

Zinc oxide/polyvinylidene fluoride composite material for optical applications

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ZnO is included in semiconductor II-VI group with interesting semiconductor properties, such as: good transparency, high electronic mobility, wide bandgap, high brightness at room temperature, etc. These properties are already being used in developing applications for transparent electrodes in liquid crystal displays and to save electricity or heat, protect windows, etc. Important applications of zinc oxide, ZnO/PVDF composite and microstructure examination as well as manufacture techniques are briefly discussed. Special attention has been paid to the effects of the microstructure and composition on the ZnO/PVDF composite properties, and various material characterization techniques are reported. The intensity of the absorption bands in ZnO/PVDF composite is lower compared to the intensity of the absorption bands of the PVDF powder.

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1. Introduction

In contrast to commercial piezoelectric ceramics, lead-free materials such as ZnO and a polymer matrix are proper candidates for use in eco-friendly applications [1].

ZnO presents a high energy excitation (60 MeV) high-energy (3.37 eV) high-energy semiconductor material that provides ultra-violet emission exciton regions efficiently at room temperature.

This bandgap corresponds to a wavelength of 328 nm, within the UV light range and is transparent to visible light as well as to the most widely used wavelengths in optical technologies. These properties combined with the piezoelectric effect make ZnO a unique, complete, perfect material for electronic and optoelectronic applications. ZnO is also biodegradable and biocompatible. Since 2009 ZnO's electronic future applications are for *thin film transistors and light emitting diodes*.

Also, ZnO was used as photocatalyst due to its high photosensitivity, non-toxic nature, stability and wide band gap. Photocatalytic activities of pure and doped ZnO were investigated for degradation of Malachite green (MG) (bis[p-dimethylaminophenyl] phenylmethylium oxalate) solution [2]. In order to enhance photocatalytic activity in the visible region it is necessary to modify ZnO, by various ways such as doping it with metals or non-metals and coupling it with other semiconductors [3].

Semiconducting metal oxides such as ZnO and Cu₂O are promising candidate materials for implementation in photovoltaic applications. ZnO is one of most the important materials in materials research today. ZnO nanowires (NW) have attracted worldwide attention because of important implications in LED, biomedical, solar cell, nanogenerators, piezotronics and electronics applications [4], detectors, sensors, pumped UV random laser diode

(LD) [5]. Once the NWs are strained, a macroscopic piezopotential is created, which can drive a flow of electrons, thus converting mechanical energy into electricity, therefore ZnO NWs may be utilized in the "self-powered nanotechnology" and small electronic devices with sensors could be easy and costless supplied. Also, ZnO nano-rods have been used to create scattering and local cavities in the construction of random lasers [6].

The Aluminium doped ZnO (AZO) thin films indicate a high transparency in the visible region and these transparent AZO films may be open a new avenue for optoelectronic and photonic devices applications in near future [7]. XRD patterns have shown that the AZO films crystallize in a hexagonal wurtzite type, and the grain sizes decrease with increasing Al doping [8]. The AZO thin films were grown on the (002)-oriented ZnO nucleation layer by the chemical bath deposition [9].

Some methods used to study the evolution of powder crystallization properties are: Non-Isothermal Differential Scanning Calorimetry (DSC), Spectroscopy of RAMAN, FTIR Spectroscopy, Spectroscopy of Photon Correlation Spectroscopy (PCS), Fourier Transform Infrared Spectrometry (FTIS), X-ray diffraction, Scanning force microscopy (SFM). Analysis of SEM images of powders and thin films obtain important data related to: *granulation, porosity, material defects, profiles, roughness, 3D viewing, thickness of layers deposited on the support, etc.* The composition of the films is analyzed with special procedures (EDAX, AES and ICP).

In the recent years, there has been considerable interest expressed in the polymer Polyvinylidene Fluoride (PVDF), because it exhibits strongest piezoelectric properties as compared to any other commercial polymer. Also, Polyvinylidene Fluoride (PVDF) is a material that has attractive properties such as pyro and ferroelectricity,

flexibility, low specific weight, good processability [10]. The polymer is widely used in high tech applications such as chemical process equipment, electrical and electronics, specialty and energy related applications.

Fig. 1 presents the molecular geometry, without defects for PVDF containing 20 monomer units: (a) α -form; (b) β -form.

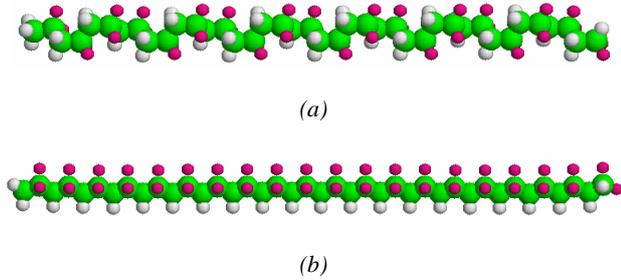


Fig. 1. Molecular geometry, without defects for PVDF containing 20 monomer units: (a) α -form; (b) β -form (color online)

PVDF has a simple structure $[H - (CF_2 - CH_2)_n - H]$ and has 5 forms of polymorphism depending on the synthesis conditions. The crystallization forms involve 3 different forms of polymer chain configuration, namely: (1) all-trans (TTTT) planar zigzag for the β phase, (2) TGTG0 for the α and δ phases and (3) T3GT3G0 for the γ and ϵ phases [11].

When packing PVDF chains in crystal lattice, PVDF dipoles are either additives leading to a final net dipole as in the case of β , γ and δ phases, or can cancel each other out resulting in a net dipole, as in the case of the α and ϵ polymorphic phases. Of the 5 polymorphic forms, the β phase shows the highest spontaneous polarization per elementary cell unit leading to the highest piezo, pyro and ferroelectric activity. The β form has the highest applicability potential for sensors and aquatics. Fig. 1 schematically shows the flawless configurations for PVDF chains for $n = 20$.

Fibers of polyvinylidene fluoride/zinc oxide (PVDF/ZnO) nanocomposites at various concentrations and structures were fabricated by electrospinning technique, this effort for modified β -PVDF crystal fibers. The nanocomposites were structured through the synthesis

of ZnO into various structures and comprised PVDF matrices at different concentrations. The crystalline phases and morphology of the nanocomposites are analyzed by x-ray diffraction and field emission scanning electron microscopy [12].

Piezoelectric PVDF/ZnO composite nanofibers are particularly desirable for their nontoxicity, breathability and flexibility. As results, by electro spraying pre-synthesized ZnO nanorods on PVDF nanofibers resulted in the highest piezoelectric response due to the combined effect of the greater piezoelectricity of aligned ZnO nanorods and PVDF nanofibers, and larger triboelectric response from increased surface roughness [13].

ZnO incorporation in PVDF under pre-ordered processing conditions has proved effective photocatalytic composites [14].

2. Experimental

2.1. Composite film preparation

A method of obtaining the ZnO/PVDF composite was used in [14], where the process consisted by a mixture of ZnO in the amount predetermined by the design of experiments and 9.78 g of DMAc. The solution was kept in an ultrasound for 15 min. Subsequently, predetermined amounts of PVDF polymer and PVP pore forming agent were added to the mixture. The vessels were shaken at 200 rpm at the temperature and time defined in the experimental design. Also, Polyvinylidene Fluoride (PVDF)/ZnO composites were prepared by solution mixing based on solid knowledge of membrane technology [15].

In this work the composite films were prepared by mixture of amounts of ZnO and PVDF powders (see Table 1), where volume fraction V_f of ZnO/PVDF of 40%, 50% and 60%, followed by hot-pressing at applied temperatures T_{max} between 160 °C and 190 °C and pressure P between 50 and 120 bar. The thickness of the films was in the range of 110 to 400 μm . The side surfaces of the composite films were metallized by brushing with Ag paste and then annealed at 180 °C in the oven. The Z6 composite films are brittle, porous and conductive, so they could not be metallized to form electrodes.

Table 1. Conditions in the ZnO/PVDF composite processing method

Sample name	ZnO/PVDF V_f (%)	T_{max} (°C)	P (bar)	Thickness (μm)	Remarks
Z6	60	190	120	390 - 400	Brittle, porous, conductive
Z5	50	170	75	290	Homogenous
Z4	40	160	50	110 - 120	Brittle

2.2. Structural characterizations

The crystalline structure analyses were performed at room temperature with FTIR spectroscopy in the transmission mode. The FTIR spectra were collected in the

range of 600 to 1600 cm^{-1} wave number for the crystal phase identification. Polyvinylidene fluoride (PVDF) shows polymorphism. Among the crystallization forms β and γ have piezoelectric properties.

According to the literature, for PVDF the α form is identified by IR peaks 411, 530, 615 (CF_2 bending), 766 (CF_2 skeletal bending), 795 (CF_2 rocking), 855, 974 (CH_2 twisting), 1149, 1210, 1383, 1402, 1432 and 1455 cm^{-1} ; the β form is identified by the peaks located at 490, 511 (CH_2 bending), 600, 810, 840 and 1275 cm^{-1} and the γ form 430, 778, 812, 832 and 1234 cm^{-1} [16] [17]. Fig. 2 presents the FTIR spectra for composites ZnO/PVDF, namely Z4, Z5, ($V_f = 40\%$; 50%) and PVDF.

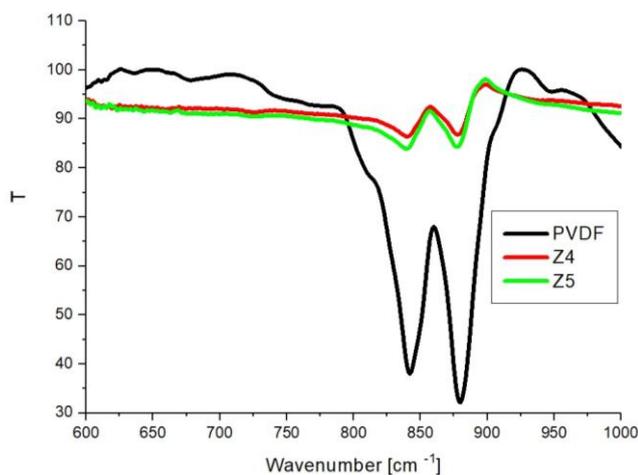


Fig. 2. FTIR spectra for composites ZnO/PVDF, namely Z4, Z5, ($V_f = 40\%$; 50%) and PVDF (color online)

The PVDF, Z4 and Z5 samples show the imprint of the forms α 878, 1400, 1431 cm^{-1} , and β at 840, 1171 and 1280 cm^{-1} , respectively. The intensity of the absorption bands in Z4 and Z5 composite samples is lower compared to the intensity of the absorption bands of the PVDF powder (Fig. 2).

3. Results and conclusions

Important applications of Zinc Oxide, Zinc oxide/Polyvinylidene Fluoride composite material and microstructure examination as well as manufacture techniques are briefly discussed. Special attention has been paid to the effects of the microstructure and composition on the Zinc Oxide / Polyvinylidene Fluoride composite properties, ZnO in different structures and various characterization techniques are reported. Also, structural characterization and composite preparation of ZnO/PVDF are presented. The intensity of the absorption bands in ZnO/PVDF composite is lower compared to the intensity of the absorption bands of the PVDF powder. ZnO/PVDF composite material is brittle, porous or homogeneous, function of the temperature and pressure applied in the hot-pressing process.

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