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# Flexible Thermoelectric ZnO–Organic Superlattices on Cotton Textile Substrates by ALD/MLD

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We investigate the thermoelectric properties of both pristine ZnO and ZnO–organic superlattice thin films deposited on a cotton textile using ALD/MLD. Hydroquinone is used as the organic precursor to fabricate the superlattices. The resulting thin-film coatings are crystalline, in particular when deposited on a textile substrate with a thin pre-deposited Al<sub>2</sub>O<sub>3</sub> seed layer. The thermoelectric properties of our ZnO and ZnO–organic superlattice coatings are comparable to those for thin films deposited on conventional inorganic substrates; Al doping can be employed to further improve the thermoelectric properties. The ZnO–organic superlattice thin films moreover show enhanced resistance to mechanical strain. Due to their higher flexibility and lower thermal conductivity in comparison to pristine ZnO thin films, the ZnO–organic superlattice thin films are a possible material platform for flexible thermoelectrics that can be integrated in textiles and applied in wearable electronics.

#### 1. Introduction

Wearable technology has evolved considerably in the past two decades,<sup>[1]</sup> encompassing cross-disciplinary research fields, with a scale of integration ranging from fibre, yarn and fabric to worn objects.<sup>[2]</sup> Developing functional fibres for smart textiles becomes relevant due to the miniaturisation and need for compact, flexible components, to achieve truly textile-like behavior.<sup>[3, 4]</sup> Examples of such wearable devices are personal textile-based health-monitoring systems, which have resulted in an urgent need for robust and mechanically flexible energy solutions such as body-heat-harvesting thermoelectrics.<sup>[5]</sup> Another class of devices requiring robust, low-profile, and cheap energy solutions are the ubiquitous low-power sensor and signaling systems, which are powered by energy harvested via thermo-, tribo-, or piezoelectric effect<sup>[6-8]</sup> and possibly stored in a supercapacitor<sup>[9]</sup> or a Li-ion microbattery.<sup>[10, 11]</sup> In the following, we focus on small-scale energy harvesting based on the thermoelectric effect.

Thermoelectric materials can be used to convert waste heat to electric energy *via* Seebeck effect. They are characterized by a dimensionless figure-of-merit  $ZT = S^2 \sigma T/(\kappa_e + \kappa_l)$ , where *S* is the Seebeck coefficient (thermopower),  $\sigma$  the electrical conductivity, *T* the temperature, and  $\kappa_e$  and  $\kappa_l$  the electronic and lattice contributions to the thermal conductivity  $\kappa_{e}^{[12]}$  **Figure 1** illustrates the basic principle of a conventional thermoelectric (TE) energy conversion device and the concept of a TE generator device combined with a flexible substrate. Furthermore, **Figure 1c** shows how the *ZT* value arises from the abovementioned individual components. Alloys of bismuth telluride (Bi<sub>2</sub>Te<sub>3</sub>) and antimony telluride (Sb<sub>2</sub>Te<sub>3</sub>) are by far the most widely used TE materials. They show high *ZT* values for near-room-temperature applications and have been utilized for decades in solid-state refrigeration applications. A major obstacle for the widespread utilization of Bi-Sb-Te based thermoelectrics is the low abundance of tellurium: it is among the rarest elements in Earth's crust. Furthermore, current thermoelectric generators based on conventional TE materials such as Bi<sub>2</sub>Te<sub>3</sub> are typically inflexible solid-

state devices, which would not be convenient for mobile small-scale applications.<sup>[12]</sup> Consequently, there is a significant interest in producing flexible and efficient TE generator solutions. In particular, a mechanically flexible TE generator solution integrated with lightweight and comfortable textile substrates could be an enabling platform for body-heat-based energy harvesting.





**Figure 1.** (a) Schematic illustration of a conventional thermoelectric module with p-type and n-type legs. (b) Schematic illustration of a thermoelectric element combined to a flexible substrate. (c) Relation between the thermoelectric figure-of-merit *ZT* and the individual components, *S*,  $\sigma$ ,  $\kappa$ , and  $\kappa_L$ . (d) Schematic illustration of an ALD/MLD-fabricated ZnO– organic superlattice which strongly scatters phonons in the superlattice cross-plane direction (the organic building block is benzene, resulting from the hydroquinone precursor).

Recently Lee *et al.* fabricated woven-yarn thermoelectric textiles by coating electrospun polyacrylonitrile nanofiber cores with n-type  $Bi_2Te_3$  and p-type  $Sb_2Te_3$  and twisting them into flexible yarns.<sup>[13]</sup> By weaving the TE-coated yarns into textiles they were able to obtain an output power of up to 8.56 W m<sup>-2</sup> for a temperature difference of 200 K in the textile

thickness direction. Another recent study on thermoelectric fabrics utilized a completely different type of material solution, where thermoelectric PEDOT:PSS polymer was used to coat a polyester fabric with a solution-based method.<sup>[14]</sup> This fabric-TE device was based on p-type PEDOT:PSS only, resulting in a so-called unileg-type device that produced an output power of about 260  $\mu$ W m<sup>-2</sup> for a temperature difference of 75 K.

Atomic layer deposition (ALD) technique offers a highly controllable way to deposit semiconducting inorganic materials on both yarns and textiles.<sup>[15]</sup> There is a significant amount of literature on ALD fabrication of various inorganic materials, many of which can be deposited as crystalline thin films at rather low temperatures.<sup>[16]</sup> Deposition of different oxides and metals on various soft materials such as polymers has been reviewed by Parsons.<sup>[17]</sup> Parsons *et al.* have also described in detail the mechanisms and reactions during ALD on polymers<sup>[18]</sup> and reviewed the recent ALD studies focused on textile substrates.<sup>[19]</sup> A particularly well-suited TE material for ALD investigations is ZnO, as it can be deposited as crystalline thin films at rather low temperatures.<sup>[20]</sup> The ALD of ZnO and Al-doped ZnO on cotton and nylon nonwoven fiber mats has already been investigated in the context of fabricating conductive coatings for sensor applications.<sup>[21],[22]</sup>

While ZnO is known to be a promising TE material for remarkably high operating temperatures (about 1000°C),<sup>[23]</sup> the relatively high thermal conductivity of bulk ZnO results in rather poor TE efficiency at low temperatures. However, the thermal conductivity of ZnO can be decreased by nanostructuring, which results in high scattering of the heat-carrying phonons while the electronic conductivity still remains at a reasonable level.<sup>[24, 25]</sup> In combination with the ALD fabrication of inorganic materials, a very convenient and highly controllable route to nanostructuring is molecular layer deposition (MLD) to produce hybrid inorganic–organic materials (**Figure 1d**).<sup>[26-32]</sup> The combined ALD/MLD technique has been used to fabricate various nanoscale oxide–organic superlattices in a highly controllable

fashion<sup>[33]</sup> and crystalline ZnO–organic superlattices fabricated using hydroquinone (HQ, benzene-1,4-diol, HO-C<sub>6</sub>H<sub>4</sub>-OH) as the organic precursor indeed show order-of-magnitude reduction of thermal conductivity.<sup>[34]</sup> The order-of-magnitude reduction of thermal conductivity has also been proven for analogous hybrid TiO<sub>2</sub>–organic superlattices fabricated by ALD/MLD, highlighting the wider applicability of the oxide–organic superlattice approach for the thermal engineering of metal oxides.<sup>[35]</sup> The atomic-level structural characteristics and thermoelectric properties of the ZnO–organic superlattices have also been investigated using quantum chemical methods, providing further mechanistic insight for the observed thermal conductivity reduction.<sup>[36, 37]</sup> An atomic-level structural model for a ZnO–organic superlattice, derived by combining quantum chemical investigations and experimental spectroscopic evidence, is illustrated in **Figure 1d**.

Here in this work we fabricate flexible thermoelectric ZnO–organic superlattices on cotton textile substrates using ALD/MLD and determine their thermoelectric power factors. Since cotton is the most widely used natural fiber cloth, combining electronic materials with cotton is particularly interesting for truly integrated wearable electronics applications.

#### 2. Results and discussion

#### 2.1 Thin-film fabrication and structural characteristics

We deposited both pristine ZnO and ZnO–organic superlattice thin films on a cotton textile using ALD and ALD/MLD, respectively. Diethylzinc (DEZ) and H<sub>2</sub>O were used as the precursor materials for ZnO and hydroquinone was used as the organic precursor (resulting in benzene molecules, ZnO–C<sub>6</sub>H<sub>4</sub>–OZn, within the final ZnO–organic superlattice). The ALD of oxide materials on cotton and other polymeric substrates differs significantly from ALD on standard substrate materials such as silicon or glass.<sup>[18]</sup> First of all, in comparison to silicon, the fibers of the cotton substrate form a porous-type fine-structure with features of ~10 µm in size. This requires much longer pulse and purge times during the ALD to attain even growth

of the film. Secondly, the ALD precursors may diffuse into the substrate, such subsurface diffusion and reactions resulting in swelling and roughening of the substrate.<sup>[18]</sup> However, cellulosic cotton is an example of a natural polymer with a large density of surface hydroxyl groups, which may help the precursors to react at the surface, thus preventing the subsurface diffusion.<sup>[18]</sup> To study the nature of ALD of ZnO on our cotton substrates, we carried out the ZnO depositions both for pristine cotton substrates and for cotton substrates coated with pre-deposited Al<sub>2</sub>O<sub>3</sub>. The ALD of Al<sub>2</sub>O<sub>3</sub> was carried out with the standard trimethyl aluminum (TMA) and H<sub>2</sub>O precursors, and since TMA is known to react readily with the surface hydroxyls of cellulosic cotton, such pre-deposition can improve the quality of the deposited ZnO thin films.<sup>[18, 21]</sup> Due to the porous nature of the cotton substrate, clearly longer precursor and subsequent N<sub>2</sub> purge pulse lengths need to be applied in comparison to typical flat and dense ALD substrates.<sup>[22]</sup>

All ZnO–organic superlattice thin films were fabricated with ALD/MLD on cotton substrates with a pre-deposited Al<sub>2</sub>O<sub>3</sub> seed layer. The thickness of the inorganic ZnO block was kept constant in all superlattices, while three different thicknesses were tested for the organic interface. A recent study showed that thicker organic interface fabricated via successive DEZ+HQ pulses further reduced the thermal conductivity in comparison to a ZnO–organic superlattice containing organic monolayers only.<sup>[38]</sup>

The textile substrate makes it highly challenging to determine the thickness of the ZnO and ZnO–organic films with the X-ray reflection (XRR) technique typically applied for ALD-fabricated thin films. Instead we estimated the textile-coating thicknesses by determining the thicknesses of ZnO and ZnO–organic films deposited on a silicon substrate using the same deposition temperature. The same approach has been previously applied for Al<sub>2</sub>O<sub>3</sub> thin films grown on various bio-based polymeric materials.<sup>[39]</sup> For example, we measured the thicknesses of our (ZnO)<sub>600</sub> and (ZnO)<sub>588</sub>:(HQ)<sub>12\*1</sub> thin films deposited on a silicon substrate

to be 102 and 108 nm, respectively. The growth-per-cycle (GPC) rates are in line with the previous studies on ZnO and ZnO–organic thin films.<sup>[40]</sup>

We investigated the cotton textiles before and after ALD by using scanning electron microscopy (SEM) **Figure 2a-c**. The cotton fibers of the textile substrate are about 10-20 µm thick, cotton fibers with similar thickness having been observed also in previous ALD studies with textile substrates.<sup>[21]</sup> The SEM images suggest that the surface of the cotton textile becomes somewhat smoother upon the ALD deposition. However, since the thickness of the deposited ZnO thin films is in the range of ~100 nm, the thin film itself may not be the main reason to the change in the appearance. It is possible that the deposition temperature (150°C) used in our ALD fabrication affects the substrate surface. **Figure 2b** clearly shows darker areas on the surface of the fibres. This may be due to some irregularities of the substrate surface, but it may also indicate uneven deposited on the cotton substrate as a seed layer before the ZnO thin film, the dark areas are not as distinct. Overall, the SEM images also highlight the porous nature of the cotton textile substrate since the distances between the cotton fibres can be even tens of micrometers.

The physical appearance of the cotton textile before and after the ALD is shown in **Figure 2d**. The color of the textile substrate changes from pure white to beige during the deposition. The deposition of a ZnO–organic superlattice thin film results in a brown color for the textile substrate apparently because of the longer deposition time required for the ALD/MLD process. In previous studies, pure ZnO has been successfully deposited on cotton substrates also at the lower temperatures of 115°C.<sup>[21]</sup>



**Figure 2.** a) SEM image of the pristine textile substrate; b) SEM image of the textile after ALD of a  $(ZnO)_{1000}$  thin film; c) SEM image of the textile after ALD of a  $(Al_2O_3)_{50}(ZnO)_{600}$  thin film; d) Appearance of the cotton textile before ALD (left); after ALD of ZnO thin film (middle); and after ALD of ZnO–organic superlattice thin film (right).

To obtain reasonable thermoelectric properties, the deposited ZnO thin films should be crystalline. X-Ray diffraction (XRD) patterns for representative thin films deposited on a cotton textile are shown in **Figure 3**. For ZnO films deposited directly on the cotton substrate, the sample with 600 DEZ+H<sub>2</sub>O cycles did not show any ZnO reflections, while with 800 cycles ZnO reflections could be observed in the XRD pattern. With 1000 cycles the XRD peak intensities increased further and a conductivity measurement of the textile substrate showed the thin film to be conductive. Al doping of 1% did not significantly reduce the crystallinity of a ZnO thin film deposited using 1000 cycles.

Depositing the ZnO on cotton substrates with a pre-deposited Al<sub>2</sub>O<sub>3</sub> seed layer had a significant impact on the crystallinity of the films. The ZnO thin film showed XRD reflections already after 600 ALD cycles. We tested Al<sub>2</sub>O<sub>3</sub> seed layers deposited using 20 and 50 ALD cycles, and the ZnO thin films deposited on the thicker seed layer were clearly more crystalline. Depositing a 600-cycle thick ZnO film with 1% Al doping resulted in a slightly reduced crystallinity. Finally, the crystallinity of the ALD/MLD fabricated ZnO–organic superlattice thin films was slightly reduced in comparison to purely inorganic ZnO thin films, but the ZnO reflections can still be very clearly seen in the XRD pattern. This difference in the XRD patterns of ZnO thin films and ZnO-organic superlattice thin films is consistent with the differences observed for ZnO thin films and ZnO-organic superlattice thin films deposited on silicon substrates.



**Figure 3.** XRD patterns for a) ZnO thin films deposited directly on a cotton textile substrate using 600, 800, and 1000 DEZ +  $H_2O$  cycles, and b) ZnO thin films and ZnO–organic superlattice thin films deposited on a cotton textile substrate that has been pre-treated with TMA +  $H_2O$  cycles to form a seed layer of  $Al_2O_3$ . The peak indices are for bulk ZnO (wurtzite structure).

#### 2.2 Thermoelectric properties

The conductivity of the ZnO and ZnO–organic thin films deposited on cotton substrates was tested immediately after the ALD or ALD/MLD fabrication process to assess whether the deposition had resulted in a conductive textile surface. For pure ZnO thin films without any pre-deposition of Al<sub>2</sub>O<sub>3</sub>, 1000 ALD cycles were required to obtain a conductive sample. When 50 cycles of Al<sub>2</sub>O<sub>3</sub> were pre-deposited on the cotton substrate, 600 ZnO cycles were already enough to obtain a conductive sample, in agreement with previous ZnO ALD studies on cotton-based substrates.<sup>[21]</sup>

The thermoelectric properties of the thin films deposited on a cotton textile are listed in **Table 1**. The Seebeck coefficient value for the ZnO film ( $-146 \ \mu V \ K^{-1}$ ) is in line with the value previously obtained for a ZnO thin film on a borosilicate substrate ( $-130 \ \mu V \ K^{-1}$ ). <sup>[41]</sup> For comparison, the Seebeck coefficient for our Al-doped (1%) ZnO film deposited on a cotton substrate is somewhat larger ( $-117 \ \mu V \ K^{-1}$ ) than the value for a similarly doped ZnO thin film deposited on borosilicate ( $-60 \ \mu V \ K^{-1}$ ). For the ZnO–organic superlattice thin films, the Seebeck coefficient clearly decreases from  $-411 \ \mu V \ K^{-1}$  to  $-136 \ \mu V \ K^{-1}$  when the thickness of the organic block is increased from one monolayer to five Zn+organic layers. This is in line with fact that the resistance also decreases as the thickness of the organic block increases. Furthermore, our preliminary data on analogous ZnO–organic superlattice thin films deposited on silicon substrates show exactly the same trend.

Thin film	<i>R</i> (Ω) <sup>a)</sup>	ρ (Ω cm)	S (µV K⁻¹)	$S^2 \sigma$ (10 <sup>-7</sup> W cm <sup>-1</sup> K <sup>-2</sup> )
ZnO (pre-deposition of $Al_2O_3$ on the textile substrate)				
(Al <sub>2</sub> O <sub>3</sub> ) <sub>50</sub> ZnO <sub>600</sub>	870	0.022	-146	9.6
$(AI_2O_3)_{50}(Zn_{0.99}AI_{0.01}O)_{600}$	34	0.001	-117	137
ZnO–organic superlattices with varying thickness of the organic part (pre-deposition of Al₂O₃ on the textile substrate)				
(Al <sub>2</sub> O <sub>3</sub> ) <sub>50</sub> (ZnO) <sub>588</sub> :(HQ) <sub>12*1</sub> (49:1)	1737	0.050	-411	33.7
(Al <sub>2</sub> O <sub>3</sub> ) <sub>50</sub> (ZnO) <sub>588</sub> :(HQ) <sub>12*3</sub> (49:3)	1052	0.026	-199	15.2
(Al <sub>2</sub> O <sub>3</sub> ) <sub>50</sub> (ZnO) <sub>588</sub> :(HQ) <sub>12*5</sub> (49:5)	912	0.025	-136	7.4

**Table 1.** Thermoelectric properties of ZnO thin films and ZnO:organic superlattice thin films deposited on a cotton textile substrate.

<sup>a)</sup> R = resistance;  $\rho$  = resistivity; S = Seebeck coefficient.

The resistance of the (Al<sub>2</sub>O<sub>3</sub>)<sub>50</sub>ZnO<sub>600</sub> thin film (870  $\Omega$ ) is comparable with the resistance of a ZnO<sub>600</sub> thin film deposited on a glass substrate (647  $\Omega$ ). For the actual resistivity values, the lack of exact thicknesses of the studied thin films is a major source of uncertainty. We simply assumed the thickness of the ZnO and ZnO–organic thin films deposited on a cotton substrate with Al<sub>2</sub>O<sub>3</sub> seed layer to be similar to the thickness of an analogous thin film deposited on a silicon or glass substrate. This assumption yielded a resistivity value for the (Al<sub>2</sub>O<sub>3</sub>)<sub>50</sub>ZnO<sub>600</sub> thin film (0.022  $\Omega$  cm) that is comparable to the resistivity of a ZnO thin film deposited on a glass substrate (0.015  $\Omega$  cm). A previous study on a ZnO thin film of 600 cycles deposited on a cotton-based material reported an effective conductivity of 24 S cm<sup>-1</sup> which translates to 0.042  $\Omega$  cm in terms of resistivity.<sup>[21]</sup> Al-doped ZnO thin films deposited on nylon nonwoven fiber mats were previously reported to be ~6 times more conductive in comparison to pure ZnO,<sup>[22]</sup> while here the Al-doped ZnO thin film is over 20 times more conductive. As discussed above, the resistance and resistivity of the ZnO–organic superlattice thin films decreases as a function of the organic layer thickness.

In terms of the thermoelectric power factor  $S^2 \sigma$ , the (Al<sub>2</sub>O<sub>3</sub>)<sub>50</sub>(Zn<sub>0.99</sub>Al<sub>0.01</sub>O)<sub>600</sub> thin film possesses the highest value, followed by the (Al<sub>2</sub>O<sub>3</sub>)<sub>50</sub>(ZnO)<sub>588</sub>:(HQ)<sub>12\*1</sub> hybrid superlattice with a four times smaller value. To obtain the final thermoelectric figure-of-merit *ZT*, the thermal conductivity of the thin films would also be needed. Accurate thermal conductivity measurements of thin films are challenging even on standard solid substrates such as glass. Therefore, it was not yet possible to measure the thermal conductivity of our ZnO or ZnO– organic thin films deposited on textile substrates. However, measurements of analogous thin films on glass substrates have shown that the cross-plane thermal conductivity of the ZnO thin films can be reduced by even two orders of magnitude by creating a ZnO–organic superlattice by ALD/MLD.<sup>[42]</sup> Since the cotton substrate itself is a very poor thermal conductor, it is likely

that the thermal conductivity of the thin films deposited on the cotton substrate will be just as low or even lower as for the thin films deposited on glass substrates.

#### 2.3 Mechanical properties

Since the cotton substrates are inherently flexible, we tested the effect of mechanical strain on the resistivity of our ZnO and ZnO–organic thin films deposited on the flexible substrate. If a thin film deposited on a flexible substrate is able to retain reasonable electric properties after mechanical strain, this could open up new possibilities towards the development of flexible conductive coatings and thermoelectric materials.

We carried out the mechanical tests for three different ZnO and ZnO–organic thin-film samples deposited on the cotton substrate:  $(ZnO)_{1000}$ ,  $(Al_2O_3)_{50}(ZnO)_{600}$ , and

(Al<sub>2</sub>O<sub>3</sub>)<sub>50</sub>(ZnO)<sub>588</sub>:(HQ)<sub>12\*1</sub>. The mechanical testing was carried out in three phases. First, the textile with the deposited thin film was folded in half. Next, the textile was folded in half for a second time. Finally, the twice-folded textile was rolled, trying to obtain as compact roll as possible. The conductivity of the textile was checked after each phase and each textile remained conducting for all the steps. However, the final resistivity measurements carried out on the samples after the mechanical testing revealed clear differences between the three thin-film samples. The resistances of the (ZnO)<sub>1000</sub> and (Al<sub>2</sub>O<sub>3</sub>)<sub>50</sub>(ZnO)<sub>600</sub> thin films increased by 123% (from 1520  $\Omega$  to 3390  $\Omega$ ) and 218% (from 870  $\Omega$  to 2770  $\Omega$ ), respectively, due to the mechanical testing resulted in a 21%-increase only (from 1611  $\Omega$  to 1943  $\Omega$ ). Apparently the presence of the organic monolayers within the ZnO–organic superlattice improves the flexibility of the thin film. This finding is in agreement with recent studies on crystalline, ALD/MLD-fabricated inorganic–organic calcium-based hybrid materials, which were found to tolerate relatively large elongations (> 20%) before breaking.<sup>[43]</sup>

#### 3. Conclusion

We have deposited both pristine ZnO and ZnO-organic superlattice thin films on a cotton textile using ALD and ALD/MLD, respectively. Hydroquinone was used as the organic precursor, resulting in a ZnO–C<sub>6</sub>H<sub>4</sub>–OZn type inorganic-organic superlattice. Crystalline ZnO and ZnO-organic superlattice thin films could be deposited and pre-deposition of a thin Al<sub>2</sub>O<sub>3</sub> seed layer on the textile substrate further improved the crystallinity of the thin films. The thermoelectric properties of the ZnO and ZnO-organic superlattice thin films deposited on the textile substrate could be measured and they were shown to possess thermoelectric properties comparable to similar thin films deposited on conventional inorganic substrates. The ZnOorganic superlattice thin films described here are to our knowledge the first inorganic-organic hybrid materials that can be fabricated directly on a flexible substrate, showing thermoelectric properties as-deposited. Al doping further improved the thermoelectric properties. Finally, the ZnO-organic superlattice thin film showed enhanced resistance to mechanical strain. In addition to the increased flexibility, the ZnO-organic superlattices are also known to possess significantly lower thermal conductivities in comparison to pristine ZnO thin films, suggesting further enhancements in the thermoelectric figure-of-merit. The flexible ZnOorganic superlattice thin films are an exciting materials platform for further research towards flexible thermoelectrics that can be integrated in textiles and applied in wearable electronics.

#### 4. Experimental Section

*Thin-film deposition with ALD/MLD*: The thin-film depositions were carried out in a Picosun R-100 ALD reactor. The deposition temperature and pressure were set to 150 °C and 11 hPa, respectively. The textile substrate was a preshrink and washed 100% cotton 2x2 basket weave fabric (two groups of weft threads cross two groups of warp threads), 30 picks per cm, 28 ends per cm, mass per unit area of 270 g m<sup>-2</sup>. Precursors for the ZnO depositions were

diethylzinc (DEZ) (Zn  $\geq$  52,0 m-%, Aldrich) and H<sub>2</sub>O. Hydroquinone (HQ) was used as the organic precursor for the ZnO–organic superlattices (99,5 %, Merck). Al<sub>2</sub>O<sub>3</sub> seed layers were deposited using trimethyl aluminum (TMA) (97 %, Aldrich) and water precursors. For Al doping of the ZnO thin films, aluminum chloride (AlCl<sub>3</sub>) (99,9 %, Aldrich) was used as the Al precursor. HQ and Al<sub>2</sub>O<sub>3</sub> precursors were kept at temperatures of 160°C and 100°C, respectively. All other precursors were kept at room temperature. The pulse/purge times were as follows: 2/10 s for DEZ and H<sub>2</sub>O (ZnO), 15/15 s for HQ, 2/20 s for TMA and H<sub>2</sub>O (Al<sub>2</sub>O<sub>3</sub> seed layer), and 2/10 s for AlCl<sub>3</sub> (Al-doping of ZnO). The pulse time of DEZ and H<sub>2</sub>O could be reduced to 1.5 s without degrading the crystallinity of the ZnO thin films significantly. *XRD measurements*: The XRD patterns of the thin films deposited on the textile substrates were obtained with a PANalytical X'Pert PRO MPD  $\alpha$ -1 powder diffractometer (Cu K $_{\alpha}$  X-ray source, Si wafer used as support during the measurement of the textile). Grazing incidence XRD and XRR data for the reference ZnO and ZnO–organic thin films deposited on a silicon substrate were obtained with a PANalytical X'Pert PRO thin-film diffractometer (Cu K $_{\alpha}$  X-ray source, 20 mm mask).

*SEM measurements*: All SEM samples illustrated in Figure 3 were sputtered with Pd-Au to ensure the conductivity of the samples. It was also possible to image non-sputtered samples due to the conductivity of the ZnO thin films. The SEM images were collected on a JEOL JSM-7500FA scanning electron microscope.

*Thermoelectric measurements*: The thermoelectric properties were measured for thin films on rectangular cotton textile substrates cut to a size of ca. 10 x 5 mm. The Seebeck coefficient and resistivity values of the samples were measured at room temperature using homemade setups. For the resistivity measurements, a simple four-point probe setup was used (using 1 mA current). Copper wires were connected to the textile samples using silver paste (DuPont) diluted with butyl acetate.

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#### Table of contents entry

#### **Flexible thermoelectrics**

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# Flexible Thermoelectric ZnO–Organic Superlattices on Cotton Textile Substrates by ALD/MLD



**Flexible thermoelectric ZnO–organic superlattices** are fabricated on cotton textile substrates using atomic / molecular layer deposition and their thermoelectric properties are characterized. Combining thermoelectric materials with cotton, the most widely used natural fiber cloth, is particularly interesting for truly integrated wearable electronics applications.