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Investigation of the structural, optical and piezoelectric properties of ALD ZnO films on PEN substrates

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Abstract. We present the results of studies on the structural, optical and piezoelectric properties of ZnO thin films deposited by ALD on flexible polyethylene naphthalate (PEN) substrates. Changes were observed in the optical transmission and crystal structures as the deposition temperature was varied. The electromechanical behavior, dielectric losses and voltage generated from ZnO flexible devices were investigated and discussed, in order to estimate their suitability for potential application as microgenerators activated by human motion.

1. Introduction

Flexible microelectronics is a fast-growing modern technology with a variety of attractive applications: energy harvesting, micro-/nano-electromechanical systems (sensors and actuators), organic light-emitting displays (OLEDs), flexible smartphones, electronic paper, wearable microelectronics and biological applications. Recently, mechanical energy scavenging from human motions has attracted great attention due to its potential application in the bioelectronics and medicine [1, 2]. These motions take place at low frequencies (up to 50 Hz), compared to other ambient sources of vibration. In addition, there exist many other sources of low-frequency vibrations in the environment, such as pumps, compressors, diesel engines, wind and fans, that could also contribute to electrical energy generation [3]. Therefore, the study is of particular interest of piezoelectric microgenerators in the low-frequency range. When used for self-sufficient power supply of biosensors, these elements must be small-sized, ultrathin, lightweight and possibly flexible [4].

An increasing number of biocompatible components would benefit from the use of such structures. Replacing the metal or metal-oxide electrodes with conductive polymers is a good starting point in the process leading to the fabrication of fully-compatible microgenerators [5, 6]. Furthermore, it results in

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more stable flexible devices that are not affected by multiple mechanical loading due to the high elasticity of the electrode [7]. Replacing the piezoelectric functional film with a polymer is still an obstacle restricting the device efficiency due to the relatively low piezoelectric coefficient d_{ij} of this class of materials [8]. This is the reason why conventional inorganic piezoelectric materials, such as piezoceramics and their composites, are still a basic component of layered microgenerators, locked between polymer-containing electrodes [9]. All this provoked the interest in zinc oxide (ZnO), which exhibits good piezoelectric properties along the [0001]-direction due to its non-centrosymmetric structure. Along with its other properties, such as high transmittance in the visible range and low DC resistivity, ZnO is the most promising environmentally-friendly (lead-free) material for energy harvesting applications, transparent electronics, solar cells and optical devices. A variety of chemical and physical deposition techniques have been reported for preparation of ZnO films, nanocoatings and nanostructures (nanowires, nanorods, etc.) [10, 11]. To obtain flexible devices, low-temperature deposition processes are needed, e.g., atomic layer deposition (ALD). The advantages of ALD over other deposition techniques are: large area thickness uniformity, atomically flat and smooth coatings, perfect 3D conformability, uniform covering on high-aspect-ratio features and possibility to control the thickness on a nanometer scale [11-13].

In this paper, we report on the structural, optical and piezoelectric properties of ZnO thin films deposited by ALD on flexible polyethylene naphthalate (PEN) substrates. We present the electromechanical behavior, dielectric losses and voltage generated by a flexible device with a piezoelectric nanocoating of atomic-layer-deposited ZnO films. Such a device is very promising for potential application as a microgenerator activated by human motion. To the best of our knowledge, this is the first report on a piezoelectric energy-harvesting flexible device with ALD-grown ZnO films.

2. Experimental

We discuss several samples based on ALD ZnO films. The films were grown directly on polyethylene naphthalate (PEN) and p-Si (100) substrates; another set of ZnO films were deposited on the top of three different contacts: Al, Au and PEDOT:PSS/Au. Thus, PEN/ZnO, Si/ZnO, PEN/Al/ZnO, PEN/Au/ZnO and PEN/PEDOT:PSS/Au/ZnO structures were obtained. The ZnO film in the PEN/Al/ZnO and PEN/Au/ZnO structures were grown at 100 ºC, the rest were grown at 80, 100 and 120 ºC.

2.1. Bottom contact deposition

The PEN substrates were cleaned by isopropanol in a supersonic cleaner. The bottom electrodes were prepared as follows: 1) for the polymer-containing ones, a poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) film with a thickness of 35 nm was spin-coated on the PEN surface at a spinning speed of 1500 rpm for 30 s; a gold (Au) ultrathin film (15 nm) was then grown by DC sputtering; 2) for the bottom Al electrode, an Al film with a thickness of 230 nm was prepared by thermal evaporation of a wire with 99.998 % purity at a basic pressure of 10^{-5} Torr.

2.2. ALD of ZnO films

Thin ZnO films were prepared in a Beneq TFS 200 ALD system on p-type Si (100), PEN, PEN/Al, PEN/Au and PEN/PEDOT:PSS/Au substrates. The deposition process was conducted at 80, 100 and 120 ºC and a pressure of 2 mbar. To obtain ZnO films, alternating deposition from DEZ and H_2O precursors was carried out. The pulse and purging durations were the same for both precursors – 200 ms and 1 s, respectively. A pure N_2 gas flow at 600 sccm was maintained during the precursor introduction and the purging steps [11]. For each temperature, 550 cycles were performed.

2.3. XRD Analysis

The XRD patterns of all samples were recorded on a Bruker D8 Advance powder diffractometer equipped with a copper tube (CuKα) and a LynxEye position-sensitive detector. The patterns were recorded in the angular range 5.5 – 80.0 °2θ, with a step of 0.04 °2θ and counting statistics of 0.1

second per detector strip (17.5 s totally). More detailed patterns were recorded in the range 30 – 38 °2θ, a step of 0.04 °2θ and counting statistics of 1 second per strip (175 s totally). The phase identification of the collected data was performed by using the ICDD PDF-2 (2014) database. According to the reference PDF file number 00-036-1451 of synthetic ZnO (Zincite), the first three lines of this compound with indices (100), (002) and (101) should appear in the range 30 – 38 °2θ.

2.4. Ellipsometric measurements

The ellipsometry measurements were performed using a Woollam M2000D rotating compensator spectroscopic ellipsometer with a wavelength range from 193 nm to 1000 nm in reflection mode. The spectroscopic ellipsometry data of Ψ and Δ were taken at room temperature at angles of incidence of 65°, 70° and 75°. The data acquisition and analysis software were CompleteEASE 5.10 J. A. Woollam Co., Inc. The ZnO thickness was extracted from the ellipsometric data of the films grown on Si substrates. Transmission intensity measurements on the PEN/ZnO samples were performed.

2.5. Piezoelectric measurements

To acquire information on the processes in the ALD ZnO grown on a polymer-covered PEN substrate, the top electrode was made of aluminium. Using top electrode same as the bottom one would result in a weaker signal due to its lower conductivity compared to aluminium. The top electrodes were cut from aluminium tape with one side covered by a conductive adhesive, forming active areas of 2 mm^2. The set-up allowed us to apply a low-frequency bending force (up to 52 Hz controlled by the rotation speed of an electric motor), similar to the targeted mechanical sources. All samples were preliminary poled in an electric field with strength of 5 V/cm^2 for one min. The samples were fixed to the bendable beam of the stand to avoid non-uniform distribution of the mechanical wave across the structure and the appearance of additional resonance modes. A reference force sensor measured the mechanical load with the data shown on the stand's display. The shape of the resulting voltage produced by the cyclic loading of the samples was recorded by a DQ2042CN digital storage oscilloscope. The piezoelectric response was excited by a mechanical stimulus of about 5 kg mass load. Additionally, the resistance, capacitance and dielectric losses were measured at a standard bias voltage of 1 V and a frequency of 1 kHz by an Instek 816 RLC meter. This measurement was carried out before and after polarization of the samples to determine how the film is affected by the polling voltage, i.e., to assess its piezoelectric susceptibility. All measurements were conducted with no electric load (open circuit mode) [6].

3. Results and discussions

The thicknesses of ZnO films grown on Si substrates at temperatures 80, 100 and 120 ºC were 50, 70 and 86 nm, respectively. The same behavior, i.e., a growth rate rise with the temperature, was also seen for ZnO grown on glass and polycarbonate substrates; we thus assumed that this applies to all PEN substrates, since this temperature range is on the front edge of the ALD window [14]. The transmission of PEN/ZnO samples and pure PEN substrate is presented in figure 1a.

For the sample grown at 120 ºC, the transmission was measured at two different points of the substrate. While all samples with ZnO films were less transparent than pure PEN substrate, the thickness dependence of transparency was more complex (figure 1). The sample of middle thickness (PEN/ZnO grown at 100 ºC) showed the lowest transmission in the wavelength range 380 – 1000 nm (which may be due to neutral oxygen vacancies and singly ionized zinc vacancies [15]). In the shorter wavelength range of 380 – 525 nm the thickest ZnO film (PEN/ZnO grown at 120 ºC) had higher transmission, whereas in the longer wavelength range (525 – 1000 nm), the thinnest ZnO film (PEN/ZnO grown at 80 ºC) displayed a higher transmission probably due to singly ionized zinc vacancies [15].

All samples discussed exhibited a polycrystalline hexagonal ZnO phase with a wurtzite-type structure (figure 1 b and figure 2). The analysis of the first three peaks of ZnO between 30 – 38 °2θ showed that at a temperature of 120 ºC, the predominant ZnO peaks were (100) and (101), while (002) was with low intensity. As the temperature decreased, the intensity of the (100) and (101) peaks

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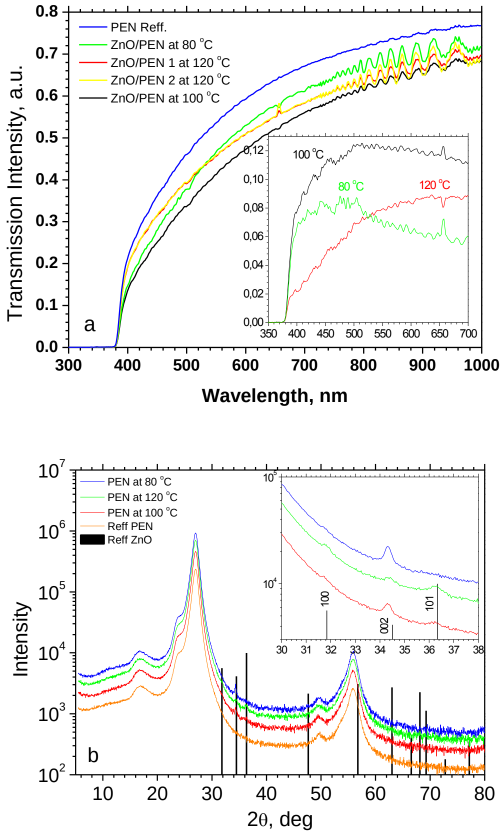

Figure 1. Optical transmission a) and X-ray 2θ intensity b) for ZnO films on PEN substrates at 80, 100 and 120 ºC deposition temperatures; inset in figure 1a – transmission with subtracted substrate; inset in figure 1b – detailed patterns in the range 30 – 38°2θ.

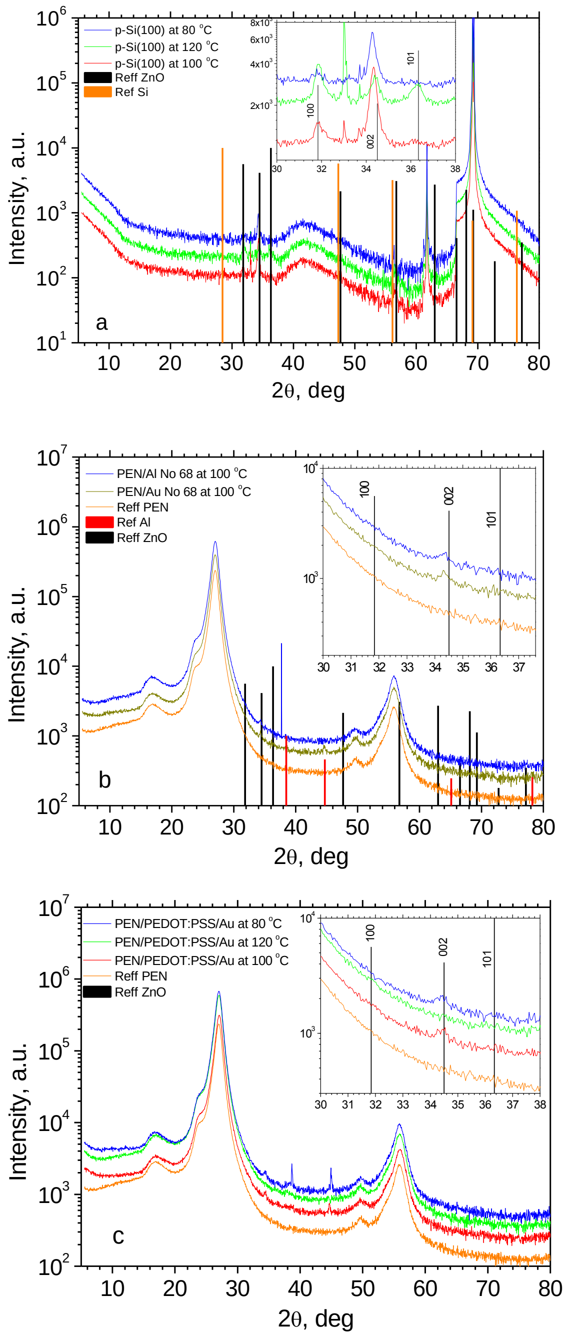

Figure 2. X-ray 2θ intensity for ZnO films on a) p-Si(100), b) PEN/Al and PEN/Au and c) PEN/PEDOT:PSS/Au substrates at 80, 100 and 120 ºC deposition temperatures. The insets show more detailed patterns in the range 30 – 38°2θ.

decreased, while that of (002) increased. Similar results have been presented in other works [12, 16]. The film grown at the middle temperature (PEN/ZnO at 100 ºC) possessed more crystallites of both orientations and, probably, of smaller sizes. This could explain its lowest transparency. To prove this, or other propositions, additional investigations are needed.

Next, we demonstrated the ability of the flexible device with ALD ZnO to generate measurable piezoelectric voltage with parameters (periodicity, effective value, distortions) suitable for application as an energy harvesting microgenerator. As is shown in figure 3 a-d, periodically bending and releasing the structures resulted in the generation of an alternating voltage that in most of the cases strictly followed the frequency of the stimulating vibration. In figure 3, we present the piezoelectric characterization of PEN/PEDOT:PSS/Au/ZnO samples (figure 3 a-c) grown at differen temperatures, and a PEN/Al/ZnO sample (figure 3 d) grown at 100 ºC. The output voltage response for a representative flexible microgenerator was measured under continuous actuation at a frequency of 52 Hz (deflection of the beam and sample of ~3–4 mm). The extracted voltages were 29.7 mV, 86.16 mV and 11.48 mV, corresponding to ZnO grown at temperatures of 80, 100 and 120 ºC, respectively. The lateral positioning of the top electrodes for the structure with an Al bottom electrode also gave promising results regarding measurable piezoelectric voltage distinguishable from the noise (figure 4).

We further found that the electrical output was strongly affected by the mechanical load frequency. At frequencies higher than 52 Hz, noise could only be registered, most probably due to high dielectric losses and inability of the dipoles to follow the mechanical wave direction change. This observation is in good agreement with the results for the RC time constant of each device, varying between 29.6 ms

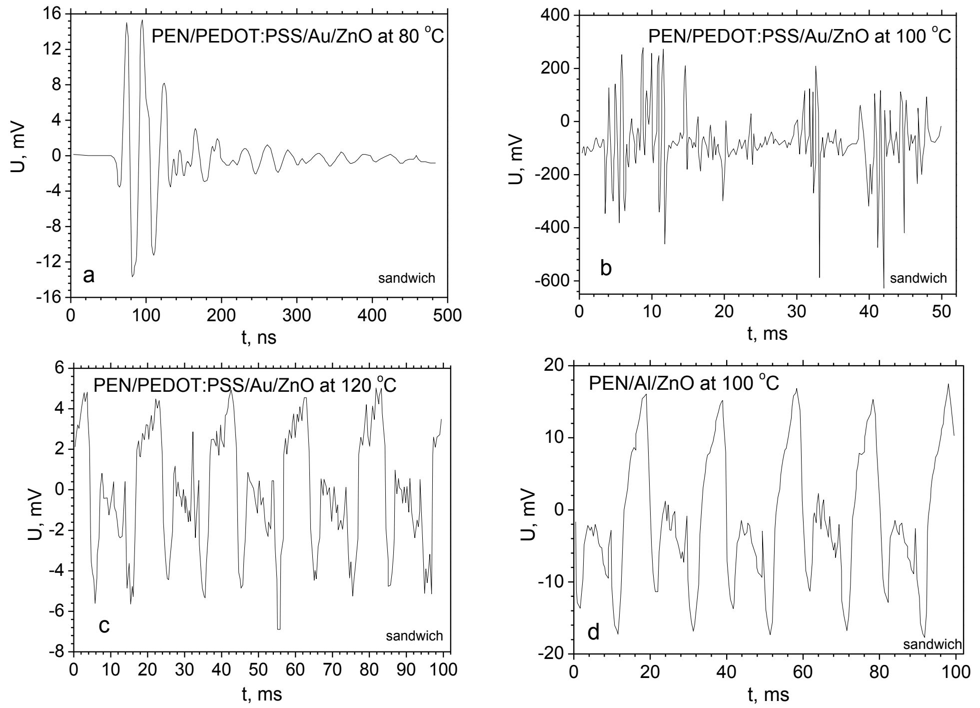

Figure 3. Piezoelectric response of flexible microgenerators with ALD ZnO films grown on PEN/PEDOT:PSS/Au substrates at temperatures a) 80 ºC; b) 100 ºC; c) 120 ºC; and on a PEN/Al substrate grown at 100 ºC d).

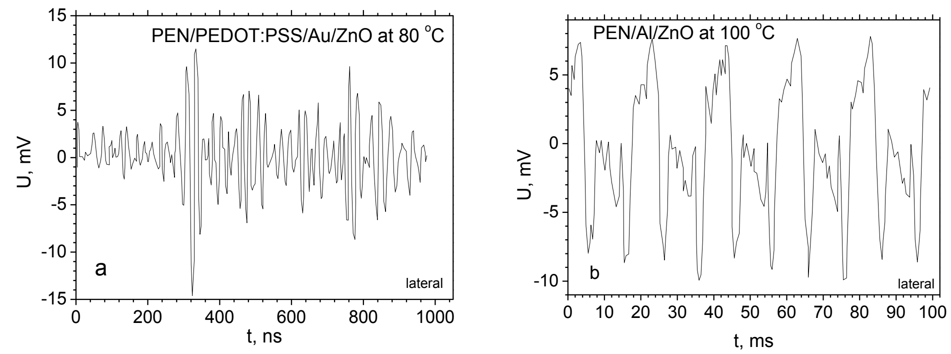

Figure 4. Piezoelectric response of (a) PEN/PEDOT:PSS/Au/ZnO/Al and (b) PEN/Al/ZnO/Al devices.

and 420 ms depending on the ZnO-growth temperature and the sample design. One period of a sinusoidal vibration with a frequency of 52 Hz is 19 ms, meaning that none of the prepared structures generating periodical signals could follow a mechanical load of higher frequency.

Moreover, we found that, due to the rising losses, the magnitude of the piezoelectric voltage was maximal in the frequency range 20-52 Hz. The sign of the measured capacitance (table 1) at stretching the samples along the poling axis was positive, which means that the voltage generated had a polarity coinciding with the poling electric field direction. This was the reason for the positive pulses seen on the oscilloscope; similarly, after discontinuing the stress, negative voltage peaks were seen.

Figure 3 a shows the lack of periodicity in the signal. Random pulses with a maximal amplitude of 29.7 mV were observed, but neither a frequency nor an effective value could be defined. This is to be expected, because the RC parameters did not change significantly after polarization. Otherwise, the resistance and capacity should be changed at least by an order of magnitude [17]. Keeping the same order of magnitudes (or less) means no response to poling or weak susceptibility of the dipoles to re-orientation, resulting in a negligible piezoelectric reaction. When the measurement was conducted between two adjacent electrodes (a lateral structure, instead of a sandwich-type one), a periodic signal was recorded (figure 4a), but its effective value was only 5.4 mV. The dielectric losses were high, as can be seen in table 1.

Table 1. Resistance, capacitance and dielectric losses of samples for different electrode configurations and ZnO-growth temperatures.

Device	R, C and tgδ before poling	R, C and tgδ after poling
PEN/PEDOT:PSS/Au/ZnO/Al, ZnO at 80 ºC	C = 37 μF R = 80 Ω tgδ = 0.105	C = 18 μF R = 44.5 Ω tgδ = 0.099
PEN/PEDOT:PSS/Au/ZnO/Al ZnO at 100 ºC	C = 1 nF R = 24 Ω tgδ = 0.098	C = 35 μF R = 12 kΩ tgδ = 0.094
PEN/PEDOT:PSS/Au/ZnO/Al ZnO at 120 ºC	C = 119 nF R = 57 Ω tgδ = 0.091	C = 15 μF R = 53 Ω tgδ = 0.068
PEN/Al/ZnO/Al ZnO at 100 ºC	C = 109 nF R = 420 Ω tgδ = 0.140	C = 2.2 μF R = 100 Ω tgδ = 0.010
PEN/Au/ZnO/Al ZnO at 100 ºC	C = 934 nF R = 1.3 kΩ tgδ = 0.068	C = 623 nF R = 1.2 kΩ tgδ = 0.041

For the device whose signal is shown in figure 3 b, the effective value measured of the generated voltage was 86.16 mV. The pulses look random, but the oscilloscope picked up repeating pulses and measured a frequency of 20,83 Hz which is lower by a factor of 2.6 than that of the exciting vibration, probably meaning that the dipoles had a relatively low mobility. One can notice a symmetry with respect to the pulses' rise and fall times – 24 ms for pulses with positive and negative polarity. This gives us reason to believe that they did not have a random nature and represented a well-defined piezoelectric signal. The lateral electrode configuration did not result in a significant voltage generation.

The structure whose signal is presented in figure 3 c was susceptible to polarization, with capacitance varying from 119 nF prior to applying the poling voltage to 15 μF after poling. Its dielectric losses decreased most significantly after polarization, compared to the other measured structures with ZnO produced at 80 °C and 100 °C. The signal was periodic with a high degree of symmetry of the positive and negative pulses. The effective value was 11.48 mV, the largest amplitudes of the positive and negative pulses were 21.9 mV and −32.4 mV, respectively. The pulses' rise and fall times were 54 ms, with a frequency of 25 Hz, or twice as low as that of the mechanical load, probably meaning that the mobility of the dipoles was relatively low.

The sandwich structure with configuration illustrated in figure 3 d produced a periodic signal with a well-expressed amplitude of 15.3 mV and an effective (rms) value of 10.85 mV. It also demonstrated the lowest value of dielectric losses of all structures prepared. The pulses' frequency was 52 Hz (exactly the mechanical stimulation frequency); therefore, the dipoles were re-orienting smoothly without delay following the mechanical wave. The pulses' rise/fall times was 10.8 ms. The lateral structure with adjacent upper electrodes (figure 4 b) with the signal measured between them was also functioning, although with twice as low amplitude of the piezoelectric voltage generated – 8.82 mV, and steeper pulses – 1.6 ms.

We also prepared a structure with all Au electrodes, but the results were not satisfactory, as a significant piezoelectric reaction was lacking. Such behavior is expected, since the capacitance after polarization remains small and even decreases, while the resistance of the polarizable medium is in the order of kiloohms.

Regarding the usability of the film for piezoelectric devices, the increased (002) peak suggests a predominant *c*-axis orientation of the crystallites [18], which coincides with the applied force direction for the sandwich structures and may be the reason for the highest achieved effective value of the generated voltage (see figure 3b). Moreover, it has been proved that samples with high crystallinity at (002) orientation are more conductive, which facilitates the electrical poles formation [19].

Compared to previous reports for thin film generators with ZnO nanostructures (nanowires, nanorods, etc.), the ALD-ZnO based one showed promising results in terms of the voltage generated. The reason is probably in the more reliable contact between the ALD film and the electrodes. In contrast, the deformation of the above-mentioned nano-formations leads to unstable interfaces between the needle-type piezoelectric film and the electrode, thus resulting in a lower yield [20].

Although the values of all measured voltages were in the order of millivolts, the current flowing through the structure was still rather small – in the range of 500 nA to 16 µA, resulting in microwatts power.

4. Conclusions

ALD-ZnO nanofilms were deposited on flexible PEN substrates and their structural, optical and piezoelectric properties were investigated in dependence of the deposition temperature and contact type. Some of the structures discussed possessed high transparency and flexibility, which could make them useful for applications in flexible optoelectronic. Other structures showed promising piezoelectric properties and are potential candidates for flexible microgenerators activated by human motion.

Our future work will be related to increasing the structures' conductivity, thus raising the electrical power density. Long-term stability studies after cyclic repeated bends should also be carried out on piezoelectric microgenerators with ALD ZnO sandwiched between symmetrical types of electrodes, especially polymer-based ones.

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References

[1] Diao L-W, Zheng J, Pan X-D, Zhang W, Wang L-F and Sun L-Z 2014 *J. Thorac. Dis.* **6**/9 1300
[2] Zheng Q, Shi B, Li Z and Wang Z L 2017 *Adv. Sci. (Weinh)* **4**/7 1700029
[3] Leventhall G 2003 *A Review of Published Research on Low Frequency Noise and its Effects* (Nobel House, London)
[4] Ani Melfa Roji M, Jiji G and Ajith Bosco Raj T 2017 *RSC Adv.* **7** 33642
[5] Cheng T, Zhang Y-Z, Zhang J-D, Lai W-Y and Huang W 2016 *J. Mater. Chem.* A **4** 10493
[6] Kolev G, Aleksandrova M, Dobrikov G, Pathan H, Fartunkov M and Denishev K 2017 Piezoelectric energy harvesting device with nanobranched ZnO on Polymer/Metal/Polymer coated flexible substrate *Proc. 15th IEEE Int. Conf. Electrical Machines, Drives and Power Systems* (Sofia, Bulgaria, 1-3 June 2017) pp 320-4
[7] Aleksandrova M, Kurtev N, Videkov V, Tzanova S and Schintke S 2015 *Microelectr. Eng.* **145** 112

[8] Ramadan K S, Sameoto D and Evoy S 2014 *Smart Mater. Struct.* **23** 033001
[9] Ponnammar D, Chamakh M M, Deshmukh K, Ahamed M B, Erturk A, Sharma P and Al-Maadeed M A-A 2017 Ceramic-based polymer nanocomposites as piezoelectric materials *Springer Series on Polymer and Composite Materials* pp 77-93
[10] Özgür Ü, Alivov Ya I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S-J and Morkoç H 2005 *J. Appl. Phys.* **98** 041301
[11] Blagoev B S, Dimitrov D Z, Mehandzhiev V B, Kovacheva D, Terziyska P, Pavlic J, Lovchinov K, Mateev E, Leclercq J and Sveshtarov P 2016 *J. Phys.: Conf. Ser.* **700** 012040
[12] Kumar A, Kumar P, Kumar K, Singh T, Singh R, Asokan K and Kanjilal D 2015 *J. All. Comp.* **649** 1205
[13] Kowalik I A, Guziewicz E, Kopalko K, Yatsunenko S, Wójcik-Głodowska A, Godlewski M, Dłużewski P, Łusakowska E and Paszkowicz W 2009 *J. Cryst. Growth* **311** 1096
[14] Guziewicz E, Kowalik I A, Godlewski M, Kopalko K, Osinniy V, Wójcik A, Yatsunenko S, Łusakowska E, Paszkowicz W and Guziewicz M 2008 *J. Appl. Phys.* **103** 033515
[15] Krajewski T A, Terziyska P, Luka G, Lusakowska E, Jakiela R, Vlakhov E S and Guziewicz E 2017 Diversity of contributions leading to the nominally n–type behavior of ZnO films obtained by low temperature Atomic Layer Deposition, *J. Alloys and Compounds* In Press Accepted Manuscript DOI 10.1016/j.jallcom.2017.08.206
[16] Malm J, Sahramo E, Perälä J, Sajavaara T and Karppinen M 2011 *Thin Solid Films* **519** 5319
[17] Chalioris C E, Karayannis C G, Angeli G M, Papadopoulos N A, Favvata M J and Providakis C P 2016 *Case Studies in Construction Materials* **5** 1
[18] Huang W 2012 C-axis oriented ZnO piezoelectric thin films prepared by RF magnetron sputtering for saw filters *Proc. 2nd Int. Conf. Computer Appl. and System Modeling* (2012 Paris France) pp 2017-20
[19] Shariffudin S S, Zakaria N Z, Herman S H and Rusop M 2011 Effect of deposition temperature on the characteristics of Zinc Oxide nanoparticles thin films deposited by thermal chemical vapor deposition *Proc. Int. Conf. Electronic Devices, Systems and Applications* (25-27 April 2011 Kuala Lumpur Malaysia)
[20] Li T, Li Y T, Qin W W, Zhang P P, Chen X Q, Hu X F and Zhang W 2015 *Nanoscale Res. Lett.* **10** 394