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Marin, Giovanni; Tynell, Tommi; Karppinen, Maarit

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Flexible thermoelectric modules based on ALD-grown ZnO on different substrates

Giovanni Marin,¹ Tommi Tynell,^{1,2} and Maarit Karppinen^{1,a)}

¹Department of Chemistry and Materials Science, Aalto University, FI-00076 Aalto, Finland ²Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research Dresden, Helmholtzstrasse 20, 01069 Dresden, Germany

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The authors have designed and tested prototype thin-film thermoelectric devices based on 100–500 nm thick layers of n-type ZnO fabricated with atomic layer deposition on different substrate materials: oxidized silicon, polyethylene naphtalate plastics, and thin flexible glass. In addition, they address the benefits of depositing intermittent organic (benzene) layers within the ZnO matrix through molecular layer deposition for thermal conductivity suppression. Thermoelectric performance of the test devices composed of several ZnO or ZnO:benzene thin-film legs was evaluated by generating the temperature difference using a hotplate and measuring the output voltage at the ends of the circuit in both open circuit and load configurations. The output voltage was found to increase with increasing ZnO film thickness. Most interestingly, the ZnO:benzene superlattice film investigated had better performance compared to plain ZnO of the same thickness, thus opening the way to further developments of thermoelectric thin-film devices. *Published by the AVS*. https://doi.org/10.1116/1.5079614

I. INTRODUCTION

With recent advances in flexible electronics, energy harvesting technologies are increasingly being seen as the key to realizing self-powered electronic applications such as biomedical sensors or wearable electronics. Several energy harvesting methods could be used for this purpose, and generators based on thermoelectricity,^{1–3} piezoelectricity,^{4,5} and triboelectricity⁶ have all been investigated as potential power sources for wearable electronic devices.⁷ Thermoelectric energy harvesting, in particular, has received a lot of attention due to its robustness and easy scalability, as well as the attractiveness of using human body heat as the power source.⁸ Thus, there have been considerable efforts to develop flexible alternatives to the conventional ceramic thermoelectric materials. Polymers and inorganic-organic hybrid materials have emerged as the most promising candidates, and flexible thermoelectric generators based on these materials have already been fabricated using techniques such as screen printing,^{9,10} inkjet printing,^{11,12} and vacuum deposition.^{13,14}

Of the various thin-film deposition methods that have been utilized to fabricate thermoelectric generators, atomic layer deposition (ALD) is one of the most suitable methods for the deposition of flexible modules. This is due to the generally low deposition temperatures used in ALD processes,^{15,16} and the possibility of combining inorganic ALD layers with thin organic layers deposited through molecular layer deposition (MLD) cycles for enhanced mechanical properties.^{17,18} The combined ALD/MLD approach, moreover, allows depositing hybrid inorganic– organic superlattice thin films where thin organic layers embedded within the inorganic thermoelectric matrix efficiently suppress the thermal conductivity.^{19–22} Finally, the ability of ALD to deposit conformal films on very complex surfaces also enables relatively simple nanostructuring through the use of templates such as nanocellulose aerogels,²³ or even the direct deposition of thermoelectric thin films on textiles or fibers.²⁴

So far, ALD-grown thin films of both conventional and hybrid materials have been investigated for their basic thermoelectric properties, but there have been few reports on the performance of thermoelectric modules made using ALD (Ref. 25) or ALD/MLD.²⁶ This is most likely because of the difficulty in achieving high power outputs due to the small temperature gradients obtained with thin-film materials. Indeed, most thin-film based thermoelectric modules are reported to have power outputs in the μ W or mW range using low-level heat sources.⁸ However, e.g., biomedical sensors have been shown to operate with a power consumption as low as 19 μ W,²⁷ thus manifesting the emerging feasibility of using a flexible thermoelectric generator as the power source for such a device.^{26,28–30}

To achieve the maximum potential of a thermoelectric generator, each module should be built with a combination of both p-type and n-type thermoelectric materials. In this research, we, however, chose—for the sake of simplicity and following the work by Suemori *et al.*⁹—to address the feasibility of the ALD thin-film technology by constructing our test devices based on a single material (n-type ZnO) only; we believe that the concept, once found feasible, can then be extended to two-material systems³¹ in a relatively straightforward manner. Here, we report our first results for the design and evaluation of such simple devices deposited on three different test substrates (silicon, plastic, and flexible glass). We will demonstrate that (i) the thermoelectric performance can be enhanced by increasing the thickness of the thermoelectric

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^{a)}Electronic mail: maarit.karppinen@aalto.fi

ZnO layer and (ii) at a fixed film thickness, ALD/MLD ZnO:organic superlattice films may outperform the ALD-ZnO films.

II. EXPERIMENT

A. Thermoelectric thin-film depositions

We used the following substrates for our thermoelectric device fabrication: oxidized silicon (wafers from Okmetic; 520 µm of SiO₂; oxidation done in Micronova, Aalto University), polyethylene naphthalate (PEN; Goodfellow; 0.25 mm thick, biaxially oriented), and flexible glass (AF32 eco thin glass from Schott; $100\,\mu m$ thick). Nitrogen (produced with a Parker HP 5000 N₂ generator, oxygen content less than 10 ppm) was used as carrier and purge gas, and the starting pressure in the reactor was 15 mbar remaining similar during depositions. The ZnO films were deposited from diethyl zinc (DEZ, Sigma-Aldrich \geq 52 wt. % Zn basis) and de-ionized water (containers kept at room temperature outside of the reactor) with the following precursor/purge pulsing sequence: 0.2 s DEZ/5 s N₂/0.5 s H₂O/5 s N₂. All these depositions were carried out in a Picosun R-100 top flow reactor at 160 °C for consistency. Additionally, we deposited ZnO:benzene superlattice thin films using hydroquinone (HQ; Sigma-Aldrich \geq 99.5%) as the organic precursor on the PEN substrate in the same reactor but at a higher temperature of 180 °C. This temperature was necessary for the ALD/MLD experiments due to the higher sublimation temperature of hydroquinone (the HQ source was kept at 180 °C, the source temperature being dependent on the source and/or reactor configuration); however, the higher deposition temperature was not ideal for the PEN substrate, and some bending of the plastic was observed at this temperature. The ZnO:benzene thin film was grown with the following precursor sequence: $100 \times [0.2 \text{ s} \text{ DEZ/5 s} \text{ N}_2/0.5 \text{ s}$ $H_2O/5 \text{ s} N_2] + [0.2 \text{ DEZ}/5 \text{ s} N_2/10 \text{ s} HQ/30 \text{ s} N_2];$ this resulted in a superlattice in which the individual ZnO-layer thickness was ca. 15 nm. This sequence was repeated six times, followed by an extra 15 nm thick ZnO top layer.

B. Device fabrication

The fabrication steps were kept simple with the focus being on the deposition of the thermoelectric material layer. To pattern the ALD-grown thermoelectric ZnO film or ALD/MLD-grown ZnO:benzene superlattice film, two different schemes, a lithography-etching route and a masking-tape route, were tested as illustrated in Fig. 1. In both of these fabrication routes, the bottom and top electrodes, made of copper, were thermally evaporated through a patterned shadow mask. Glass and PEN substrates are insulants, but the Si wafers are needed to be oxidized to insulate the circuit from the conductive silicon.

We started the device prototyping on the oxidized silicon wafer substrates, owing to the ease of fabrication and the reliability of the processing on a well-known substrate type. For the silicon substrates, both the fabrication schemes described in Fig. 1 were initially tested; for the final device fabrication, the lithography-etching route was chosen. The masking-tape route (masking tape from Bertech, resistant up to 200 °C) was found to interfere during the ALD growth of ZnO at high temperatures, preventing the uniform film growth. In the chosen lithography-etching route, the ZnO layer was patterned with standard lithography and etching with a 1:1:50 mixture of H₃PO₄, acetic acid, and water through a photoresist masking pattern. After this, the top contacts were evaporated to close the circuit and to finalize the device.

The same lithography-etching route was utilized with the flexible glass substrate. In this case, the masking-tape route turned out to be impossible as the tape sticks to the glass,



Fig. 1. Fabrication schemes: (A) silicon or glass substrate: (a) metal evaporation through shadow mask for the bottom contact; (b) ALD of ZnO on the entire sample surface; (c) application, exposure, and development of photoresist to pattern the ZnO surface; (d) ZnO etching and photoresist removal; (e) metal evaporation through shadow mask for the top contact; (f) fully connected device. (B) PEN substrate: (a), (d), and (e) as above; (b) masking tape applied on the surface and cutting the pattern, (c) ALD of ZnO on the entire sample surface, and (d) upon tape removal ZnO remains only on nontape-protected areas.

which—being only $100 \,\mu$ m thick—was easily broken when the tape was removed. With the PEN substrate, on the other hand, the masking-tape route was used both to make the process easy and to accommodate for eventual deformation of the substrate during the deposition. Even a small bending of the PEN substrate would make the lithography step complicated and less accurate. The ALD of ZnO on PEN was performed after the substrate was covered with the masking tape, and the pattern for the thermoelectric pads was then cut. With the masking tape, the depositions were carried out at 160 °C to avoid the deformation of the PEN substrate. Finally, the masking tape was removed, and the sample was ready for the last metallization. The masking tape works similarly to a lift-off resist, and the film on top of the tape is removed, but there is no need for strippers.

C. Electrical measurement setup

The thermoelectric performance was evaluated for each device using a simple hotplate for the heating, see Fig. 2. The temperature gradient ΔT between the top and the bottom of the thin film (measured to be around 0.1 K) was maintained using a simple metal heatsink cooled with a 12 V fan placed on top of the sample. Upon the heating and cooling cycle, the temperature of the substrate was monitored using a resistive thermometer. The generated voltage was measured both while heating and cooling the hotplate with a device connected to a second multimeter; the whole setup was controlled with a custom LABVIEW program. During the measurements, the heating rate could not be directly controlled so the somewhat different heating and cooling rates affected the measurements. The generated voltage was first measured in

an open circuit mode and then with a 1.4Ω (including wires resistance) resistance connected to the circuit to measure the voltage produced by the device under load. A low resistance value was needed to obtain a measurable voltage from the circuit, as the power of the device was not enough to drive higher loads.

III. RESULTS AND DISCUSSION

A. Oxidized silicon substrate and different device designs

The device fabrication on the oxidized silicon wafer substrates was the most straightforward, as all the steps are standard and the wafers are easy to handle, and no material incompatibility issues existed during the deposition, lithography, and etching steps. Therefore, we tested different device designs with the oxidized Si wafers.

In Fig. 3, we compare two different device designs. In Design-1, the contact pads are stacked on top of each other. In this case, small defects in the ALD-ZnO layer (common if the deposition is not performed in a clean-room) are likely to cause contact issues in the final device. Moreover, the thermoelectric power generation happens only in the vertical direction, i.e., along the film thickness. In Design-2, the contact pads are shifted such that the defect issue can be avoided and at the same time the configuration allows the use of the lateral dimension (millimeters compared to the hundreds of nanometers) of the thermoelectric ALD-ZnO layers. From the V-T curves shown in Fig. 3 for devices with 500 nm thick ZnO layers, it can be seen that the performance is remarkably better for Design-2.



Fig. 2. Schematic illustration of the measurement in the open and closed (with a load) circuit modes (a) of the heating setup (b). (c) Photo of the measurement setup.



Fig. 3. (a) Two device designs tested, with both top and side views: in Design-1 contact pads are stacked on top of each other, in Design-2 shifted; the former/latter utilizes the film thickness/lateral dimension. (b) Comparison of the V-T curves for the two designs with 500 nm thick ZnO layers.

B. Flexible PEN substrate and effect of the hybrid superlattice

Most of the measurements were made for devices fabricated on PEN substrates, as these devices were readily fabricated and also turned out to show the best performances in general. With these devices, we could, for example, investigate the effect of the ALD-ZnO film thickness on the device performance. In Fig. 4(a), we plot the voltages measured at the two ends of the circuit upon the heating and cooling processes in the open circuit configuration for devices with different ZnO-layer thicknesses (100 nm yellow, 150 nm purple, and 500 nm green). The wavy shape of the curves (most visible for the purple ones) is due to the nonconstant heating rate of the hotplate during the measurements. Each measurement was repeated multiple times, cycling the temperature from 30 to 100 °C and then back to 30 °C. In each case, the temperature cycling resulted in hysteresis output curves such that the higher voltages were obtained upon heating as the heating rate was faster than the cooling rate. The cycling behavior was quite reproducible, with most variations coming from the heating rate of the hotplate; the cooling rate could be kept quite constant in all measurements with the CPU cooler on top of the hotplate spinning at a constant speed. Overall, the open circuit voltage data in Fig. 4(a) clearly reveal the increasing voltage generated by the devices with the increasing thickness of the ZnO film; note that the data are plotted with a log scale.

To test the performances of the devices under a load, the 1.4 Ω resistor was added to the circuit, see Fig. 4(b). The produced voltages are, as expected, lower compared to those achieved in the open circuit case, but the trend of increasing voltages with increasing ZnO film thickness is the same. However, at temperatures below 60 °C, the thickness of the film does not affect the performance. We tentatively attribute this to the fact that the Seebeck coefficient is higher at higher temperatures³² such that the difference between the 100 and 500 nm thick ZnO films become larger at the higher temperatures.

In Fig. 4(b), we also show measurement data for the device fabricated from a 100 nm thick ZnO:benzene superlattice film. Excitingly, the superlattice performs remarkably better than the ZnO film of the same thickness (100 nm).



Fig. 4. V–T curves measured without (a) or with (b) a load in the circuit for devices deposited on PEN for ZnO layers with different thicknesses (100 nm yellow, 150 nm purple, and 500 nm green) and for a 100 nm thick ZnO:benzene layer (only in the case of the closed circuit with the load).



Fig. 5. (a) Photo of the device fabricated on flexible glass. (b) V-T curve for the device fabricated on flexible glass based on a 100 nm thick ZnO film.

This proves that the considerably lowered thermal conductivity values obtained in our previous work for similar ALD/ MLD ZnO:benzene superlattice thin films²¹ are indeed directly translatable to the overall device performance.

In general, the electrical power outputs of our simple test devices based on n-type thermoelectric legs only are very poor still, ranging from 0.01 to $0.23 \,\mu\text{W/m}^2$ for the devices based on 100 and 500 nm thick ZnO films, respectively; this is mostly due to the difficulty in maintaining large enough temperature gradients. Considering the typical power requirement of microelectrical mechanical systems being in the $\mu\text{W}^{27,33}$ (Refs. 27 and 33) to mW range,^{34,35} we still have a lot to improve. Suemori *et al.*⁹ achieved two orders of magnitude higher power outputs for their flexible devices based on one-type thermoelectric material, but their module was an order of magnitude thicker than ours.

C. Flexible glass substrate

Finally, we made efforts to fabricate some test devices on flexible glass to confirm the feasibility of the process. The fabrication of the very fragile glass proved to be challenging and only the device with a 100 nm thick ZnO layer was investigated for the thermoelectric performance. As displayed in Fig. 5, the V-T data show rather large hysteresis in the voltage between the heating and cooling curves.

Relatively high voltage values are generated upon heating when the heating rate is high and constant. Then, after the maximum temperature is reached and the hotplate is turned off, the rate of changing temperature suddenly considerably decreases. At this point, the drop in voltage is caused by the absence of a temperature gradient since the glass substrate stores heat more efficiently than the other substrates. This seems to be positive upon heating owing to the larger temperature gradient achieved, but affects negatively during the cooling. However, more studies are needed to fully understand this behavior.

D. Substrate comparison

Comparing the voltages obtained from devices deposited on different substrates, it is clear that the substrate has a significant influence on the performance of the thermoelectric device. The V-T curves of the different ZnO thickness and substrate combinations are summarized in Fig. 6. There are two direct comparisons that can be made between the devices: (i) the performance of 500 nm thick ZnO layers on Si/SiO₂ and PEN substrates and (ii) the performance of



FIG. 6. (a) Comparison of devices deposited on different substrates. (b) Optical microscope images of different positions in the pads fabricated on different substrates confirming the expected layer alignment and stacking. The lower-quality ZnO edges in the device fabricated on PEN is due to the tape patterning fabrication; the other devices were fabricated using photolithography.

100 nm ZnO layers on PEN and flexible glass substrates. The first comparison reveals that the 500 nm ALD-ZnO device fabricated on PEN shows a voltage value that is approximately one magnitude higher than the one achieved with an identical device deposited on Si/SiO₂. Secondly, the comparison between the PEN and glass substrates for the 100 nm ALD-ZnO devices again shows a difference of approximately one magnitude, but it is the flexible glass substrate that offers the superior performance in this case.

There are two main factors that can be considered to be causing the observed substrate-specific differences in device performance: the thermal conductivity and the thickness of the substrates. Since the voltage generated by a thermoelectric device is determined by the temperature gradient over it, and the heat flow from the heater has to pass through the substrate first, a thinner and more thermally conductive substrate would be expected to lead to a higher hot-side temperature experienced by the ZnO films and thus the higher voltage generation. Thermal conductivities of the substrates within the measured temperature range, based on the values provided by the manufacturers, are estimated to be $0.2 \text{ W m}^{-1} \text{ K}^{-1}$ for PEN, $1.2 \text{ W m}^{-1} \text{ K}^{-1}$ for the flexible glass, and $1.3\,W\,m^{-1}\,K^{-1}$ for SiO_2 (the Si part of the Si/SiO₂ substrate has a thermal conductivity two magnitudes higher and is thus thought to have little effect on the temperature gradient). Therefore, based on the thermal conductivity alone, the PEN substrate would be expected to have the worst performance, while the glass and Si/SiO₂ substrates would produce similar voltage values. This does not fit the observations, so thermal conductivity is not thought to be the main factor influencing the device performance.

There is, however, a clear correlation between the substrate thickness ($520 \,\mu$ m for SiO₂, $250 \,\mu$ m for PEN, and $100 \,\mu$ m for the flexible glass) and the performance of the thermoelectric device, with the thinnest substrate resulting in the highest voltage output. Therefore, we conclude that the different device performances on different substrates are most likely the result of the substrate thickness influencing the temperature gradient over the thermoelectric device. The thermal conductivity is thought to have an effect on the temperature gradient as well, but at least in this case, with all the substrates having relatively low thermal conductivity values, the effect of the substrate thickness is much larger.

IV. CONCLUSIONS

In this work, we have demonstrated that it is possible to fabricate functional thermoelectric devices based on ALDgrown thin films. The devices were fabricated on oxidized Si wafers as well as on flexible PEN and glass substrates. In addition to the module design itself, the substrate type employed seems to have a large impact on the device performance, with the thinner substrates resulting in the better performance due to a larger temperature gradient over the ZnO films.

The comparison between different ALD-ZnO film thicknesses on the same substrate (PEN) showed that the device performance crucially depended on the film thickness, as expected. The thicker films not only generated more power but were also able to maintain higher temperature gradients. Furthermore, adding organic benzene layers into the film to form a ZnO:benzene superlattice was shown to lead to a considerably enhanced performance of the thermoelectric device.

Electrical power generated by the best performing device based on 500 nm thick ALD-ZnO legs on a PEN substrate was only of the nW level. Nevertheless, these very first results were encouraging and verified the feasibility of the concept. Moreover, our work revealed several ways to improve the performance in future, including the use of inorganic–organic superlattice films and also looking for suitable p-type components for the device, thus inspiring further research to improve the power generated by ALD thin-film thermoelectric modules and their integration with microbatteries, electronics, and sensors.

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