



Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Influence of metallic and semiconducting nanostructures on the optical properties of dye-doped polymer thin films

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ARTICLE INFO

Article history:

Received 7 September 2015

Received in revised form 7 December 2015

Accepted 9 December 2015

Available online xxx

Keywords:

Dye-doped polymer thin film

Ni nanowires

ZnO nanowires

Electron microscopy

Luminescence

ABSTRACT

Dye-doped polymer thin films were obtained by spin-coating of 8% polyvinylpyrrolidone (PVP) solutions (in ethanol). Ni or ZnO nanowires were incorporated in Rhodamine 6G doped polymer films (10^{-4} M dye concentration). Optical and morphological properties of simple dye-doped polymer films and films containing metallic or semiconducting nanostructures were investigated. Optical microscopy and scanning electron microscopy were used to image the nanowires. The presence of Ni nanowires induces a small shift (2–3 nm) to longer wavelengths on the emission band of Rh 6G doped PVP film. The ZnO nanowires' presence was confirmed by X-ray diffraction measurements. An enhancement of the emission of the dye doped polymer is induced by the semiconducting structures.

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1. Introduction

In the era of nanotechnology, when it is possible to manipulate matter at a scale of one millionth of a millimeter, common materials are regarded in a special way. On such small scale, these materials present extraordinary properties that can lead to new applications and technologies. One example is constituted by polymers, materials intensively studied over a long period of time for which ultra-miniaturization permitted their use in many new applications.

The devices based on polymers embedding inorganic compounds, attracted, recently, increasing attention due to the possibility of combining the great advantages of using polymers (flexibility, cheapness) with the special properties and phenomena induced by the inorganic compound (magnetic, optic, electric, surface enhanced plasmon resonance etc.). The devices based on polymers are gaining attention considering the possible applications, especially the ones requiring the processing on large areas with low costs. Potential applications of doped polymers are ranging from medicine to sensors or electrical and optical applications [1–4].

An emerging research area is the synthesis and characterization of doped polymers with special optical properties [5,6]. In this case, doping of the polymer is used in order to improve and tailor their optical behaviors [7–13]. Several types of dopants can influence the optical properties of polymers. Among those, dyes and semiconducting or metal nanoparticles are the most interesting. Dyes are currently

used for applications in fields as varied as the coloring of textile fibers, medical imaging, lasers, photonic devices and organic light emitting diodes, their spectroscopic behavior in solutions being known. When used as dopants in polymers, dyes can generate emission over the whole visible spectral region, with enhanced excitation efficiency and low excitation power operation [14]. Differences in the optical behaviors of the dyes might be related with preferential pattern of dye's incorporation into the host [15,16]. One of the most interesting features of doped polymer is the change of refractive indexes by using as dopants semiconducting or metallic nanoparticles [17,18]. Recently, polymer thin films doped with dyes or metal particles were intensively studied [19,20]. Polymers doped with dyes are used as modern light sensing materials, white light diodes [21,22], light amplifiers [23] or waveguides [24]. In this context, our aim was to obtain doped polymers with enhanced and tailored optical properties. Thus, the influence of the metallic or semiconducting nanostructures on the optical properties of the dye-doped polymer films was studied.

One of the most used methods for obtaining of polymer films is spin coating. Thus, thin films of polyvinylpyrrolidone (PVP) doped with different concentrations of Rhodamine 6G were produced. Nickel nanowires prepared by the template method (electrodeposition in nanoporous polycarbonate foils obtained by ion-irradiation and subsequent chemical etching) were embedded in Rhodamine 6G doped polymer films. Also, zinc oxide nanowires produced by templateless electrodeposition were covered with the dye-doped films. The optical and morphological properties of both dye-doped polymer films and dye-doped polymer films containing metallic or semiconducting nanostructures were evaluated.

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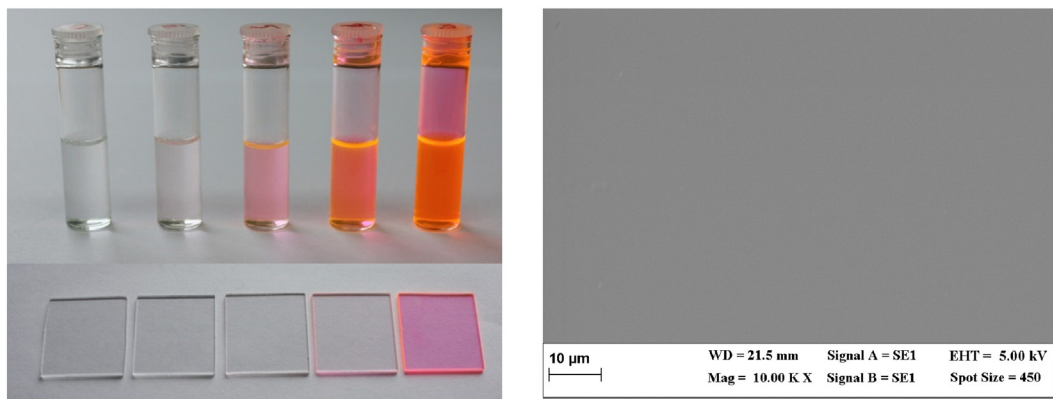


Fig. 1. a) Thin films deposited by spin coating from solutions of Rh 6G in PVP with different concentrations of dye (0 M, 10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M); b) SEM image of a transparent Rh 6G (10^{-4} M) doped PVP thin film deposited by spin coating on microscope glass.

2. Experimental details

Commercial polyvinylpyrrolidone of Mw = 1,300,000 molecular weight, with chemical formula $(C_6H_9NO)_n$, and Rhodamine 6G Basic Red 1 of 99.9% purity, with chemical formula $C_{28}H_{31}N_2O_3Cl$, from Aldrich were used without further purification. Solutions of 8% PVP were prepared by dissolving the polymer in ethanol. Thin film samples were produced by spin coating using a KW-4A CHEMAT. PVP thin films doped with different concentration of Rhodamine 6G (Rh 6G) were deposited on glass substrates of $2.5\text{ cm} \times 2.5\text{ cm}$. The spin coater was set at 2000 rpm for 5 s.

Morphological and optical properties of the dye-doped PVP films obtained by spin coating were studied. We used a Carl Zeiss EVO 50 XVP scanning electron microscope (SEM, Oberkochen, Germany) operating at a voltage of 5 kV to prove the uniformity of polymer films and operating at a voltage of 20 kV to evaluate the morphologies of the nanostructures.

Ni nanowires (of $20\ \mu\text{m}$ long and $\sim 200\text{ nm}$ diameter) were obtained by electrochemical deposition inside the nanoporous polycarbonate (PC) membranes. The template deposition is a versatile method to produce nanostructures with controlled properties [25–28]. In order to obtain the templates, PC foils of $30\ \mu\text{m}$ thickness were irradiated with swift heavy ions of high kinetic energies (11.4 MeV/nucleon) at the UNILAC linear accelerator of GSI, Darmstadt. By subsequent chemical etching, the tracks were transformed into pores which further were filled with Ni via electrochemical deposition. The membranes were fully dissolved and a suspension of Ni nanowires was obtained. The nanowires were visualized with a Carl Zeiss AxioMat optical microscope. Thin films of PVP doped with 10^{-4} M concentrations of Rhodamine 6G containing Ni nanowires were deposited on glass substrates of $2.5\text{ cm} \times 2.5\text{ cm}$.

The Ni nanowires' suspension was previously sonicated and the dye-doped PVP solution containing the Ni nanowires was immediately spin coated on the glass substrate. The nanowires form a (semi) stable suspension in the time required for coating the glass.

In order to obtain a relative alignment of the Ni nanowires, a part of the samples containing the metallic nanostructures were spin coated in the presence of a magnet. The magnet was placed near the substrate holder, in a fixed spot. Due to the rapid evaporation of the solvent (ethanol), the Ni nanowires remain aligned in the dye doped polymer films.

ZnO nanowires' arrays were electrodeposited on glass from zinc nitrate aqueous bath. The glass substrates were previously covered with a thin layer of gold deposited by evaporation. A thin layer of titanium ensured the adherence of gold on the glass substrate. Thin films of PVP doped with 10^{-4} M concentration of Rhodamine 6G were deposited on top of the ZnO nanowires.

The crystalline phase of ZnO was identified by X-ray diffraction (XRD) on a Bruker AXS D8 Advance instrument (Karlruhe, Germany) with Cu $K\alpha$ radiation ($\lambda = 0.154\text{ nm}$). The source was operated at

40 kV and 40 mA and the $K\alpha$ radiation was removed using a nickel filter. The XRD experiment was performed in a Bragg–Brentano reflection geometry. The $K\beta$ radiation was eliminated using a nickel filter.

The optical properties of dye-doped films, dye-doped films containing Ni nanowires and dye-doped films deposited on ZnO nanowires arrays were analyzed using a Varian Cary 5000 UV–Vis–NIR spectrometer (200–3300 nm) and an Edinburgh Instruments FL920 (200–900 nm) fluorescence spectrometer with 450 W Xe lamp.

3. Results and discussion

Thin films of PVP doped with different concentrations of Rhodamine 6G (0 M, 10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M) were deposited on glass substrates using spin coating, as it can be observed in Fig. 1a. Using scanning electron microscopy we demonstrated that the films are uniformly deposited (Fig. 1b).

The emissive properties of the dye-doped thin films were evaluated. Thus, as can be observed in Fig. 2, the emission band due to the presence of the dye in the polymer film increases in intensity with the increasing of the dye concentration. In these measurements the excitation wavelength was the same for all the spectra (500 nm). In the same time, the wavelength of the peak is shifting towards longer wavelengths with the increasing of the dye concentration, this being a typical behavior for most of dyes [29].

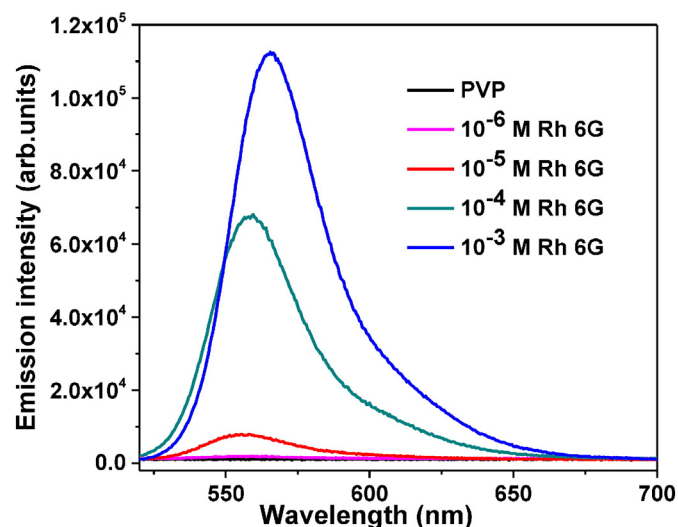


Fig. 2. Emission spectra of dye-doped PVP films, excited with 500 nm, doped with different concentrations of Rhodamine 6G deposited by spin coating on glass.

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