A novel piezoelectric ZnO nanogenerator on flexible metal alloy substrate

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***Abstract*—In this paper, we report a novel piezoelectric ZnO nanogenerator on flexible metal alloy substrate (Phynox alloy) for energy harvesting and sensing applications. The vertically aligned ZnO nanowires are sandwiched between Au electrodes. The aligned growth of ZnO nanowires have been successfully synthesized on Au coated metal alloy substrate by hydrothermal method at low temperature (95±1 °C). The as-synthesized vertically aligned ZnO nanowires were characterized using FE-SEM. Further, PMMA is spin coated over the aligned ZnO nanowires for the purpose of their long term stability. The fabricated nanogenerator is of size 30mm x 6mm. From energy harvesting point of view, the response of the nanogenerator due to finger tip impacts ranges from 0.9 V to 1.4V. Also for sensing application, the maximum output voltage response of the nanogenerator is found to be 2.86V due to stainless steel (SS) ball impact and 0.92 V due to plastic ball impact.**

Keywords: ZnO nanowires, nanogenerator, piezoelectricity

I. INTRODUCTION

Powering nano scale devices is the main challenge in the present day nanotechnology world. The potential power sources for nano devices are vibrational energy, mechanical energy, solar energy, hydraulic energy [1]. Moreover the miniaturization of portable electronic devices is very difficult without batteries. The problems associated with the use of batteries include limitation in the size of the device and frequent recharging process. However in place of batteries, if we adopt nanogenerators, mechanical energy is always available in and around us for powering these nano devices. Nanogenerator is a device which converts random mechanical energy into electrical energy to drive nano scale level devices.

Zinc Oxide (ZnO) is one of the promising potential materials for energy harvesting and sensing applications. ZnO is a semiconducting piezoelectric material having energy band gap of 3.37 eV and large excitation binding energy of 60 meV at room temperature [2]. It is a prominent material because of its structural, semiconducting, mechanical and piezoelectric properties. The advantages of ZnO are: it exhibits both semiconducting and piezoelectric properties, environmental friendly, biocompatible, growth occurs on large variety of substrate materials [1, 3]. The applications of ZnO are plenty and it is used in electronic, electrochemical, electromechanical devices such as light–emitting diodes, field emission devices, micro/nano sensors, solar cells, nanopiezotronics and piezoelectric nanogenerators [2].

Various techniques are used for the synthesis of ZnO nanostructures such as physical vapour deposition (PVD), chemical methods, molecular beam epitaxy (MBE), pulsed laser deposition (PLD). Among these techniques, solution based chemical methods are more advantageous because they are simple, convenient, low cost, less hazardous, compatible for flexible substrates, capable of large scaling up and growth occurs at relatively low temperatures [2]. The use of these nanogenerators for sensing applications further eliminate the requirement of batteries and make them single independent system. Hence, in the present work, we have reported piezoelectric ZnO nanowires synthesized on flexible alloy substrate as independent energy harvesting and sensing system. Various literature reports on different kinds of flexible substrate materials (Kapton [4], Polythylene naphthalate (PEN) [5], PS (polyester) [6]) for the fabrication

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of nanogenerators. To the best of our knowledge, there are no reports on flexible alloy substrates for the nanogenerator fabrication. We are introducing for the first time, a flexible alloy substrate for the fabrication of nanogenerators.

II. EXPERIMENTAL

A. Deposition of ZnO seedlayer on alloy substrate

Phynox metal alloy substrate was properly cleaned with standard cleaning procedure. Cr/Au (20/50 nm) layer was deposited by RF magnetron sputtering over the substrate for the purpose of bottom electrode contact. Later ZnO thin film (100 nm) as a seed layer was deposited over the Cr/Au layer for the growth of ZnO nanowires.

B. Synthesis of ZnO nanowires

Chemical agents used for this method are Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and Hexamethylenetetramine ((HMTA) $(CH2)_6 N_4$)). The $Zn(NO_3)_2$ salt provides Zn^{2+} ions for the growth of ZnO nanowires. The HMTA during the ZnO nanowires growth would slowly hydrolyze in water solution and gradually produce OH^- ions.The growth process of ZnO nanowires can be controlled by the following chemical reactions [2,7].

$$(CH_2)_6N_4 + 6\ H_2O \longleftrightarrow 4\ NH_3 + 6HCHO$$
$$NH_3 + H_2O \longleftrightarrow NH_3.H_2O$$
$$NH_3.H_2O \longleftrightarrow NH^{4+} + OH^-$$
$$Zn^{2+} + 2OH^- \longleftrightarrow Zn\ (OH)_2$$
$$Zn\ (OH_2) \longleftrightarrow ZnO + H_2O$$

An equi-molar concentration (25 mM) of $Zn(NO_3)_2$ and HMTA was used for the growth of nanowires. The substrate was kept upside down over the surface of solution and due to surface tension it was standing on the solution. The growth process was carried out in mechanical hot air oven at low temperature (95±1 °C) for the growth time of 5 hrs. The synthesized nanowires on substrate were cooled at room temperature and cleaned with DI water. Further, the cleaned sample was dried at room temperature

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C. Fabrication of nanogenerator

In order to fabricate the nanogenerator, 3-4 µm thick PMMA was spin coated over as-synthesized ZnO nanowires. Spin coating was done for the purpose of long term stability of nanowires and mechanical robustness of the complete structure. Also, it helps to prevent possible short-circuiting between the bottom and the top electrodes [3]. Later, oxygen plasma etching was done to etch out the fine thickness of PMMA coating for the purpose of top electrode contact. The depth of etching was 1 - 1.5 µm and the etch time was 90 sec. Now the tips of nanowires are clean and are ready to use for the top electrode contact purpose. The top electrode of Cr/Au (20/100 nm) was deposited on to the kapton film and was kept upside down over the tips of the nanowires for contact. The schematic diagram and the actual photograph of the fabricated nanogenerator are shown in Fig. 1. and Fig. 2. respectively.

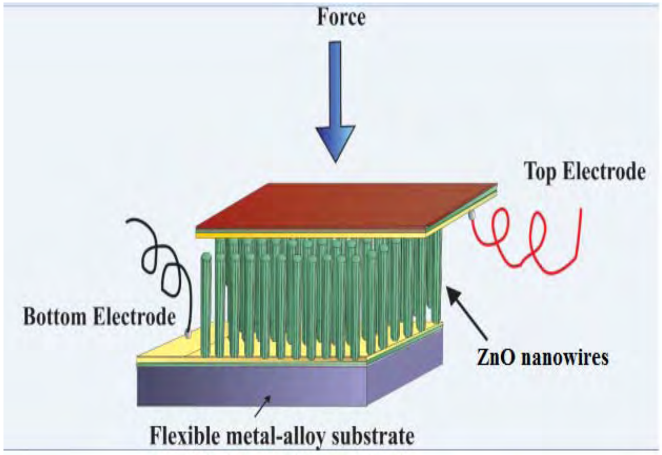

Figure. 1: Schematic diagram of nanogenerator

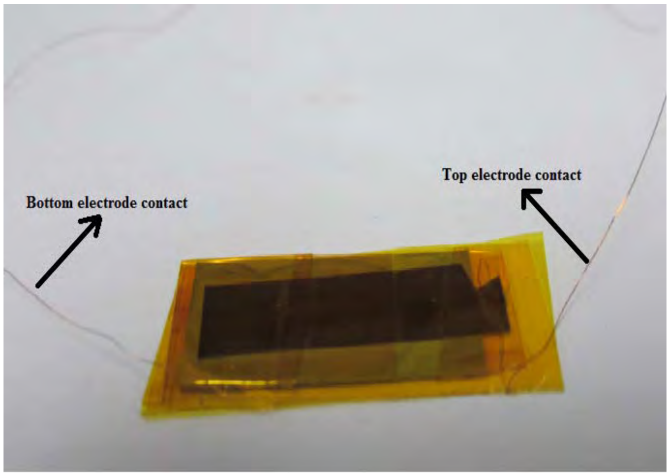

Figure. 2: Fabricated nanogenerator on flexible metal alloy substrate

III. RESULTS AND DISCUSSIONS

A. Characterization of ZnO nanowires

The morphology of ZnO nanowires grown on alloy substrate was observed using field emission scanning electron microscopy (FE-SEM (Carl Zeiss), ULTRA 55). Fig. 3a shows the top view of the vertically grown ZnO nanowires. Fig. 3b shows the cross sectional view of grown nanowires. The average length and diameter of the synthesized vertical nanowires are found to be 3 µm and 170 nm respectively.

Most of the ZnO nanowires are vertically aligned as well as highly dense over the entire surface of the alloy substrate.

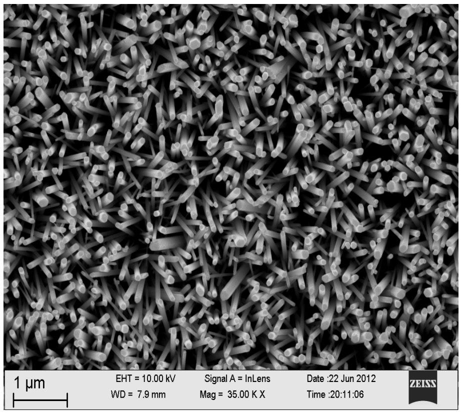

Figure.3: Top view of vertically grown ZnO nanowires

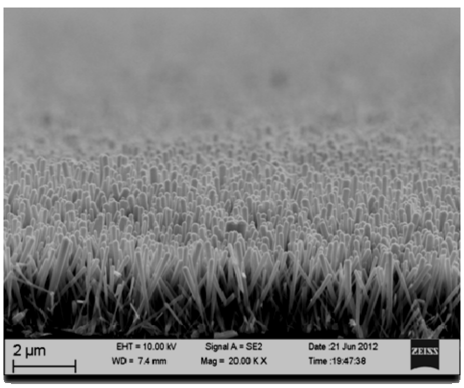

Figure.4: Cross sectional view of vertically grown ZnO nanowires

B. Performance of fabricated nanogenerator

The fabricated nanogenerator was directly connected to CRO (Yokogawa, DLM 2022). In order to see the suitability for energy harvesting application, dynamic force was applied on the fabricated nanogenerator using finger tip impacts. The typical response obtained from the nanogenerator due to the dynamic force of human finger impact is given in Fig. 5. The maximum output voltage obtained is 0.93V.

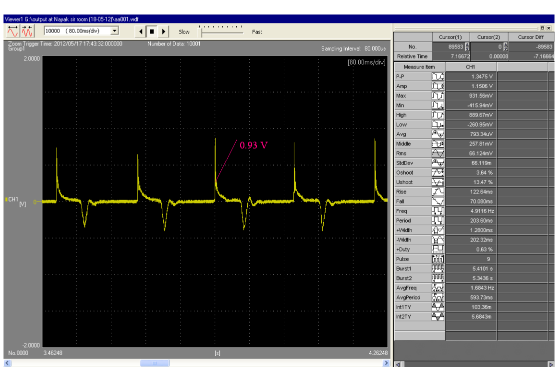

Figure 5: Response of the nanogenerator due to finger tip impacts.

For the sensing application point of view, stainless steel and plastic balls of equal diameter were used. The balls were dropped from four different random heights (8.5, 11, 16 and 23 cms) on to the nanogenerator. When the balls were dropped from the maximum height of 23 cms, the response of the nanogenerator for stainless steel ball was found to be 2.86 V (Fig. 6) and 0.92 V for plastic ball (Fig. 7). Fig .8 shows the relationship between output voltage and the ball drop height for both the balls. The output voltage generated due to stainless steel ball impact is almost 3 times greater than the output voltage generated due to plastic ball impact.

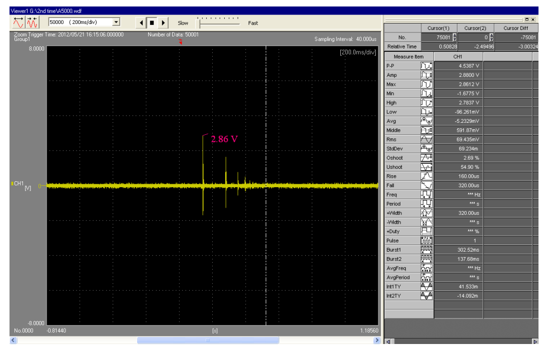

Figure .6: Response of the nanogenerator for stainless steel ball impact.

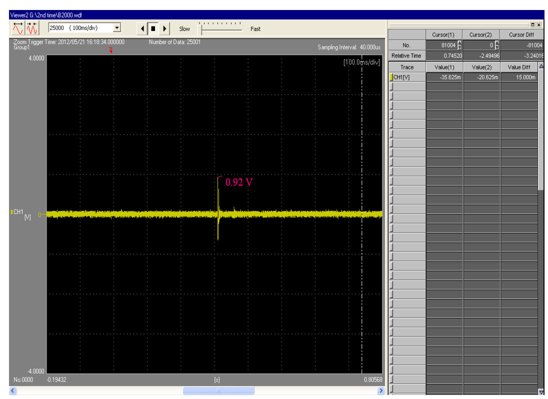

Figure. 7: Response of the nanogenerator for plastic ball impact.

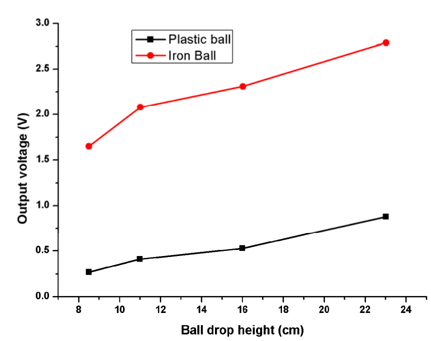

Figure 8: Output of nanogenerator due to SS ball and plastic ball dropped from different heights.

IV. CONCLUSION

We have reported on the fabrication of piezoelectric ZnO nanogenerators on flexible metal alloy substrate. The vertically aligned ZnO nanowires were synthesized by hydrothermal method and were characterized using FE-SEM. The response of the nanogenerator was studied due to human finger tip impacts as well as ball drop impacts. Results obtained indicate the potential application possibilities of the nanogenerator for energy harvesting and sensing applications.

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