Enabling high-quality transparent conductive oxide on 3D printed ZrO₂ architectures through atomic layer deposition

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The conformal atomic layer deposition of a transparent conductive oxide composed of Al-doped ZnO (AZO) over three-dimensional (3D) shaped ZrO₂ microarchitectures produced using two-photon lithography (TPL) is reported here for the first time. The effect of ZrO₂ morphology, surface roughness, and crystallographic phase (tetragonal and monoclinic) on the quality and properties of the deposited ZnO and AZO thin films is investigated. No discontinuities, domains, or areas differing from the desired chemical composition have been found in films grown over the 3D structures. Three different Al dopant concentrations (4.0 %, 4–5 %, and 5.0 % Al doping cycles) are examined and compared to undoped ZnO. AZO and ZnO optical and electrical properties are studied using cathodoluminescence (CL) and Hall effect measurements. The CL study confirms that the observed emissions from the ZnO and AZO films are associated with the near band emission of ZnO and defects, i.e., zinc and oxygen vacancies and interstitial oxygen. The AZO films exhibit n-type semiconductor behavior, and a minimum resistivity of 1.2 × 10⁻³ Ω cm is achieved. From a broad perspective, AZO deposition on 3D microarchitectures opens a new route towards dimensionally refined optoelectronic devices in which the ZrO₂/AZO can serve as an enabling role for the production of electrodes.

1. Introduction

The combination of optical transparency while maintaining electrical conductivity is vital for fabricating advanced electrodes, functioning as building blocks across optoelectronic devices, such as displays,[1] photovoltaic cells,[2] thin-film transistors,[3] or light-emitting diodes.[4] Transparent conductive oxides (TCOs) are the most investigated and applied among the various materials offering these characteristics. Fundamentally, TCOs must be highly transparent within the visible range (a band gap > 3 eV) and exhibit low electrical resistivity (ρ < 10⁻⁴ Ω cm).[5,6] The most prevalent examples of TCOs include n-type derivatives of In₂O₃, SnO₂, and ZnO.[7]

Al-doped ZnO (AZO) is an attractive alternative that does not compromise optical and electrical properties, which are essential in electronics used in information systems. The precise control of Al doping in AZO is crucial to tailor its electronic and optical properties. For instance, Deng et al. studied the influence of the Al content (0–8.06 at%) within ZnO wurtzite films.[8] The authors demonstrated that with increased dopant concentration, the optical bandgap abruptly increases (3.26 eV for ZnO and 3.50 eV for AZO with 1.80 at.% Al) and gradually

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shifts towards higher values, up to 3.66 eV for 4.50 at.% Al.[8] The optical bandgap increase is associated with the Burstein-Moss effect, i.e., the absorption edge is blue-shifted due to the increased population of states close to the conduction band. [8,9] Alongside the optical bandgap shift, the average transmittance (in the 400 – 1500 nm range) is also higher for the AZO (1.80–5.24 at.% Al) than for pristine ZnO. [8] Such transparency and reduced resistivity have allowed AZO to be used in solar cells as conductive electrodes. In another work, Kan et al. reported that indium tin oxide (ITO) replacement by AZO in a polymer solar cell is possible. [10] The results reveal similar power conversion efficiencies, if not better, than ITO. [10] The power conversion efficiencies are attributed to reduced resistivity and increased transparency compared to undoped ZnO. Low resistivity is associated with the Al substitution effect in ZnO, resulting in oxygen vacancies (V_O) or interstitial Zn (Zn_i). [8]

In most cases, AZO is utilized in a film form to minimize the light absorption of conductive layers by reducing the optical path length. Various thin film fabrication approaches have been developed for AZO, i.e., sputtering, [11] electrodeposition, [12] chemical vapor deposition, [13] and atomic layer deposition (ALD). [14] ALD offers several advantages, including exceptional conformity, uniformity, and precise thickness control (Å - μm range). [15,16] The films are usually free of inhomogeneities and discontinuities. [15] Furthermore, the precise control of the chemical composition is advantageous, especially the possibility of introducing dopants in a well-controlled fashion. [15]

Recently, a novel ALD technique called atomic partial layer deposition (APLD) was formulated for the conformal growth of complex oxides, such as HfO_2-TiO_2. [17,18] Later, Ramírez-Esquível et al. used the APLD method for growing AZO films with Al doping cycle contribution up to 4 at%.[19] APLD relies on the variation of the metal precursor flow rates and the exposure time to deposit two or more species on the same surface (depicted in Fig. 1), which is not feasible with conventional ALD. [17]

Shortcomings have been addressed, such as the formation of undesired aluminum oxide or metallic aluminum domains at higher doping percentages (Al concentration > 4 at.%), [19–22] Despite the possibility of the APLD for the fabrication of well-controlled coats on a single atomic layer scale, the studies on AZO grown using ALD/APLD are oriented towards the film deposition over planar surfaces, i.e., glass substrates, [19] probably because of industrial demands on planarized systems. However, there are examples of AZO deposition over complex structures, i.e., nanopillars, [23] nanowires, [24] or nanostructured glass. [25] Even ALD deposition over genuinely 3D microarchitectures has been the subject of only a limited number of studies, including Al_2O_3, [26,27] SiO_2, [28] and TiN, [29] with none exhibiting characteristics similar to AZO.

The common feature among the mentioned 3D microarchitectures and the referred works is the usage of two-photon lithography (TPL) to fabricate the 3D polymeric scaffolds as templates for the deposition of the inorganic materials. [26–29] However, such acrylate-based polymers are usually not directly applicable in optoelectronic technologies unless unreacted functional groups (e.g., vinyl) on the surface of 3D-printed polymeric features are employed to promote targeted functionalization. [30] From a surface chemistry perspective, using ceramic 3D microarchitectures as templates is an attractive option to maximize the geometrical surface area of a TCO, which functionality can be applied over relatively high temperatures without the risk of decomposition. For example, ZrO_2 (zirconia) owns outstanding mechanical feasibility, nontoxicity, chemical stableness, and high affinity to oxygen-including groups. [31] A key property to account for ZrO_2/AZO architectures is understanding the effect of the underlying substrate crystallinity and shape that might affect the optoelectronic characteristics of deposited AZO thin films. [32] A way to generate such understanding is using the APLD method optimized for AZO deposition over glass and silicon. Important to mention is that no studies have been conducted on complex 3D ceramic structures varying the Al doping levels (>4%). [19] In this regard, merging APLD and TPL holds the potential to pave the path toward a new generation of 3D devices in which the AZO (nano)layer can serve as an enabling role, such as a transparent electrode for light emission.

In this work, a fundamental investigation to expand the applicability of AZO as an optoelectronic component is driven by two strategies: (i) nucleation study of AZO over the non-studied 3D solid-beam micro-structured ZrO_2 and (ii) tuning the AZO electrical and optical properties by varying the Al dopant concentrations to demonstrate that AZO can be conformally deposited over complex ZrO_2 architectures. The results can grant the possibility of exploring the fabrication of 3D optical microstructured materials to direct light-matter interaction in optoelectronics.

2. Results and discussion

2.1. APLD of AZO

Ceramic 3D micro-optics is an emerging field where additive manufacturing methods can contribute. [33] However, 3D micro-optics might require electrical conductive interfaces to demonstrate functionality. Therefore, in this section, the deposition of AZO nanolayer is studied over complex high refractive index 3D ZrO_2 microstructures fabricated via TPL. The 3D ZrO_2 microarchitectures are manufactured on diced pieces of Si, following the methodology of Winiczewski et al. [34] Three different ZrO_2 architectures (octet-truss lattice, gyroid, and C60 buckyball-inspired structure, denoted as a buckyball) are selected as a platform for testing the geometrical and conformality limits of APLD.

APLD relies on mixing two metalorganic precursors in a specific number of cycles to facilitate doping. In this research, diethylzinc (DEZ)
is used as a precursor forming the ZnO matrix of the thin film, while trimethylaluminum (TMA) is the Al-rich dopant. The schematic representation of the APLD process is presented in Fig. 1. The typical cycles (tc) and doping cycles (dc) are utilized. In the dc, DEZ is introduced in a sufficiently short pulse to produce an unsaturated surface with few remaining reactive –OH groups on the surface (Fig. 1 (a-b)). A non-saturated layer of monoethyl zinc is adsorbed and controlled with the exposure time, in which ethane is released as a side-product. It has previously been reported that DEZ exposures of 0.1—0.24 s do not result in total surface saturation, as the growth per cycle (GPC) variation is below 0.05 Å/cycle. A DEZ pulse is followed by a short TMA pulse, which is the base for the APLD method (Fig. 1 (b-c)). As a result, dimethyl aluminum and monomethyl aluminum sites are introduced on the remaining sites on the same atomic layer, and methane is released as a by-product. In the case of AZO deposition, a 0.24 s dosing exposure leads to a nearly saturated surface that ensures efficient doping using the TMA precursor. Consequently, TMA is dosed to react with the remaining groups or adsorption sites to incorporate a small quantity of aluminum-rich reagent (Fig. 1 (b-c)). For obtaining AZO 4%, AZO 4–5 %, and AZO 5 %, the pulse duration and number of TMA pulses during the second subcycle are modified, as indicated in Table S1. Finally, an oxidation pulse to hydroxylate and thus reactivate the surface is conducted (Fig. 1 (c-d)). At this point, a single dc is completed, and zinc and aluminum species co-exist on the same layers separated by complete oxygen layers (Fig. 1 (d)). As by-products of reactions, ethane, and methane are released.

In the case of tc, DEZ saturating pulse is followed by the purge, H$_2$O oxidation pulse, and a purge, which results in the formation of a ZnO layer. Coverage of the entire surface is achieved by repeating tc and dc at the accurate precursor dosage and exposure times to saturate the surface. A detailed description of the methodology can be found in the experimental section. Furthermore, it is important to mention that the APLD method was previously optimized for AZO deposition (≤4% dc) over planar substrates, i.e., glass and silicon. However, no studies have been conducted for higher Al doping levels (>4% dc contribution) and using non-conventional, complex 3D ceramic microstructures. In this study, three different recipes are used to obtain films with higher aluminum concentrations (>4% dc contribution), accomplished by varying the TMA pulses as indicated in the scheme (Figure S2 and Table S1). The AZO deposition methodology is also applied over 3D ZrO$_2$ microstructures. The structures have been annealed at 600 and 1200 °C to obtain zirconia in two crystallographic phases, i.e., tetragonal (t-ZrO$_2$) and monoclinic (m-ZrO$_2$).

### 2.2. Microstructural and elemental characterisation

For ceramic 3D micro-optics, the film morphology, surface roughness, and conformality are important, as such characteristics can affect either optical or electrical outcomes. The study starts with the AZO coating of ZrO$_2$ microstructures. For reference, top-view images of the 3D t- and m-ZrO$_2$ gyroid microstructures before and after the AZO 5% deposition are presented in Fig. 2. The high-magnification micrographs (Fig. 2a’ and c’) reveal the granular, irregular surface of the pristine ZrO$_2$ structure. In the vertical direction, the individual, stepped layers stacked over each other can be differentiated, typical for the additively-manufactured structures (Fig. 2a” and d”). Fig. 2b and d show corresponding images of the same microstructures after the AZO 5% deposition. The visual qualitative analysis of the images confirms high surface coverage and conformal deposition of the thin films. The high magnifications of the labeled regions (Fig. 2b’, b”, d’ and d”) show that the films grow following the original topography, where the lateral

**Fig. 2.** SEM images of (a) t-ZrO$_2$ gyroid before and (b) after AZO 5% deposition, (c) m-ZrO$_2$ gyroid before and (d) after AZO 5% deposition. Sections (a’ – d’) present the magnified areas labeled within the (a – d) images, and sections (a” – d”) present the magnified regions labeled in the (a’ – d’) images.
dimensions of the 3D microarchitectures are increased (Figure S3). As a result of film growth, distances between microarchitecture beams are reduced (Figure S3). The analysis implies that chemisorption reactions and nucleation processes proceed on surfaces of 3D-printed ZrO₂ microstructures.[38] The charging of the microstructures by the electron beam of the SEM instrument is visibly reduced upon the deposition of AZO 5%, indirectly proving the electrical conductivity of the film. The AZO 5% crystals are observed to grow as needle-like grains, which agrees with previous reports.[19] SEM image of AZO 5% crystals deposited over silicon substrate is shown. The silicon substrate has been chosen for SEM contrast purposes. Similar growth behavior is expected over t-ZrO₂ and m-ZrO₂ microstructures but with a lower crystallization which is challenging to resolve with SEM (Fig. 2). Regardless of the t-ZrO₂ and m-ZrO₂ microstructure geometry (octet-truss lattices, gyroid, or buckyballs) with AZO 4%, AZO 4–5%, and AZO 5%, lower crystallization is observed. Octet-truss lattices coated with ZnO, AZO 4%, AZO 4–5%, and AZO 5% are shown in Figures S4-S7. Gyroid coated with ZnO, AZO 4%, AZO 4–5% and AZO 5% are shown in Figures S8-S11. Buckycrystal coated with ZnO, AZO 4%, AZO 4–5% and AZO 5% are shown in Figures S12-S15.

A planar surface of the Si/SiO₂ substrate is presented next to the area where 3D ZrO₂ microstructures are located (Figures S16 and S17). The surface is covered with an oxide layer grown during the thermal annealing of the pre-ceramic structures.[34,39] It should be noted that needle-like crystals have been challenging to resolve due to SEM contrast. The SEM images collected for the AZO 4%, AZO 4–5% needle-like crystals have been challenging to resolve due to SEM annealing of the pre-ceramic structures. [34,39] It should be noted that the Si substrate is revealed under the base octet-truss lattice (Fig. 4). The elemental distribution matches the expected allocation of elements for the AZO grown over ZrO₂. No specific hot spots, e.g., Al or Zn domains, undesired aluminum oxide islands, or areas differing from the desired film morphology grown over a 3D structure, are found within the spatial resolution of the map. It is concluded that the analyzed AZO film is continuous and conformal, also within the central areas of the specimen, which may be difficult to reach for other methods of surface deposition or materials composed of porous nanoparticles.[15,16] An important parameter not yet mentioned is the chemical content of the multiple specimens encountered over the microstructures after AZO deposition. Therefore, the EDX spectrum is collected from the outer beam of a buckyball-inspired architecture coated with AZO 4% to assess the chemical composition of the thin films. EDX spectrum (Figure S19) reveals the chemical composition 62 at.% O, 13 at.% Zn, 1 at.% Al, 10 at. % Zr, and 14 at.% Si. After excluding Zr and Si, both oxidized and Si substrates are observed with a lower significance of the substrate role.

The ZnO films grown with different Al doping cycle contributions (AZO 4%, AZO 4–5%, and AZO 5%) and pure ZnO deposited on the t-ZrO₂ octet-truss lattices are visually inspected at three magnifications (Fig. 3) to evaluate any potential variation of the printed structure. The statistical analysis is described in Section S5. The respective SEM images are shown in Figure S18. The results are given in Table 1. The aspect ratio (AR, i.e., l to w) of crystallites for all the AZO films is comparable but more consistent over the Si/SiO₂ substrate for t-ZrO₂. More consistent crystallite sizes are observed over the substrate on which t-ZrO₂ microstructures are located, which could be related to lower t-ZrO₂ surface roughness than the m-ZrO₂. The observation is likely related to the higher annealing temperature of the latter one (1200 °C versus 600 °C). For ZnO, more round crystallites are observed with a lower magnitude of the substrate role.

The ZnO films grown with different Al doping cycle contributions (AZO 4%, AZO 4–5%, and AZO 5%) and pure ZnO deposited on the t-ZrO₂ octet-truss lattices are visually inspected at three magnifications (Fig. 3) to evaluate any potential variation of the printed structure configuration during AZO deposition. The different microstructure types are shown in Figures S4-S15. For the Al-doped ZnO in Fig. 3, high aspect ratio needle-like grains are noticed at the highest magnifications. In contrast, the ZnO film appears to form more uniformly, possibly hexagonal habit grains, with no additional level of morphology observable. To compare the size of crystallites grown over the planar Si/SiO₂ substrates and 3D ZrO₂ structures, the width, length, and aspect ratio are determined for images presenting the flat round t-ZrO₂ base for all AZO film compositions. The length, width, and aspect ratio for AZO 4% are 96 ± 12 nm, 22 ± 3 nm, and 4 ± 1 nm, respectively. For AZO 4–5%, 93 ± 10 nm, 21 ± 3 nm, and 5 ± 1 values are determined. The parameters are 91 ± 12 nm, 20 ± 2 nm, and 5 ± 1 in the case of AZO 5%. The ZnO films are not distinguishable from the t-ZrO₂ crystallites. For m-ZrO₂, only AZO 5% crystallite dimensions can be accurately measured with 81 ± 8 nm length, 20 ± 3 nm width, and 4 ± 1 ratio.

Although AZO has been successfully deposited over complex 3D microarchitectures, an important point should be confirmed, which is conformity. For such an assessment, we use a representative microstructure. In this case, the m-ZrO₂ octet-truss lattice with AZO 4–5% on the surface of the 3D ZrO₂ microstructure is milled by a focused ion beam (FIB) to reveal the structure’s core. SEM-EDX maps showing the elemental distribution (Zr, Zn, O, Al, C, Si) are collected (Fig. 4). A thin Zn, Al, and O film is observed over solid beams containing Zr and O (Fig. 4(b)). The contrast in the image corresponding to Al (Fig. 4(e)) is adjusted to increase the initially low readability due to the low Al content. C signals are assigned to both the printed microstructure and the grown thin film (Fig. 4(f)), which origin can be the incomplete decomposition of precursors used for the 3D printing and ALD or the contamination from the chamber and FIB processing. Carbon is often an impurity in ceramic structures printed using TPL and tailor-made resins. The Si substrate is revealed under the base octet-truss lattice (Fig. 4(g)), which surface is oxidized due to the annealing step used in the additive manufacturing of the ZrO₂ architectures.[34] Finally, the Zr and Zn distribution maps with 75% opacity overlapped in post-processing (Fig. 4(h)). The elemental distribution matches the expected allocation of elements for the AZO grown over ZrO₂. No specific hot spots, e.g., Al or Zn domains, undesired aluminum oxide islands, or areas differing from the desired film morphology grown over a 3D structure, are found within the spatial resolution of the map. It is concluded that the analyzed AZO film is continuous and conformal, also within the central areas of the specimen, which may be difficult to reach for other methods of surface deposition or materials composed of porous nanoparticles.[15,16]

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Crystallite length (l), width (w), and aspect ratio (AR) of ZnO, AZO 4%, AZO 4–5%, and AZO 5% films deposited over Si/SiO₂ substrates, next to which 3D t-ZrO₂ and m-ZrO₂ microstructures are situated.</th>
<th>ZnO</th>
<th>AZO 4%</th>
<th>AZO 4–5%</th>
<th>AZO 5%</th>
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<tbody>
<tr>
<td>Si/SiO₂ next to t-ZrO₂</td>
<td>l (nm)</td>
<td>49 ± 7</td>
<td>70 ± 14</td>
<td>64 ± 10</td>
<td>65 ± 9</td>
</tr>
<tr>
<td></td>
<td>w (nm)</td>
<td>26 ± 6</td>
<td>16 ± 2</td>
<td>14 ± 2</td>
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<td></td>
<td>AR</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
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<tr>
<td>Si/SiO₂ next to m-ZrO₂</td>
<td>l (nm)</td>
<td>55 ± 6</td>
<td>62 ± 8</td>
<td>54 ± 6</td>
<td>75 ± 12</td>
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<tr>
<td></td>
<td>w (nm)</td>
<td>26 ± 4</td>
<td>16 ± 3</td>
<td>13 ± 3</td>
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Fig. 3. SEM images of t-ZrO$_2$ octet-truss lattices with deposited thin films of (a) ZnO, (b) AZO 4%, (c) AZO 4–5%, and (d) AZO 5%. In (a’–d’), close-up images of the areas labeled with boxes in images (a–d) are given. High magnifications of regions enclosed within the boxed-in images (a’–d’) are presented in (a’’–d’’).

Fig. 4. Elemental mapping of the octet-truss lattice cross-section prepared via FIB milling: (a) secondary electron image of the inspected area, and (b–h) EDX maps showing the distribution of (b) Zr, (c) Zn, (d) O, (e) Al, (f) C, (g) Si, and an overlaid image (h) of (b) and (c) at 75% opacity. The scale bar presented in (a) is shared across the (b–h) images.
lattice deformation from Al incorporation in the crystalline structure, can be observed among the recipes according to the dc % contribution. [20–22].

To estimate the GPC values for the films deposited over 3D ZrO₂ structures, the feature size increment is determined by analyzing the SEM images. An example of such measurement is given (Figure S3). The images are collected before and after deposition for each film composition. The number of cycles, GPC values are computed (Figure 5). The standard deviation for the thickness increase is the square root of the squared standard deviations of populations. Due to different measurement methods, this contributes to a higher error than for planar substrates. The planar surfaces of glass and silicon are typically chemically pre-cleaned to remove organic contamination and hydroxylate species from the outer layer. Even though the 3D ZrO₂ structures are not cleaned before the deposition and are used directly after storage, all architectures have reactive surfaces with similar GPC values to planar substrates. The GPC values are comparable between the t-ZrO₂ and m-ZrO₂ phases. In most cases, the GPC value is slightly higher for the m-ZrO₂ structures, which may be correlated with higher porosity and granularity of t-ZrO₂, and in turn, higher active surface area.

Concerning film conformality, the buckyball can be considered an open architecture. In contrast, the octet-truss lattice consists of an intricate network of beams that may interact differently with the precursor vapor during the deposition. It can be observed that despite the architecture, all of the microstructures show a similar trend in GPC values when the Al content is varied. The holes or cavities within the presented architectures (∼1 μm 2.5 μm long) and their polycrystalline porous nature do not impede the precursor flow or cause uneven nucleation. [38,41] The qualitative analysis demonstrates a conformal deposition at the top-view surface growth. Neither the irregular surface of the structures nor the external network of beams seemed to divert AZO nucleation in a different ratio. The reaction seems mainly influenced by the high DEZ, TMA, and H₂O reactivity.

2.4. Chemical state characterization

To provide insights into the chemical environment, potential defects, and impurities of the deposited films, X-ray photoelectron spectroscopy (XPS) analysis is conducted. Since the spot sizes of most of the conventional XPS instruments are relatively larger than the 3D structures presented in this study, planar areas of the samples are analyzed instead. [42] The core spectra of the Al 2p, Zn 2p, and O 1s core levels are recorded for ZnO, AZO 4%, AZO 4–5%, and AZO 5% samples deposited over Si substrates (Fig. 6). Within the Al 2p range, a narrow single doublet with 0.55 eV spin–orbit splitting is observed for all AZO samples (Fig. 6 (a)). For simplicity, the 2p½/2 and 2p½ levels are not individually plotted. The peak area increases with the Al content and is 1.23, 1.36, and 1.52 square units for AZO 4%, AZO 4–5%, and AZO 5%, respectively. This trend is expected according to the increasing Al saturation in the monolayer within the recipes. In the Zn 2p½/2 range, two main contributions are found for all the analyzed samples (Fig. 6 (c)). The lower binding energy (BE) peak (ZnI) corresponds with the Zn lattice within the ZnO wurtzite phase (Fig. 6 (c)). [43] The peak at the higher BE (ZnII) has been related to zinc point defects such as Zn₂ or zinc hydroxide (Fig. 6 (c)). [44,45] Two contributions are found in the O 1s spectra (Fig. 6). The more intense peak (O₂) is associated with the ZnO wurtzite crystalline structure lattice oxygen (Fig. 6 (b)). [44,45] The second peak (O₃) may be related to low-coordinated ZnO₄[46] which forms hydroxylated species upon exposure to the ambient. V₅ might also be present but cannot be resolved due to their high reactivity to moisture. [47] Nevertheless, the presence of V₅ is confirmed optically in the next section.

The Al 2p½ signal is observed at BE around 74.1 eV in AZO 4%, AZO 4–5%, and AZO 5% (Fig. 6 (a)). In all cases, and since only one contribution is found, the peak locations can signify that Al constitutes a substitutional dopant in the wurtzite, likely as Al⁺⁺ point defects. [43,48] Al 2p position shifts for varying concentrations are generally insignificant because no local chemical changes are introduced for the Al species. The Zn 2p½/2 photoemission line highly depends on the local chemical environment, i.e., local structure changes, morphology variation, and oxygen-deficient lattices. [49,50] A significant difference in ZnI and ZnII peak positions is observed for all AZO compositions compared to ZnO (Fig. 6 (c)). The BE of AZO 4–5% is also lower than the AZO 4% and 5%. The decrease in BE upon doping ZnO with Al may indicate the inclusion of Al⁺⁺ defects in the crystalline structure as the dopant increases the free electron density. [19] Similarly, the O₁ and O₃ peak positions are consistently shifted to lower BE for all the Al-doped films. In addition to the free electron density augmentation, the oxygen components are susceptible to Al dopant, which suggests the observations are related to the different local structures in AZO films.

2.5. Optical properties

The role of defects present in AZO is an important factor. Defects can modify the optical properties of the aimed optical ceramic material. Previously, we characterized the optical properties of t-ZrO₂ and m-ZrO₂ microstructures using cathodoluminescence (CL) [34] and similar

![Fig. 5. Growth per cycle (GPC) analysis for deposition of ZnO, AZO 4%, AZO 4–5%, and AZO 5% over (a) t-ZrO₂ and (b) m-ZrO₂ buckyballs, gyroids, and octet-truss lattices.](image-url)
results have been found in Figure S20. In this study, we further inves-
tigate the influence of the composition of the AZO thin films deposited
over the Si substrates and 3D m-ZrO₂ microstructures using the same
technique. The selection of 3D m-ZrO₂ microstructures with deposited
thin films is made since, after the deconvolution of CL spectra, consid-
erably fewer components are found for this phase when compared with
t-ZrO₂. [34] This way, fewer defect-related ZnO, AZO, and m-ZrO₂
emissions might overlap. The CL spectra are recorded for spots on the
over the Si substrates and 3D microstructures over which films are grown are also sources of the
interpretation. The surface of the Si substrate is covered with a
native oxide grown during the thermal annealing in the air, reaching
several hundred nm, thus exceeding the thickness of the thin films
grown over it in this study. [34,39] According to the literature, for ZnO nanorods, the penetration depth depends on incident electron accelerating voltage (e.g., 0.4 µm for 10 kV and 1.14 µm for 20 kV). [51]

Therefore, for the 15 kV beam used in this study, the substrate or 3D m-ZrO₂ microstructures with deposited which films are grown are also sources of the
analytical signals detected.

The CL spectrum collected for the undoped ZnO film deposited over substrate features several contributions (Fig. 7 (a)), with the most intense signals centered around 3.60 eV (344 nm), 3.23 eV (383 nm), 2.96 eV (419 nm), 2.62 eV (473 nm), a weaker red band at 1.95 eV (636 nm) and a peak at 1.62 eV (765 nm). The dominant component at around 3.23 eV (≈ 383 nm) is assigned to the ZnO near band emission (NBE), stemming from the free exciton recombination occurring after exciton collisions. [52,53] Previously, peaks at 3.27 eV and 3.65 eV have been distinguished for thick and thin ZnO rods. [54] The latter signals are due to the increased free-bound exciton emission combined with the confinement effect in the thin structure. [54] In SEM images of the films at high magnifications, needle-like features could be resolved (Figure S16 – S17), which may imply the existence of two NBE components. Due to oxygen and zinc vacancies (Vₒ), blue (2.96 – 2.62 eV shoulder) excitonic emission can be observed. [55,56] This signal is assigned to the electron transitions from the Vₒ to the valence band and from the conduction band to the Vₐₒ. [55] The near-infrared (near-IR) peak at 1.62 eV indicates the presence of structural imperfections, Vₐₒ, and interstitial oxygen (Oᵢ). [57,58] The peak at 1.65 eV was previously attributed to Vₒ below the conduction band in ZnO nanotubes. [59] The origin of the peak at approximately 1.9 eV is debatable and may relate to the Vₐₒ point defects or a non-bridging oxygen hole center in the underly-
der SiO₂ formed during the annealing of the Si substrate. [34,57] Since the luminescence spectra are typically not presented in the UV but mostly visible range, the accurate attribution and referencing of the 3.94 eV (315 nm) peak are nontrivial. The signal might be related to Fermi-level electrons recombining with valence band holes. [61] A shoulder ranging to higher energy (≈ 290 nm) was also observed for ZnO nanorods. [62]

For AZO 4% (Fig. 7 (b)), the main peak maximum is shifted to 3.35 eV (367 nm). The optical bandgap depends on the electron-hole mobility within the semiconductor and is reported to widen from 3.28 eV for undoped ZnO to 3.35 eV for AZO 4%, consistent with our observations. [63] No new distinct signals are found. In the case of the AZO 4–5% on Si/SiO₂ (Fig. 7 (c)), the local maxima are found at 3.94 eV (315 nm), 3.6 eV (344 nm), 3.35 eV (372 nm), 2.96 eV (419 nm), 2.62 eV (473 nm), 1.95 eV (636 nm), and 1.65 eV (752 nm). For AZO 5% on Si/SiO₂ (Fig. 7 (d)), the maxima are found around 3.65 eV (340 nm), 3.35 eV (372 nm), 2.96 eV (419 nm), 2.62 eV (473 nm), 1.82 eV (681 nm) and 1.65 eV (742 nm). An additional contribution at 2.20 eV (564 nm) can be distinguished, likely stemming from the donor–acceptor shallow-level transitions from Vₒ to Vₐₒ. [55] The shoulder at around 3.65 eV (≈ 340 nm) is more intense in all AZO samples when compared with ZnO, correlating with the higher crystallite aspect in Table 1. [54] For AZO 5%, the broadening towards higher energy is observed with a weak peak at 4.22 eV (294 nm). Such broadening of the emission into the UV range was also previously observed with increased Mg concentration in doped ZnO films grown by ALD. [64]
Within the indigo-blue-green region (2.9 – 2.3 eV), contributions from underlying 3D m-ZrO$_2$ structures, ZnO and AZO, can be superpositioned. The typical CL spectrum collected for the additively manufactured m-ZrO$_2$ microstructures is deconvoluted into the components around 2.3, 2.6, and 2.9 eV. The dominant peak at 2.6 eV can be assigned to V$_{O}$ or the electronic transitions between the F$^{*+}$ and F$^{+}$ levels. The 2.3 and 2.9 eV contributions are associated with interstitial carbon (C$_{i}$), likely in ceramics obtained from the metal-organic precursor and carbon-rich polymer. Consequently, due to the overlap of the main ZnO and m-ZrO$_2$ contributions, in the case of thin films grown over the 3D ZrO$_2$ structures, the main focus is dedicated to the most intense ZnO signals correlated with the NBE. For ZnO deposited over m-ZrO$_2$ buckyball, the CL spectrum is deconvoluted into the components at 2.28, 2.56, 2.9, and 3.18 eV (Fig. 8 (a)). The latter, the most intense signal, can be assigned to ZnO NBE. A weak near-IR signal around 1.62 eV is found, previously attributed to structural imperfections, V$_{Zn}$, and O$_{i}$.

Besides the broader band deconvoluted to peaks at 2.3 eV, 2.6 eV, and 2.9 eV, for AZO 4%, AZO 4–5%, and AZO 5% grown over 3D m-ZrO$_2$ structures, the NBE peak is found at 3.34, 3.30, and 3.34 eV (Fig. 8 (a-d)). With the increase of Al content in AZO, a minor widening of the band gap can be expected. The intensity of the NBE peak is significantly lower than for the ZnO deposited over m-ZrO$_2$ and the ZnO and AZO films grown over the substrate. These differences indicate that the radiative emission recombination paths may be modified. As in the CL, the carriers are excited with high-energy electron beams, and the abundant electrons could be trapped in unfilled defect levels related to V$_{O}$. In turn, the electrons are unavailable for transitions associated with other CL bands.

In addition, complimentary transmittance spectra of the thin films deposited on glass slides are recorded in the ultraviolet–visible-near-infrared range (UV–Vis-NIR) (Figure S21(a)). Since only minor differences have been observed between ZnO and AZO (with 1 – 4% dc contributions), in this study, AZO 4% and AZO 5% are representative samples. There is no significant difference in the UV range concerning the absorption edge between the samples. The increased Al doping results in slightly higher transmittance over the visible range, correlated with the higher charge carrier concentration and Burstein-Moss effect. Using the Tauc plot (Figure S21(b)), an optical band gap of 3.5 ± 0.1 and 3.6 ± 0.1 eV for AZO 4% and AZO 5%, respectively, are determined, which are higher than the NBE positions determined by CL.

Monochromatic cathodoluminescence images of the m-ZrO$_2$ gyroid with deposited AZO 4% are collected (Fig. 9) to study the spatial signal distribution at 2.58, 2.88, and 3.30 eV over the conformally deposited film. Interestingly, no increase in CL intensity is noted for the edges of lamellas composing gyroid, which could be expected due to the higher specific free surface area. For 2.58 and 2.88 eV, higher intensity is noted within inner regions of the 3D structures between parallel segments of lamellas, which may occur due to the increased electric field amplitude inside a cavity. The intensity of the signals at 3.30 eV, associated with NBE, is lower but homogenous throughout the architecture, illustrating the uniformity of the AZO layer. It is important to note that the shape of the 3D microstructures does not influence the optical properties of the m-ZrO$_2$ octet-truss lattice, gyroid, and buckyball coated with AZO 5% (Figure S20). The only observable difference concerns the minor...
Fig. 8. Cathodoluminescence spectra collected from $m$-ZrO$_2$ 3D structures with deposited (a) ZnO, (b) AZO 4%, (c) AZO 4–5%, (d) AZO 5% thin films.

Fig. 9. SEM and monochromatic cathodoluminescence images of the 3D $m$-ZrO$_2$ structure coated with AZO 4%: (a) SEM image of a gyroid, and CL image at (b) 2.58 eV, (c) 2.88 eV, and (d) 3.30 eV; (a' – d') close-up images of the areas labeled with boxes in images (a – d).
difference in the relative intensity of the 2.3, 2.6, and 2.9 eV peaks.

2.6. Electronic properties

2.6.1. Hall effect measurements

The AZO electrical properties (carrier concentration, mobility, and resistivity) are determined via Hall effect measurements. Upon the placement of an electrical conductor carrying electric current in the transverse magnetic field, a potential difference is produced, termed the Hall effect.[70,71] The principle is often employed to determine the material electronic properties.[71] To establish the Hall effect, measurements are conducted using a dedicated system for depositing thin films on glass substrates by applying a magnetic field of 0.5 T. The derived results are shown in Table 2.

All AZO films exhibit n-type semiconductor behavior, as can be expected for Al-doped ZnO.[19] As a reference, the bare ZnO film showed a mean resistivity (ρ) value of 6.02 × 10^{-12} Ω cm, following the lowest values reported.[72] The n-type extrinsic semiconductor resistivity (ρ) is inversely proportional to the elemental electric charge (e), the free electron density (n), and the electron mobility (μe), as given in Equation (1).

\[
\frac{1}{\rho} = n\mu_e
\]  

Thus, the charge carrier concentration and electron mobility play an important role in resistivity evaluation as intrinsic contributions. Regarding the fabricated AZO-ZrO₂ heterostructures, the electrical resistivity shows values reaching a minimum of 1.1 × 10^{-10} Ω cm, which is an improvement from previous results using the supercycle (sc) approach by APLD.[19] Compared with ZnO and AZO 4%, the carrier concentration shows an increment for the AZO 4-5% and 5% films with values near 7.7 × 10^{20} cm^{-3}.[19] The donor doping effect may explain the latter, in which Al atoms substituting Zn in the ZnO crystalline structure (as discussed in XPS) impact the electrical properties. For AZO 4%, 4-5%, and 5%, the mobility is reduced compared with AZO of lower Al content and reaches the minimum value of 5.79 cm² V⁻¹ s⁻¹ for AZO 4-5%. The mobility behavior is mainly influenced by the charge carrier concentration, which can be detrimental to electron mobility if scattered by impurities.[73] In this study, no clear plateau of electrical properties is observed within the range of conditions, and possibly further modification can be achieved for doping cycle contributions exceeding 5%. The values obtained are comparable with those reported in the literature for planar substrates.[21,22,74–76]

3. Concluding remarks

Conformal deposition of ZnO and AZO over complex 3D ZrO₂ microstructures has been achieved via atomic partial layer deposition using diethylzinc, trimethylaluminum, and water as reagents. Thin films of AZO at 4%, 4-5%, and 5% Al doping cycle contributions have been conformally deposited. The crystallographic phase of 3D ZrO₂ microstructures (z-ZrO₂ and m-ZrO₂) has not affected film growth. No specific cleaning of the 3D-printed ZrO₂ structures is required, and structures can be applied as-annealed (1 h at 600 or 1200 °C) after storage. Qualitative chemical analysis confirmed homogenous elemental distributions throughout the films grown over the 3D ZrO₂ microstructures. No domains, undesired aluminum oxide islands, or areas differing from the desired film morphology grown over the 3D structure were found. The GPC is not significantly affected by the shape of 3D architectures.

Furthermore, the CL study confirms the emissions from the ZnO and AZO films associated with V₀, V₂₀, and O₁. Interestingly, for thin films on planar substrates, two components of the NBE can be distinguished, attributed to the high aspect ratio of crystallites, confirmed by SEM. In CL spectra for ZrO₂, we previously found components associated with V₀ and C₁, which may overlap with defect-related emissions in thin films grown in this study, especially under the beam acceleration conditions (15 kV) required to analyze the 3D ZrO₂ structures. Only one NBE component can be distinguished for ZnO and AZO grown over ZrO₂ 3D structures. The NBE peak position changes with the Al content and is respectively 3.18 eV, 3.30 eV, 3.30 eV, and 3.34 eV for ZnO, AZO 4%, AZO 4-5%, and AZO 5%.

All AZO films exhibit n-type semiconductor behavior, as expected for Al-doped ZnO. For AZO 4%, 4-5%, and 5%, the mobility is lower than for AZO of Al < 4% and reaches the minimum of 5.79 cm² V⁻¹ s⁻¹ for AZO 4-5%.[19] The electrical resistivity of AZO 5% reaches a minimum of 1.2 × 10^{-8} Ω cm, an improvement from previous results using the supercycle (sc) approach by APLD.[19] Compared with ZnO and AZO 4%, the carrier concentration increments for the AZO 4-5% and 5% films with values near 7.7 × 10^{20} cm³. The electrical parameters are not plateaued, and tuning might be possible by increasing the Al doping cycle contribution. The effective impurification methodology (APLD) for Al as a substitutional dopant in the wurtzite has resulted in defects leading to improved charge carrier concentration and reduced resistivity. The values obtained are comparable with the literature for planar substrates.

The study concludes that the deposition of thin conductive oxides using the APLD is feasible. The characteristics of the ZnO and AZO films deposited over 3D ZrO₂ microstructures resemble their typical optical and electrical properties. Supercycle methodology enables the development of an auspicious reproducible approach, addressing intrinsic and persistent issues emerging when doping is done via conventional ALD, showcased even for complex 3D microstructures. Further studies on APLD could result in the foundation of a reproducible approach permitting the manufacturing of functional thin transparent electrode materials for optoelectronics, integrated optics, or light-emitting diodes. [34,77,78] The ability to deposit TCOs over 3D-printed microstructured ceramics is a step towards achieving dimensionally refined electro luminescent devices and other diodes, utilizing lanthanide-doped phosphors, e.g., ZrO₂:Eu³⁺, as emitters.[34,79] The advantages of such integration include improved heat dissipation and higher phosphor resolution, combined with reduced optical cross-talk and scattering through structural design and precise positioning.[34,80]

4. Experimental section

4.1. Materials

Diethylzinc and trimethylaluminum, of microelectronics grade, used as ALD precursors, were purchased from Sigma-Aldrich. The AGR reagent grade acetone, ethanol, isopropanol, sulphuric acid, and hydrogen peroxide were acquired from Fermont. Industrial-grade N₂ was purchased from Grupo INFRA MX. Deionized water was obtained from the ultrapure filtration system. The photoresin was prepared using the recipe established before.[34]

4.2. Additive manufacturing of ZrO₂ microstructures

The ZrO₂ microarchitectures were additively manufactured using a Zr-rich tailor-made photoresin. The custom recipe and methodology
reported by Winczewski et al. were applied.\[34\] A commercial direct laser writing setup (Photonic Professional GT, Nanoscribe) was used to print three types of pre-ceramic microstructures (buckyball, gyroid, and octet-truss lattice) on Si (8 \times 8 \text{ mm}) substrates. The substrates with the fabricated pre-ceramic structures were subsequently annealed at 600 and 1200 °C for 1 h to obtain tetragonal zirconia (t-ZrO₂) and monoclinic zirconia (m-ZrO₂) miniaturized replicas.

4.3. Atomic layer deposition (ALD) of AZO and ZnO films

The depositions of AZO and ZnO were conducted in a custom-built TFS-200 Atomic Layer Deposition reactor (Beneq Oy), operated in thermal mode, following the recipe presented in the previous work.\[19\] In total, four different film compositions were studied: ZnO, ZnO:Al-4.0\% (AZO 4\%), ZnO:Al-4-5\% (AZO 4-5\%), and ZnO:Al-5\% (AZO 5\%), where Al \% refers to the percentage of cycles involving the Al-rich precursor, trimethylaluminum. The films were deposited over 3D-printed t-ZrO₂ and m-ZrO₂ structures and two types of control samples, i.e., Fisherfinest™ Premium plain glass microscope slides (Fisher Scientific) and commercial-grade silicon substrates. Before deposition, the Si substrates were sequentially sonicated for 10 min in baths of acetone, ethanol, isopropl alcohol, and piranha solution (H₂SO₄:H₂O₂ 4:1 v/v) to be finally dried under an N₂ stream. The flow rate of ultrapure N₂ was 200 sccm for the process and 300 sccm for the vessel; a viscous flow regime was followed. The reactor temperature was set at 200 °C. The 3D-printed ZrO₂ microstructures and the control samples were placed in the process chamber 10 min before the deposition to equilibrate the temperature. As a baseline, the ZnO deposition recipe consists of a fixed number of cycles. A typical individual cycle (tc) includes a diethylzinc (DEZ) dose of 0.240 s, a purge of 2.0 s, an H₂O dose of 0.240 s, and a 2.0 s purge. The ALD regime for high-quality films (= 100 nm growth for 625 cycles) is maintained, as schematically depicted in (Figure S2). A supercycle recipe was followed for the deposition of AZO at all studied dopant concentrations (4.0\%, 4-5\%, and 5.0 Al doping cycle \%). In such a recipe, a tc is replaced with a doping cycle (dc), corresponding to the desired dopant percentage. The dc includes an extra trimethylaluminum (TMA) pulse and proceeds as follows: i. DEZ dose, ii. purge, iii. TMA dose, iv. purge, v. H₂O dose, vi. purge, as depicted in Figure S2. For instance, the ZnO:Al-4\% (AZO 4\%) sc contains 24 tcs, followed by a single dc. After 25 repetitions (625 cycles in total), the dopant agent constitutes 4\% of the dc 25 cycles, as presented in Fig. 1 and Figure S2. Table S1 shows the specific conditions for each recipe for AZO 4\%, AZO 4-5\%, AZO 5\%, and ZnO (without Al doping). A complete deposition was driven nonstop to obtain ≈ 100 nm thickness.

4.4. Field emission scanning electron microscopy (SEM)

The electron micrographs of the deposited films and the 3D ZrO₂ structures were obtained using a field emission scanning electron microscope (SEM, FEI Nova Nano SEM 200) equipped with an immersion lens secondary electron detector. An acceleration voltage of 15 kV was applied.

4.5. Crystallite size determination – Image analysis

The high-magnification SEM images of the ZnO, AZO 4\%, AZO 4-5\%, and AZO 5\% films deposited over Si substrates earlier annealed at 600 and 1200 °C were analyzed using the Fiji image processing package (2.9.0 release) to determine the average crystallite sizes. Forty spots were analyzed in each case.

4.6. Scanning electron microscopy (SEM)

The images of the m-ZrO₂ microstructures after the deposition of AZO 4-5\% were collected at 15 kV acceleration voltage using a JSTM-IT500 InTouchScope™ scanning electron microscope.

4.7. Energy dispersive X-ray spectroscopy (EDX)

Chemical characterization was conducted using an energy dispersive X-ray microanalysis system (Oxford, INCA X-Sight) attached to the SEM. The data was collected using INCA Energy software.

4.8. Spectral reflectance analysis

The thickness of the deposited layers was determined in spectral reflectance measurements conducted on the glass and Si control samples. A commercial thin-film thickness measurement system (Filmetrics F20-UV, KLA Corporation) with a source operating in a 200 nm – 1100 nm spectral range was used.

4.9. X-ray photoelectron spectroscopy (XPS)

The high-resolution XPS of the deposited films were registered using a Thermo Scientific™ ESCALAB™ 250Xi XPS system. A monochromatic Al K \(\alpha\) (h\(\nu\) = 1486.7 eV) XRF X-ray source and the 180° hemispherical energy analyzer were used. The photoelectrons were measured at the perpendicular (\(\theta = 90°\) ) orientation of the magnetic field to the sample surface. The spectra were acquired from a 650 μm spot at 10 eV pass energy, with compensation for potential charging effects using an electron flood gun. The position of the adventitious C 1 s peak (284.8 eV) was monitored, and specimens were scrupulously sputtered using an Ar gun, operated at 2000 eV and 10 μA until the disappearance of the surface C peak, thus resulting in a clean sampling area. The peaks were fitted with the AAnalyzer software version 1.20.\[81\] The background was subtracted using the active background approach function. Binding energy was normalized by individually deconvoluting the C Is region and adjusting the BE of carbon sp² peak position to 284.1 eV. The spectra were then deconvoluted using Chi-square fitting.

4.10. Hall effect measurements

The electrical properties of the thin films were characterized via Hall Effect measurements using the control samples. The DX-50 (Dexing Magnet Tech.) The Hall effect system with a magnetic field of 0.5 T was used. The carrier concentration (n), resistivity (\(\rho\)), and mobility (\(\mu\)) were obtained at room temperature by measuring the Hall voltage using the van der Pauw method to study the electrical properties of the deposited AZO.

4.11. Cathodoluminescence (CL)

The cathodoluminescence study was conducted with a Gatan MonoCla4 detector attached to a JEOL JIB-4500 SEM. During the measurements, a 15 kV acceleration voltage was used.

4.12. Ultraviolet-visible-near-infrared transmittance measurements (UV–Vis-NIR)

The UV–Vis-NIR transmittance spectra of the thin films deposited on glass were recorded using a Cary 5000 (Agilent Technologies) spectrophotometer in the 190 – 1100 nm range. Pristine glass substrates were used for reference.

4.13. Confocal Raman spectroscopy (Raman)

The Confocal Raman Spectroscopy measurements were conducted at ambient conditions using an Alpha 300 (Witec) with a 100x/0.9NA air objective (MPlan FL.N, Olympus) and a 600 g/mm grating. The samples were excited with a 532 nm laser at 5.0 mW power. The presented data are an average of 60 acquisitions of 1 s. CrystalSleuth software
4.14. Focused ion beam (FIB) tomography and SEM-EDX imaging

The 3D AZO/ZrO₂ structures were milled using the focused ion beam workstaton (Thermo Scientific Helios 5 UX DualBeam). The EDX maps were recorded using an integrated EDX detector and 5 kV beam voltage.

CRediT authorship contribution statement

Joel Arriaga Dávila: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration. Jędrzej P. Winczewski: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration, Supervision. Manuel Herrera-Zaldívar: Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing. Crisian Rosero Arias: Formal analysis, Investigation. Nayely Pineda Aguilar: Conceptualization, Validation, Writing – review & editing, Supervision. Jorge L. Cholula-Díaz: Conceptualization, Validation, Writing – review & editing, Supervision. Israel De Leon: Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Funding acquisition. Han Gardeniers: Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Funding acquisition. Arturo Suarrey Arce: Conceptualization, Validation, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. Eduardo Martínez-Guerra: Conceptualization, Validation, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

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