

PFM Characterization of Piezoelectric PVDF/ZnO-Nanorod thin films

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Abstract—The present work reports the development and the piezoelectric characterization of nano-engineered thin-films of Polyvinylidene Fluoride (PVDF) and vertical array of zinc oxide nanorods (ZnO-NRs). In particular, the piezoelectric response of the produced samples was investigated by evaluating the piezoelectric coefficient (d_{33}), through Piezoresponse Force Microscopy (PFM). We compared the piezoelectric response of three different samples: a neat PVDF thin-film, an array of vertically oriented ZnO-NRs and an array of vertically oriented ZnO-NRs embedded in PVDF. We tested two types of substrates: a flexible substrate namely PET-ITO and a rigid substrate namely ITO coated glass. The highest piezoelectric response was found to be exerted by the hybrid system made of vertically aligned ZnO-NRs array embedded in PVDF on PET-ITO substrate, showing a piezoelectric coefficient, as high as 14.91 pm/V.

I. INTRODUCTION

Poly (vinylidene fluoride), PVDF, is one of the most investigated polymers due to its piezo-, pyro- and ferroelectric properties. Such traits make it a very promising material in various application, especially in the fields of sensors and actuators [1]. PVDF can exist in five different crystalline phases, namely α , β , γ , ϵ and δ . The first two phases are the most common crystalline phases observed in PVDF. The β -phase is the one that exhibits the strongest ferroelectric and piezoelectric properties and it is generally obtained through spin coating or phase inversion [2]. The obtained films show a random distribution of the β -phase and a high porosity that make it unsuitable for electroactive application. It is well known that a highest piezoelectric coefficient is originated by uniform orientation of the PVDF β -phase, which can be obtained through uniaxial or biaxial stretching of melt-crystallized films [3] or applying a high electric field [4]. In order to obtain a self-polarized PVDF β -phase thin film, we used a spin-coating deposition method and low temperature phase inversion. Several studies have shown that inorganic nanofillers enhance the β -phase formation, producing hybrid structures with better electrical and mechanical properties [5]. Among the inorganic nanofillers, nanostructured zinc oxide (ZnO), which is a piezoelectric metal oxide semiconductor with a wide bandgap energy (3.37 eV) and large exciton binding energy (60 meV), has attracted much attention. ZnO

can be easily prepared in the form of nanostructured thin films of micro-, nanorods (NRs) or nanowires (NWs) [6].

The purpose of this work is to investigate the piezoelectric response of PVDF/ZnO-NR systems, taking advantage of the synergistic effect of an aligned array of vertically oriented ZnO-NRs and of PVDF thin-film with enhanced β -phase. We have tested two kinds of substrates: ITO coated glass substrate and PET-ITO. We evaluated the synergic effect of the hybrid PVDF/ZnO-NR system through measurement of the piezoelectric coefficient (d_{33}), and we compared the obtained result with different samples made on the over aforementioned substrates e: a) PVDF thin film; b) aligned array of vertically oriented ZnO-NRs; c) aligned array of vertically oriented ZnO-NRs embedded in PVDF. Each sample has been characterized morphologically through Scanning Electron Microscopy Field Emission (FE-SEM). The piezoelectric response, of each sample, has been evaluated measuring the piezoelectric coefficient (d_{33}), through Piezoelectric Force Microscopy (PFM).

II. MATERIALS AND METHOD

A. Production of PVDF thin-film

PVDF thin-films were prepared dissolving 20 wt% of PVDF (Solvay 6061) in N,N-Dimethylformamide (DMF), heating at 70°C and under magnetic stirring for about 2 hours. PVDF was then deposited by spin coating on substrates at 7500 rpm for 10s with an acceleration of 7500 rpm/s. Immediately after the deposition, the substrate with the PVDF thin film was quenched at -20°C in a glycerol/water solution for 30 min.

B. Production of aligned array of vertically oriented ZnO-NRs

A thin-film of oriented ZnO-NRs over substrates is produced by a two steps process [7]: a) Seed layer deposition; b) Zinc oxide growth by chemical bath deposition (CBD). The first step consists in the deposition of a seed layer in order to obtain nucleation points for the following growth step. The seed solution is prepared dissolving $0.2 \cdot 10^{-3}$ mol of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in 40 ml of isopropanol ($\text{C}_3\text{H}_8\text{O}$). The solution is then stirred at 250 rpm for 30 minutes at room temperature. The seed layer is deposited by deep coating, i.e. by immersing for 5 s the substrate into the seed solution, followed by placement in an oven for 15 minutes at 300°C for ITO coated glass substrate and at 150°C for PET-

ITO. This first procedure is repeated 5 times. In the second step an equimolar concentration ($2 \cdot 10^{-3}$ mol) of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HTMA) are dissolved in 100 ml of deionized water (DI water), then stirring the resulting solution for 1 h at room temperature. The substrate was immersed inside the solution perpendicularly to the water-air meniscus for 4.5 h at $60^\circ C$ without stirring.

C. Production of aligned array of vertically oriented ZnO-NRs embedded in PVDF

The hybrid PVDF/ZnO-NR sample was produced through a combination of the processes reported in sections A and B. A ZnO-NRs array (section B) was embedded by spin coating, in a PVDF thin-film, following the process described in section A.

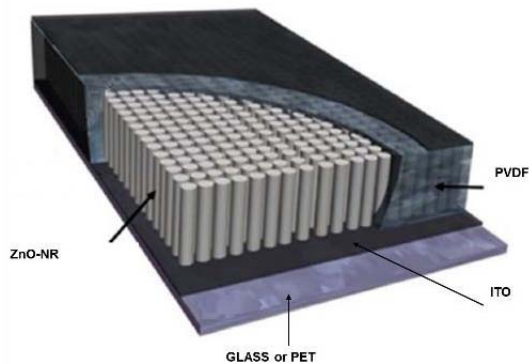


Fig.1 Hybrid PVDF/ZnO-NR sample

III. RESULTS AND DISCUSSIONS

A. Piezoresponse Force Microscopy (PFM) Characterization

The piezoelectric response of the produced samples was evaluated using a commercial Atomic Force Microscope, equipped with a PFM module (Dimension Icon, Bruker). In this work the PFM measurements were performed under the following conditions: silicon cantilever (Bruker) with nominal spring constant 5 N/m, resistivity 0.01-0.025 Ωcm , nominal resonance frequency 150 kHz. The piezoresponse was measured when an AC voltage was applied trough the tip with amplitude up to 10 V, with a 2V step and frequency of 15 kHz. Scan rate was 0.5 Hz and the scan area was $(1 \times 1) \mu m^2$ [8]. Figure 1 shows the measured displacement vs applied AC voltage of the analysed samples.

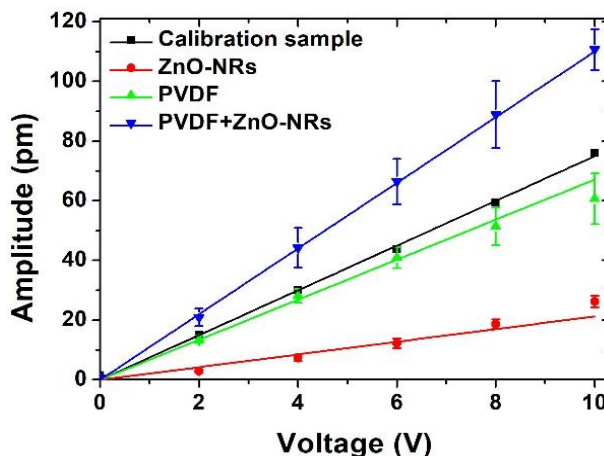


Fig.2. Piezoelectric signal versus the applied a.c voltage for ITO coated glass substrate.

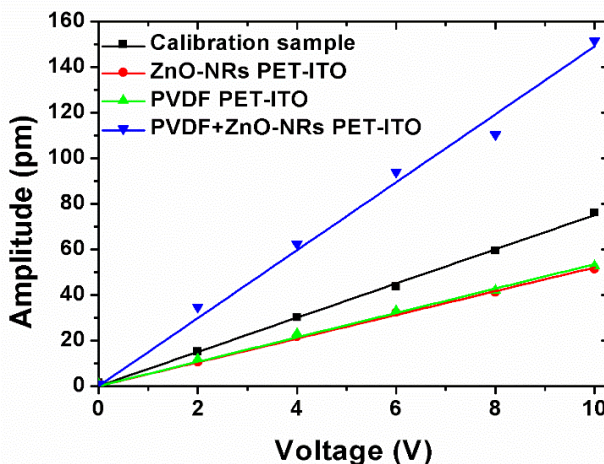


Fig.3. Piezoelectric signal versus the applied a.c voltage for PET-ITO substrate.

As we can see we obtained a very good linear behaviour, in agreement with the converse piezoelectric effect theory, according to which the displacement of the material is proportional to the applied a.c voltage. The d_{33} value was estimated by using a periodically poled lithium niobate (PPLN) as a reference sample. The obtained d_{33} -values are reported in Table 1.

Table 1. Piezoelectric coefficient of the produced samples.

	ITO coated glass substrates	PET-ITO Substrates
Sample	d_{33} (pm/V)	d_{33} (pm/V)
ZnO-NRs	2.13 ± 0.07	5.20 ± 0.30
Quenching PVDF	6.71 ± 0.30	5.35 ± 1.42
Quenching PVDF+ZnO-NRs	11.07 ± 1.07	14.91 ± 4.39

B. Field Emission-Scanning Electron Microscopy (FE-SEM) Characterization

Figs. 4-5 (a), (b) show SEM images of the ZnO-NRs array grown on the two different substrates considered in this study. The diameter of the ZnO-NRs, forming a dense array, is ~ 30 nm. Figs. 4-5 (c), (d) show the influence of the substrate on quenched-PVDF. In particular, the morphology of the film over the ITO coated glass substrate is characterized by a low porosity and spherulitic pattern, while the one of the film over the PET-ITO substrate the morphology is characterized by high porosity around $1\mu\text{m}$. In Fig.4-5 (e), (f), we can observe the morphology of hybrid PVDF/ZnO-NR. The images show that the presence of the ZnO-NR does not influence the morphology of the corresponding neat PVDF thin film.

I. CONCLUSIONS

The piezoelectric properties of a hybrid piezoelectric material, consisting of an array of vertically oriented ZnO-NRs embedded in PVDF matrix is reported. PFM characterizations, carried out on both the basic piezoelectric components (PVDF thin film and ZnO-NRs) and on the resulting hybrid structure, showed a much higher piezoresponse of the hybrid structure, indicating a synergistic effect of ZnO-NRs and PVDF, when combined together.

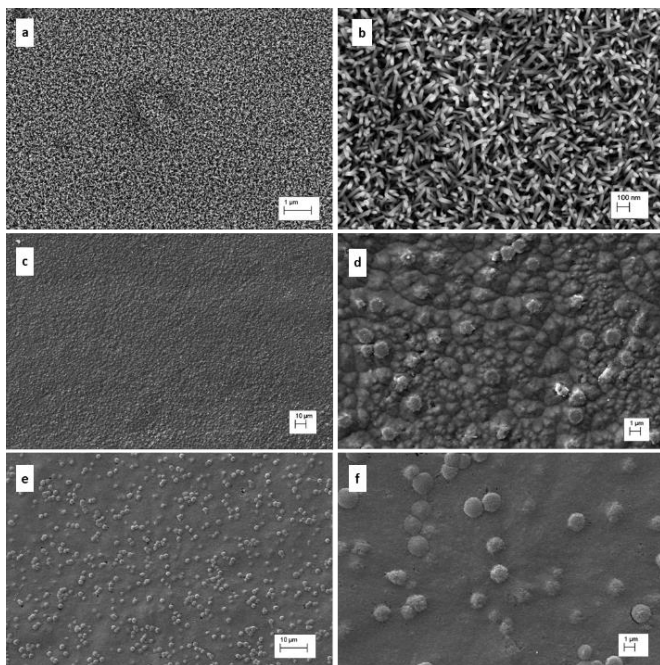


Fig.4 a), b) SEM images of aligned array of vertically oriented on the ITO-coated glass substrate; c), d) SEM images of the top surface of the hybrid PVDF/ZnO-NR on the ITO-coated glass substrate; e), f) SEM images of the hybrid PVDF/ZnO-NR sample on ITO-coated glass substrate.

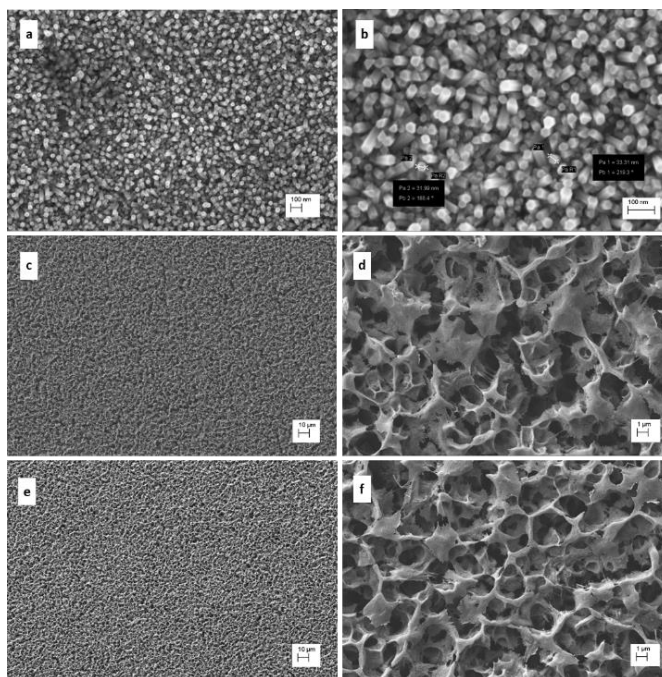


Fig.5 a), b) SEM images of aligned array of vertically oriented on the PET-ITO substrate; c), d) SEM images of the top surface of the hybrid PVDF/ZnO-NR on the PET-ITO substrate; e), f) SEM images of the hybrid PVDF/ZnO-NR sample on PET-ITO substrate.

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