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Investigations on the influence of substrate temperature in developing enhanced response ZnO nano generators on flexible polyimide using spray pyrolysis technique

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ABSTRACT

Zinc oxide was deposited on flexible substrate over a large area to demonstrate nano charge generation capability using spray pyrolysis technique for the first time. The influence of growth substrate temperature towards piezoelectric property has been investigated. It is observed that the samples deposited at 300 °C showed best output peak voltage of 1.91 V. A direct relation between piezoelectric output and intrinsic defects from photoluminescence spectra is observed. A load v/s voltage output along with capacitance-voltage analysis is performed to investigate the effect of loading on the polarization of ZnO. The enhanced piezoelectric response of ZnO compared to previous reports is due to very low intrinsic defects, smooth morphology and pre-strained behavior of substrate. The curved profile nano generator harvests electricity by d_{31} mode. ANSYS stress-strain simulation of arched shape film is performed, in which large stress due to large strain even at very low load is observed.

1. Introduction

The need for flexible devices is quite visible on the recent developments in the field of electronics and semiconductor industries [1–12]. Flexible piezoelectric nano generators (F-PENG) are one of the upcoming domains under the category of flexible devices. Flexible nano generators have wider applications over the nano generators developed on the rigid substrate owing to their capability of withstanding intensive vibrations, deflections and also their low damping coefficient, which enhances the coupling efficiency. Wide varieties of piezoelectric materials have been reported such as aluminum nitride, zinc oxide (ZnO), polyvinylidene fluoride, lead zirconia titanate etc [12,13]. However, it is observed that ZnO is considered as one of the promising materials owing to its property of generating different kind of nano-structures/composite, versatile multi-functional behavior, high stability, environment friendly applications, higher order of reaction control, high piezoelectric coefficient and ability to get deposited on the flexible substrates [14–22]. Researchers have tried to deposit ZnO nano structures on the polyimide substrate using RF sputtering, PLD etc. [23,24]. However, depositing ZnO on a flexible substrate in a large area at a lower cost remains as a challenging issue. In the present work, an attempt has been made for the first time to deposit ZnO using a low-cost spray pyrolysis technique on flexible polyimide sheet, which has not been reported elsewhere. Previous reports on spray pyrolysis technique using ZnO have discussed successful applications in photocatalytic, gas sensors, temperature sensor, transistors etc [25–28]. ZnO based flexible nano generator using spray pyrolysis is being discussed for the very first time in this paper. Spray pyrolysis technique has the capability to deposit ZnO nano structures on 200 × 200 mm in very short time at a very low cost which makes it as a good alternate process for the production of practical devices. Spray pyrolysis gives many advantages over other techniques like pulsed laser deposition and sputtering. Neither it requires high-quality targets nor does it have a need of vacuum, which is a big advantage to scale-up for industrial requirements. Moreover, the process can be done using moderate range of temperature and it offers an exceptionally simple and easy way to dope thin films. In this paper, the influence of growth substrate temperature towards the demonstration of piezoelectric behavior has been discussed in detail.

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2. Experimental details

The precursor solution for spray pyrolysis has been prepared by taking 0.1 M solution of anhydrous zinc acetate (Sigma-Aldrich), methanol (Sigma-Aldrich) and deionized (DI) water (3:1). Glycol acetic acid (Renkem) was added to decrease the pH of the solution to 4. The solution was stirred at high rpm using magnetic stirrer at room temperature. It was kept for some time for the settling of undissolved particles which was again followed by stirring for 24 h. The beakers were tightly sealed. Later, the solution was transferred to 50 ml solution holder which was used for the spraying. Fresh nylon tubes were thoroughly cleaned with acetone and DI water to avoid any sort of contamination. Polyimide films (thickness 50 μm) was thoroughly sonicated for 5 min each using DI water, acetone and isopropyl alcohol. Fig. 1 shows the schematic diagram spray pyrolysis setup used for the deposition. The substrate was coated with 60–70 nm aluminum (Sigma-Aldrich) using physical vapor deposition system prior to spray deposition. Experimental parameters used are mentioned in Table 1.

The deposition reaction kinetics and piezoelectric output were studied at three different substrate temperatures viz. 300, 350 and 400 °C. The reaction in spray pyrolysis takes place in the way as shown below

$$Zn(CH_3COOH)_2 + H_2O + CH_3OH \longrightarrow Zn^{2+}(aq.) + OH^{-}(aq.) + CH_4\,(g) + 2CH_3COOH\,(aq) \quad (1)$$

$$Zn^{2+}(aq.) + OH^{-}(aq.) + CH_4\,(g) + 2CH_3COOH\,(aq) \xrightarrow{\blacktriangle} Zn(OH) \quad (2)$$

$$Zn(OH)_2 \xrightarrow{\blacktriangle} ZnO(s) + H_2O(g) \quad (3)$$

The crystallinity and phase information were examined by powder XRD (Rigaku Smart Lab system) with Cu-Kα radiation operating at 40 kV and 40 mA and with wavelength (λ) = 1.5418 Å. The morphology, structures and energy dispersive x-ray (EDAX) of the as-prepared ZnO nanograins were further studied by field emissionscanning electron microscope (FE-SEM, Carl Zeiss Sigma series supra-55). The CV measurement was carried out using Hioko LCR meter. To measure the voltage change in the thin film, voltmeter feature incorporated in the source measurement unit (Keithley 2612) was used. The photoluminescence (PL) spectrometer (Dongwoo Optron DM 500i) having an excitation source consisting of a continuous wave He-Cd laser (excitation wavelength 325 nm, PMT detector) was used to measure the PL emission at room temperature. Standard weights were used for the weight vs voltage analysis.

Table 1
Reaction parameters taken during deposition.

Parameters	Values
Carrier Gas	Air
Air pressure	1 Bar
Temperatures varied	300, 350, 400 °C
Flow rate	3–5 ml/min
Solution volume	50 ml each
Nozzle Substrate Height	120 mm

3. Results and discussion

3.1. Morphology analysis

Fig. 2 shows the FE-SEM micrographs and EDAX results of synthesized samples. The variation in morphology due to temperature is strikingly visible. Image J analysis is performed and it is observed that the average grain size increased with increasing the temperature. At 300 °C,the morphology of deposited film seemed to be like a larva shaped grains as shown in Fig. 2(a). Grain size continued to increase with the increase in temperature which agrees with previously reported results [29,30]. Fig. 2(b) shows FE-SEM image of the film grown at 350 °C. In this film cracks and porosity is observed whereas, in the film grown at 400 °C the surface morphology is rough but uniform with elongated grains. High temperature favors rapid growth of crystallites due to

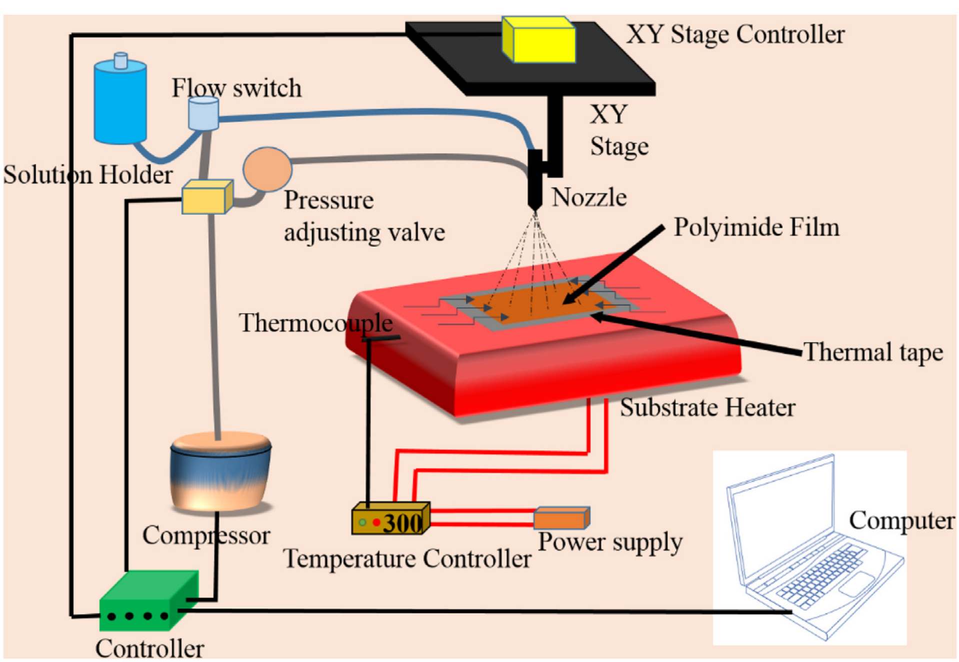

Fig. 1. Spray Pyrolysis setup.