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Polyethylene terephthalate thin films; a luminescence study

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ABSTRACT

Polyethylene Terephthalate (PET) films doped with Rare Earths (RE^{3+}) have been deposited on glass by spray pyrolysis technique at 240 °C, using recycled PET and (RE^{3+}) chlorides as precursors. Cerium, terbium, dysprosium and europium were used as dopants materials, these dopants normally produce luminescent emissions at 450, 545, 573 and 612 nm respectively; the doped films also have light emissions at blue, green, yellow and red respectively. All RE^{3+} characteristic emissions were observed at naked eyes. Every deposited films show a high transmission in the visible range (close 80% T), films surfaces are pretty soft and homogeneous. Films thickness is around 3 μm.

1. Introduction

Over years the synthesis and studies about rare-earth ions (RE^{3+}) doped materials have attained great importance for a wide variety of potential applications in optical technology, such as phosphors [1–3], lasers [4–6], fiber amplifiers [4,6], high-density optical storage [4,6], and electroluminescent display devices [2,3]. In particular, RE^{3+} doped thin film phosphors structures have drawn a special attention due to their promising applications in flat panel displays (FPDs) [2].

The development of flexible, thin displays is a much sought-after goal, and has attracted a great deal of research effort [7–11]. By integrating, for example, the high information content of a traditional flat-panel liquid–crystal display (LCD) into a thin, flexible sheet of plastic, one could obtain a durable, lightweight product suitable for many applications in the growing market of pagers, cell phones, and personal digital assistants (PDAs), as well as future "electronic paper". By eliminating the need to rely on thin and fragile glass substrates, flexible displays should also bring benefits in the form of improved manufacturing yield, large area display capability, and less material and lower production costs.

Oxide-based phosphors such as yttrium, aluminum and hafnium [12–14] have been considered as potential thin film phosphors because of their high transparency, excellent chemical and thermal stabilities, and relatively high luminescence brightness performance [2–6,15] however, it is fair to say that it is necessary to use high reaction temperatures (above 500 °C) in order to achieve these characteristics. Nowadays, another kind of properties are also important like flexibility, environment friendly and low manufacturing cost; this properties are present in polymer films, since recycled materials could be employed to synthesize and low reaction temperatures are used. Polymeric thin films are common; some of them with luminescent properties [16–18] by the use of RE^{3+}; many techniques are used to synthesize them such as: spin-coating, sol–gel, electrospinning and MAPLE (matrix assisted pulsed laser evaporation) between others [19–22].

Polyethylene Terephthalate (PET) is a polymer, mainly used as container for beverages, with excellent characteristics as high transparency, flexibility and excellent chemical and thermal stabilities. However, PET water bottles are a serious pollution problem around the world, because they end up in landfills and take centuries to decompose.

In order to reduce the presence of PET in the landfills, the search for alternative uses of PET are continually present [23,24]. In the present work, the use of PET as host lattice is reported. Cerium, terbium, dysprosium and europium were used as dopant materials, films doped with them, give rise to luminescent emissions at 450, 545, 573 and 612 nm respectively; films also have high light emissions at blue, green, yellow and red respectively. PET films were made by spray pyrolysis technique using corning glass, quartz and crystalline (111 and 110) silicon as substrates.

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Photoluminescence (PL) and cathodoluminescence (CL) emissions of these films are reported as well as optical and structural characteristics (by UV–Vis, IR spectroscopy AFM and SEM measurements). White light was also achieved using double dopant materials on PET films.

This work aims to present a new way to deal with plastic waste, through a technological implementation. By using spray pyrolysis technique, the polymeric films deposition ensures low cost of a possible development of light emitting devices based on polymer films of PET and at the same time, at the best of our knowledge, this is the first time in which this deposition technique has been used to elaborate polymeric thin films. Similar studies, using other deposition techniques [25,26], report some drawbacks such as clusters formation and low homogeneity; the above is mainly due to the use of micrometer size powders or light emitting organic inks as active luminescent centers. In our case, rare earths were introduced as dopants into a polymer matrix, which ensures an even distribution of light emission sites and avoids the occurrence of clustering of light emission centers at localized points. This fact has been reported before in other host materials [27–29].

2. Experimental details

PET films were prepared from recycled powdered water bottles, in powder shape; dissolved in N,N-Dimethylformamide (N,N-DMF), supplied by J.T. Baker heated at 120 °C. The films were deposited at 240 °C on corning glass, quartz and crystalline silicon (1 1 1 and 1 0 0) by spray pyrolysis technique. This technique has been widely used to obtain films or coatings of different materials, mainly metallic oxides, since the technique is used under atmospheric pressure conditions. The spray pyrolysis technique is considered an inexpensive and scalable technique to obtain films and coatings with excellent properties. The technique consists in supplying an aerosol from a chemical solution which undergoes a pyrolytic decomposition on a hot substrate, leading to a solid film or coating on top of the surface used as substrate. However, the technique has not been attempted to obtain films thinner than 300 Å. Most of the films that are obtained with this technique usually range from 0.1 up to a few microns.

For this work, PET films were prepared with a 0.0005 mol/l chemical solution formed with recycled powdered PET in N,N-DMF, and using Rare Earths (RE^{3+}) as dopants (RE chlorides) previously dissolved into diethyleneglycol in a 0.01 mol/l chemical solution; 6 ml were taken of these kinds of solutions and were added to PET chemical solutions; REs used at this work were cerium, terbium, dysprosium and europium in order to achieve blue, green, yellow and red light emissions. A molten tin bath was used as thermal energy source for substrates to get a pyrolytic reaction, furthermore, nitrogen (N_2) at a flow rate of 5 l/min was used as carrier gas.

It is important to mention that the reproducibility characteristics on parameters such as roughness, and IR measurements for these films are excellent. Actually spray pyrolysis is a technique known for the quality of the synthesized films and high reproducibility; including very thin films (around 30 nm) [30]. In addition, around 80 samples were synthesized and characterized, in order to make this report, to ensure the reproducibility of the different film characteristics including luminescence, transparency and roughness.

Optical transmittance spectra were obtained with a Perkin Elmer Lambda 25 spectrophotometer in a wavelength range of 200–1100 nm, and a Thermo Scientific Nicolet 6700 FT-IR spectrophotometer in a wavelength range of 500–40,000 nm was used to achieve infrared analysis.

Roughness and morphology were measured with an Atomic Force Microscope Veeco CP Research, that is capable to measure both arithmetic average and root mean square roughness (RMS), at this work RMS measurements are reported. RMS parameter represents the standard deviation of the distribution of surface heights, so it is an important parameter to describe the surface roughness by statistical methods. This parameter is more sensitive than arithmetic average height to large deviation from the mean line.

The mathematical definition and the digital implementation of this parameter are as follows:

$$R_q = \sqrt{\frac{1}{l}\int_0^1 \{y(x)\}^2 dx}$$

$$R_q = \sqrt{\frac{1}{n}\sum_{i=1}^{n} y_i^2}$$

where R_q is the root mean square roughness, n is the number of intersections of the profile at the mean line and y is the relative height. The RMS mean line is the line that divides the profile so that, the sum of the squares of the deviations of the profile height from it is equal to zero [31].

SEM images were obtained in a Scanning Electron Microscope JEOL using an acceleration voltage of 1 kV and ×500 as magnification. Photoluminescence (PL) measurements were carried out using a SPEX Fluoro-Max-P spectrophotometer. Finally CL measurements were performed in a stainless steel vacuum chamber with a cold cathode electron gun (Luminoscope, model ELM-2 MCA, RELION Co.). The thin films were placed inside the vacuum chamber and evacuated to $\sim 10^{-2}$ Torr. The electron beam was deflected through a 90° angle to focus onto the luminescent film normal to the surface; the diameter of the electron beam on the film was 3 mm approximately. The emitted light was collected by an optical fiber and fed into a SPEX Fluoro-Max-P spectrofluorimeter. The applied current of electron beam was 0.05 mA with an accelerating voltage in the range from 1 kV to 2 kV for all kinds of thin films. All measurements were carried out at room temperature.

3. Results and discussion

Fig. 1(a) shows the IR spectrum of an undoped PET film, which is similar to the one previously reported by Marck [32]. The rest of images Fig. 1(b to f) show the IR spectra characteristics of doped PET films, it is possible to observe that those spectra are similar to only PET film spectrum, save for two bands (at 1540 and 1410 cm^{-1}) that are associated to the presence of (—CH_2—) bonds

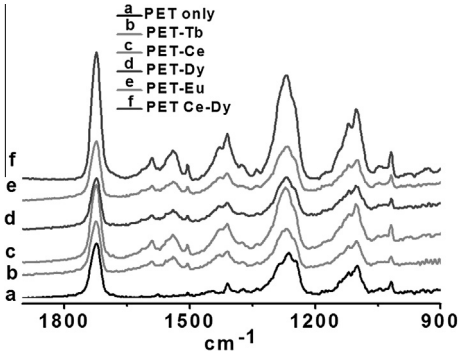

Fig. 1. IR spectra from undoped PET films (a). Rare earths doped PET films (b–f).