Optimization of dielectric matrix for ZnO nanowire based nanogenerators

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Abstract. This paper reports the role of selection of suitable dielectric layer in nanogenerator (NG) structure and its influence on the output performance. The basic NG structure is a composite material integrating hydrothermally grown vertical piezoelectric zinc oxide (ZnO) nanowires (NWs) into a dielectric matrix. To accomplish this study, three materials - poly methyl methacrylate (PMMA), silicon nitride (Si$_3$N$_4$) and aluminium oxide (Al$_2$O$_3$) are selected, processed and used as matrix dielectric in NGs. Scanning electron microscopy (SEM) analysis shows the well-aligned NWs with a diameter of 200±50 nm and length of 3.5±0.3 μm. This was followed by dielectric material deposition as a matrix material. After fabricating NG devices, the output generated voltage under manual and automatic bending were recorded, observed and analyzed for the selection of the best dielectric material to obtain an optimum output. The maximum peak-to-peak open-circuit voltage output for PMMA, Si$_3$N$_4$ and Al$_2$O$_3$ under manual bending was recorded as approximately 880 mV, 1.2 V and 2.1 V respectively. These preliminary results confirm the predicted effect of using more rigid dielectrics as matrix material for the NGs. The generated voltage is increased by about 70% using Si$_3$N$_4$ or Al$_2$O$_3$, instead of a less rigid material as PMMA.

1. Introduction
Considering the present energy crisis, the scientific world is in search of alternate technological solutions to generate energy from the ambiance. Biomass, wind, solar, thermal and mechanical energies are the potential sources. Out of these, mechanical vibrations and impacts are omnipresent when compared to other sources. These mechanical inputs can be implemented for energy harvesting by typical approaches such as electromagnetic induction, electrostatic, magnetostrictive as well as piezoelectric effects [1]. The piezoelectric nanowires (NWs) based energy harvesters are widely researched considering their compatibility with the silicon fabrication technology and flexible substrates. The vertical integrated nanogenerator (VING) is one of the most common modes of harvesting energy using piezoelectric NWs [1, 2]. The basic VING structure consists of piezoelectric NWs inside dielectric matrix is shown in Fig. 1. Besides preventing the electrical leakage and short-circuit between the electrodes, the dielectric material influence the mechanical robustness and stability of the nanogenerator (NG). Moreover, Young’s modulus of the dielectric material also affects the mechanical energy transfer and therefore influences overall device performance.

According to the basic VING structure in Fig.1, the dielectric medium can be categorized into two layers –matrix layer and top dielectric layer. The previous FEM analysis reported from our group described the use of polymethyl methacrylate (PMMA), silicon nitride (Si$_3$N$_4$) and aluminium oxide (Al$_2$O$_3$) as top or matrix dielectric materials in the NG fabrication [3–5]. According to these studies, the use Al$_2$O$_3$ and Si$_3$N$_4$ instead of PMMA improves the device performance under compression when used as top dielectric layer and under bending when used as whole matrix material. The present paper reports the experimental validation of these works by studying the role of suitable dielectric matrix in
NG and its influence on the output performance. To accomplish this, three dielectric materials – PMMA, Si₃N₄ and Al₂O₃ are selected, processed and used in NGs. The output performance is studied by applying strain through manual bending and automatic bending using an actuator controlled by a stepper motor.

![Figure 1. Schematic diagram of the nanogenerator](image)

2. Device preparation
In the present work, piezoelectric ZnO NWs were grown using a solution growth method (Chemical Bath Deposition) on cleaned flexible stainless steel substrates with 40nm thick Atomic Layer Deposition (ALD) coated ZnO seed layer. The growth solution was comprised of a 1:1 ratio of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA). The growth temperature was kept at 85 °C for the growth of 15 hours. Scanning electron microscopy (SEM) analysis shows the well-aligned ZnO nanowires grown with a diameter of 200±50 nm and length of 3.5±0.3 μm (Fig. 2(a)). This was followed by dielectric material deposition as a matrix material on three different samples. The PMMA matrix layer was deposited by spin coating consisting of a double coating of 495PMMA A2 and A6 resists using the parameters from the datasheet provided by MicroChem®. The resulting estimated thickness of the top layer is about 1 μm. The other dielectrics were deposited using sputtering for Si₃N₄ (250 nm) and ALD for Al₂O₃ (240 nm). Aluminium was deposited as a top electrode over the dielectric matrix by evaporation. The cross-sectional SEM images of these samples are shown in Fig 2(b). The active area (11 mm × 13 mm) was based on the surface area of the top electrode.

![Figure 2.](image)

3. Performance analysis
After fabricating NG devices, the performance analysis of piezoelectric NWs based NG devices were carried out by measuring open-circuit potential generation when subjected to strain. For this, the NG devices were tested under manual bending and automatic bending for minimum 3 different sets of readings. The data were recorded using digital oscilloscope (LeCroy WaveSurfer 424) and high
impedance passive probe (LeCroy PP007-WS). The manual bending provides the first-hand working of the device test. However, it lacks the repeatability of the data as the bending amplitude varies every time. The automatic bending fulfills this drawback. Nevertheless, the amount of maximum strain applied to the device is limited.

3.1. Manual bending
Under manual bending tests, the peak-to-peak voltage ($V_{pp}$) generation for PMMA, Si$_3$N$_4$ and Al$_2$O$_3$ were recorded as approximately 880 mV, 1.24 V and 2.07 V respectively (Fig. 3(a-c)). The bending frequency was measured to be in the range of 2–2.4 Hz. These preliminary results confirmed the predicted effect of using more rigid dielectrics as matrix material for the NGs. The generated voltage is increased by about 41% using Si$_3$N$_4$ and 135% Al$_2$O$_3$, instead of a less rigid material as PMMA.

![Figure 3](image)

**Figure 3.** Generated voltage from the NGs where (a) PMMA (b) Si$_3$N$_4$ and (c) Al$_2$O$_3$ material was used as dielectric matrix, respectively. (d) Comparison of NGs performance ($V_{pp}$) with different dielectric materials (inset photograph shows normal bending direction for the analysis)

3.2. Automatic bending
Although the manual results were promising, it lacked repeatability and quantification of the applied strain. Hence, a cantilever setup was made and the deflection of the cantilever was controlled using an Arduino-controlled stepper motor. The NG device was placed near the fixed-end where the strain in the cantilever is the maximum [6]. Here, the shaft deflected the cantilever by approximately 4 mm (0.4% strain) consistently to ensure the same strain in the NG. The deflection frequency was kept to be approximately 2–2.8 Hz. Si$_3$N$_4$ and Al$_2$O$_3$ based NG device generated a maximum $V_{pp}$ of 123 mV and 271 mV respectively (Fig. 4 (b - c). However, no output was observed in the PMMA based NG device at 4 mm cantilever deflection (Fig. 4(a)). The deflection of 7 mm (0.65% strain) generated $V_{pp}$ of 85 mV only (Fig. 4(d)). Al$_2$O$_3$ based NG device generated 220% more compared to PMMA based NG with almost half the cantilever deflection.
Conclusions
From the above study, it can be concluded that the dielectric matrix in the NG device plays significant role in the device performance as predicted by theoretical studies. The performance of the device have been studied under manual bending as well as automatic bending using an Arduino-controlled stepper motor setup. Out of the three materials tested in the present work, Al₂O₃ based NG generated 135% more potential compared with those based on PMMA. These results confirmed the predicted effect of using more rigid dielectrics as matrix material for the NGs. The detailed analysis is ongoing on these samples on several aspects: (I) to better quantify and to increase the controlled applied strain and (II) to understand the origin of the oscillation on the output potential. Further work will include the estimation of the total generated power using variable resistive loads.

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