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Evaluation of Transverse Piezoelectric Coefficient of ZnO Thin Films Deposited on Different Flexible Substrates: A Comparative Study on the Vibration Sensing Performance

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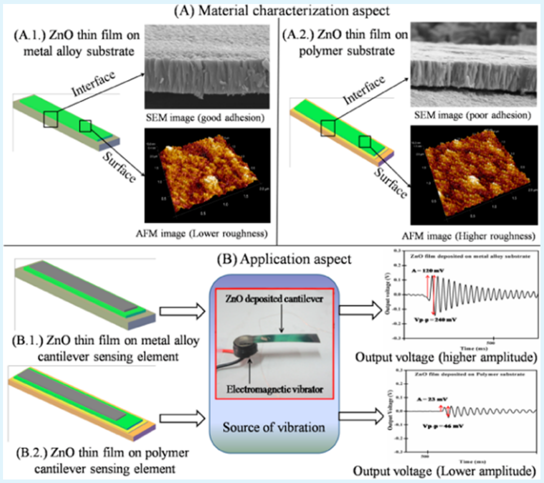
Supporting Information

ABSTRACT: We report on the systematic comparative study of highly *c*-axis oriented and crystalline piezoelectric ZnO thin films deposited on four different flexible substrates for vibration sensing application. The flexible substrates employed for present experimental study were namely a metal alloy (Phynox), metal (aluminum), polyimide (Kapton), and polyester (Mylar). ZnO thin films were deposited by an RF reactive magnetron sputtering technique. ZnO thin films of similar thicknesses of 700 ± 30 nm were deposited on four different flexible substrates to have proper comparative studies. The crystallinity, surface morphology, chemical composition, and roughness of ZnO thin films were evaluated by respective material characterization techniques. The transverse piezoelectric coefficient (d_{31}) value for assessing the piezoelectric property of ZnO thin films on different flexible substrates was measured by a four-point bending method. ZnO thin films deposited on Phynox alloy substrate showed relatively better material characterization results and a higher piezoelectric d_{31} coefficient value as compared to ZnO films on metal and polymer substrates. In order to experimentally verify the above observations, vibration sensing studies were performed. As expected, the ZnO thin film deposited on Phynox alloy substrate showed better vibration sensing performance. It has generated the highest peak to peak output voltage amplitude of 256 mV as compared to that of aluminum (224 mV), Kapton (144 mV), and Mylar (46 mV). Therefore, metal alloy flexible substrate proves to be a more suitable, advantageous, and versatile choice for integrating ZnO thin films as compared to metal and polymer flexible substrates for vibration sensing applications. The present experimental study is extremely important and helpful for the selection of a suitable flexible substrate for various applications in the field of sensor and actuator technology.



KEYWORDS: *flexible substrate, piezoelectric coefficient, sputtering, vibration sensing, ZnO thin film*

1. INTRODUCTION

The substrate plays a fundamental role in determining the structural, physical, optical, and mechanical properties of deposited thin films and the extent of their applications. The selection of a suitable substrate is of immense importance because it significantly affects the surface morphology, and other characteristic properties of the deposited thin film. Hence, the substrate material acts as a foundation stone for thin film deposition. The deposition of thin films on flexible substrates offers several advantages, as compared to films deposited on other conventionally and generally used stiff substrates, such as borosilicate and Pyrex glass, silicon, and sapphire substrates. The remarkable advantages of flexible substrates over other commonly employed substrates are that they are light-weight, portable, wearable, and economical and possesses greater impact resistance and robustness.[1] The integration of thin films on flexible substrates provides a sensing and actuation functionality element to microsystems, which is a much sought after feature in biomedical, structural health monitoring, and energy harvesting applications. These attributes of flexible substrates makes it an attractive choice as compared to other conventionally used stiff substrate materials.[2]

Piezoelectric thin films deposited on flexible substrates are desirable for numerous applications in various areas. Recently, quite a few investigators and research groups have demonstrated the application possibilities of numerous piezoelectric thin films deposited on different flexible substrates in several areas. Applications in fields like flexible and printed electronics,[3] organic electronics,[4] thin film transistors (TFTs),[5] paper batteries,[6] antibacterial clothes for biomedical applications,[7] smart skin,[8] dye synthesized solar cells (DSSC),[9] and sensor

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and actuator technology[10] have been demonstrated. Therefore, integrating piezoelectric thin films on to flexible substrates opens up several exciting possibilities in various fields. It is the requirement of the present day technology, to explore the suitability of new flexible substrates leading towards the successful development of handy, cost-effective, large area, robust, and high performance functional microsystems. In general, the available flexible substrates can be broadly categorized into two types: metal/metal alloy type and polymer type. To date, numerous flexible substrates have been used for thin film deposition, but none of the reported literature works systematically addresses the comparative study on properties of piezoelectric thin films deposited on different types of flexible substrates and their application aspect. Therefore, it is difficult to find appropriate and comprehensive literature in this regard. Our experimental efforts presented in this paper are a step forward in this regard, and it will definitely bridge the previously existing gaps present in this field.

In recent years, ZnO (zinc oxide) thin films have captivated greater attention and are a promising candidate with their application possibilities in a wide spectrum of areas. ZnO thin films exhibit exceptional piezoelectric, mechanical, structural, and optical properties.[11] It is a compositionally simple binary oxide material, which can be deposited on a wide variety of substrate materials.[12] The stoichiometry, texture, morphology, and other structural properties can be tailored with ease depending upon the intended application.[13] When compared with PVDF (polyvinylidene fluoride) and PZT (lead zirconate titanate) films, ZnO thin film does not require any thermal-electric poling.[14] ZnO thin film possesses higher values of piezoelectric coupling coefficient as compared to that of AlN (aluminum nitride) thin film.[15] As a result, in view of the above mentioned points, ZnO thin film was selected as a suitable candidate for the present experimental study. The piezoelectric constants of ZnO thin films are smaller than that of PZT and PVDF films, but it possesses several effective functionalities such as large mechanical deflections[16] and the potential to tune the Fermi surfaces at metal contacts;[16] it is also a bio-safe and biocompatible material.[17] The evaluation of transverse piezoelectric coefficient (d_{31}) value of ZnO thin films is of immense importance, in order to assess their suitability in sensing and actuation applications. Previously, piezoelectric ZnO thin films have been employed for vibration sensing applications.[18] Therefore, in the present experimental work, we have conducted a comparative study on the d_{31} coefficient value of piezoelectric ZnO thin films deposited on four different types of flexible substrates for vibration sensing.

In the present paper, we report on the comparative study of the structural and morphological properties of ZnO thin films deposited on four different flexible substrates. The substrates chosen for the present experimental study includes a metal alloy (Phynox), metal (aluminum), polyimide (Kapton), and polyester (Mylar). The four-point bending method was used for the measurement of piezoelectric d_{31} coefficient value of ZnO thin films. A suitable in-house developed experimental set-up, for evaluating the vibration sensing performance of ZnO thin films, is discussed. The material characterization studies of ZnO thin films were performed by XRD (X-ray diffraction), FESEM (field emission scanning electron microscopy), EDAX (energy dispersive X-ray diffraction), and AFM (atomic force microscopy) techniques.

2. EXPERIMENTAL SECTION

2.1. Flexible Substrates Used in the Present Experimental Study. The important physical and mechanical properties of four different flexible substrates employed in the present experimental study are shown in Table 1. The brief description about substrate materials is given below:

Table 1. Important Physical and Mechanical Properties of Flexible Substrates Employed for the Present Experimental Study

		flexible substrates			
sr. no.	properties	Phynox	aluminum	Kapton	Mylar
1	thermal expansion coefficient (ppm/°C)	12	16	32	65
2	ultimate tensile strength (UTS) (N mm^{-2})	2600	310	230	200
3	modulus of elasticity (N mm^{-2})	2×10^5	69×10^3	2500	3100
4	yield strength (N mm^{-2})	2200	276	68	103
5	density (g cm^{-3})	8.30	2.70	1.42	1.39

(1) The first one is a Phynox alloy substrate, which is basically a flexible, austenitic alloy of cobalt, chromium, and nickel. Phynox alloy strips (thickness 40 μm) were procured from Lamineries, MATTHEY SA Company (Switzerland). It possesses good physical, chemical, and mechanical properties. Additionally, it is a good thermal and electrical conductor. Its biocompatibility adds to its application as an electrode material in pacemakers as well as in implant components for biomedical applications. Furthermore, several industries such as aerospace, telecommunication, and process control plants also employ Phynox alloy in relays and switches and as membranes for pressure sensors.

Recently, our research group has used Phynox alloy in several diverse applications. The applications of piezoelectric ZnO thin films deposited on Phynox alloy as a flow sensor,[19] impact sensor for nondestructive material discrimination,[20] thin film sensor array (TFSA),[10] and micro-actuation[21] have been demonstrated. (**Please see Supporting Information Section I. Selection of Phynox alloy over commonly used metal alloy flexible substrate (SS-304L) for vibration sensing studies**).

(2) The second one is an aluminum metal substrate. Strips of aluminum metal (thickness 40 μm) were also procured from Lamineries, MATTHEY SA Company (Switzerland). It is one of the commonly employed flexible substrate for thin film deposition. As aluminum is electrically conductive hence, it acts well as an electrode material. Additionally, it is used as a substrate material for metal core copper clad laminates used in high brightness LEDs. It is also used as a heat sink for electronic appliances. It is a biocompatible and nontoxic material; hence, it finds application possibilities in the biomedical field.

(3) The third one is Kapton, which is basically a polyimide film. Kapton was procured from DuPont Teijin Films (USA). It possesses a unique combination of good physical, electrical, and mechanical properties. Therefore, it opens new design and application possibilities in various fields. It is used in a variety of electrical and electronic insulation applications, as a substrate for flexible printed circuits, and in pressure-sensitive tapes.

(4) The fourth one is Mylar, which is basically a polyester film. Mylar was also procured from DuPont Teijin Films (USA). Its higher thermal expansion coefficient value makes its application prospects limited. Therefore, it is generally used in situations where the physical requirements are not as demanding.

2.2. Deposition of Thin Films and Fabrication of Cantilever Element for Vibration Sensing Studies. The flexible substrates under consideration were properly cleaned with the standard cleaning procedure. The substrates were first cleaned by ultrasonicating them in a soap solution, followed by an organic solvent i.e. iso-propyl alcohol (IPA). Figure 1a and b shows thin film deposition steps for the

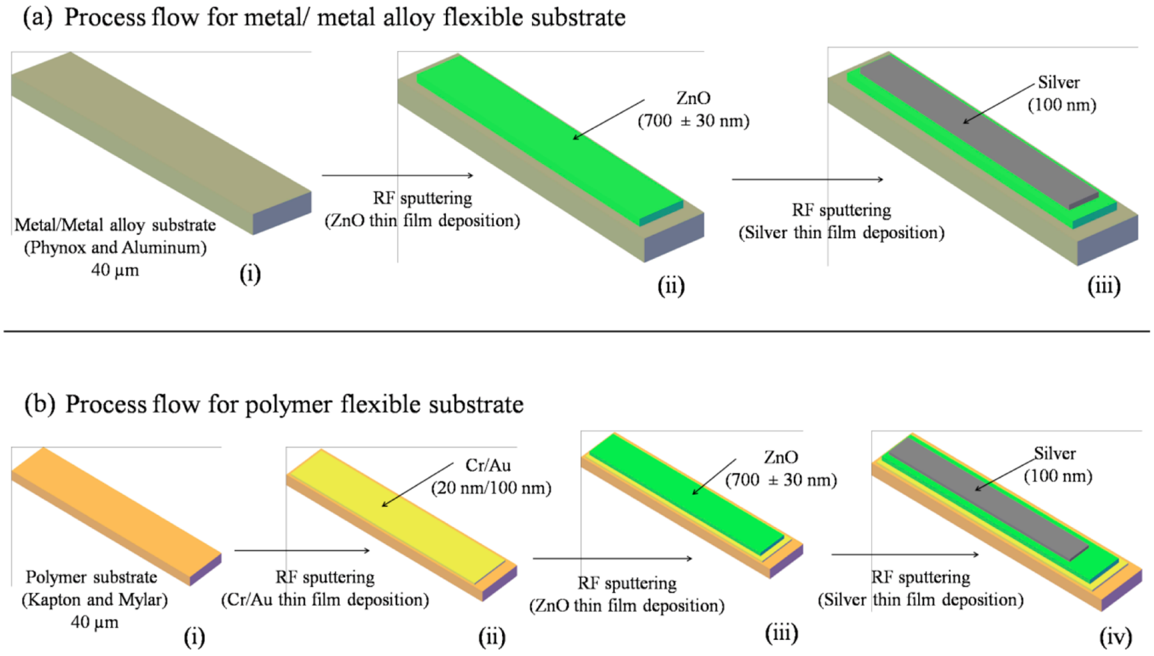


Figure 1. Thin film deposition steps for the fabrication of cantilever sensing element for vibration sensing studies [(a) metal/metal alloy substrates and (b) polymer substrates].

fabrication of the cantilever element for comparing the vibration sensing performance. Initially, thoroughly cleaned polymer substrates (Kapton and Mylar) were loaded into a multitarget thin film deposition chamber. A bottom adhesion layer of chromium thin film (thickness ~20 nm), followed by a seed layer of gold thin film (thickness ~100 nm), was deposited by RF magnetron sputtering. Both thin films (Cr and Au) were deposited without breaking the vacuum conditions. The deposition of gold thin film on polymer substrates serves two purposes. First, in the case of sensing applications, wherein an MIM (metal insulator metal) structure is required, the gold thin film serves as a conducting bottom metallic electrode. Secondly, gold film serves as a seed layer, as it is known to enhance the *c*-axis orientation of ZnO thin film.[22] Furthermore, the deposition of the seed layer also helps in the surface modification by greatly reducing the surface roughness of native Kapton and Mylar substrates.

In the second step, the metal alloy (Phynox) and metal (aluminum) substrate along with the gold thin film coated polymer substrates were loaded into a single target thin film deposition chamber for ZnO thin film deposition. The target employed for deposition was a stoichiometric ZnO circular target with purity of 99.99% (VIN Karola instruments, Norcross, USA). In our earlier work, we have optimized sputtering process parameters for the deposition of good quality piezoelectric ZnO thin film.[19] High quality piezoelectric ZnO thin films (thickness 700 ± 30 nm) were deposited on four flexible substrates. In the present experimental study, a little modification was done with the substrate temperature alone as compared to the earlier work. This was done in order to allow the worthy comparison of deposited ZnO thin films on four different flexible substrates. The substrate temperature was kept at 100 °C during the deposition process, as the presently employed polymer substrates (Kapton and Mylar) find it difficult to withstand higher temperatures.

In the final step, a silver thin film of thickness ~100 nm was deposited as a top electrode by RF magnetron sputtering on all four ZnO thin film deposited flexible substrates. This was done in order to complete the MIM structure for vibration sensing studies. The dimensions of the fabricated cantilever sensing element were, length 50 mm, width 5 mm, and thickness 40 μm. In the last step, double enameled thin copper wires of diameter 0.07 mm were attached to the top and bottom electrodes by silver epoxy for the electrical contact purpose.

On comparing the process flow (see Figure 1a and b), it is clear that, the metal alloy/metal substrates have one step lesser than the polymer substrates. The Phynox and aluminum itself acts as a bottom electrode layer for electrical contact purposes. As a result, there was no need for Cr/Au deposition on Phynox alloy and aluminum substrate. In the case of polymer substrates (Kapton and Mylar), the gold thin film was required as it serves the purpose of a conducting bottom metallic electrode. (**Please see Supporting Information Section II. Experimental conditions maintained during the deposition of thin films**).

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Analysis. The X-ray diffraction studies were performed by using Bruker D8 Advance X-ray diffractometer. Figure 2a–d shows the X-ray diffraction spectra of as-deposited ZnO thin films on Phynox, aluminum, Kapton,

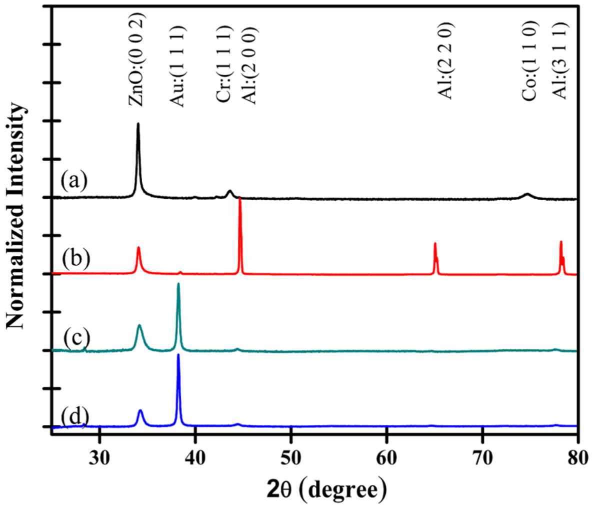


Figure 2. X-ray diffraction spectra of as-deposited ZnO thin films deposited on different flexible substrate [(a) Phynox alloy (black), (b) aluminum (red), (c) Kapton (green), and (d) Mylar (blue)].

and Mylar substrates, respectively. The as-deposited ZnO thin film on all four flexible substrates showed a diffraction peak at about 34.4°, which corresponds to the diffraction from the (002) plane of ZnO. The lattice parameters of these films were found to be a = 3.35 Å and c = 5.22 Å ((International Centre for Diffraction Data), ICDD PDF no. 751533). These values were similar to the values reported for good quality piezoelectric ZnO thin films.[23] The presence of the (002) peak indicates that the as-deposited ZnO thin films have strong *c*-axis orientation perpendicular to the substrate. Higher degree of *c*-axis orientation and (002) preferred crystalline structure improve the piezoelectric properties of the ZnO thin film.[11] The (002) peak with relatively higher intensity was obtained for a ZnO thin film deposited on Phynox and aluminum substrates followed by Kapton and Mylar. Therefore, ZnO films deposited on Phynox and aluminum substrates were relatively more *c*-axis oriented and highly crystalline. The probable reason for higher crystallinity was that, during the process of ZnO thin film deposition on Phynox and aluminum substrate, the incoming adatoms acquire sufficient thermal energy from the substrate surface (kept at 100 °C). As a result, these adatoms will try to loose this energy by relocating themselves to the suitable location, resulting in proper crystallization leading towards better structural development. On the other hand, polymer substrates are not good thermal conductors, so they will not transfer the thermal energy to these incoming adatoms. As a result, the above process of proper relocation of adatoms will not take place, and hence, the films were relatively less crystalline. Moreover, in the case of polymer substrates, the lack of rigidity of the substrate surface further precludes effective crystallization, which is not the case in metal and metal alloy substrates. Furthermore, the lack of crystallinity of ZnO thin films on polymer substrates is specific to deposition conditions during sputtering to some extent. It may be possible to deposit ZnO thin films with better crystallinity and preferred orientation by hydrothermal and solution based growth processes.

It is clearly visible in Figure 2a–d that the FWHM value of the (002) peak shows an increasing trend as we move from Phynox to Mylar (i.e., from a to d). The ZnO thin film deposited on Phynox substrate possesses the lowest FWHM value of the (002) peak followed by aluminum, Kapton, and Mylar. The smaller FWHM value means larger crystallite size resulting in the improved crystal quality of the deposited thin film and hence better piezoelectric properties.[24] The crystallite size of ZnO thin film deposited on Phynox substrate was highest as compared to the crystallite size of films on aluminum, Kapton, and Mylar substrates. Therefore, the as-deposited ZnO thin film with higher crystallinity, preferred *c*-axis orientation, high intensity of the (002) peak, and lower FWHM value was obtained on the metal alloy and metal substrate. On the other hand, polymer substrates yielded comparatively inferior quality ZnO films in terms of crystallinity, preferred orientation, and FWHM value. The additional peaks which are seen in the XRD spectra were originated from the base substrate materials. More information regarding these extra peaks is given in detail in the supporting information (**Please see Supporting Information Section III. Crystallographic characteristics**). EDAX analysis was also performed for ZnO thin films deposited on different flexible substrates (**Please see Supporting Information Section IV. Composition analysis using EDAX**).

3.2. Analysis of Surface Morphology using FESEM.

The microstructure and surface morphology of ZnO thin films were investigated using FESEM (ULTRA 55, Karl Zeiss). Figure 3a–d shows high-magnification cross-sectional images, and Figure 3e–h shows top surface FESEM images of as-deposited ZnO thin films on all four substrates. The as-deposited ZnO thin film on all four substrates possesses homogenous columnar structure perpendicular to the substrate surface, as evident from cross-sectional images (see Figure 3a–d). This is an indication of highly *c*-axis oriented piezoelectric ZnO thin film.[25] The measured thicknesses of ZnO thin films on all four substrates were about 700 ± 30 nm. It is clearly visible in case of Phynox and aluminum substrates (see Figure 3a and b), the as-deposited ZnO thin films were having good adherence with the substrate and were not detached off from the surface. Whereas, in case of Kapton and Mylar substrates layers of as-deposited ZnO thin films were detached off from the substrate surface, indicating poor adhesion with the substrate surface (see Figure 3c and d). The reason for poor adhesion resulting in the detachment of ZnO thin films was the induced stresses in deposited films due to the self bending of polymer substrates. This self-bending of polymer substrates was the result of increased temperature because of incoming

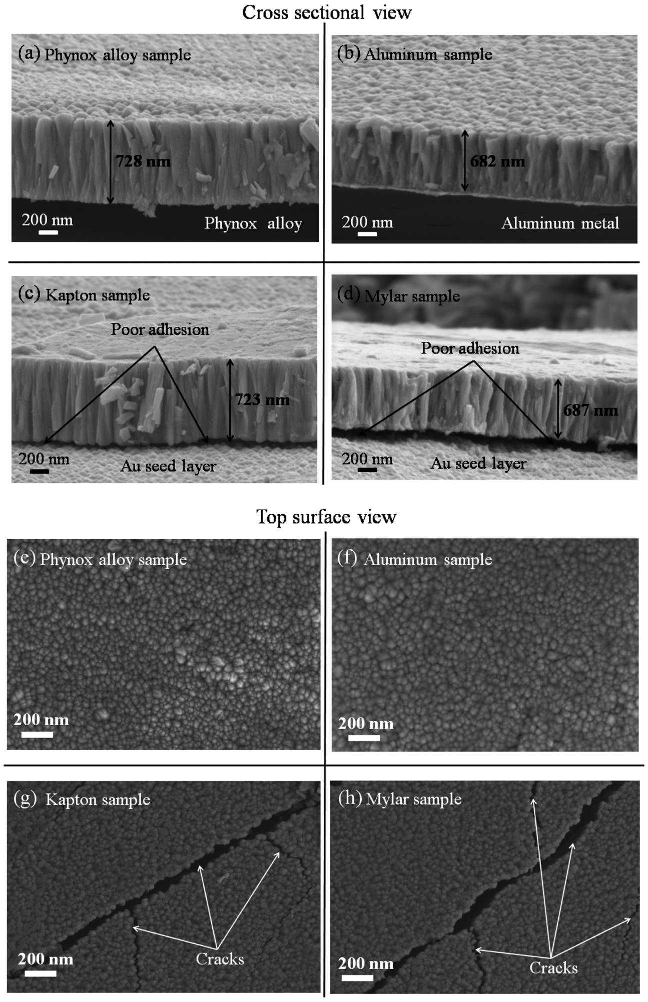
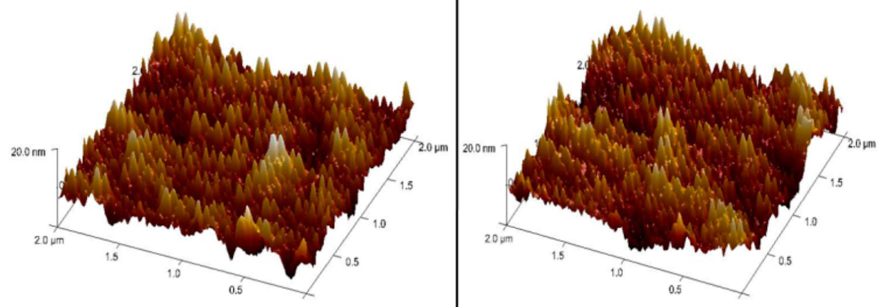


Figure 3. Cross-sectional (a–d) and top surface (e–h) FESEM images of as-deposited ZnO thin films on Phynox, aluminum, Kapton, and Mylar substrate, respectively.

(a) Phynox alloy sample (b) Aluminum sample



(c) Kapton sample (d) Mylar sample

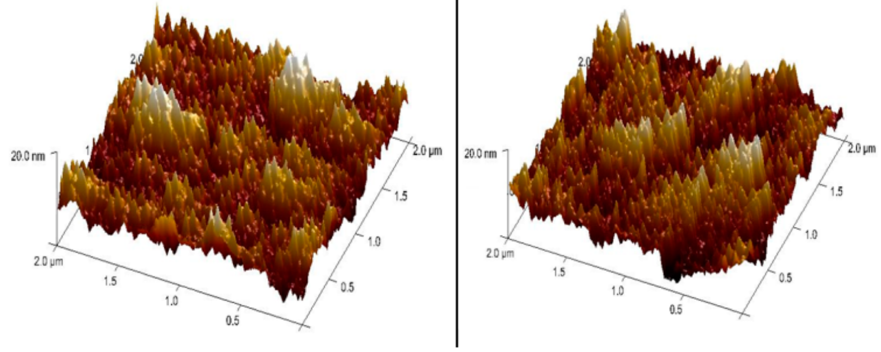


Figure 4. 3D AFM images of as-deposited ZnO thin films on (a) Phynox, (b) aluminum, (c) Kapton, and (d) Mylar substrates.

sputtered atoms. The key factor responsible for induced stresses in ZnO thin films was the highly mismatched thermal expansion coefficient value of polymer substrates with that of the ZnO. Kapton (32 ppm/°C) and Mylar (65 ppm/°C) have relatively very high thermal expansion coefficient value, as compared to that of the ZnO (6.2 ppm/°C),[26] resulting in the huge mismatch of thermal expansion coefficient. This results in the larger expansion of polymer substrate materials relative to the ZnO thin film during the deposition process and, hence, induces stresses in films. Finally, as a result ZnO thin films on Kapton and Mylar substrates started to get detached off from the substrate surface and, hence, have poor adhesion. On the other hand, the thermal expansion coefficient value of Phynox alloy is 12 ppm/°C and that of aluminum is 16 ppm/°C. Hence, ZnO thin films on Phynox and aluminum substrates have comparatively very little mismatch of thermal expansion coefficient. Therefore, the ZnO thin films on Phynox and aluminum substrate showed good adhesion and were not detached from the substrate surface.

In case of top surface FESEM images (see Figure 3e−h), as can be clearly seen in Figure 3e and f, the ZnO thin films deposited on Phynox and aluminum substrate were dense and possessed well oriented, uniform, and closely packed grains of size about 65−75 nm. The ZnO thin film surface on polymer substrates (Kapton and Mylar) was relatively rough, with randomly oriented, non-uniform, and smaller grains. Moreover, in Figure 3g and h, cracks induced in as-deposited ZnO thin films on polymer substrates due to the induced stresses resulting from the mismatch of thermal expansion coefficients are clearly visible. These cracks were not seen in ZnO thin films deposited on Phynox and aluminum substrates (see Figure 3e and f).

3.3. Analysis of Surface Roughness Using AFM. The average rms surface roughness (R_q) values of ZnO thin films was measured using AFM (ESPM 3D AFM, Novascan Technologies, USA) and were analyzed using Nanoscope software. Figure 4a−d shows 3D AFM images of as-deposited ZnO thin films on Phynox, aluminum, Kapton, and Mylar substrate, respectively. The 2 μm × 2 μm squared scan area was taken into consideration for measuring the average rms surface roughness value. The R_q value was measured for a particular ZnO thin film deposited sample from 10 different locations. It is clearly evident from AFM images that there is a difference in the surface roughness of ZnO thin films deposited on different flexible substrates. Table 2 summarizes the measured R_q and standard deviation values of ZnO thin films deposited on different flexible substrates. The surface roughness of ZnO thin film is a dominant factor, which influences the piezoelectric d_{31} coefficient value and, hence, affects the sensing performance of ZnO thin films.[18] The lowest value of R_q of about 4.35 nm was measured for the ZnO thin film deposited on Phynox substrate. The surface of the film was comparatively smooth and free from defects due to the proper microstructural development. The observed smooth surface indicates desirable two dimensional (2D) layer by layer growth mode (Frank−van der Merwe Mode).[27] In case of aluminum substrate the surface roughness value of ZnO thin film was bit increased to about 6.32 nm. The native rough surface of the aluminum substrate has contributed towards this increase. The measured values of

Table 2. Average rms Surface Roughness (R_q) and Standard Deviation Values of ZnO Thin Films Deposited on Four Different Flexible Substrates

sr. no.	sample	R_q (nm)	standard deviation (nm)
1	Phynox alloy	4.35	0.7237
2	aluminum	6.32	0.7523
3	Kapton	12.28	0.6535
4	Mylar	15.28	0.7439

R_q for ZnO thin films on Kapton and Mylar substrate were 12.28 and 15.28 nm, respectively. These values were relatively much higher than the surface roughness values of ZnO thin films deposited on Phynox and aluminum substrate. The above observation of higher surface roughness of ZnO thin films deposited on polymer substrates was mainly attributed to two main reasons. Firstly, polymer substrates were not thermally conductive as a result they have not provided sufficient kinetic energy to incoming adatoms to get diffused on to the proper location. This results in the improper microstructural development and, hence, increases the surface roughness. Secondly, the surface roughness of the native substrates itself was also responsible to some extent. However, the effect of surface roughness of native substrate can easily be overcome by depositing the seed layer of gold thin film and ZnO thin films with higher thicknesses.

3.4. Comparison of Piezoelectric d_{31} Coefficient Value.

In the present experimental study, the piezoelectric d_{31} coefficient value was measured by using four-point bending method (aixACCT four-point bending system, model: aix-4PB). (**Please see Supporting Information Section V. Measurement of transverse piezoelectric coefficient (d_{31}) value**). Figure 5 shows the variation of piezoelectric d_{31} coefficient value of as-deposited ZnO thin films with respect to the type of substrates. The reported value in the bar graph is averaged over five measurement readings performed for a particular ZnO thin film deposited sample. The higher d_{31} coefficient values of about 4.72 and 4.23 pm V^{-1} were obtained on the metal alloy (Phynox) and metal (aluminum) substrates, respectively. The reason for the higher d_{31} coefficient values was the larger grain size of the as-deposited ZnO thin films.[28] Additionally, the deposited films on Phynox and aluminum substrates were highly crystalline and possess lower surface roughness values. The d_{31} coefficient values of ZnO thin films deposited on polymer substrates (Kapton and Mylar) was found to be relatively lower of about 2.72 and 1.23 pm V^{-1}, respectively. The reason for the relatively lower d_{31} coefficient values was attributed to the fact that deposited films have smaller grain size.[28] Moreover, films were comparatively less crystalline, with higher surface roughness values, as compared to films deposited on Phynox and aluminum substrates. The higher the d_{31} piezoelectric coefficient value, the better the sensing performance of the ZnO thin film.[18] Therefore, metal alloy (Phynox) substrate proves to be a preferable choice over the metal (aluminum) and other two polymer (Kapton and Mylar) substrates for sensing and actuation applications.

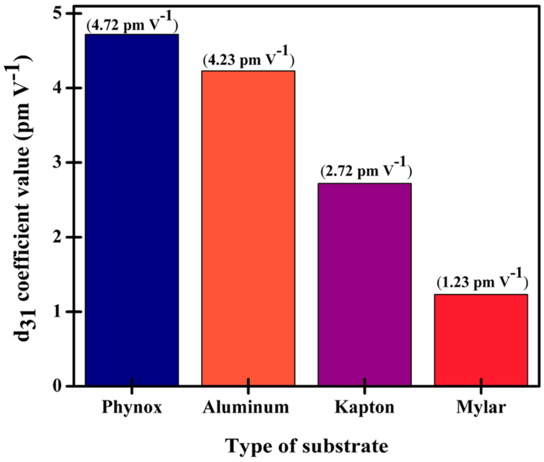


Figure 5. Variation of piezoelectric d_{31} coefficient value (pm V^{-1}) with respect to the type of substrate [Phynox alloy substrate (blue), aluminum substrate (orange), Kapton substrate (purple), and Mylar substrate (pink)].

3.5. Comparative Study on the Vibration Sensing Performance.

3.5.1. Experimental Setup. In order to experimentally compare the piezoelectric property of as-deposited ZnO thin films on four different flexible substrates, a vibration sensing study was performed. Figure 6 shows the actual photograph of the in-house developed experimental test set-up, employed for vibration sensing studies. It consists of a function generator (Agilent 33220A), digital storage oscilloscope (Yokogawa DLM-2022), and a cantilever sensing element mounted on the electromagnetic vibrator. The magnified view (see Figure 6 inset) gives a comprehensible picture of the cantilever element mounted on to the electromagnetic vibrator. The cantilever sensing elements were firmly mounted with a carbon tape on the electromagnetic vibrator. In order to have a worthy comparison of the vibration sensing performance, the electromagnetic vibrator was operated at a voltage of 10 V p−p for all four cantilever samples. This ensures exactly same magnitude of vibrations for all four ZnO thin film deposited cantilever samples.

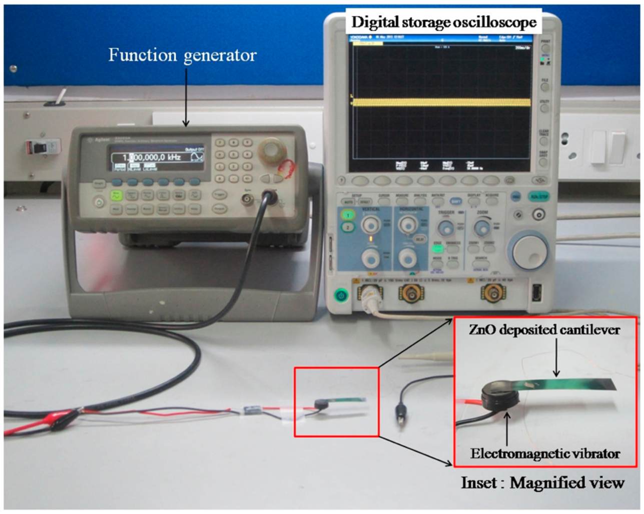


Figure 6. Photograph of in-house developed experimental setup employed for the evaluation of vibration sensing performance of ZnO thin films deposited on different flexible substrates. (inset) Magnified view of the cantilever sensing element mounted on to the electromagnetic vibrator.

The four substrates under consideration had different values of elastic modulus, so it becomes necessary to vibrate them at their fundamental natural frequency. The system is considered to be a continuous system in which the beam mass is considered to be distributed along with the stiffness of cantilever element. The fundamental natural frequency is given by

$$f_n = \frac{\alpha_n^2}{2\pi}\sqrt{\frac{EI}{mL^4}} \tag{1}$$

Where, f_n is the natural frequency, n is the order of mode of vibration, E is the modulus of elasticity of cantilever element, I is the moment of inertia, m is the mass per unit length, L is the length of cantilever element, and α_n is a constant whose value

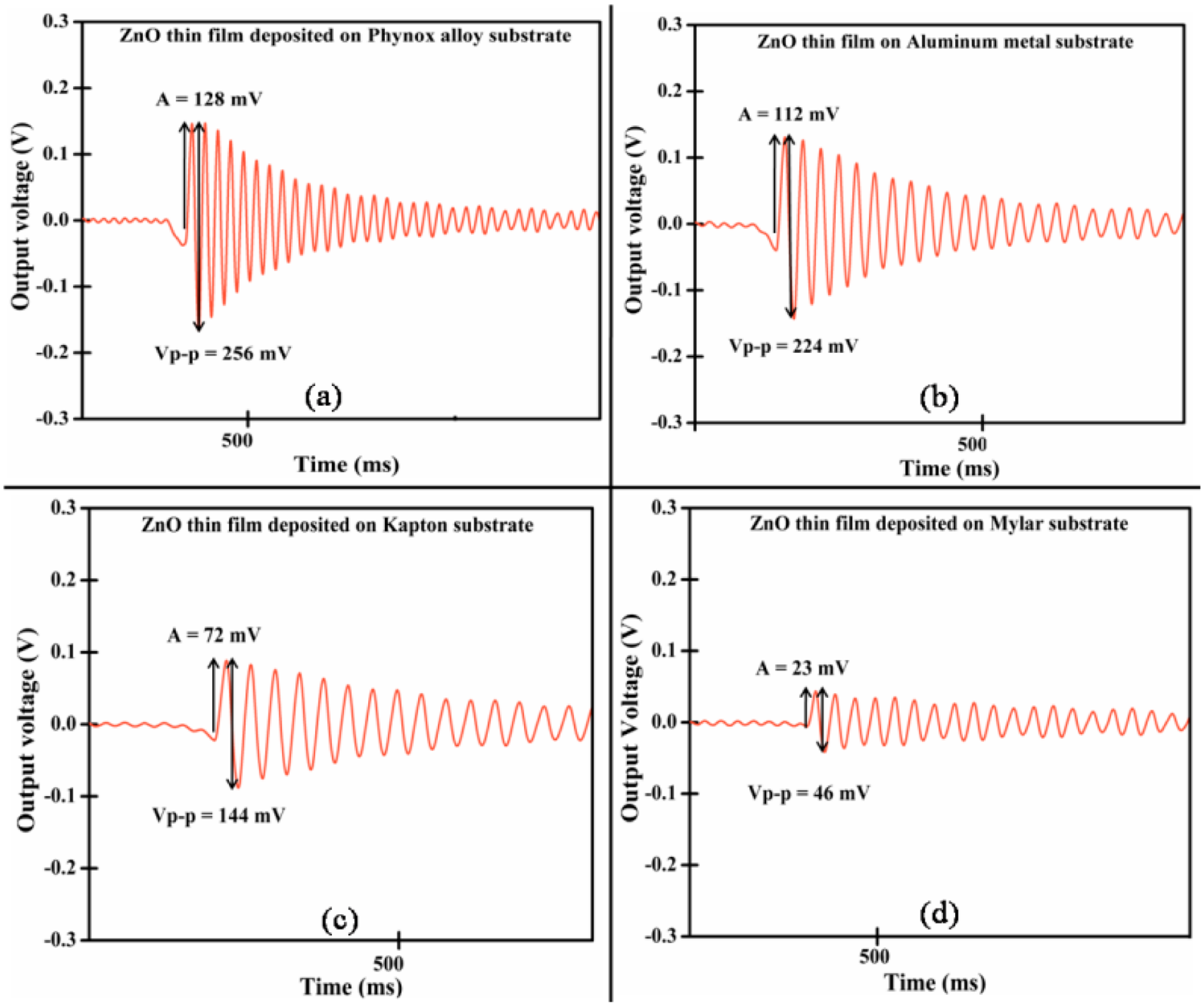


Figure 7. Output voltage signals generated from as-deposited ZnO thin films on Phynox, aluminum, Kapton, and Mylar cantilever sensing elements, respectively.

depends on the mode of vibration of the cantilever. In the present experimental study, the cantilever elements were vibrated in their first mode. Therefore, the above eq 1 can be further written as

$$f_n = \frac{(1.875)^2}{2\pi}\sqrt{\frac{EI}{mL^4}} \tag{2}$$

From the above equation, the fundamental natural frequencies for the first mode of vibration for different cantilever samples were calculated. The Phynox, aluminum, Kapton, and Mylar cantilever sensing elements were vibrated at frequencies of 258, 140, 65, and 64 kHz, respectively. (**Please see Supporting Information Section VI. Calculation of fundamental natural frequency of different cantilever samples**). The electromagnetic vibrator was given the respective frequency for the particular cantilever sensing element. This was done because the piezoelectric ZnO thin film deposited cantilevers will generate the highest output voltage at their fundamental natural frequencies. The overall thicknesses of deposited ZnO thin films and two electrode layers (920 ± 20 nm) was very little as compared to the thickness of the cantilever (40 μm); hence, the presence of deposited thin films will not have any effect on the vibration behavior of the cantilever element.

3.5.2. Vibration Sensing Analysis. The vibration sensing experiment was repeated five times for a particular cantilever sample mounted on to the electromagnetic vibrator. The individual cantilever sample has generated an almost similar amplitude of the first peak of output voltage with a variation of ±3.2 mV. As a result, we have reported a representative output voltage signal from each of the cantilever samples. Initially, the cantilever element under consideration was firmly mounted on to the electromagnetic vibrator and the vibrator was energized and switched off quickly. This sets up the mounted cantilever sensing element into vibration. These vibrations of the cantilever sensing element were damped out due to the elastic restoring force, and the cantilever element comes to the rest position. This damping will cause a gradual dissipation of vibration energy, which in turn will result in the gradual decay of the vibration amplitude of the cantilever. This trend of gradual decrease of the amplitude is also faithfully followed by electrical output voltage signals generated by all four cantilever samples. The envelope of the generated voltage signals clearly indicates this gradual decrease in the amplitude in Figure 7a−d. Hence, the generated output voltage is in synchronization with the vibrations of the cantilever element. The generated output voltage signal is an exponentially decaying sinusoidal waveform, which can be described by the following relation:

$$V = A\exp(-t)\,\sin(\omega t) \tag{3}$$

Where, A = amplitude of the peak, t = time on x-axis, and ω = frequency.

When the cantilever sensing element is subjected to vibrations from the electromagnetic vibrator, a periodically varying longitudinal tensile and compressive stress is generated along the deposited ZnO thin film. This stress will cause mechanical deformation in the as-deposited ZnO thin film, resulting in the generation of piezoelectric potential across the thickness of the ZnO thin film. The generated piezoelectric potential is a result of the relative displacement of Zn^{2+} cations with respect to O^{2-} anions due to the piezoelectric effect in ZnO wurtzite crystal structure.[17] This piezoelectric potential will cause the flow of electrons from the top electrode to the bottom electrode and, hence, generates an output voltage signal. In the present experimental case, vibrations of the cantilever will induce longitudinal stress in the ZnO film, which in turn generates the electrical field and output voltage along the vertical direction. Therefore, d_{31} piezoelectric coefficient is responsible for the vibration sensing.[18]

Figure 7a−d shows the recorded output voltage signals generated by as-deposited ZnO thin films on Phynox, aluminum, Kapton, and Mylar cantilever, respectively. The ZnO film deposited on Phynox cantilever has generated higher amplitude of the first peak of about 128 mV. This is attributed to the higher d_{31} piezoelectric coefficient value of 4.72 pm V^{-1}, which is an indication of good piezoelectric property. In the case of the aluminum sample (Figure 7b), the first peak voltage amplitude was bit less, about 112 mV. It is evident from Figures 7c and d that the first peak voltage amplitudes generated by ZnO thin film on Kapton and Mylar cantilevers were relatively low, about 72 and 23 mV, respectively. The d_{31} coefficient value of ZnO thin film was also comparatively less on Kapton (2.72 pm V^{-1}) and Mylar (1.23 pm V^{-1}) substrates. As expected the observed better vibration sensing performance in the case of ZnO thin film deposited on Phynox alloy cantilever was due to better structural and morphological properties and higher piezoelectric d_{31} coefficient value as compared to that on aluminum, Kapton, and Mylar cantilevers.

Figure 8 shows the variation of the first peak voltage amplitude with respect to the type of substrate. The reported first peak voltage amplitude value in the bar graph was averaged over five measurement readings performed for a particular ZnO thin film cantilever sample. As can be seen that, the trend of variation of the output voltage amplitude is exactly similar to the variation of piezoelectric d_{31} coefficient value (see Figure 5). Therefore, the higher the d_{31} coefficient value of ZnO thin film, the greater the amplitude of the first peak and the better the vibration sensing performance. Hence, the results obtained from vibration sensing studies are in corroboration with observations and conclusions made from material characterization studies.

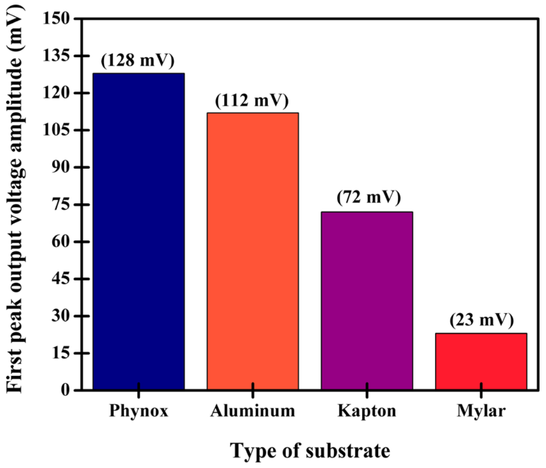


Figure 8. Variation of first peak output voltage amplitude value (mV) with respect to the type of substrate [Phynox alloy substrate (blue), aluminum substrate (orange), Kapton substrate (purple), and Mylar substrate (pink)].

In vibration sensing studies, ZnO thin film deposited on Phynox alloy cantilever showed relatively better performance by generating highest amplitude peak voltage. On the other hand, there are some disadvantages with remaining flexible substrates (aluminum, Kapton, and Mylar). Aluminum has a tendency to get oxidized easily, and this creates problems when it is used as a bottom electrode. The work function of aluminum increases after its oxidation. As a result of this increased work function, the flow of charges at the ZnO/aluminum interface decreases. Hence, the cantilever sensing element generates lesser output voltages over a period of time. This affects the overall performance of the sensor. This problem does not arise with a Phynox alloy as a bottom electrode, as it does not oxidize. Moreover, as can be seen from Table 1, the values of ultimate tensile strength (UTS) and yield strength of aluminum, Kapton, and Mylar are less compared to that of Phynox alloy. Therefore, the cantilever sensing elements fabricated from these materials will possess lower spring retaintivity and will get completely bent at higher deflection values. Therefore, ZnO thin film deposited on Phynox alloy proves to be a better and preferable choice for vibration sensing applications, as compared to other flexible substrates used in the present experimental study.

4. CONCLUSION

ZnO thin films were deposited by an RF reactive magnetron sputtering technique on four different flexible substrates for analyzing their potential application in vibration sensing. The major conclusions that can be drawn from the present experimental study are the following:

(1) ZnO thin films deposited on metal alloy and metal (Phynox and aluminum) substrate were highly crystalline and possessed uniform grains of larger size and lower rms surface roughness value. Additionally, ZnO thin films also have a higher d_{31} coefficient value. The metal alloy/metal substrates take the advantage of special features such as easily withstanding high temperature and no need of depositing bottom metal electrode, as the substrate itself act as one of the electrode. ZnO thin films deposited on Phynox and aluminum substrates have generated relatively higher peak output voltage amplitude and, hence, resulted in comparatively better vibration sensing performance. Due to some limitations of aluminum metal, Phynox alloy becomes the preferable choice. The ZnO thin film deposited on Phynox substrate has noteworthy advantages and, hence, opens up several exciting possibilities towards the realization of flexible thin film devices useful for varied applications.

(2) ZnO thin films deposited on polymer substrates (Kapton and Mylar) were not properly crystalline and possessed nonuniform grains of lesser size, higher rms surface roughness value, and lower d_{31} coefficient value. The as-

deposited ZnO thin films on polymer substrates showed relatively poor vibration sensing performance. Therefore, ZnO thin film deposited on polymer substrates may find limited applications as compared to films deposited on metal alloy and metal substrates.

■ ASSOCIATED CONTENT

Supporting Information

Selection of Phynox alloy over other commonly used metal alloy flexible substrate (SS-304L) for vibration sensing studies. Description of the experimental conditions maintained during the deposition of thin films. Crystallographic characteristics. Composition analysis using EDAX. Measurement of transverse piezoelectric coefficient (d_{31}) value of ZnO thin films deposited on different flexible substrates. Calculation of fundamental natural frequency of different cantilever sample. This material is available free of charge via the internet at http://pubs.acs.org.

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Notes

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