Atomic layer deposition of B-doped ZnO using triisopropyl borate as the boron precursor and comparison with Al-doped ZnO†

Diana Garcia-Alonso, Stephen E. Potts, Cristian A. A. van Helvoirt, Marcel A. Verheijen and Wilhelmus M. M. Kessels

Doped ZnO films are an important class of transparent conductive oxides, with many applications demanding increased growth control and low deposition temperatures. Therefore, the preparation of B-doped ZnO films by atomic layer deposition (ALD) at 150 °C was studied. The B source was triisopropyl borate, B(OiPr)3 (TIB), which has a significantly lower vapour pressure and is a safer alternative precursor to highly toxic diborane(6), B2H6. The doping fraction (DF) of the films was varied by the ratio of ZnO and dopant ALD cycles. The electrical, structural and optical properties of the ZnO:B films were studied as a function of the dopant concentration and deposition temperature, and were compared with ZnO:Al films, where dimethylaluminium isopropoxide, [Al(CH3)2(OiPr)]2 (DMAI) and trimethylaluminium, Al2(CH3)6 (TMA) were the Al sources. A low resistivity of 3.5 mΩ cm was achieved for 45 nm-thick ZnO:B deposited at 150 °C with a doping fraction (DF) of 0.016, which was similar to the results obtained for ZnO:Al films prepared with DMAI and lower compared to the 8 mΩ cm achieved for ZnO:Al prepared with TMA at an optimized DF of 0.040. Hence TIB, as well as DMAI, outperformed the conventionally employed TMA in terms of doping efficiency at 150 °C. It was found that the optical band gap could be easily tuned over the range of ~3.2–3.7 eV by modifying the doping fraction.

1 Introduction

Tin-doped indium oxide (ITO) is the most popular transparent conductive oxide (TCO) for optoelectronic devices, but the scarcity and relative expense of indium has led to alternative TCO materials being sought.1,2 ZnO has many intrinsic properties that makes it a good candidate for a TCO material as it has a direct wide band gap of ~3.4 eV, a refractive index of ~2.0 and electronic mobilities as high as 50–60 cm2 V−1 s−1.3,6 ZnO films exhibit good optical transparency below the band gap and their conductivity can be increased by doping with a group 13 element (i.e., ZnOx where x = Al, B, Ga, In).7,8

ZnO (either intrinsic, i.e. without intentional doping, or doped) is especially of interest for application fields with very strict cost requirements, such as the field of photovoltaics (PV).

For example, ZnO is employed on the front and/or rear of silicon heterojunction (SHJ) solar cells,9–11 used as multifunctional front contact on thin film solar cells such as amorphous silicon, Cu(In,Ga)(S,Se)2 (CIGS), CdTe, or organic solar cells,12,13 or it acts as a buffer layer or semi-transparent cathode in organic photo-voltaics (OPV)14,15 or as a nanostructured photoanode or interlayer in dye-sensitised solar cells (DSCs).16,17

For many TCO applications, particularly in PV, ultrathin (doped) ZnO films with a low resistivity (< 1 mΩ cm) and a high transparency (> 80%) in the spectral region of interest are required.6,18 Preferably, the low resistivity should be a result of high carrier mobility rather than high free-electron density, the latter resulting in a decrease in transparency, especially in the infrared region.19 Low deposition temperatures (< 200 °C) and a tuneable roughness are other requirements for certain types of solar cells, such as CIGS, flexible plastic DSCs and SHJ cells.

ZnO and doped ZnO thin films have been grown by various methods such as spray pyrolysis,20,21 sol–gel deposition,22,23 sputtering,24,25 pulsed laser deposition (PLD),25,26 chemical bath deposition (CBD),27,28 metal–organic chemical vapour deposition (MOCVD),29,30 and atomic layer deposition (ALD).31–33 ALD, in particular, is becoming a popular deposition technique as it allows for deposition at low temperatures, it is a ‘soft’ method without highly energetic species and it is scalable. Furthermore, the fact...
that ALD operates via self-limiting surface reactions in cycles means that doping materials can be introduced with greater control and tuning than other deposition methods. Recent reviews emphasise the potential of ALD to contribute towards achieving high-efficiency solar cells.33,34

Many articles have been published on the ALD of intrinsic ZnO and ZnO:Al, mostly using TMA as an Al source, but far fewer using other dopant materials. TMA is a highly reactive molecule, which has led to its popularity as an ALD precursor. However, this high reactivity can lead to difficulty in controlling doping levels. Furthermore, it is pyrophoric, making it potentially difficult to handle and dangerous in high quantities such as those used in high-volume manufacturing. In this article, we investigate the ALD of ZnO:B using an alternative B source, triisopropyl borate (TIB), in conjunction with a ZnO ALD process comprising diethylzinc (DEZ) and H2O half-cycles. First, a brief review of the state-of-the-art of ALD ZnO:X (X = Al, B) and the precursors used to date is reported. Second, the electronic, structural and optical properties of the ZnO:B films obtained using TIB are presented and compared with the properties of the ZnO:Al films obtained using conventional TMA and alternative DMAI precursors under the same conditions.15,16

2 ALD of ZnO:X and precursors

ALD is an ultrathin film deposition technique comprising alternating exposures of gaseous precursors, known as half-cycles, to a surface (substrate) separated by purging steps to ensure the precursors do not mix.37,38 ALD excels in producing highly uniform and conformal films with a precise growth control and is compatible with deposition temperatures from room temperature up to ~350 °C,39-41 where the higher end of the temperature range is limited by the decomposition temperature of the metal-organic precursor.40-42 The cyclic nature of ALD means that doses of dopant sources can easily be incorporated into the process. The technique also allows for the deposition of virtually defect-free films with tailored compositions (via doping) and it can easily be used to produce multilayer structures.43-47 Doping is often achieved by combining the steps of two normal ALD processes in a supercycle, where m cycles of the base material process (in this case ZnO) are followed by one cycle of the doping material (Fig. 1). The number of cycles m is chosen to obtain the desired film composition, and the supercycle (m + 1) is repeated x times until the desired film thickness is reached. The value of m can also be varied in the supercycles throughout the deposition process in order to obtain films with graded doping.

A wide selection of elements with a different valency to Zn can be used to dope ZnO, such as Al, B, Ga, Ge, H, Hf, Mn, N, P, S, Si, Sn, Ti, and Zr. A complete review of doping materials for ZnO by ALD can be found in the recently published review by Tynell et al.12

Reported ALD processes for ZnO:X (X = Al, B) are summarised in Table 1. In almost all cases of ZnO ALD, DEZ is used as the Zn source. The most commonly-employed dopant is Al and the most frequently used Al-source for the ALD of ZnO:Al is trimethylaluminium (TMA), as evidenced by the large number of publications reporting it.8,43,44,48-77 The main reason behind this is that TMA is a well-documented precursor and is extensively used within the ALD community. However, TMA is a highly volatile molecule,79,80 and it is very reactive towards a variety of surface groups, which is ideal for pure Al2O3 ALD processes but that can make doping using ALD difficult to control because it is too reactive to afford a sufficiently low surface density of Al atoms. Aluminium isopropoxide (AIP) has also been reported as an alternative Al source in the ALD of ZnO:Al,79 where its potential advantage is that AIP is less reactive than TMA towards surface groups, which makes doping potentially easier to control.

![Fig. 1](https://example.com/fig1.png)

A schematic representation of two ALD supercycles used to dope the ZnO films with a doping element, X (X = Al, B, Ga, etc.). For uniform doping, a constant value of m is used (m1 = m2 = \cdots = m_x) whereas for films with graded doping, the value of m can be varied. Details of the ALD processes are shown in the lower part of the figure: the process for the ZnO based material comprises two half-cycles in which DEZ and H2O are dosed; in most cases, the ALD process of the doping material also comprises two doses: dopant precursor dosing and H2O dosing. Other co-reactants such as O2 or O2 plasma can also be employed instead of H2O, for both the ZnO and the doping element.
However, AIP is a solid at room temperature and exists as a tetramer. Consequently, the low volatility of AIP could prove to be challenging in some ALD systems as it can require heating up to \( \sim 130 \) °C before an optimum vapour pressure for growth is obtained. A compromise in reactivity and volatility between TMA and AIP can be found in the heteroleptic precursor dimethylaluminium isopropoxide, \([\text{AlMe}_2(\text{OiPr})]_2\) (DMAI), which has been employed as an ALD precursor to both \( \text{Al}_2\text{O}_3\) \(^{81,82}\) and ZnO:Al thin films.\(^{36,83}\) We recently reported the ALD of ZnO:Al using DMAI, which led to higher doping efficiencies (i.e., higher active dopant densities) and lower resistivities than those obtained when TMA was used.\(^{36}\) This improved doping efficiency resulted from a lower surface density of Al atoms due to the lower reactivity of DMAI and the steric hindrance caused by the bulky OiPr ligands on the precursor.

The most commonly reported B source for thin film deposition is diborane(6) (\( \text{B}_2\text{H}_6\)), which is an extremely flammable gas at room temperature. It is also highly toxic\(^{89}\) and is consequently typically used as a 1–10% solution in H\(_2\).\(^{B2H6}\) has been the most widely used as a CVD precursor to \( \text{ZnO:B} \)\(^{90–98}\) with, to date, relatively few reports of its use in ALD.\(^{85–88}\) We believe that the reason behind this low number of publications on the use of \( \text{B}_2\text{H}_6\) for ALD is its extremely high vapour pressure,\(^{139}\) which is not easy to control under ALD conditions. Furthermore, the highly toxic nature of \( \text{B}_2\text{H}_6\) means it is undesirable to handle, which has led to alternatives being sought.

Potential candidates for the B source were considered based on the precursors that had been used for CVD of B-containing films. CVD processes using precursors such as borazine,\(^{100}\) \(B,B',B''\)-trichloroborazine\(^{101}\) and tris(dimethylamido)borane\(^{102–106}\) have been reported, although in those cases the target material was BN. Boron tribromide (\( \text{BBr}_3\)) has been used as an ALD precursor to \( \text{B}_2\text{O}_3\)\(^{107}\) and \( \text{BN}\)\(^{108}\), however, bromide impurities in the film can be extremely detrimental to its electrical properties. Specifically concerning ZnO:B, a recent study was carried out in order to investigate safer precursors than \( \text{B}_2\text{H}_6\) for CVD,\(^{109,110}\) wherein \(N,N',N''\)-trimethylborazine, trimethyl borate and triisopropyl borate (TIB) were employed as the B sources. The ZnO:B films deposited using these aforementioned precursors had comparable resistivities to films where \( \text{B}_2\text{H}_6\) was used. Based on these results, the selection of a potential B-source candidate for ALD was done for this work. In terms of their use as an ALD precursor, \(N,N',N''\)-trimethylborazine was not considered because, being isostructural with benzene, it was unclear how it could react with surface groups in an ALD mechanism. Regarding trimethyl borate, its vapour pressure (100 Torr at 20 °C)\(^{119}\) was unpractical. On this basis, TIB was chosen as the most promising ALD precursor for ZnO:B.

We report here the use of TIB as an alternative B precursor for the ALD of ZnO:B and we compare the results with ZnO:Al films deposited using DMAI and TMA as Al sources. We extended the temperature range of the recently reported ZnO:Al ALD process using DMAI\(^{36}\) from 250 °C down to 150 °C in order to compare the film properties given by the two different dopants. A comparison of these two precursors with their more traditional counterparts is given in Table 2. The TIB and DMAI molecules, which contain OiPr ligands, are large compared to TMA. The presence of OiPr results in possible steric hindrance, thus affording a lower surface density of the doping element and

![Table 1](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>Zn source</th>
<th>Dopant source</th>
<th>Co-reactant</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:Al</td>
<td>ZnEt(_2)</td>
<td>[AlMe(_3)](_2)</td>
<td>H(_2)O</td>
<td>8, 43, 44, 48–76 and this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Al(OiPr)(_3)](_2)</td>
<td>H(_2)O</td>
<td>37, 77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[AlMe(_2)(OiPr)](_2)</td>
<td>H(_2)O</td>
<td>99, 79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[AlMe(_3)](_2)</td>
<td>H(_2)O</td>
<td>36, 83 and this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[AlMe(_2)(OiPr)](_2)</td>
<td>H(_2)O</td>
<td>48</td>
</tr>
<tr>
<td>ZnO:B</td>
<td>ZnEt(_2)</td>
<td>B(_2)H(_6)</td>
<td>H(_2)O</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B(OiPr)(_3)</td>
<td>H(_2)O</td>
<td>85–88</td>
</tr>
</tbody>
</table>

\(^*\) Me = methyl, CH\(_3\); Et = ethyl, CH\(_2\)CH\(_3\); iPr = isopropyl, CH(CH\(_3\))\(_2\).

![Table 2](image)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Zn precursor</th>
<th>B precursors</th>
<th>Al precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>DEZ</td>
<td>B(_2)H(_6)</td>
<td>TMA</td>
</tr>
<tr>
<td>Full name</td>
<td>Diethyl zinc</td>
<td>Diborane(6)</td>
<td>Trimethyl aluminium</td>
</tr>
<tr>
<td>Formula</td>
<td>Zn(CH(_2)CH(_3))(_2)</td>
<td>B(_2)H(_6)</td>
<td>Dimethylaluminium isopropoxide</td>
</tr>
<tr>
<td>Physical state (R.T.P.)</td>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>−28</td>
<td>−165(^{109})</td>
<td>n/a</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>117</td>
<td>−92.5(^{109})</td>
<td>140(^{109})</td>
</tr>
<tr>
<td>Decomposition temperature (°C)</td>
<td>&gt; 200(^{118})</td>
<td>&gt; 200(^{118})</td>
<td>n/a</td>
</tr>
<tr>
<td>Vapour pressure at 25 °C (Torr)</td>
<td>~ 160(^{211})</td>
<td>~ 35400(^{29})</td>
<td>~ 1300(^{119})</td>
</tr>
<tr>
<td>Flammability</td>
<td>Highly flammable, pyrophoric</td>
<td>Extremely flammable, non-phyrophoric</td>
<td>Highly flammable, pyrophoric</td>
</tr>
</tbody>
</table>

Flammability: Highly flammable, pyrophoric

This journal is © The Royal Society of Chemistry 2015.

---

This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.
3 Experimental

The ZnO doping ALD processes were carried out in an open-load ALD reactor (OpAL, Oxford Instruments), as reported previously.\textsuperscript{35,36} Samples were deposited with different doping concentrations over a range of substrate temperatures (150–240 °C). 7059 corning glass, silicon wafers with a native oxide layer, and silicon wafers with a 450 nm-thick thermally-grown SiO\textsubscript{2} layer were used as substrates. Diethyl zinc (DEZ > 99.999%, Dowchemester Chemicals) and trisopropyl borate (TIB > 98%, Air Liquide) were used as Zn and B-doping precursors respectively. Dimethylaluminium isopro-poxide (DMAI > 99.999%, Air Liquide) and trimethyl aluminium (TMA > 99.999%, Air Liquide) were used as reference Al doping precursors. Deionized water vapour (DI-H\textsubscript{2}O) was used as the co-reactant in all cases. The ZnO:B ALD process details will follow in Section 4.1. The ZnO:Al ALD processes using DMAI and TMA as doping precursors are described elsewhere.\textsuperscript{35,82}

Spectroscopic ellipsometry (SE) was used to measure the film thickness and the dielectric function of the films.\textsuperscript{122} The in situ and ex situ measurements were performed using a Woollam, Inc. M2000 visible and near-infrared ellipsometer (0.75–5 eV). The SE data were analysed using a Drude oscillator model.\textsuperscript{35}

The film compositions (doping and impurity concentrations) were analysed by X-ray photoelectron spectroscopy (XPS Thermo Scientific K-Alpha KAI066, monochromatic Al Kα (h\textnu = 1486.6 eV), X-ray spot: 400 μm). The sensitivity factors used for quantification were: B 1s, 0.470; O 1s, 2.881; Zn 2p 3/2, 21.391; Al 2p, 0.75; C 1s, 0.919. Rutherford backscattering spectroscopy (RBS; 2 MeV He\textsuperscript{+} beam in channelling configuration under perpendicular incidence with the detector at 170° scattering angle) and proton-induced gamma ray emission (PIGE; 2700 keV H\textsuperscript{+} beam with an angle of incidence of 6.5° between the beam and sample surface and the gamma detector at an angle of 90° with respect to the beam) were used to calibrate the sensitivity factors used in XPS quantification and to obtain the areal density of the doping elements. The RBS/PIGE measurements were carried out at AccTec B.V. The film composition is presented as the doping fraction (DF) calculated by

\[
\text{DF} = \frac{X_{\text{at\%}}}{X_{\text{at\%}} + Z_{\text{at\%}}} = \frac{X_{\text{at\%}}}{X_{\text{at\%}} + Z_{\text{at\%}}}, \quad \text{where} \quad X = \text{Al or B}.
\]

The resistivity (\rho) and sheet resistance (R_S) of all samples were obtained by four-point probe (4pp) measurements using a Keithley 2400 SourceMeter and a Signaton S-301-6 probe. The carrier concentration (n) was extracted from SE data assuming an effective mass of 0.4 and cross-checked using a Hall measurement system (BIO-RAD) using the van der Pauw configuration. The electron mobility (\mu) of the films was calculated following the formula 

\[
\mu = \frac{(n+\rho\epsilon)}{\epsilon}, \quad \text{where} \quad \epsilon \quad \text{is the elementary charge}.
\]

The structural properties of the samples were studied by X-ray diffraction (XRD; PanAlytical X’pert PRO MRD) and transmission electron microscopy (TEM; JEOL ARM 200 probe corrected TEM, operated at 200 kV). UV-VIS-NIR spectroscopy (Cary 5000, Agilent Technologies) was used to study the optical transparency of the films. The absorption coefficient (\alpha) was calculated from the extinction coefficient (k) of the films as obtained by the SE data. The optical band gap of the films was calculated using the so-called Tauc plots extracted from the SE data as well.\textsuperscript{35,124}

4 Results and discussion

4.1 Process properties and atomic composition of ALD films

The ZnO doping ALD processes were carried out using so-called supercycles as illustrated in Fig. 1. In principle, the concept of supercycle is effective when the two individual ALD processes (i.e., the base material ALD process and the dopant ALD process) are compatible with each other. Additionally, the ALD supercycle should be in saturation when the two individual ALD processes are in saturation. This is in fact the case for the ZnO and Al\textsubscript{2}O\textsubscript{3} ALD processes used to obtain Al-doped ZnO films that we reported previously.\textsuperscript{35,36,82}

Attempts to obtain a B\textsubscript{2}O\textsubscript{3} ALD process using TIB with either water or an O\textsubscript{2} plasma as co-reactants resulted in no growth at all temperatures investigated. As part of their studies on the BBr\textsubscript{3}–H\textsubscript{2}O ALD process, Putkonen and Niinistö suggested that volatile boric acid, B(OH)\textsubscript{3}, was formed instead of B\textsubscript{2}O\textsubscript{3} when the boron precursor came into contact with excess water under reduced pressure.\textsuperscript{107} The boric acid was then carried away in the vacuum rather than being incorporated into a growing film. We believe that a similar mechanism might take place when TIB is the precursor, which would account for the lack of growth of B\textsubscript{2}O\textsubscript{3}. However, it was still possible to grow ZnO:B films using TIB incorporated into a supercycle using the DEZ–H\textsubscript{2}O process. For this reason, the parameters of the ALD process for the B dopant were tuned during the ZnO doping ALD process at 150 °C using a supercycle with m = 4 (i.e., 5 cycles consisting of 4 ZnO + 1 TIB) and using the already-optimised ZnO ALD process parameters (50 ms DEZ dose, 5 s purge, 20 ms H\textsubscript{2}O dose, 6 s purge).\textsuperscript{35} For the process development, in situ spectroscopic ellipsometry (SE) was used to measure the film thickness after every supercycle. Growth per supercycle (GPSC) values were determined from the slope of the growth curves or sufficient purging. For example, nucleation delays or etching.\textsuperscript{35}

The saturation curves for the gas exposures and purges of the B cycle of an ALD supercycle corresponding to four DEZ cycles and one TIB cycle for the ZnO:B process are depicted in Fig. 2. These data were obtained by varying the duration of one of the ALD cycle steps, while keeping the duration of other steps sufficiently long to ensure either saturation of surface reactions or sufficient purging. The saturation GPSC was
respectively) both reached saturation at pulse times of ~50 ms. It would be expected that longer precursor doses would increase the GPSC until the process is saturated. However, the TIB dose (Fig. 2a) showed a drop in GPSC such that, after saturation, it was ~0.12 nm per supercycle lower than that for the intrinsic ZnO process (i.e., TIB dose = 0 s in Fig. 2a) at 150 °C (GPSC = 0.73 nm per supercycle, corresponding to 4 DEZ cycles). The water dose (Fig. 2c) showed a gradual increase in GPSC, which is typical of water doses.125 Purge times of 5 s were necessary to remove the volatile reaction products and the excess precursor (Fig. 2b and d). These dosing/purging times for the B doping process (i.e., TIB and DI-H₂O doses of 50 ms separated by purge steps of 5 s) were used for all further experiments.

The reduction in GSPC with increasing TIB dose observed in Fig. 2a could be the result of a slight etching of the ZnO by the TIB (as observed for TMA36,69,72) but it could also be due to the inhibition of ZnO growth after a TIB pulse, as observed for DMAI.36 To establish which effect played a role, an experiment in which a supercycle with (m = 4) at 150 °C. (a) TIB precursor dose, (b) TIB precursor purge, (c) DI-H₂O dose, and (d) DI-H₂O purge. (a) TIB precursor dose, (b) TIB precursor purge, (c) DI-H₂O dose, and (d) DI-H₂O purge. The growth per supercycle (GPSC) for each condition was averaged over 10 supercycles. The ZnO standard conditions are specified elsewhere (50 ms DEZ dose, 5 s purge, 20 ms H₂O dose, 6 s purge)35 and the process saturated at a GPC of 0.2 nm per cycle for an intrinsic ZnO film deposited at 150 °C.

~0.61 nm per supercycle. The TIB and H₂O doses (Fig. 2a and c, respectively) both reached saturation at pulse times of ~50 ms. It would be expected that longer precursor doses would increase the GPSC until the process is saturated. However, the TIB dose (Fig. 2a) showed a drop in GPSC such that, after saturation, it was ~0.12 nm per supercycle lower than that for the intrinsic ZnO process (i.e., TIB dose = 0 s in Fig. 2a) at 150 °C (GPSC = 0.73 nm per supercycle, corresponding to 4 DEZ cycles). The water dose (Fig. 2c) showed a gradual increase in GPSC, which is typical of water doses.125 Purge times of 5 s were necessary to remove the volatile reaction products and the excess precursor (Fig. 2b and d). These dosing/purging times for the B doping process (i.e., TIB and DI-H₂O doses of 50 ms separated by purge steps of 5 s) were used for all further experiments.

The reduction in GSPC with increasing TIB dose observed in Fig. 2a could be the result of a slight etching of the ZnO by the TIB (as observed for TMA36,69,72) but it could also be due to the inhibition of ZnO growth after a TIB pulse, as observed for DMAI.36 To establish which effect played a role, an experiment was carried out in which the film growth after every cycle (either DEZ or TIB cycle) was monitored by spectroscopic ellipsometry. The data presented in Table 3 show that approximately 2.7 at per nm² B and 5.8 at per nm² Zn were deposited in each individual respective cycle in a supercycle with m = 4. The number of Zn atoms deposited in this supercycle is therefore overall lower than expected for four cycles of the intrinsic ZnO process, which led to 7.1 at per nm² Zn deposited per individual cycle of intrinsic ZnO. Furthermore, the number of Zn atoms deposited per individual cycle of ZnO is higher than this value when employing a supercycle with m = 19. Similar observations can be noted for ZnO:Al when using DMAI or TMA as the doping precursor (see Table 3).

In order to investigate the dopant adsorption, the B doping fraction (DF) was studied at 150 °C as a function of the dopant ALD cycle fraction \( R_m = \frac{m}{m+1} \), where m was varied from 3 to 40. The DF was assessed using XPS, where the sensitivity factors for Al and B were calibrated by RBS/PIGE. We benchmarked the developed process with the ZnO:Al ALD processes using DMAI and TMA as alternative and conventional sources of Al, respectively. No C impurities were detected within the ZnO:X (X = Al, B) films by RBS and XPS above the detection limit of these methods. Only adventitious C was observed on the surface of the films by XPS. The incorporation of doping elements was the lowest in the case of the TIB and the greatest in the case of TMA for a given cycle ratio m (Fig. 3). This is in agreement with the data obtained by RBS/PIGE analysis, where the areal densities of B or Al per cycle were, on average, ~3.2 at per nm² per supercycle (TIB), ~4.4 at per nm² per supercycle (DMAI) and ~9.0 at per nm² per supercycle (TMA).
Table 3 Rutherford Backscattering Spectrometry (RBS) and Proton-Induced Gamma Ray Emission (PIGE) data of selected ZnO: X films deposited at 150 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Doping precursor</th>
<th>Cycle ratio</th>
<th>ZnO: X</th>
<th>Dopant ALD cycle fraction, $R_s$</th>
<th>Doping fraction by RBS/PIGE, DF</th>
<th>Dopant areal density (at per nm²) per dopant cycle</th>
<th>Zn areal density (at per nm²) per ZnO cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:B</td>
<td>TIB</td>
<td>19:1</td>
<td>0.05</td>
<td>0.024 ± 0.002</td>
<td>3.6 ± 0.1</td>
<td>7.7 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>ZnO:B</td>
<td>TIB</td>
<td>5:1</td>
<td>0.17</td>
<td>0.085 ± 0.009</td>
<td>2.7 ± 0.1</td>
<td>5.8 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>DMAI</td>
<td>18:1</td>
<td>0.05</td>
<td>0.033 ± 0.003</td>
<td>4.5 ± 0.2</td>
<td>7.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>DMAI</td>
<td>9:1</td>
<td>0.10</td>
<td>0.065 ± 0.007</td>
<td>4.3 ± 0.2</td>
<td>6.9 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>TMA</td>
<td>17:1</td>
<td>0.06</td>
<td>0.064 ± 0.007</td>
<td>8.0 ± 0.3</td>
<td>6.9 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>TMA</td>
<td>8:1</td>
<td>0.11</td>
<td>0.17 ± 0.02</td>
<td>10.0 ± 0.4</td>
<td>5.9 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>7.1 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

Note that the dopant areal density per supercycle is equal to the dopant areal density per dopant cycle, as there is one doping cycle per supercycle. The Zn areal density per supercycle is equal to $m$ times the Zn areal density per ZnO cycle.

4.2. Electrical properties

The electrical properties of the 45 ± 5 nm-thick ZnO:B films deposited on glass substrates at a temperature of 150 °C are presented in Fig. 4. The addition of a small amount of B sharply reduced the resistivity of the films to a minimum of ~3.5 mΩ cm for a DF of 0.016 (Fig. 4a). The films were benchmarked with ZnO:Al films of the same thickness and deposited at the same temperature using DMAI and TMA as Al precursors. The addition of Al also reduced the resistivity of the films to a minimum in both cases. Doping with DMAI resulted in ZnO:Al films with the same minimum resistivity than ZnO:B films at the same DF of 0.016, while doping with TMA resulted in ZnO:Al films with a higher minimum resistivity of 8 mΩ cm for a higher DF of 0.040. The resistivity of ZnO:Al films increased in both cases after achieving the minimum resistivity value, but this increase was more gradual than observed for the ZnO:B films.

The carrier concentration extracted from the modelling of the SE data assuming an effective mass of 0.4 (Fig. 4b) was consistent with the carrier concentration obtained by Hall measurements (not shown). The carrier concentration increased with the addition of B until a maximum of $3.1 \times 10^{20}$ cm$^{-3}$ for a DF of 0.034 was achieved, after which the carrier concentration decreased abruptly. This trend is consistent with previous reports in the literature for ZnO:B layers deposited by chemical spray pyrolysis. In the case of ZnO:Al films doped with DMAI, the carrier concentration reached a maximum value of $2.6 \times 10^{20}$ cm$^{-3}$ for a DF of 0.016, before gradually decreasing to a value of $2.2 \times 10^{20}$ cm$^{-3}$ for higher doping fractions. For ZnO:Al films doped with TMA, the carrier concentration reached a maximum value of $1.4 \times 10^{20}$ cm$^{-3}$, which did not vary significantly at higher DF values than 0.06. Based on literature reports, it is expected that the carrier concentration will decrease abruptly for higher Al doping concentrations than those studied in this work. The increase of the carrier concentration for low doping fractions in the three cases can be assigned to the effective doping of B and Al, respectively (i.e., substitution of Zn$^{2+}$ by B$^{3+}$ or Al$^{3+}$). The sharp decrease of the carrier concentration for TIB and the local saturation for DMAI and TMA might occur as a result of dopant occupying interstitial sites, dopant clustering, formation of oxides, or formation of metastable phases, making dopant inactive, which is possibly related to reaching the solubility limit of the B and Al into the ZnO lattice. For low doping fractions, the maximum mobility value for the ZnO:B films (i.e., $11.4$ cm$^2$ V$^{-1}$ s$^{-1}$) was 57% higher at low doping fractions relative to the maximum values determined for the ZnO:Al films. Based on the Masetti model for ionized impurity scattering, a mobility as high as $42$ cm$^2$ V$^{-1}$ s$^{-1}$ would be expected for the maximum carrier concentration of $3.1 \times 10^{20}$ cm$^{-3}$ in this work (ZnO:B film with DF = 0.034). Therefore, the overall lower values obtained for the
three doping materials and the trend of mobility decreasing with increasing doping fraction over the full range studied (Fig. 4c) can most likely be attributed to grain boundary scattering.\textsuperscript{128} Furthermore, it is rather striking that the carrier concentration decreases slightly, despite the slight increase in carrier concentration with temperature. From Fig. 5, it can be concluded that a further increase in film thickness has a relatively minor impact on $R_s$. All films had a thickness of 45 nm and were deposited on glass substrates at 150 °C.

4.3 Structural properties

The crystal structure of the ZnO:B films was characterized by XRD, and selected spectra are presented in Fig. 6. Similar patterns were observed for ZnO:Al doped using the DMAI precursor (see Fig. S3 of the ESI†). The intrinsic ZnO films were polycrystalline and exhibited an hexagonal wurzite structure with a weak (002) peak. The doping fraction increased with temperature that processing at 150 °C led to lower absolute values of conductivity (i.e. a higher resistivity), carrier concentration, mobility and doping efficiency. For this reason, the effect of deposition temperature on the electrical properties of the ZnO:B films and the doping efficiency was investigated. ZnO:B films with thicknesses of 45 ± 5 nm were deposited at different temperatures (150–240 °C) using a cycle ratio with $m = 24$, which led to an optimised resistivity in the ZnO:B doping series shown in Fig. 4. The resistivity of the ZnO:B films decreased from 3.5 mΩ cm at 150 °C to 2.2 mΩ cm when deposited at temperatures of 200–240 °C. This was due to an increase in carrier concentration from $2.2 \times 10^{20}$ cm$^{-3}$ to $2.8 \times 10^{20}$ cm$^{-3}$ and an increase in mobility from 8 to $10.5$ cm$^2$ V$^{-1}$ s$^{-1}$. We would like to underline that the doping fraction increased with increasing deposition temperature, whereas the doping efficiency decreased slightly, the slight increase in carrier concentration with temperature. From Fig. 5, it can be concluded that ~200 °C is the optimum deposition temperature for ZnO:B.

In this equation, $n$ and $n_0$ are the carrier densities of doped (X = Al, B) and intrinsic ZnO films respectively; and $N_{Zn}$ is the atomic density of Zn as measured by RBS (4.0 $\times 10^{22}$ cm$^{-3}$).\textsuperscript{36} As can be seen in Fig. 4d, the alternative precursors, TIB and DMAI, showed the highest doping efficiency at low doping levels, i.e., 30–40% for a range of DF of 0.016–0.018 that resulted in the lowest resistivities for the ZnO:B and ZnO:Al (doped with DMAI) films.\textsuperscript{129} Both alternative precursors out-performed TMA in terms of doping efficiency, as a maximum doping efficiency of 6% was achieved using this conventional precursor. This is in line with previously reported results for ZnO:Al films doped with DMAI and TMA deposited at 250 °C.\textsuperscript{36}

Compared to ZnO:Al films deposited at 250 °C, we found that processing at 150 °C led to lower absolute values of conductivity (i.e. a higher resistivity), carrier concentration, mobility and doping efficiency. For this reason, the effect of deposition temperature on the electrical properties of the ZnO:B films and the doping efficiency was investigated. ZnO:B films with thicknesses of 45 ± 5 nm were deposited at different temperatures (150–240 °C) using a cycle ratio with $m = 24$, which led to an optimised resistivity in the ZnO:B doping series shown in Fig. 4. The resistivity of the ZnO:B films decreased from 3.5 mΩ cm at 150 °C to 2.2 mΩ cm when deposited at temperatures of 200–240 °C. This was due to an increase in carrier concentration from $2.2 \times 10^{20}$ cm$^{-3}$ to $2.8 \times 10^{20}$ cm$^{-3}$ and an increase in mobility from 8 to $10.5$ cm$^2$ V$^{-1}$ s$^{-1}$. We would like to underline that the doping fraction increased with increasing deposition temperature, whereas the doping efficiency decreased slightly, the slight increase in carrier concentration with temperature. From Fig. 5, it can be concluded that ~200 °C is the optimum deposition temperature for ZnO:B.

In this equation, $n$ and $n_0$ are the carrier densities of doped (X = Al, B) and intrinsic ZnO films respectively; and $N_{Zn}$ is the atomic density of Zn as measured by RBS (4.0 $\times 10^{22}$ cm$^{-3}$).\textsuperscript{36} As can be seen in Fig. 4d, the alternative precursors, TIB and DMAI, showed the highest doping efficiency at low doping levels, i.e., 30–40% for a range of DF of 0.016–0.018 that resulted in the lowest resistivities for the ZnO:B and ZnO:Al (doped with DMAI) films.\textsuperscript{129} Both alternative precursors out-performed TMA in terms of doping efficiency, as a maximum doping efficiency of 6% was achieved using this conventional precursor. This is in line with previously reported results for ZnO:Al films doped with DMAI and TMA deposited at 250 °C.\textsuperscript{36}
texture (i.e., preferential growth orientation), consistent with what is reported in the literature.\textsuperscript{60,131} No peaks indicative of (crystalline) boron oxide phases were observed in the studied range of doping fractions. The intensity of the peaks decreased abruptly at a doping fraction of $DF = 0.053$ for ZnO:B films as expected for highly-doped ZnO films. Similar observations hold for the ZnO:Al films prepared with DMAI.

The XRD patterns of both the ZnO:B and ZnO:Al films revealed several interesting features. First of all, the intensity of the (002) peak decreased while that of the (100) peak increased for increasing doping fractions, indicating a change in texture of the ZnO:X films. This effect was more pronounced in the case of DMAI than in the case of TIB as shown in Fig. 7a. As a guide to the eye, the ratio $I_{002}/I_{100}$ for a powder pattern, i.e., the pattern characteristic for a film with randomly oriented crystals, has been included to illustrate the change in texture from (002) to (100). Secondly, a significant shift of the peaks to higher 2\(\theta\) values was observed for increasing B fractions, which was likely due to compressive stress in the ZnO unit cell caused by the substitution of Zn\textsuperscript{2+} (ionic radius of 0.60 Å, assuming a four-coordinate environment as expected for wurtzite structures)\textsuperscript{132} with smaller B\textsuperscript{3+} ions (four-coordinate ionic radius of 0.11 Å).\textsuperscript{132} This effect was significantly smaller in the case of ZnO:Al films doped by DMAI (Al\textsuperscript{3+}, four-coordinate ionic radius of 0.39 Å).\textsuperscript{132} Fig. 7b shows the shift of the (002) peak as a function of the doping fraction, as a consequence of the compression of the unit cell (i.e., a decrease of the $c$-lattice parameter) with increasing doping fractions. It should be noticed that the $c$-lattice parameter for the pure ZnO films (i.e., $DF = 0$) was slightly larger (5.219 Å) than the value reported for the wurtzite ZnO crystal lattice (5.207 Å).\textsuperscript{6} This slight difference could be attributed to a combination of measurement inaccuracies (i.e., scan step size or a small sample misalignment in the $z$-direction), and sample conditions (i.e., stress in the film, or relatively small crystals).

To further understand the nanostructure of the films, a TEM study was performed on two ZnO:B films with two different cycle ratios ($m = 30$ and 19) and a ZnO:Al (DMAI) film with $m = 18$ (Fig. 8). As visible in the bright field (BF) TEM images shown in Fig. 8a, both ZnO:B films were characterized by columnar grains stretching from the substrate to the surface, while the ZnO:Al film showed a somewhat interrupted grain growth, i.e., at several heights within the layer new crystals have
nucleated and grown. The latter can most likely be attributed to the local presence of amorphous AlOx preventing epitaxial growth of ZnO on the underlying ZnO crystals after a DMAI cycle. In both ZnO:B films, it was difficult to distinguish the B-doped layers from the rest of the film, due to limited difference in average atomic number compared to the undoped ZnO. Only close to the interface with the substrate, these layers are vaguely discernible, as indicated by the arrows on the high-angle annular dark field (HAADF) STEM images in Fig. 8b. In contrast, the Al-doped layers were more clearly visible in the lower part of the ZnO:Al film than the ZnO:B films. The fact that the doped layers were only visible close to the interface to the substrate can be attributed to the surface roughness of the films, which increases as a function of vertical position in the layer due to the pyramid-shaped top facets of the growing ZnO crystals.

4.4 Optical properties

The transmittance spectra of selected ZnO:B layers with different DF (0.000–0.063) are shown in Fig. 9. The transmittance values were over 90% in the major part of the visible and near-infrared (NIR) range. A decrease in transmittance was observed in the NIR region with increasing doping fraction until DF = 0.034. For higher DF values, the transmittance in the NIR increased again. This behaviour can be attributed to free-carrier absorption. Furthermore, a blue shift was observed in the ultraviolet absorption edge with increasing doping concentration from intrinsic ZnO to doped ZnO:B films with a DF of 0.063. This is due to the increase of the optical band gap. Both these aspects will be considered more in detail below.

The transmittance (T) of the ZnO:B films deposited on glass does not correct for interference effects in the films nor for the strong absorption peak of the glass substrates. Additionally, the transmittance is a film property and depends therefore on the film thickness. For these reasons, the ALD ZnO:B optical properties were assessed by studying the absorption coefficient.

![Fig. 7](image_url) Intensity ratio I_{002}/I_{100} of the (002) and (100) peaks measured by XRD on the ZnO:X (X = Al, B) films reflecting the change in texture from (002) to (001) and (b) c-lattice parameter of the ZnO wurtzite unit cell and the corresponding 2θ position of the (002) peak as a function of the doping fraction in the ZnO:X (X = Al, B). The films were deposited at 150 °C on glass substrates. The c-lattice parameter of the wurtzite ZnO crystal is 5.207 Å.

![Fig. 8](image_url) Transmission electron microscopy images: (a) bright-field (BF) TEM of two ZnO:B films (m = 30 and m = 19) and a ZnO:Al film (m = 18); and (b) high-angle annular dark field (HAADF) STEM images of ZnO:B (m = 30) and ZnO:Al (m = 18). The B- and Al-doped layers are indicated by arrows.

![Fig. 9](image_url) Transmittance of selected ZnO:B samples (DF = 0.000–0.063) deposited at 150 °C and with thicknesses of 45 ± 5 nm.
Absorption coefficient (\(a\)) which was calculated from the SE data. Fig. 10 shows \(a\) as a function of the DF for ZnO:B films on a wide DF region (DF = 0.000–0.094). Clearly in the NIR region, the absorption decreases with increasing DF up to 0.034 whereas it increases again for higher DF values. This can be attributed to the free-carrier absorption in the films as described by the Drude model.\(^{133}\)

The correlation of \(n\) with the free carrier density (\(n\)) is shown in the legend of the figure. The absorption coefficient of ZnO:Al films doped with DMAI follows a similar trend with \(n\) (see Fig. S4 for the absorption coefficient data of ZnO:Al using DMAI and TMA, ESI†).

The optical band gap (\(E_{g,\text{opt}}\)) of the ZnO:X films was extracted from so-called Tauc plots\(^{35,124}\) (i.e., \((\varepsilon_2 E^2)^2\) as a function of the photon energy \(E\), where \(\varepsilon_2\) is the imaginary part of the dielectric function extracted from the SE data) as shown in Fig. S5 (ESI†). The optical band gap energies, calculated by linear fits to the data in the Tauc plots, are presented in Fig. 11 as a function of the DF. For ZnO:B, as well as for ZnO:Al, the optical band gap increases with increasing doping fraction. This increase can be attributed to the Burstein–Moss shift, but only for the range of DF values for which the carrier concentration \(n\) increases.\(^{60,68}\) For higher DF values (DF > 0.034), in the case of ZnO:B and ZnO:Al (DMAI), the increase in the optical bandgap can be attributed to effects related to the grain size,\(^{134}\) strain and other types of imperfections.\(^{135}\) Additionally, the fact that films start to have a considerable fraction of amorphous oxide with a higher bandgap than intrinsic ZnO plays probably a role. This holds especially for the case of Al-doping for which the formation of amorphous AlO\(_x\) regions has become clear.\(^{15}\)

5 Conclusions

Doped zinc oxide is a key transparent conducting oxide (TCO) material for many thin-film-based applications in optoelectronics. Atomic layer deposition (ALD) is a very promising technique to deposit high quality TCOs as doping materials can be introduced with greater control than with other deposition methods. Aluminium is by far the most common element to dope zinc oxide and especially trimethyl aluminium (TMA) is used as a precursor during ALD. The application of other dopants has been far less reported. For instance, B as a dopant has been scarcely reported for ALD probably due to the highly toxic nature of the traditional boron precursor diborane. We report here the feasibility of using a new, relatively safe boron precursor, triisopropyl borate (TIB), for the atomic layer deposition of ZnO:B. To benchmark the properties of the ZnO:B films, we also deposited ZnO:Al films using dimethylaluminium isopropoxide (DMAI) and TMA as alternative and conventional Al sources, respectively.

Process wise, the use of the TIB precursor led to the better control over the doping (i.e., less dopant atoms per doping cycle are deposited) and to very high doping efficiencies, as compared to doping using TMA. The DMAI precursor resulted in similar high doping efficiencies (\(\eta \sim 30–40\%) to TIB. The conductivities and carrier concentrations of the films deposited using TIB and DMAI were significantly higher at lower doping fractions than that of ZnO:Al films where TMA was the aluminium source. The mobilities of ZnO:B films were significantly higher than those of the ZnO:Al films where TMA and TMA at low doping fractions. Additionally, the transparency of the ZnO:B films was very high in most of the visible and near-infrared range. The excellent electrical and optical properties of selected ALD ZnO:B films deposited using TIB can be exploited to prepare, for instance, transparent conductive oxide films for silicon heterojunction solar cells for which the required thickness is \(\sim 80\) nm due to the fact that the film acts also as antireflection coating. The results showed that resistivities as low as 1.5 and 0.9 m\(\Omega\) cm (i.e., sheet resistances \(R_s = 204\) and...
128 Ω sq\(^{-1}\)) can be achieved for ~80 nm-thick ZnO:B films deposited at temperatures of 150 °C and 200 °C, respectively. In both cases, transmittances higher than 80% for wavelengths >370 nm, but over 90% for wavelengths in the range 700–1750 nm can be achieved.

In light of these results, it is demonstrated that the use of novel alternative precursors for ALD can open new ways of doping ZnO more efficiently resulting in excellent electrical and optical film properties even at low temperatures.

Acknowledgements

The authors thank J. W. Weber, Dr H. C. M. Knops and B. W. H. van de Loo (TU/e) for their invaluable input into the analysis of the SE data. We would also like to thank W. Keuning, B. Macco, and H. Gatz (TU/e) for their help with the XRD, AFM, and transmission measurements, respectively. This work was financially supported by the European Community’s 7th Framework Programme through the Marie Curie Intra-European Fellowship of D.G.-A. ([ALD4PV], FP7-MC-IEF-272444) and by the Dutch Technology Foundation STW through the Flash VI CI programme). Air Liquide is acknowledged for the donation of the DMAI and TIB precursors. Solliance, a solar energy R&D initiative of ECN, TNO, Holst, TU/e, imec and Forschungszentrum Jülich, and the Dutch province of Noord-Brabant are acknowledged for funding the TEM facility.

Notes and references

This journal is licensed under a Creative Commons Attribution 3.0 Unported Licence.