, *tof*, which can be approximated by

$$tof = (d \cdot A_{burner}) / (Q_{air} + Q_{gas} + Q_{prec}), \quad (3)$$

where A_{burner} is the area of the outlets being 415.8 mm², d is the distance between the burner outlet and the substrate surface (working

Table 1

Binding energies and concentration values of the C1s, O1s and Zn2p_{3/2} of the XPS-lines for the three samples shown in Fig. 2. All binding energy values have a preciseness of ±0.1 eV and the concentration values of ±0.3%.

Emission line	Binding states	Binding energy/eV			Concentration/%		
		20 °C	100 °C	200 °C	20 °C	100 °C	200 °C
C1s	C _I	285.5	285.4	285.8	13.6	14.7	15.5
	C _{II}	287.0	286.9	287.2	2.0	2.0	1.9
	C _{III}	289.5	289.3	289.7	2.7	3.1	2.3
O1s	O _I	530.7	530.5	530.9	22.8	23.3	24.9
	O _{II}	532.1	531.9	532.3	19.0	17.5	15.7
Zn2p _{3/2}	Zn	1021.9	1021.8	1022.1	39.7	39.1	39.3

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