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# Conductive zinc oxide thin film coatings by combustion chemical vapour deposition at atmospheric pressure

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ABSTRACT

We have established a combustion chemical vapour deposition (C-CVD) system for the deposition of zinc oxide (ZnO) at atmospheric pressure. This C-CVD process has the advantage of a short exposure of the substrates to the flame. It is also potentially applicable as an inline coating system.
Fundamental studies were performed on undoped ZnO. The specific resistivity of these layers strongly depends on the film thickness and decreases with increasing thickness. As the lowest resistivities, values of about $2.0 \cdot 10^{-1}$ Ωcm are achieved. Ultra-violet photoemission spectra show the valence band structure of the deposited ZnO. The work function and valence band edge were determined. UV–vis spectra were taken to investigate the transmission of the coated glass samples. From these spectra the band gap energy was obtained. Raman spectroscopy as well as infrared spectroscopy confirmed the presence of ordered ZnO crystallites. The X-ray diffraction verified this result and illustrates the hexagonal structure. In the mid-infrared range precursor deposits were detected for low substrate temperatures.



## 1. Introduction

As n-type II–VI semiconductor zinc oxide (ZnO) has a wide direct band gap of about 3.37 eV [1] at room temperature. There is a high interest in ZnO because of its wide direct band gap, high optical transparency, good conductivity for doped ZnO and low production costs. Thus doped ZnO is a good candidate as a replacement for the commonly used transparent conductive indium tin oxide thin films.

Undoped as well as doped ZnO thin films with resistivities ranging from $10^{-4}$ Ωcm to $10^{7}$ Ωcm were produced by several aerosol assisted chemical vapour deposition (AA-CVD) [2,3], atmospheric pressure CVD [4], plasma enhanced CVD [5], pulsed laser deposition [6], spray pyrolysis [7] or sol–gel [8] techniques.

The films presented here were prepared by combustion CVD (C-CVD) using aerosol droplets. It is a variant of the conventional combustion CVD process in which the precursor is transported within the carrier gas and fed directly into the flame. The established C-CVD system can possibly be used as an inline coating system. There is only a very short exposure of the substrates to the flame and therefore the substrate surfaces are hardly affected by the heat of the flame. It is also possible to coat large-area substrates and the process is comparatively cheap. Commonly published C-CVD or its variants [2,3] were assigned to static systems, where a C-CVD burner is used to form thin films on a static substrate in a reaction chamber. In these systems the substrates are exposed for several minutes to the flame and are thus intensely heated up.

## 2. Experimental details

### 2.1. Deposition process

ZnO films were prepared using a variant of the classic C-CVD technique. The precursor was fed directly into the flame as aerosol droplets. These droplets were generated using a compressed air nozzle. As precursor zinc nitrate ($Zn(NO_3)_2$) was dissolved in a mixture of 2-propanol and deionised water with a concentration of 0.2 M. This zinc salt has significant advantages for the deposition of ZnO films at atmospheric pressure compared to other commonly used metal organic substances like zinc acetylacetonate [2], zinc acetate [3,7,8] or diethylzinc [4]. It dissolves very well in water; improved concentrations are therefore possible. It also does not clog the nozzle of the aerosol jet and is very easy in handling.

The liquid solution was pumped into the jet pistol. The supplied compressed air raptures the precursor droplets and thus forms the aerosol. The aerosol is directly introduced into the flammable gas air mixture flow, which guides the precursor to the flame. A schematic view of the system used is shown in Fig. 1.

We used a burner designed at Innovent for thin layer deposition [9]. It is equipped with two slot shaped outputs. They are equally dimensioned and therefore allow doubled growth rates. The substrates, silicon(100) wafers and 4 mm soda lime silicate float glass (Guardian Industries), were placed on a heated table, which was driven by a

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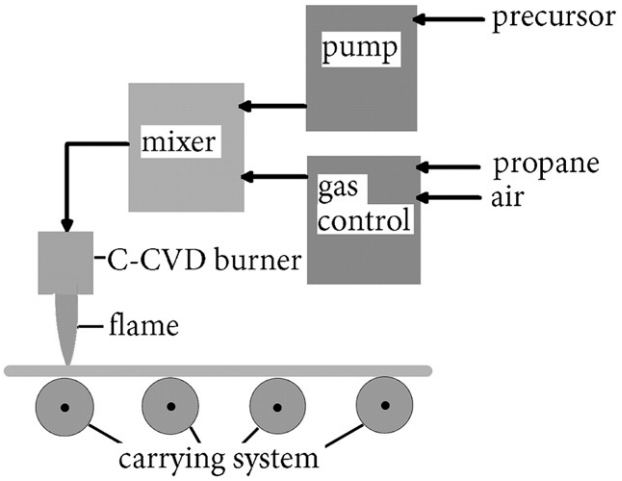


**Fig. 1.** Sketch of the coating system used.

linear axis. So the substrates move below the burner and the number of passes is adjustable. Typically the process parameters were chosen in the following range:

Propane: 0.8–1.2 l/min
Air: 14–32 l/min
Velocity: 10–50 mm/s
Substrate temperature: 20–300 °C
Burner distance: 2–9 mm
Precursor feed: 0.8–2.5 ml/min

This parameter field contains all relevant working points. It does not make sense to vary all the parameters independently of each other. The propane–air ratio should be chosen for example as a stoichiometric ratio. The velocity, burner distance and precursor feed are associated closely to each other. When changing the burner distance, the size of the particles can be controlled; lower distances lead to smaller particles but intensively heating up the substrate surfaces when the reductive part of the flame is reached. The velocity has also great influence on the substrate temperature and also controls the mass flow of particles reaching the surface.

### 2.2. Measurements

The thicknesses of all films were characterised using a surface profilometer Dektak3ST (Veeco) with a scan length of 2000 μm. In order to get the step height, the substrates were prepared with a dissolving material, which is easily dissolved after the coating process. All samples were treated in the same way. Hence, the error due to possible solvent resists is equal for all samples and they are comparable. The electrical properties of the ZnO films were measured at room temperature in the form of a two point measurement of the resistivity using a tip distance of 5 mm. Ultra-violet photoemission spectra (UPS) were taken with an ARUPS10 (VG) at normal emission conditions. A He I excitation source (21.22 eV) was used at an angle of 45° and a base pressure of $10^{-8}$ Pa. The scanning electron microscopy (SEM) investigation was carried out by a Supra 55 VP (Zeiss) using the inlense detector and an operating voltage of 5 kV. Additionally, X-ray diffraction (XRD) was performed using a Siemens D5000 with a copper channel ($K_{\alpha 1}$ and $K_{\alpha 2}$ 2:1) and a secondary monochromator as a source. The samples were measured using the grazing incidence method at 1°. Resonant Raman spectra were taken using a Horiba LabRam HR spectrometer. The excitation source was the HeCd laser line at 325.03 nm with a power of 0.4 mW at the surface of the substrates. The UV–vis spectra were obtained by a Spectrometer Lambda 2 (Perkin Elmer). Fourier transform Infrared (FT-IR) transmission spectra were measured using a Vertex 80v (Bruker) in the spectral range from 50 $cm^{-1}$ to 4000 $cm^{-1}$ with a resolution of 2 $cm^{-1}$. For statistical analysis the software statgraphics of StatPoint Inc. was used.

## 3. Results and discussion

Typical film thicknesses of ZnO deposited by the C-CVD process at atmospheric pressure were in a range between (16 ± 3) nm for 20 passes and (130 ± 10) nm for 100 passes. With an increasing number of passes one could observe that the samples became hazy. Small particles are formed during deposition which agglomerate and adhere to the surface (Fig. 2) and thus form the thin film. When the thickness reaches a certain value, the formation of a loose porous powder from these agglomerates is observed. The exact value of this critical thickness is difficult to specify, because further investigations on the formation process are missing yet. A similar observation is made when $SiO_2$ is coated by C-CVD [10]. These loose particles are washed away when the substrates are cleaned.

The influence of a single process parameter (factor) to a specific property was estimated by a systematic design of experiments. Only optimized process parameters were considered and therefore the number of extensively characterised samples was limited to an acceptable number. With respect to the resistivity, the best set of parameters was selected and a selection of these samples is presented here.

A preliminary test was done in order to check the reproducibility of the results. At different times three samples were prepared with the same set of parameters. Multisample comparison is a good statistical tool to compare the samples in order to expose significant differences in their properties. The specific resistivity was determined and the following set of tests was performed.

First fitting of the three datasets to the normal distribution is tested by the Anderson–Darling test [11]. The following variance check (Levene test [12]) tests the hypothesis that the standard deviation is the same. These are the two requirements for the analysis of variance sample comparison [13]. The analysis of variance tests whether the mean values of the properties are significantly different from each other. The Kruskal–Wallis test [14] was done to control the significance between the samples based on the medians. It was found that all data of the three samples can be described by the normal distribution. No statistically significant difference amongst the standard deviations, means, or medians at the 95% confidence level was found. The multiple range test (Scheffé test [15]) supports this results and shows that there are no statistically significant differences. For visualisation a box-and-whisker plot is shown (Fig. 3). Additionally, the confidence interval of the median is added to each of the boxes. The resulting notched plots [16] expose significant differences between the samples, when the notches do not overlap.

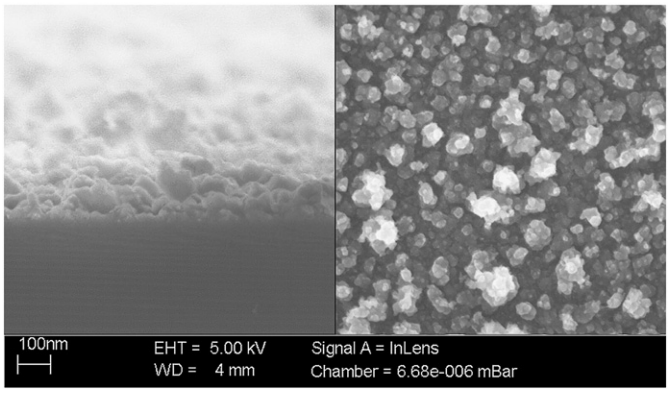


**Fig. 2.** Typical morphology of the ZnO thin films coated by C-CVD at atmospheric pressure as observed by SEM. Left: cross section, right: top view.