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Layer-by-Layer Design of Nanostructured Thermoelectrics: First-principles Study of ZnO:Organic Superlattices Fabricated by ALD/MLD

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Crystalline atomic/molecular layer deposited ZnO:organic superlattices form a fundamentally new exciting family of coherent multilayered thermoelectric materials. They retain the n-type electrical transport properties derived from the parent ZnO lattice, while the organic molecular layers reduce the thermal conductivity. The controlled nanostructuring opens up the possibility of improving the thermoelectric characteristics of the parent oxide. Here we employ quantum chemical methods to rationalize our experimental results on the ZnO:organic superlattices and determine the thermoelectric structure-property relationships arising from the nanoscale layer-by-layer engineering of ZnO. Our results reveal the importance of systematic tailoring of the organic superlattice component and provide us with atomic-level guidelines for the rational design of novel hybrid inorganic–organic thermoelectrics.

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TOC Graphic:

Research Highlights:

- 1) Crystalline thermoelectric ZnO:organic superlattice thin films can be designed and deposited in a layer-by-layer manner.
- 2) Quantum chemical methods provide thermoelectric structure-property correlations for the nanostructured hybrid superlattices
- 3) Simple modifications of the organic building block enable rational engineering of the thermoelectric properties of the superlattices

Keywords: Thermoelectrics; Nanocomposites, Hybrid Materials; Inorganic-organic interfaces; Atomic Layer Deposition; Ab initio calculations

Introduction

Thermoelectric materials are being investigated due to their high potential to provide new unconventional solutions for improving the energy efficiency of numerous heat-involving processes. Materials showing high thermoelectric efficiency can be used both to convert waste heat to electric energy (Seebeck effect) and to enable efficient solid-state cooling (Peltier Effect). Thermoelectrics are characterized by a dimensionless figure-of-merit $ZT = S^2\sigma T/(\kappa_e + \kappa_l)$, where S is the Seebeck coefficient (thermopower), σ the electrical conductivity, T the temperature, and κ_e and κ_l the electronic and lattice contributions to the thermal conductivity κ , respectively. The improvement of ZT is complicated by the fact that the coefficients S , σ , and κ_e are all coupled, as they depend on the electronic structure of the material. Thus, the challenge in discovering new materials with high ZT arises from the requirement that the power factor $S^2\sigma$ should be maximized at the same time when the thermal conductivity κ needs to be minimized.[1]

Currently, the most efficient thermoelectric materials are heavily doped semiconductors where the lattice thermal conductivity κ_l is reduced by nanostructuring or other structural features that result in high scattering of the heat-carrying phonons while the electronic conductivity still remains at a reasonable level.[2] A very efficient strategy for increasing the phonon scattering is the preparation of superlattices, that is, periodic structures of at least two different materials. For example, by creating $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices, Venkatasubramanian *et al.* were able to realize thermoelectric materials with a greatly improved efficiency in comparison to bulk Bi_2Te_3 .[3] they coined the term phonon-blocking/electron-transmitting structures for the $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices. In addition to conventional inorganic superlattices such as $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$, hybrid inorganic–organic superlattices have been recently been shown to possess highly promising thermoelectric properties due to their low thermal conductivity.[4]

There are many ways to fabricate superlattices for thermoelectric applications, but only a very few of the techniques are able to match the atomic-level precision offered by the Atomic Layer Deposition (ALD) technique. The ALD growth process is based on sequential, self-limiting gas-surface reactions, offering a highly controllable approach for producing semiconductor thin films and superlattices.[5,6] An ALD process can be further combined with Molecular Layer Deposition (MLD) of organic molecules,

which opens up the possibility of synthesizing hybrid inorganic-organic thin films and superlattices.[7] In fact, hybrid inorganic-organic superlattices provide a new avenue for the preparation of efficient thermoelectric materials, where the thermal conductivity of the host inorganic compound is significantly controlled by the organic interfaces introduced by the ALD/MLD process.

The preparation of hybrid inorganic-organic superlattices by means of ALD/MLD is a particularly attractive option for inorganic oxide materials. Many potentially interesting oxide materials are composed of abundant elements and are easy to grow with ALD, but at the same time their applicability as thermoelectric materials has been greatly limited by their inherently high thermal conductivity. A prime example is ZnO; it is a moderately efficient high temperature thermoelectric material ($ZT = 0.30$ for Al-doped n-type $\text{Zn}_{0.98}\text{Al}_{0.02}\text{O}$ at 1000°C [8,9]) but it also possesses too high bulk thermal conductivity ($54 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K [10]) to be truly efficient thermoelectric material.[11] The thermoelectric efficiency of Al-doped ZnO can be further improved with dual (Al,Ga)-doping using high dopant concentrations such $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$, [12] which might be related to the fact that the thermoelectric efficiency of materials can often be improved via nanostructuring that increases phonon scattering. For example, Al-doped ZnO nanocomposites and nanoparticles have been recently reported to show reasonably high thermoelectric efficiencies.[13,14] The thermoelectric characteristics reported in literature for (Zn,Al)O bulk and thin film samples have been recently summarized Loureiro *et al.*, [15] who also used radio frequency and pulsed direct current magnetron sputtering to fabricate (Zn,Al)O thin films with $ZT > 0.1$ at room temperature. The ZnO films with optimized Al doping of 2 wt% Al_2O_3 turned out to have rather low thermal conductivity of less than $1.2 \text{ W m}^{-1} \text{ K}^{-1}$. The room temperature power factor of $0.39 \text{ mW m}^{-1} \text{ K}^{-2}$ is larger than the power factors of 0.2 and $0.04 \text{ mW m}^{-1} \text{ K}^{-2}$ obtained in recent studies on (Zn,Al)O thin films prepared using ALD, suggesting that the ALD processes for Al-doped ZnO thin films can still be improved for higher thermoelectric efficiency.[16,17]

Since the ALD fabrication of ZnO thin films is a well-known process,[18] ZnO does provide an excellent platform for proving the benefits of phonon scattering introduced by hybrid inorganic/organic superlattices grown by the ALD/MLD technique. We have demonstrated that the ALD/MLD growth of ZnO:hydroquinone (HQ, benzene-1,4-diol, $\text{HO-C}_6\text{H}_4\text{-OH}$) hybrid thin films yields crystalline superlattice

structures with an accurately controllable periodicity for the ZnO:HQ ratios from 14:1 to 199:1.[19,20] The ZnO:HQ thin films can be further doped with Al to produce n-type (Zn,Al)O:HQ superlattices with thermoelectric functionality.[17] Combined experimental-theoretical spectroscopic analysis of the films proved that the formation of the superlattice is indeed due to hydroquinone interfaces introduced with the MLD process.[21] The ALD/MLD fabrication process of such (Zn,Al)O:HQ superlattice thin films is outlined in Figure 1a, together with atomic-level models of a ZnO:HQ superlattice with a ZnO block thickness of 1.2 nm (Figures 1b and 1c).[21]

All efficient thermoelectric materials should have low thermal conductivity, preferably in the order of $1 \text{ W m}^{-1} \text{ K}^{-1}$ or less. For polycrystalline ZnO thin films of different thicknesses, fabricated by ALD, room temperature thermal conductivities between $43\text{--}55 \text{ W m}^{-1} \text{ K}^{-1}$ have been obtained using the 3ω technique.[22] For (Zn,Al)O thin films, room temperature thermal conductivities of 6.68 ± 1.15 , 4.89 ± 0.81 , and $8.8 \pm 2.1 \text{ W m}^{-1} \text{ K}^{-1}$ have been reported in recent studies.[23-25] Notably, thermal conductivity measurements using the time-domain thermoreflectance (TDTR) technique have proved that the introduction of the HQ layers within ZnO does indeed suppress the thermal conductivity with respect to normal ZnO thin films.[23] The thermal conductivity of a hybrid ZnO:HQ superlattice with the 49:1 ratio turned out to be only $4.15 \pm 0.43 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, which is an order of magnitude lower than the values of $43\text{--}55 \text{ W m}^{-1} \text{ K}^{-1}$ obtained for polycrystalline ZnO thin films at the same temperature.[22] The Al-doping resulted in a further decrease in the thermal conductivity to $3.56 \pm 0.27 \text{ W m}^{-1} \text{ K}^{-1}$. Recent investigation of the phonon scattering and heat transport mechanisms in the ALD/MLD fabricated ZnO:HQ superlattices suggested that reduction in the thermal conductivity is a boundary-scattering dominated process that is limited by the period thickness of the ZnO blocks.[26][27] Considering the thermal conductivity reduction demonstrated for the ZnO:HQ superlattices, the preparation of hybrid metal oxide/organic superlattices by means of the ALD/MLD process is a very promising way to improve the thermoelectric efficiency of earth-abundant and easily-processable oxide materials.[28]

Figure 1. a) Diagram describing the ALD/MLD process for preparing Al-doped ZnO:HQ superlattice ($\text{Zn}_{0.98}\text{Al}_{0.02}\text{O}:\text{HQ}$), where the ratio of ALD and MLD cycles is 49:1. b) A schematic model of a ZnO:HQ superlattice thin film fabricated by the ALD/MLD process (blue = Zn, red = oxygen, green = HQ). c) Optimized atomic-level model of ZnO:HQ superlattice **1** viewed along the b axis (DFT-PBE0/TZVP level of theory, thickness of the ZnO block 1.2 nm, gray = Zn, red = O, brown = C, white = H). d) ZnO:HQ superlattice **1** viewed along the a axis.

To engineer ZnO:organic superlattices with even lower thermal conductivity, it is important to understand the atomic level mechanisms behind the observed thermal properties. Very recently we studied the structural and electronic characteristics of the ZnO:HQ superlattices by means of atomistic quantum chemical calculations, deriving the first atomic-level structural models for the ZnO:HQ superlattices.[21] By comparing the theoretical results with our experimental data we could provide a detailed interpretation of experimentally measured infrared spectra, proving the presence of organic

interfaces within the crystalline ZnO:HQ superlattices. The availability of the detailed structural information enables the detailed quantum chemical investigation of the various properties of the ZnO:HQ superlattices and here we investigate the thermal conductivity and thermoelectric properties of the hybrid inorganic-organic ZnO:HQ superlattices. The theoretical results are compared with the existing experimental evidence and the structure-property correlations discovered here provide further insights for the improvement of the thermoelectric properties of the ZnO:HQ superlattices.

Experimental and Computational details

1. ALD/MLD fabrication of the ZnO:HQ superlattices

The non-doped[19] and Al-doped[17] ZnO:HQ superlattice thin films were fabricated according to the previously reported ALD/MLD processes. The thermal conductivity and thermoelectric properties were investigated for five systems: pristine ZnO, ZnO:HQ (99:1), ZnO:HQ (49:1), $(\text{Zn}_{0.98}\text{Al}_{0.02})\text{O}$, and $(\text{Zn}_{0.98}\text{Al}_{0.02})\text{O}:\text{HQ}$ (49:1), where the (n :1) ratio corresponds to the ratio of the ALD and MLD cycles used to deposit ZnO and HQ, respectively. The thin films were deposited using a Picosun R-100 ALD reactor at a deposition temperature of 220°C. The precursors used in the deposition were diethylzinc (DEZ), trimethyl aluminum (TMA), HQ and H₂O. The HQ precursor was heated to 160 °C, while the others were kept at room temperature. N₂ was used as the purge gas. The deposition consisted of 605 ALD/MLD cycles where 600 cycles were first deposited according to the targeted composition (see Figure 1a) and then 5 additional layers of ZnO were added on top, resulting in approximately 100 nm thick films. Seebeck coefficient and resistivity data measured for the films using homemade setups,[17] and thermal conductivity data measured using time-domain thermoreflectance (TDTR) technique[23] have been reported in detail earlier.

2. Computational methods

The atomic-level structures of the ZnO:HQ superlattices were taken from our previous study,[21] where they had been optimized using the PBE0 hybrid density functional method (DFT-PBE0).[29,30]

Hybrid density functional methods have been recently applied in several computational studies on hybrid ZnO/organic interfaces.[21,31-33] All DFT-PBE0 calculations reported here were carried out using the CRYSTAL14 program package and the applied computational parameters are identical to ref [21].[34,35] Triple-zeta-valence + polarization (TZVP) level all-electron, Gaussian-type basis sets derived from the molecular Karlsruhe basis sets were applied for all atoms.[21,36] The reciprocal space was sampled using 3x4x1 and 8x8x6 Monkhorst-Pack-type k -point grids for ZnO:HQ superlattices and bulk ZnO, respectively.[37]

The thermoelectric properties of bulk ZnO and the ZnO:HQ superlattices were studied using the BoltzTraP code, which employs the Boltzmann Transport Equation within the rigid band and constant relaxation time approximations for the evaluation of the electronic transport properties of materials.[38] The band structures that were used as the input for the BoltzTraP code were calculated with CRYSTAL at the optimized geometries, using denser k -point meshes and tight SCF convergence criterion (TOLDEE 9). 21x28x12 and 48x48x24 k -meshes were applied for the ZnO:Organic superlattices and bulk ZnO, respectively. In the BoltzTraP calculations, the number of interpolated lattice points per k -point (LPFAC) was set to five.[38]

The phonon properties of ZnO and the ZnO:HQ superlattice **1** were calculated using density functional perturbation theory (DFPT) as implemented in the the Quantum ESPRESSO program package (QE).[39,40] Here we applied the PBE density functional together with the projector augmented wave method (PAW). [29,41] The Pslibrary 1.0.0 PAW datasets were applied for all atoms.[42] In all DFT-PBE/PAW calculations, we applied kinetic energy cutoffs of 44 Ry and 352 Ry for wavefunctions and charge densities, respectively. We also compared our PBE/PAW results for both bulk ZnO and ZnO:HQ superlattices to calculations with PBE/Ultrasoft pseudopotentials[43] designed for respective kinetic energy cutoffs of 40 Ry and 200 Ry and found a very good agreement between the two levels of theory. We applied the same k -point meshes as in the CRYSTAL calculations and tight convergence criteria for the structural optimizations (10^{-6} a.u. and 10^{-5} a.u. for energies and forces, respectively). In the DFPT phonon dispersion calculations, we applied tight threshold for the self-consistency ($\text{tr2_ph} = 10^{-15}$) and q -

point meshes of 3x3x1 and 6x6x3 for the ZnO:HQ superlattice **1** and bulk ZnO, respectively. The long-range electrostatic interactions that affect the interatomic force constants in polar compounds were taken into account using the approach developed by Gonze *et al.*[44]

The lattice thermal conductivities were calculated using the ShengBTE program package.[45] ShengBTE enables the full iterative solution of the Boltzmann Transport Equation for phonons from first-principles. The second-order force constants were taken from the QE calculations described above, while the third-order force constants were determined up to fourth-nearest neighbors with the `thirdorder.py` tool included with ShengBTE.[46] The finite displacement calculations for the third-order force constants were carried out with QE, applying 2x2x1 and 4x4x3 supercells for the ZnO:HQ superlattice **1** and bulk ZnO, respectively. Very tight SCF convergence criterion (10^{-12} a.u.) and Γ -point k -sampling were used in the supercell calculations. In the ShengBTE calculations we applied q -meshes of 8x8x6 and 30x30x24 for the ZnO:HQ superlattice **1** and bulk ZnO, respectively. To make the calculations on the ZnO:HQ supercells computationally feasible, the proportionality constant scalebroad was set to 0.1 after convergence tests (the constant is related to the adaptive Gaussian broadening technique used in ShengBTE for obtaining energy-conserving three-phonon scattering processes[47]). The effects of long-range electrostatic interactions on the phonon dispersions were accounted for in similar fashion to QE and the dielectric tensor and Born effective charges required for this were obtained from DFPT calculations with QE. All thermal conductivity calculations with ShengBTE included phonon scattering due to isotopic disorder arising from the natural isotopic distribution for each element.

Results and Discussion

1. Description of the basic structural and electronic properties

We investigated bulk ZnO and ZnO:Organic superlattices at the DFT-PBE0/TZVP level of theory (see Computational Methods for details). So far, very few computational studies employing explicit atomistic models have been carried out on thermoelectric inorganic/organic superlattice materials and according to Yang *et al*, the fundamental understanding of phonon and electron transport across inorganic/organic

molecular junctions remains at a very rudimentary level.[48] One example of the state-of-the-art studies on the thermoelectric properties of hybrid inorganic/organic superlattices is a recent computational study of SiGe/thiophene superlattices using a combination of DFT and Green's function formalism.[49] The formalism applied by Carrete *et al.* required only the electronic and phonon properties of the constituent components and it was not necessary to consider explicit atomistic models of the actual inorganic/organic interfaces.

The explicit atomic-level structural models of the ZnO:Organic superlattices considered here have been described in detail in our previous study.[21] Based on the experimental evidence on the preferred growth direction of ZnO, the ZnO:HQ superlattice **1** illustrated in Figure 1 was derived using the [100] growth direction for ZnO. The actual ZnO:HQ interface has HQ molecules at 50% of surface Zn-sites and H₂O molecules at the other 50% of surface Zn-sites. 50% of the surface O-sites are strongly hydrogen-bonded with the H₂O molecule of the neighboring Zn-site, while the other 50% of the O-sites remain saturated by a hydrogen atom because the neighboring Zn-site is bonded with an HQ molecule and cannot function as a proton acceptor. The unit cell of the ZnO:HQ superlattice considered is orthorhombic with $a = 6.50 \text{ \AA}$, $b = 5.21 \text{ \AA}$, $c = 20.22 \text{ \AA}$. Experimentally, the ZnO:HQ superlattices prepared with ALD/MLD show good crystallinity at least down to ZnO:HQ ratios of 14:1. The thickness of the ZnO block in the ZnO:HQ superlattice **1** studied here is 1.2 nm, which is of the same magnitude as the thickness of an experimentally characterized ZnO:HQ superlattice with 9:1 ratio (ca. 1.5 nm, based on the growth rates reported in [18]).

In addition to the fundamental structural and spectroscopic properties of the ZnO:HQ superlattices, we have also investigated their basic electronic properties such as band structures and band gaps.[21] Detailed understanding of the thermoelectric efficiency of a material requires detailed information on its band structure, and before reporting the thermoelectric properties of the ZnO:HQ superlattices in detail, we discuss the key points about their basic electronic structure. Starting with bulk ZnO, the band structure calculated at the PBE0/TZVP level of theory is shown in Figure 2a. The predicted direct band gap of 3.55 eV compares well with the experimental 0 K estimate of 3.44 eV.[50] Notably, the standard

DFT-GGA functionals such as PBE clearly underestimate the band gap of ZnO, typically predicting $E_{\text{gap}} = 0.9$ eV. The band structure of the ZnO:HQ superlattice **1** illustrated in Figure 2b possesses two rather flat valence bands within a pseudo band-gap arising from the ZnO part of the structure. Detailed inspection of these molecular-type valence bands shows them to originate practically exclusively from the HQ molecules.[21] The same conclusion can be drawn from the density of states plot in Figure 2b. The lowest conduction bands are predominantly ZnO-type delocalized bands.

The major impact of the HQ molecules on the electronic structure of the ZnO:HQ superlattice **1** interface suggests the systematic modification of the organic part has significant potential for tuning the thermoelectric efficiency of the ZnO:organic superlattices. This point is readily illustrated by replacing the HQ molecule by a saturated 1,4-cyclohexanediol molecule where all hydrogen atoms have been replaced with fluorine atoms (ZnO:CHDF superlattice **2**, Figure 2c). This modification brings the highest energy band of the organic part to the level of the topmost ZnO valence bands,[21] resulting in a direct band gap of 3.91 eV (the band gap of **2** is even larger than that for bulk ZnO (3.91 vs 3.55 eV) due to quantum confinement effects arising from the nanostructuring). The tunability of the electronic properties of the ZnO:organic superlattices is a very important feature for their rational engineering towards improved thermoelectric efficiency.

Figure 2. Band structures and density of states (DOS) plots for a) ZnO, b) ZnO:HQ superlattice **1**, and c) saturated + fluorinated ZnO:CHDF superlattice **2**. The Fermi level (zero energy) is at the top of the valence bands. For the DOS plots, Org. = Organic and Surf. = Surface (the saturating H₂O and H surface species at the ZnO:Organic interface). For the ZnO:Organic superlattices **1** and **2**, the ZnO DOS has been cut to 20% of the maximum DOS value to highlight the features arising from the organic part of the superlattice.

2. Thermal conductivity

To understand the thermal conductivity properties of the ZnO:HQ superlattices, it is helpful to first investigate the thermal conductivity of bulk ZnO. For bulk ZnO, the main drawback from the point of view of thermoelectric applications is its high thermal conductivity, arising from the ordered wurtzite crystal structure ($54 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K).[10] The lattice thermal conductivity κ_l of bulk ZnO, calculated *via* full iterative solution of the Boltzmann Transport Equation for phonons using the ShengBTE program package,[45] is shown in Figure 3a together with the experimental data from Slack.[10] For the calculated values, the symmetry-independent, non-zero components of the thermal conductivity tensor are shown ($\kappa_{l,xx}$ and $\kappa_{l,zz}$, the total value κ_l can be calculated from $1/3(2\kappa_{l,xx} + \kappa_{l,zz})$). The predicted thermal conductivity is slightly lower in the a direction of the ZnO lattice in comparison to the c direction and the total value of κ_l is $46 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K. Overall, the predicted lattice thermal conductivities for bulk ZnO are in reasonable agreement with the experimental values over the studied temperature range.

Figure 3. a) Lattice thermal conductivity (κ_l) of bulk ZnO (experimental data from Slack).[10] b) Cumulative lattice thermal conductivity of bulk ZnO at 300 K. c) Lattice thermal conductivity of the ZnO:HQ superlattice 1.

For understanding the effect of the HQ interfaces on the thermal conductivity of ZnO in the ZnO:HQ superlattices, it is very useful to study the cumulative thermal conductivity to bulk ZnO plotted in Figure 3b. To obtain the cumulative κ_l , only the heat-carrying phonons with a mean free path below a certain threshold are taken into account (the maximum mean free path is shown as the x -axis of Figure 3b). In the limit of very long maximum mean free path, all phonons can contribute and the value of cumulative κ_l

is identical to the normal bulk value. From the point of view of the ZnO:HQ superlattices, the cumulative κ_l can be used to estimate how much the organic interfaces would reduce the thermal conductivity of ZnO if the interfaces are considered to block all phonons beyond the organic interlayer spacing (equal to ZnO block thickness).

The experimentally observed room temperature thermal conductivities for the ZnO:HQ superlattices with ZnO:HQ ratios of 49:1 and 99:1 are 4.15 ± 0.43 and 7.16 ± 1.44 W m⁻¹ K⁻¹, respectively.[23] The corresponding superlattice periods were estimated to be 8 and 16 nm, which allows comparisons with the predicted cumulative κ_l . Setting the maximum mean free path to 16 nm yields a cumulative κ_l of 5.0 W m⁻¹ K⁻¹, which is in line with the experimental value measured for the 99:1 ZnO:HQ superlattice. Decreasing the maximum mean free path further down to 8 nm yields a cumulative κ_l of 2.0 W m⁻¹ K⁻¹, again in line with the experimental findings for the 49:1 ZnO:HQ superlattice. The predicted cumulative κ_l values are smaller than the thermal conductivities actually measured for the ZnO:HQ superlattices, which is perfectly reasonable considering the fact that the HQ interfaces are not expected to work as complete phonon blocking barriers as assumed in the estimates made using the cumulative κ_l . The quality of the κ_l estimates for ZnO:HQ superlattices that can be reached already by the simple application of the concept of cumulative κ_l for bulk ZnO is very encouraging considering theory-assisted synthesis planning of novel inorganic-organic superlattices.

In addition to the cumulative κ_l investigation based on bulk ZnO, we also carried out an explicit thermal conductivity calculation for the ZnO:HQ superlattice **1** with superlattice spacing of about 1.2 nm. The predicted κ_l values plotted in Figure 3c convincingly illustrate the reduction of κ_l resulting from the HQ interfaces. The total κ_l value at the temperature of 300 K is only 0.7 W m⁻¹ K⁻¹. As expected, the lowest thermal conductivity is obtained in the direction of the superlattice ($\kappa_{l,zz}$, *c*-axis). However, the κ_l values obtained for the *a* and *b* directions are also reduced greatly in comparison to bulk ZnO. Currently there are no experimental thermal conductivity data for ZnO:HQ superlattices with superlattice periods as short as 1.2 nm, but such superlattices have already been fabricated experimentally (ZnO:HQ ratio of about 9:1). Comparison with the cumulative κ_l data for bulk ZnO suggests that the lattice thermal

conductivity for a maximum mean free path of 1.2 nm should be only $0.10 \text{ W m}^{-1} \text{ K}^{-1}$, which is in good agreement with the κ_l value obtained from the explicit calculation on **1** in the superlattice direction ($\kappa_{l,zz} = 0.14 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K).

3. Thermoelectric properties

We investigated the thermoelectric properties of ZnO:organic superlattices **1** and **2** using the BoltzTraP program package.[38] BoltzTraP employs the Boltzmann Transport Equation within the rigid band and constant relaxation time approximations for the evaluation of the electronic transport properties of materials. The same approach has also been used previously to investigate the thermoelectric properties of *n*-type bulk ZnO[51] and ZnO nanowires.[52] All thermoelectric properties reported here are calculated at 600 K. The superlattice structure of the Al-doped ZnO:HQ superlattices has been shown to remain completely unaffected at least up until 723 K.[17]

The Seebeck coefficients of ZnO and ZnO:organic superlattices **1** and **2** as the function of carrier concentration are illustrated in Figure 4. Reliable p-type doping of ZnO still remains a major challenge [53] and the thermoelectric properties of p-type ZnO poorly understood in comparison to n-type ZnO. Here we report the thermoelectric properties resulting from both hole (*p*) and electron (*n*) doping for all studied materials. For the ZnO:organic superlattice materials, the anisotropy of thermoelectric properties in the *ab*-plane and along the *c*-axis (superlattice direction) is of particular interest. The S_{xx} values in Figure 4 refer to *ab*-plane and S_{zz} values to the *c*-axis (in ZnO, $S_{xx} = S_{yy}$ and in the ZnO:organic superlattices, the S_{yy} values are very close to the reported S_{xx} values). For all three systems, the anisotropy of the Seebeck coefficient is small for the p-type doping. For bulk ZnO, the anisotropy is very small also for n-type doping, while for the ZnO:organic superlattices the Seebeck coefficients are somewhat smaller in the superlattice direction in comparison to the *ab*-plane.

For all materials, the highest absolute values of the Seebeck coefficient are obtained for p-type doping, which has been so far very hard to realize experimentally for ZnO. However, when comparing the Seebeck coefficients at the carrier concentrations that result in the maximum power factor, the values are rather similar for both p- and n-doped materials. For ZnO, the Seebeck coefficient is 130 and $-131 \mu\text{V K}^{-1}$

¹ for p- and n-type carrier concentrations of $1.9 \times 10^{21} \text{ cm}^{-3}$ and $3.5 \times 10^{19} \text{ cm}^{-3}$, respectively. For ZnO:organic superlattice **1**, the corresponding values are 191 and $-169 \mu\text{V K}^{-1}$ for p- and n-type carrier concentrations of $2.2 \times 10^{21} \text{ cm}^{-3}$ and $2.4 \times 10^{19} \text{ cm}^{-3}$, respectively. Finally, for the superlattice **2**, the Seebeck coefficients are 175 and $-169 \mu\text{V K}^{-1}$ for p- and n-type carrier concentrations of $1.0 \times 10^{21} \text{ cm}^{-3}$ and $2.4 \times 10^{19} \text{ cm}^{-3}$, respectively. Overall, the ZnO:organic superlattices possess larger Seebeck coefficients in comparison to bulk ZnO at carrier concentrations resulting in the maximum power factor. Experimentally, the ZnO:HQ superlattices have been shown to possess higher Seebeck coefficients (and lower conductivity) in comparison to Al-doped ZnO.[17]

Figure 4. Seebeck coefficient of a) ZnO, b) ZnO:HQ superlattice **1**, and c) saturated + fluorinated ZnO:CHDF superlattice **2** ($T = 600 \text{ K}$).

In the case of electronic conductivities, we focus on relative electronic conductivities in different crystal directions instead of absolute conductivity values. Presently it is not feasible to predict the

electronic relaxation times of complex materials from first principles and therefore we only can access σ/τ , the electronic conductivity relative to electronic relaxation time. However, previous studies have shown that τ is largely direction independent[38] and when considering relative quantities such as σ_{xx}/σ_{yy} , τ is canceled out. The relative electronic conductivities in different crystal directions as a function of carrier concentration are illustrated in Figure 5.

Figure 5. The relative electronic conductivities in different crystal directions for a) ZnO, b) ZnO:HQ superlattice **1**, and c) saturated + fluorinated ZnO:CHDF superlattice **2** ($T = 600$ K).

In the case of bulk ZnO ($\sigma_{xx} = \sigma_{yy} \neq \sigma_{zz}$) the anisotropy between σ_{xx} and σ_{zz} is rather small: for n-type ZnO, the conductivity is slightly higher ($\sim 5\%$) along the c axis, while for p-type ZnO, the conductivity is $\sim 16\%$ higher in the ab -plane. In contrast to bulk ZnO, the ZnO:organic superlattices ($\sigma_{xx} \neq \sigma_{yy} \neq \sigma_{zz}$) show significant anisotropy in their conductivity. The anisotropy in the ab plane is rather small, only p-type doped ZnO:HQ superlattice **1** showing $\sim 10\%$ difference between σ_{xx} and σ_{yy} . As can be expected from the structural characteristics and the band structures of the superlattices, it is the superlattice direction c which shows significant differences to the ab plane. For ZnO:HQ superlattice **1**, the

conductivity in the c-direction is over 10^4 times smaller in comparison to the *ab* plane for the p-type material and $\sim 10^3$ times smaller for the n-type material. In particular for the p-type material, the flat topmost valence bands arising solely from the HQ molecules result in very low conductivity. However, modifying the organic building block significantly affects the electronic structure (Figure 2) and for the ZnO:CHDF superlattice **2**, the conductivity of the p-type material increases by almost four orders of magnitude in comparison to **1**. This change can be traced back to the fact that the topmost valence bands become again more ZnO-like in **2** (Figure 2). The conductivity of the n-type ZnO:CHDF superlattice **2** remains very similar to the ZnO:HQ superlattice **1**.

The calculated relative conductivities suggest that modifying the electronic conductivity of the ZnO:organic superlattices is possible via rational tuning of the organic building block. Of particular interest would be to find organic building blocks that could improve the conductivity of the n-doped ZnO:organic superlattices in the superlattice direction. Experimentally, the electronic conductivities (resistivities) have been so far measured only in the in-plane direction of the ZnO:HQ superlattices.[17] The obtained values show that the ZnO:HQ superlattices possess higher resistivity in comparison to bulk ZnO, but the resistivity can be decreased by controlled Al-doping.

Similar to electronic conductivities, the thermoelectric power factor $S^2\sigma$ can only be currently predicted relative to the electronic relaxation time τ . However, the $S^2\sigma/\tau$ values do give a very good picture of the relative thermoelectric efficiencies of n- and p-doped ZnO and the ZnO:organic superlattices. The power factors relative to the electronic relaxation time are illustrated in Figure 6 as a function of carrier concentration. The maximum $S^2\sigma/\tau$ values at 600 K in units of $10^{14} \mu\text{W cm}^{-1} \text{K}^{-2} \text{s}^{-1}$ are 43.5 (p) and 5.9 (n) for ZnO, 2.3 (p) and 4.0 (n) for superlattice **1**, and 8.9 (p) and 4.0 (n) for superlattice **2**. Notably, p-type bulk ZnO shows very high power factor in comparison to n-type ZnO, but due to the experimental difficulties in preparing p-type ZnO it might not be possible to exploit this property. For the ZnO:HQ superlattice **1**, the n-type material shows in fact the higher power factor in comparison to p-type. The power factor of the p-type ZnO:HQ is lowered significantly due to the low conductivity arising from the flat topmost valence band. In the case of the ZnO:CHDF superlattice **2**, the differences in the band

structure are again reflected in the predicted power factors and the overall trends somewhat resemble ZnO. The p-type material has a larger power factor in comparison to n-type, but the maximum value obtained for p-type material is only two times larger in comparison to n-type, whereas it is seven times larger for bulk ZnO.

Figure 6. Thermoelectric power factor (relative to electronic relaxation time τ) for a) ZnO, b) ZnO:HQ superlattice **1**, and c) saturated + fluorinated ZnO:CHDF superlattice **2** ($T = 600$ K).

Even though we cannot presently directly compare absolute power factor values of bulk ZnO and the ZnO:organic superlattices, some very interesting comparisons can be carried out by using the predicted relative power factors and calculated thermal conductivities. If one could fabricate ZnO:organic superlattice samples where the electronic relaxation time is similar to the electronic relaxation time of bulk ZnO, the resulting ZT values could be significantly higher for the ZnO:organic superlattices due to their lower thermal conductivity. At 600 K, the maximum power factor of n-type ZnO would be 1.5 times higher than that of ZnO:HQ superlattice **1**. However, at the same temperature, the lattice thermal conductivity of **1** is over 50 times smaller than the lattice thermal conductivity of ZnO (Figure 3). As the

electronic thermal conductivity is likely to be rather small and of similar size in both materials, the ZnO:organic superlattices could improve the thermoelectric efficiency even by a factor of 30 (assuming that the ZnO and superlattice samples possess similar electronic relaxation times). At the higher temperatures, where the lattice thermal conductivity of ZnO is further reduced, the efficiency improvement due to the superlattice decreases correspondingly. Table 1 summarizes all comparisons between experimental and theoretical data for the studied materials

Table 1. Summary of the experimental and theoretical data for the studied materials.

Lattice thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)			
Material	Experiment	Theory^a	Temperature (K)
Bulk ZnO (single cryst.)	54 ^b	46	300
ZnO thin films (polycryst.)	43–55 ^c		300
ZnO:HQ 99:1 superlattice	7.16 ± 1.44 ^d	5.0 ^e	300
ZnO:HQ 49:1 superlattice	4.15 ± 0.43 ^d	2.0 ^e	300

Seebeck coefficient ($\mu\text{V K}^{-1}$) and carrier concentration (n) in 10^{19}cm^{-3} for the max. power factor value.			
Material	Experiment	Theory^a	Temperature (K)
Bulk ZnO	–150 ($n \approx 6.5$) ^f	–131 ($n = 3.5$)	600
ZnO thin film	–120 (non-doped) ^g		300
ZnO:HQ 99:1 superlattice	–140 (non-doped) ^g		300
ZnO:HQ 99:1 superlattice	–60 ($n \approx 20$) ^g		300
ZnO:HQ superlattice 1		–169 ($n = 2.4$)	600
ZnO:HQ superlattice 2		–169 ($n = 2.4$)	600

^a All theoretical values from this work. ^b Ref. [10]. ^c Ref [22]. ^d Ref. [23]. ^e Estimated from the cumulative κ_l of bulk ZnO, see text. ^f Ref. [9] ^g Ref. [17].

Conclusions

We used quantum chemical methods to investigate the thermal conductivity and thermoelectric properties of ZnO:organic superlattices fabricated by a combined atomic and molecular layer deposition (ALD/MLD) process. Systematic comparisons with bulk ZnO were carried out to understand the impacts of the nanoscale inorganic-organic superlattice on the electronic, thermal, and thermoelectric properties of ZnO. The lattice thermal conductivities predicted for the materials are in agreement with the corresponding experimental values, the ZnO:organic superlattices showing significantly reduced thermal conductivities in comparison to bulk ZnO. Notably, very reasonable estimates on the lattice thermal conductivity of the ZnO:organic superlattices could be reached already by a simple application of the concept of cumulative lattice thermal conductivity for bulk ZnO. Further calibration and application of this technique could enable high-throughput screening of potential novel oxide materials for thermoelectric oxide:organic superlattices. The first-principles investigation of the thermoelectric properties of the ZnO:organic superlattices provided important atomic-level details in particular on the anisotropy of the thermoelectric properties. Where experimental data were available, the predicted trends were in line with the experiment. The structure–property correlations discovered here can be used as guidelines for the further optimization of thermoelectric properties of the inorganic–organic superlattices. Detailed understanding of the electronic structure of such superlattices opens up the possibility for rational tuning of the electronic properties by modifying the organic part of the hybrid superlattice. In summary, combining rational first-principles-based design of novel nanostructured inorganic-organic superlattices with the atomic-level control brought by the ALD/MLD enables the synthesis of next-generation thin-film thermoelectrics.

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Vitae

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