Plasma-enhanced chemical vapour deposition of ZnO for photovoltaic TCO application

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ABSTRACT

In terms of material properties, plasma-enhanced chemical vapour deposition (PECVD) of ZnO has advantages over sputtering techniques, due to the variety of available precursors, and the different dopants for achieving certain levels of n-type and, controversially discussed, p-type transparent conductive oxides (TCOs) on various substrate materials. This paper considers the deposition of boron-doped zinc oxide for n-type TCO-application on substrates of dimensions up to 50×50cm² and at a temperature range of 50 to 450°C using a PECVD reactor with a plasma frequency of 13.56MHz. The materials' characteristics such as transparency, carrier concentration and structural properties are discussed as a function of the deposition parameters. The deposition temperature strongly affects the crystallographic and morphological appearance of the deposited thin films, which was investigated using field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD) methods. The electronic band structure-dependent characteristics were studied using ultraviolet-visible (UV-vis) spectroscopy and Hall measurements. Secondary ion mass spectrometry (SIMS) measurements complete the characterization methods for qualitatively verifying the incorporation of dopants and impurities. Results are reported for columnar-grown boron-doped ZnO with optical transparency greater than 80% in the visible range and a maximum carrier concentration of 10^{20}cm^{-3}.

Introduction

Transparent conductive oxides (TCOs) are known for their use as electrode materials for thin-film photovoltaic devices and other optoelectronics. Their unique properties of sufficiently high electrical conductivity while maintaining high transparency in wide spectral ranges, combined with further enhancing benefits such as stray-light tailoring, have stimulated significant increasing efforts in scientific and technological research. Materials commonly used as TCOs are ITO, SnO_2:F and ZnO:X. Doping zinc oxide with group 13 elements (Al or B) leads to n-type conductivity that is widely known and used [1–3]. To achieve p-type conductivity, many investigations are based on dopants of group 15 elements (N or P) [4–6] or co-doping of group 13 and group 15 elements [7,8] for tailoring the electronic band structure. But, so far, no long-term stable and reproducible results have been demonstrated; in contrast, fundamental physical research supports the assumption that p-type conductivity of ZnO is not feasible [9]. Due to the rising costs of indium, ZnO is increasingly used instead of ITO in photovoltaic TCO applications.

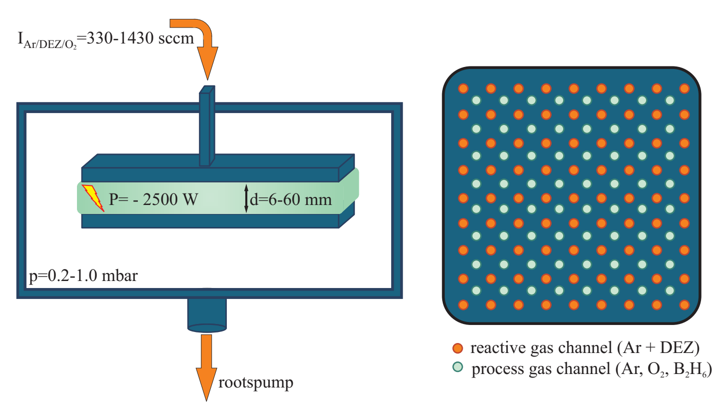

Figure 1. Schematic drawing of the PECVD reactor (left), and a top view of the two-channel direct gas distribution electrode (right).

The deposition of ZnO is carried out by means of a wide variety of physical and chemical methods. Industrially proven techniques are widely and abundantly reported: sputtering, reactive sputtering [2] and chemical vapour deposition (CVD) [10–12]; some wet chemical deposition approaches (e.g. sol-gel [1]); and more scientifically and educationally oriented methods such as molecular beam epitaxy [13], pulsed laser deposition [7], ultrasonic spray pyrolysis [14] and atomic layer deposition [15]. Among these methods, magnetron sputtering and metal organic CVD (MOCVD) are the main techniques for growing ZnO thin films applied to thin-film silicon solar cells [10]. The CVD methods can be classified into two groups: the first comprises the thermal CVD methods, which cover thermally driven reaction kinetics; the second includes the plasma-enhanced methods (e.g. PECVD). Plasma enhancement enables processes to take place below the usual temperatures for chemical reactions [16]. Lower deposition temperatures allow temperature-sensitive substrates such as polymeric foils to be used or the thermal exposure of heterojunction solar cell systems to be minimized. The main process parameters that influence the film properties encompass plasma parameters and chemical reactance flow, as well as the reaction conditions: process pressure and substrate temperature. By adjusting these parameters, the film conductivity and transparency properties, as well as the film morphology, roughness and microstructure, can be varied. The careful preselection of the precursors affects the species formed in the plasma during the process and therefore affects the chemical reaction in the plasma and the film properties.

Deposition set-up

The plasma reaction chamber at Fraunhofer IKTS is part of a plasma CVD tool manufactured by Roth&Rau Microsystems

Parameter	Lower limit	Upper limit
Electrode distance	8mm	60mm
Chamber pressure	0.1mbar	1mbar
O_2:DEZ	0.5	10
Plasma power	50W	2500W
DEZ flow	20 sccm	80 sccm
Substrate temperature	50°C	450°C

Table 1. List of basic process parameters for PECVD deposition of ZnO.

> “To achieve a homogeneous plasma reaction over the whole substrate, the ratio of carrier gas (argon), process gas (oxygen) and reactive gas (zinc precursor diluted in argon) plays a key role.”

(Meyer Burger AG). The tool is equipped with a parallel plate electrode assembly (similar to a plate capacitor): the substrate is placed at the bottom electrode and the upper electrode consists of a unique separate gas inlet system (Fig. 1). This gas inlet is designed to avoid the reaction of the educts before being injected into the plasma and ensures that the whole reaction to ZnO begins in the reaction chamber. Using highly reactive precursors such as diethyl zinc (DEZ, $Zn(CH_5)_2$) requires these particular design features in order to prevent a premature chemical reaction in the gas inlet. DEZ is a fluid under normal conditions, and therefore a bubbler set-up is necessary, in which a carrier gas (argon) is passed through the DEZ. The diluted amount of DEZ in argon, and thus the precursor flow in the plasma chamber, is controlled via an argon flow through the bubbler at a certain temperature and specific pressure according to the calculated vapour pressure.

The construction of the chamber (shown schematically in Fig. 1) allows the adjustment of the distance between substrate and showerhead from 6 to 60mm. The substrate sizes can be freely chosen up to $50\times50cm^2$; depending on the adjustable distance, even substrates thicker than common glass or silicon wafers can be used. All the results reported here pertain to ZnO thin films deposited on n-type silicon substrates at 50W plasma power. The plasma chamber is equipped with a 13.56MHz RF generator, which can be exchanged to provide higher (up to 40 or 100MHz) or lower frequencies. For µc-Si thin-film deposition, higher frequencies lead to higher deposition rates [17,18]; carrying this over to TCO deposition is currently the subject of ongoing research. For the PECVD process, the careful control of process parameters, particularly the electrode distance, strongly influences the deposition rate as well as homogeneity and therefore the economic aspects. To achieve a homogeneous plasma reaction over the whole substrate, the ratio of carrier gas (argon), process gas (oxygen) and reactive gas (zinc precursor diluted in argon) plays a key role. Controlling the applied plasma power and reactor pressure increases the field of parameters but narrows down the process window for appropriate film characteristics.

The possible process conditions for deposition of ZnO with this equipment are summarized in Table 1. Optical emission spectroscopy (OES) and monitoring of the bias voltage facilitates feedback and control of the plasma process. The OES spectra examine light emissions of excited ions that are representative for certain species. Thus, plasma chemical reactions can be deduced as reported by Groenen et al. [19] and the relative density of the species (e.g. Zn) can be calculated as reported by Robinson et al. [20]; from this, a set of parameters can be estimated. The characteristics of the plasma can be indirectly assessed from the bias voltage, which expresses a complex interaction between plasma power, gas flow and geometry of the plasma volume. Therefore, the bias voltage has to be stable over the process time and, for reproducibility, over every single deposition.

Film deposition

In order to deposit zinc oxide during PECVD, a plasma power of at least 50W is required, otherwise no reaction between the metal organic precursor and oxygen is observable, even at temperatures up to

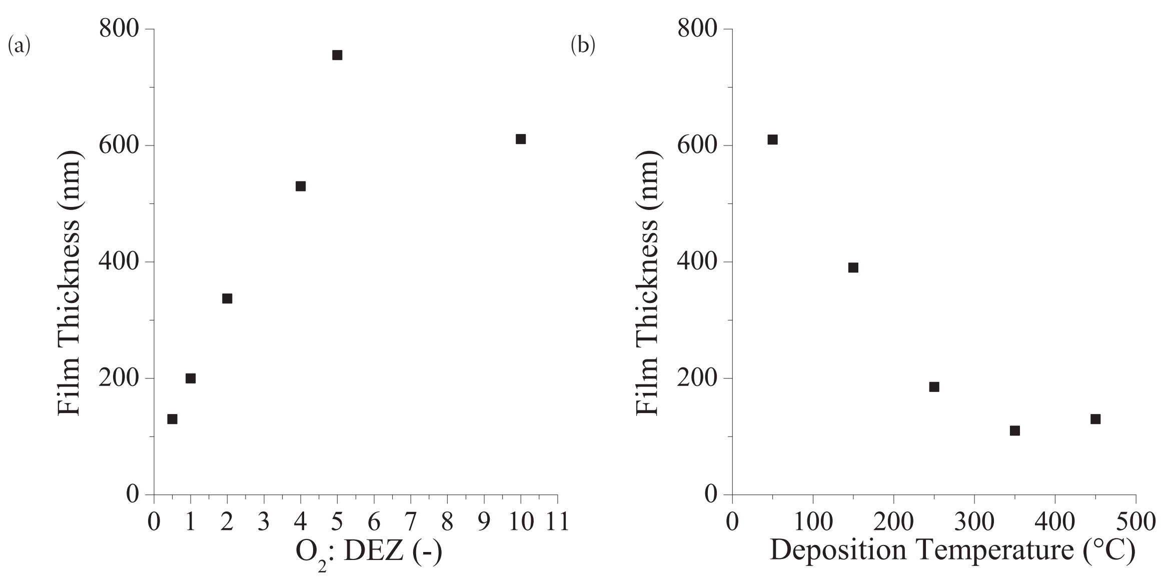

Figure 2. ZnO thickness of undoped films for (a) different O_2:DEZ ratios (at T=300°C), and (b) different substrate temperatures (for O_2:DEZ ratio of 0.5). A higher oxygen flow increases the deposition rate, and higher substrate temperatures lead to lower deposition rates.

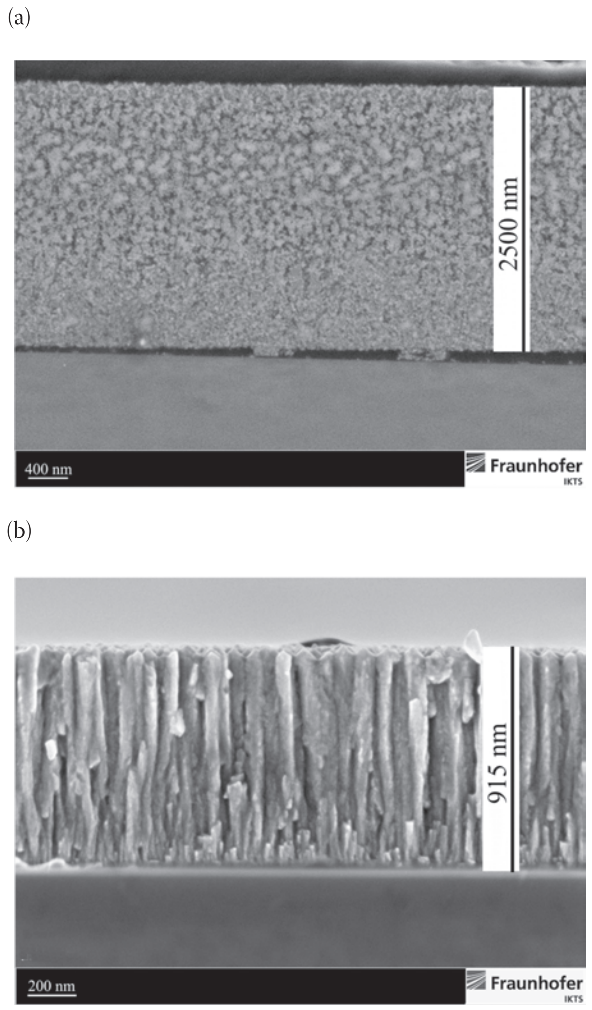

Figure 3. FESEM images of fractured surfaces of undoped ZnO films deposited at temperatures of (a) 50°C and (b) 350°C. Columnar grain growth is revealed at elevated temperatures.

450°C. In CVD processes that use other oxygen sources (e.g. water), this is reported differently in the literature [12]. For thermal expanding plasma CVD processes, Groenen et al. [19] reported that the main reactions (1) and (2) can be expected, driven by charge exchange with argon ions and a dissociative recombination with electrons:

$$Zn(C_2H_5)_2 + 5O_2 \rightarrow 4CO + 5H_2O + ZnO \quad (1)$$
$$Zn(C_2H_5)_2 + 7O_2 \rightarrow 4CO_2 + 5H_2O + ZnO \quad (2)$$

Therefore, an excess of oxygen is necessary to obtain high-quality ZnO films and economic deposition rates. For different ratios of O_2:DEZ, the film thickness increased with increasing amounts of oxygen (Fig. 2a) up to a ratio of 5, and then reached a plateau. When all other process parameters were kept constant, the film thickness decreased with increasing substrate temperature (Fig. 2b).

In a substrate temperature range of 50 to 450°C, the deposition rate, film morphology and microstructure changed dramatically. Low substrate temperatures resulted in high deposition rates, but the deposited films were of low quality and had high porosities (Fig. 3a). Spectroscopic ellipsometry measurements on these porous films reflected the low quality by a low dispersion coefficient n less than 1.8. They mainly consisted of nm-scaled and irregularly orientated crystallites. When temperatures rose above 350°C, the ZnO films were deposited uniformly with low porosities and typical columnar grain growth (Fig. 3b), and a dispersion coefficient n greater than 1.95.

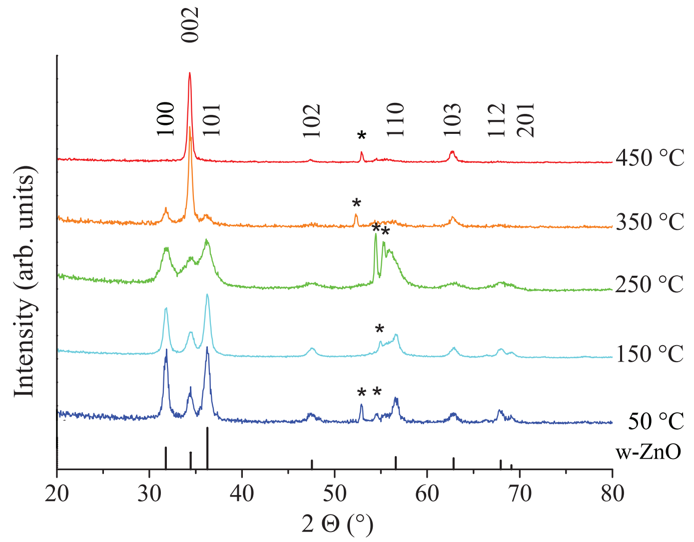

Figure 4. XRD patterns of undoped ZnO layers deposited at different substrate temperatures (for O_2:DEZ ratio of 0.5). Above 250°C, the change in crystal orientation from irregular (powder-like) to the preferred orientation of the c-axis perpendicular to the substrate surface is indicated by an increase of the relative intensity of the 002 reflection. Some silicon reflections, caused by the recording geometry, are visible and indicated by asterisks.

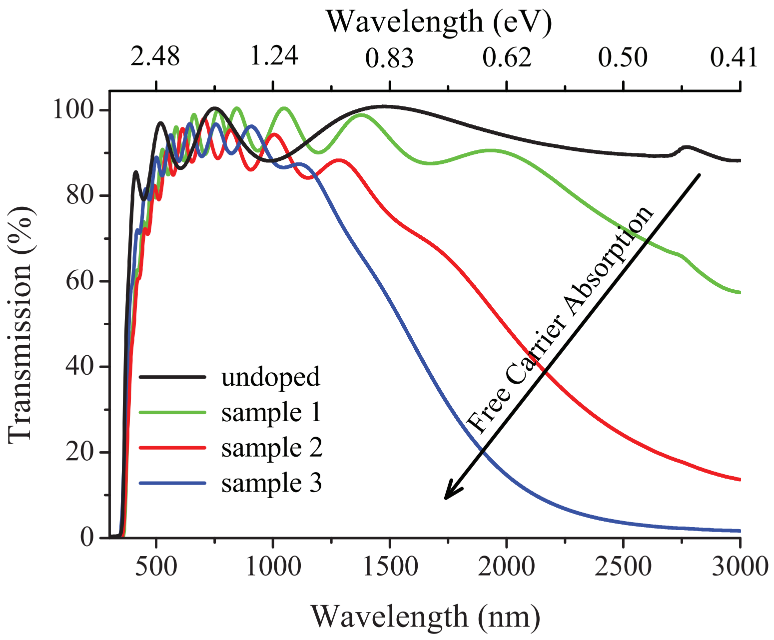

Figure 5. UV-vis transmission measurements of ZnO:B samples. Absorption in the IR region rises with increasing dopant flow, due to the free-carrier absorption.

> “Low substrate temperatures resulted in high deposition rates, but the deposited films were of low quality and had high porosities”

The influences of the substrate temperature on crystal growth direction, crystal habit and preferred orientation were measured using X-ray diffraction (XRD) at grazing incidence (1°). Fig. 4 shows the XRD patterns of a specimen series deposited at different temperatures: a strong crystal orientation with the c-axis perpendicular to the substrate surface at temperatures above 350°C is evident. The XRD patterns below a deposition temperature of 350°C all revealed Bragg reflections of hexagonal wurtzite-structured ZnO powder (according to PDF 00-36-1451 [21]). The crystals were deposited with relatively small crystallite sizes in a randomly orientated fashion, in agreement with the XRD results and the film microstructure (Fig. 3a).

Boron doping

The doping of TCO requires precise control of impurities as well as of dopant flow; otherwise, the transparency and resistivity of the films cannot be reproduced. Therefore, at Fraunhofer IKTS, all gases used in the CVD reactors are of high purity – at least grade 5.0 (99.999%), but usually grade 6.0 (99.9999%), is used. As the dopant source, diborane (B_2H_6) diluted to 2 vol% in argon was injected in various amounts into the plasma through the oxygen channel. High carrier concentrations (> 10^{19}cm^{-3}) in the films were confirmed for B_2H_6:(DEZ+O_2) ratios of 0.05 (sample 1), 0.125 (sample 2) and 0.25 (sample 3), and verified independently by Hall measurements and by analyzing the ultaviolet-visible (UV-vis) spectra by using the Drude model for free-carrier absorption (Fig. 5), as well as by an analysis of the Burstein-Moss shift (Fig. 6).

The carrier concentrations are summarized in Table 2 and agree with results reported in the literature

	Film thickness [nm]	B_2H_6:(DEZ+O_2)	Carrier concentration [cm^{-3}]		
			Burstein-Moss shift	Drude model	Hall measurements
Undoped	420	0	n/a	n/a	n/a
Sample 1	1090	0.05	$> 5.0*10^{19}$	$1.1*10^{20}$	n/a
Sample 2	1090	0.125	$> 5.6*10^{19}$	$3.7*10^{20}$	$9.8*10^{19}$
Sample 3	900	0.25	$> 1.3*10^{20}$	$6.5*10^{20}$	$1.8*10^{20}$

Table 2. Comparison of carrier concentrations derived from the UV-vis spectra and Hall measurements for three samples of varying film thicknesses and different dopant ratios (T=350°C, P=50W).

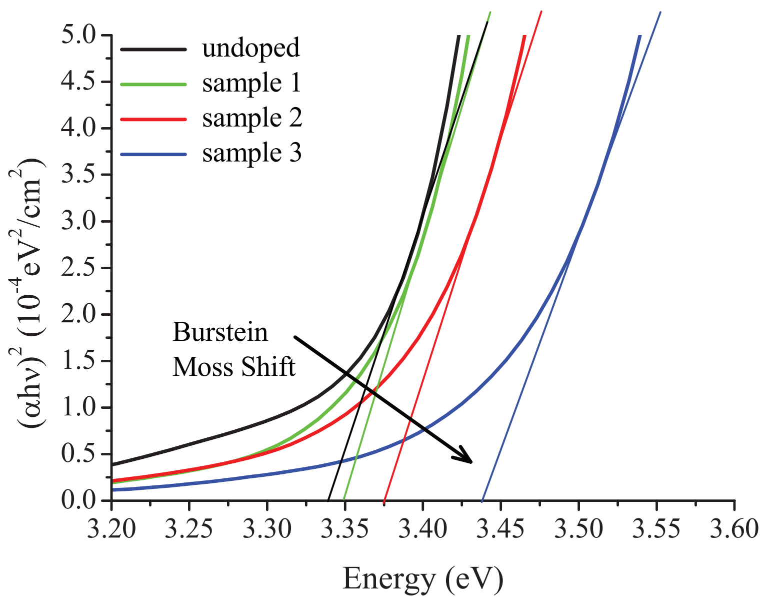

Figure 6. Tauc plot of ZnO:B samples calculated from the UV-vis data in Fig. 5. Note the blue shift of the fundamental band edge (Burstein-Moss shift) with increasing diborane flow.

[3,7,10,22]. The presence of boron throughout the whole ZnO layer was determined qualitatively from SIMS measurements (Fig. 7). The layers consist of a homogeneous distribution of boron over the entire film thicknesses, but a comparison of sample 1 and sample 3 indicates that the overall content of boron differs depending on the boron flow rate during deposition. All results shown were collected on specimens deposited under identical conditions of a substrate temperature of 350°C and an O_2:DEZ ratio of 1: higher carrier concentrations with higher boron content are therefore emphasized.

The strong 002 reflection refers to the growth in the c-axis perpendicular to the substrate surface (Fig. 8). The intensity of the 103 reflection compared to the 002 reflection and the shift of the 2Θ position may indicate an influence of the boron incorporated into the lattice. Investigations to clarify this fact are currently in progress.

> "The main parameter influencing the film morphology and crystal orientation was the deposition temperature."

Conclusion

Homogenous thick crystalline ZnO:B transparent thin films were deposited in a PECVD chamber by a reaction of diethyl zinc with an excess of oxygen in a capacitively coupled argon plasma. Both reaction gases were separately injected into the plasma by a two-channel showerhead. The dopant source B_2H_6 was transported through the oxygen channel in various quantities. Plasma power and electrode distance were optimized to 50W and 16mm, respectively. It was found that the deposition rate was strongly influenced by

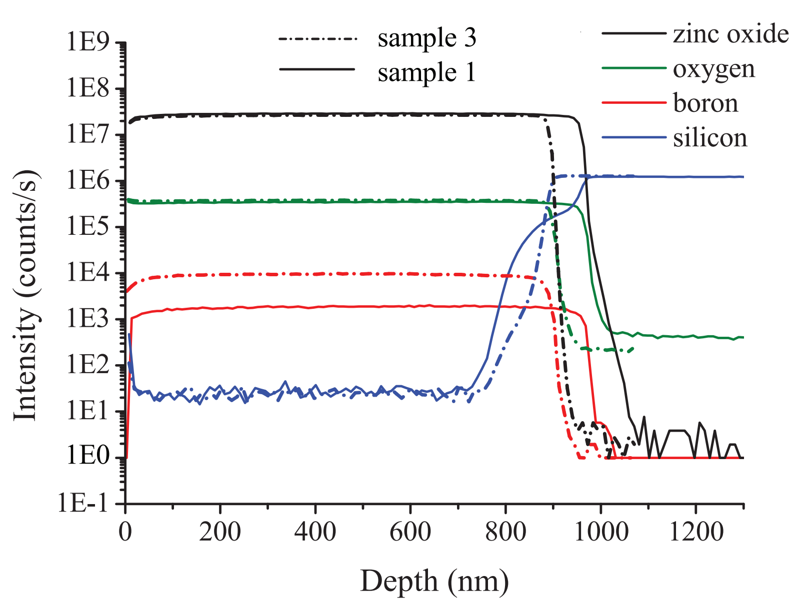

Figure 7. SIMS measurements for sample 1 (continuous line) with a 0.05 (low dopant flow) boron ratio, and for sample 3 (dashed line) with a 0.25 (high dopant flow) boron ratio. The elemental distribution as a function of ZnO layer depth was recorded. Concentrations of different elements are not comparable.

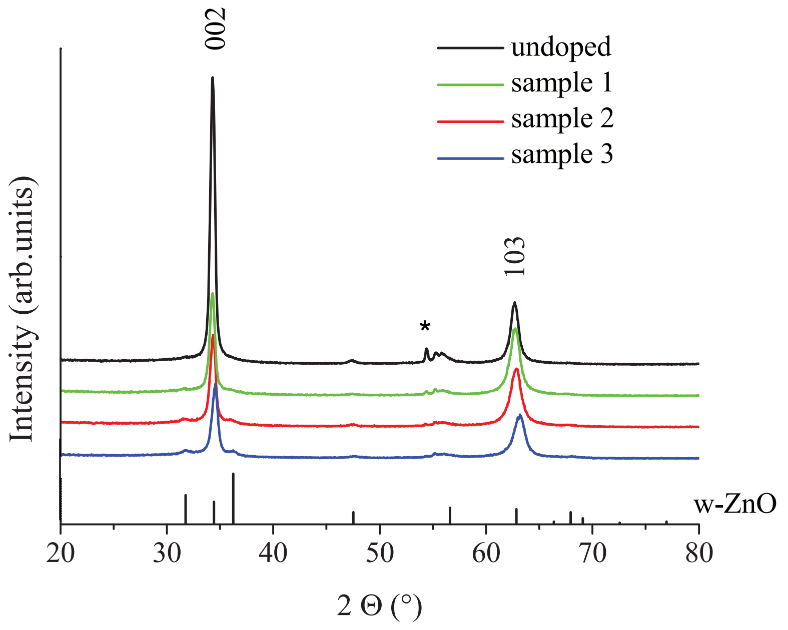

Figure 8. Comparison of the XRD measurements of an undoped sample (black line) with those of samples 1–3. The intensities are normalized to the 103 reflection in order to show more clearly how the relative intensity ratio of the 002 to 103 reflection changes with boron content.

the ratio of O_2:DEZ and by the deposition temperature. A higher temperature decreased the deposition rate, whereas the deposition rate was increased up to the stoichiometric ratio of DEZ and oxygen according to the main reaction in Equations (1) and (2).

The main parameter influencing the film morphology and crystal orientation was the deposition temperature. Above a substrate temperature of 350°C, columnar grain growth with a preferred orientation of the c-axis of hexagonal wurtzitic ZnO perpendicular to the substrate surface was revealed. The resulting boron-doped films exhibited a high carrier concentration of greater than 10^{19}cm^{-3}, which was homogenously distributed in the layer over the whole film depth. An optical transparency of greater than 80% in the visible region was demonstrated by UV-vis spectroscopy.

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