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Efficiently suppressed thermal conductivity in ZnO thin films *via* periodic introduction of organic layers

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A combination of atomic and molecular layer deposition techniques is used to fabricate thin films of hybrid inorganic–organic superlattice structures with periodically repeating single layers of hydroquinone within a ZnO or $(Zn_{0.98}Al_{0.02})O$ framework. A significant reduction of up to one magnitude in the thermal conductivity of the films as evaluated with the time-domain thermoreflectance technique is observed upon introduction of the organic layers, resulting in a greatly improved thermoelectric performance.

The need to improve the performance of thermoelectric materials beyond the limits of conventional materials has led to increased attention to various nanostructuring approaches. Among the most straightforward of these approaches is the fabrication of superlattice (SL) structures with periodicity which may hinder the transport of phonons and/or bring about charge confinement effects. Remarkable improvements in a material's thermoelectric figure of merit have been theoretically predicted and experimentally shown for a number of SL structures composed of two types of inorganic nm-scale layers by reducing the lattice thermal conductivity without significantly affecting the transport of electrons/holes.[1–4] Here we demonstrate that regularly repeating single layers of organic molecules embedded in a thicker inorganic framework may also efficiently reduce the thermal conductivity and thereby enhance the thermoelectric performance.

Atomic layer deposition (ALD) is a chemical thin film deposition method for inorganics that is based on self-limiting reactions between sequentially pulsed precursors. The technique is particularly well suited for the fabrication of

superlattices and other multilayered structures due to the self-limiting nature of the surface reactions. Combined with the strongly emerging molecular layer deposition (MLD) technique for organics, it can be used to deposit hybrid thin films consisting of alternating inorganic and organic layers.[5–9] Here we employ the combined ALD/MLD technique to deposit SL structures of (Zn,Al)O and single layers of hydroquinone (HQ).

The ALD process for ZnO is very well established, which along with the relative simplicity of the compound and the promising thermoelectric properties achieved with Al doping makes the Al-doped ZnO system ideal for investigating the effects of organic layers on thermoelectric performance.[10–12] Moreover, the relatively high lattice thermal conductivity of ZnO enables the realization of potentially large gains in thermoelectric performance if it could be reduced.[12,13] Recently, we successfully fabricated inorganic–organic SL structures of Al-doped ZnO and HQ by the combined ALD/MLD technique and demonstrated that the addition of organic layers into the structure of Al-doped ZnO does not result in a notable impairment of the Seebeck coefficient and electrical conductivity of the material; the Seebeck coefficient and resistivity values were -60 μV K^{-1} and 70 mΩ cm, respectively, for a $(Zn_{0.98}Al_{0.02})O$ sample with a 49 : 1 inorganic to organic ratio.[14] In this communication, we report a significant decrease in thermal conductivity in our ALD/MLD-fabricated $(Zn_{0.98}Al_{0.02})O$: HQ SL structures, which along with the aforementioned electrical transport properties results in a pronounced improvement in the thermoelectric figure of merit of ZnO.

Non-doped and Al-doped ZnO thin films containing periodically repeating single HQ layers were prepared on sapphire (0001) substrates using a Picosun R-100 ALD reactor. Five different samples were prepared for this study: ZnO, ZnO : HQ (with layer ratios of 99 : 1 and 49 : 1 and SL thicknesses of *ca.* 16 and 8 nm, respectively), $(Zn_{0.98}Al_{0.02})O$ and $(Zn_{0.98}Al_{0.02})O$: HQ (with a ratio of 49 : 1). All the depositions consisted of 605 ALD/MLD cycles, resulting in films approximately 100 nm thick. A schematic presentation of the periodic layer-structure of our SL thin-film samples is shown in Fig. 1, along with Fourier-

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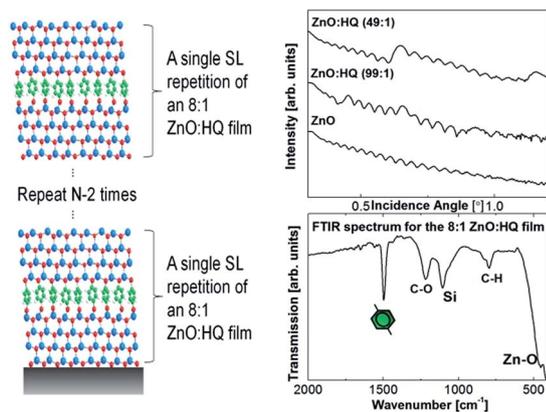
Fig. 1 The layered SL structure of the (Zn,Al)O : HQ thin films; the XRR and FTIR data are for the ZnO : HQ compositions of 99 : 1, 49 : 1 and 8 : 1 (made for FTIR only), respectively.

transform infrared (FTIR) and X-ray reflectivity (XRR) data for representative samples to evidence, respectively, the presence of the targeted organic layers and the SL repetition. A more detailed description of the sample preparation is found in ref. 14.

The thermal conductivities of the samples were measured at room temperature using the time-domain thermoreflectance (TDTR) technique. TDTR is an optical pump-probe technique used to measure the thermal properties of materials by relating the change in reflectance at the sample surface, and related temperature change, to thermal properties of the underlying layers.[15,16] The values for the thermal conductivities of the samples, determined by fitting of the TDTR measurement data are presented in Table 1. A more detailed description of the measurement technique and corresponding analyses are given in ref. 17–19. The calibration data for the thermal conductivity of the ZnO film was taken from ref. 20.

The introduction of organic layers into ZnO causes a significant reduction in the thermal conductivity of the films. Studies on the effects of SL period thickness on thermal conductivity have shown that increasing incoherent boundary scattering by decreasing the period thickness leads to decreased thermal conductivity.[21] This is consistent with the decrease in thermal conductivity we see between the thicker period (99 : 1) sample compared to the thinner period (49 : 1) sample. Aluminum doping also has a reducing effect on the thermal conductivity of ZnO thin films, as reported in a recent study.[22] Compared to the ZnO : HQ films, the reduction in thermal conductivity from Al

doping is of the same order of magnitude. However, combining both Al doping and introduction of HQ layers resulted in the lowest thermal conductivity value (3.6 W m^{-1} K^{-1}) within this study, although the value is only slightly lower than that achieved with HQ layers only.

The observed reductions in the thermal conductivities of the hybrid SL thin-film samples are attributed to the effects of phonon inhibition resulting from the periodic incorporation of HQ layers within the ZnO structure. The effect is pronounced already at relatively low numbers of HQ layers, *i.e.* in SL thin films with the 99 : 1 inorganic-to-organic ratio resulting in HQ layers repeating every ~16 nm of film thickness; by decreasing the SL thickness down to ~8 nm for the 49 : 1 films the thermal conductivity was further slightly decreased. These results are in line with a recent report on appreciably low thermal conductivity values achieved for homogeneous hybrid thin films.[23] Although those films by Liu *et al.*[23] achieved even larger reductions in thermal conductivity than the ones in the present study, they also contained much higher proportions of organic layers. The current results demonstrate that a comparable effect can be obtained with much lower ratios of organic layers, thus influencing film properties such as crystallinity and stiffness to a lesser extent. Indeed, the crystallinity of the (Zn,Al)O : HQ films was found to be high and essentially unchanged compared to pure ZnO.[14] The reductive effect from Al doping on the thermal conductivity as confirmed for our samples is well known and is usually attributed to the increased number of phonon scattering sites, which leads to a lower phonon contribution to thermal conductivity.[13]

The reduced thermal conductivity can be particularly useful for thermoelectric applications, where the control of thermal conductivity independent from the Seebeck coefficient and electrical conductivity can greatly improve the performance of a material. We reported the Seebeck coefficients and electrical conductivities of the (Zn,Al)O : HQ films in a previous study, and little change was observed in the power factor of the hybrid SL samples compared to ZnO.[14] These results were also confirmed for the current films in terms of resistivity values (the sapphire substrate is not ideal for measuring the Seebeck coefficient in our setup). Thus, it would seem that the ten-fold decrease in thermal conductivity observed in the current study would bring about a greatly increased thermoelectric figure of merit for the material. However, care should be taken when drawing conclusions on this point, because while the TDTR technique measures the cross-plane thermal conductivity of the thin films, our existing power factor measurements were made in-plane.[14] Thus, the values may not be comparable, especially in a highly anisotropic structure such as the current layered (Zn,Al)O : HQ thin films. Nonetheless, the observed thermal conductivity values represent a significant reduction and should prove effective in improving the thermoelectric performance of ZnO thin films.

We foresee that the concept of utilizing organic layers to form a hybrid superlattice structure should be applicable to a range of inorganic materials. The present work provides proof-of-concept for using organic layers to provide a large reduction in thermal conductivity *via* incoherent boundary scattering.

Table 1 Thermal conductivity values measured for the (Zn,Al)O : HQ thin films at room temperature

Sample	κ (W m^{-1} K^{-1})
ZnO	43
ZnO : HQ (99 : 1)	7.16 $\pm$ 1.44
ZnO : HQ (49 : 1)	4.15 $\pm$ 0.43
(Zn$_{0.98}$Al$_{0.02}$)O	6.68 $\pm$ 1.15
(Zn$_{0.98}$Al$_{0.02}$)O : HQ (49 : 1)	3.56 $\pm$ 0.27

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Similar effects should also be achievable with other organic precursors, and indeed, the wealth of available organic molecules that contain suitable functional groups for forming hybrid inorganic–organic superlattices is such that there is virtually no limit to the number of material combinations that can be utilized in these structures.

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