

Poly(*N*-vinylcarbazole) (PVK) deposited by evaporation for light emitting diodes thin films structures

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Abstract

The sandwich structures have been obtained by deposition of organic thin films on commercial tin oxide. Then the organic films were covered by a thin aluminium film. All the films were deposited by evaporation. The organic component was either a thin (150 nm) poly(*N*-vinylcarbazole) (PVK) film or a bilayer constituted of a thin PVK layer covered with a 8-hydroxyquinoline, aluminium (Alq₃). When PVK is deposited by classical thermal evaporation there is a shortening effect of the chain length, however, the main properties of the vinylcarbazole molecules are preserved. These films are photoluminescent with blue light emission. The *I*–*V* characteristics of the sandwich structures are typical of such organic sample. They exhibit a rectifying behaviour, with a forward polarisation when the SnO₂ electrode is positively biased. They also exhibit electroluminescence. When a single PVK film is used, the signal is quite faint. It is improved when an organic bilayer is used. However, simultaneously there is a red shift of the signal. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 73.61.Ph; 78.60.Fi

Keywords: Diodes; Photoluminescent; Polymer; Evaporation

1. Introduction

Poly(*N*-vinylcarbazole) (PVK) is not only a photoconductive polymer [1], but also a photoluminescent one. These properties are well known for a long time, but since, electroluminescent organic diodes (OLED) have been achieved [2], electroluminescent devices, emitting blue light, based on PVK thin films are under studies [3]. Usually the PVK films are deposited by spin coating, some structures have been grown by evaporation process [4]. Earlier we have studied the properties of evaporated PVK thin films [5]. We have shown that if the vinylcarbazole function is persevered during the heating process, the chain length of the PVK is strongly decreased and the films are essentially composed of oligomers and not polymers has shown by their solubility. In the present work, these thin films have been used to achieved OLED.

2. Experimental

OLED were obtained by thermal evaporation under high vacuum (10^{−5} Pa) of organic PVK powder onto SnO₂ coated

glass substrates. PVK is a well known hole transport layer [1] and therefore, for some devices, an electron transport layer has been deposited above the PVK. The dye used was the 8-hydroxyquinoline aluminum (Alq₃). Aluminum was finally deposited from a tungsten boat to form the top electrode. To prevent metal diffusion during this last evaporation the samples were cooled by liquid nitrogen.

Two types of diodes have been used.

- Series 1: ITO/PVK/Al
- Series 2: ITO/PVK/Alq₃/Al

The active area of the diodes was 2 mm × 2 mm and the thickness of the films was 150 and 60 nm for PVK and Alq₃, respectively. The thickness and the deposition rate were measured in situ by a hf quartz monitor. The thicknesses were checked by cross-section visualization with a scanning electron microscope (SEM). Electrical measurements (current–voltage: *I*–*V* and electroluminescence–voltage: *EL*–*V*) were performed using a Lambda IEEE programmable power supply coupled with a Keithley 2000 multimeter in the case of *I*–*V* and a photodiode in the case of electroluminescence.

The photoluminescence (PL) spectra were recorded using the Jobin-Yvon TG HG2S spectrophotometer with holographic gratings. The signal was detected with a Peltier-cooled photo multiplier. The sample was excited with the 337 nm line of a filtered xenon lamp (150 W). The laser

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power at the sample was kept below 2 mW. Experiments were performed at room temperature. These measurements were carried out in air at room temperature conditions.

3. Results and discussion

Fig. 1 shows the absorption and emission spectra of a PVK film deposited by evaporation, also is reported the emission spectrum of the reference PVK and vinylcarbazole powders. It can be seen that, not only the chain length of the evaporated polymer thin film is far smaller, as shown by the solubility test [5–7], but the emission spectrum is sensibly different to that of the PVK reference powder. Three maxima PL occur at about 450, 475 and 500 nm, which corresponds for the first one to PVK, while the two others can be attributed to vinylcarbazole.

This confirms the decrease of the chain length during evaporation. The absorbance shows a maximum at 350 nm, which is characteristic of PVK [1]. In order to identify the electroluminescence in multilayer diodes the spectra of Alq₃ is reported in Fig. 2, it can be seen that while the maximum PL of PVK and Alq₃ films occurs at around 475 and 550 nm, respectively that of the PVK/Alq₃ bilayer occurs at 550 nm, which means that the emission originates from the Alq₃. This means that the excitons are not confined within the PVK layer and that the use of the electron transport layer induces a red shift of the emitted light. Similar result has been obtained in the case of spin coated PVK films [5], which shows that the red shift of the emission in the presence of the Alq₃ film is not related to the deposition technique of the PVK.

Figs. 3 and 4 show the typical *I*–*V* and electroluminescence–voltage (EL–*V*) characteristics for the two series of devices. The improved performance of the bilayer diodes is clearly visible in these figures, it can be seen that the emission intensity of the two layer diode is two orders of magnitude higher.

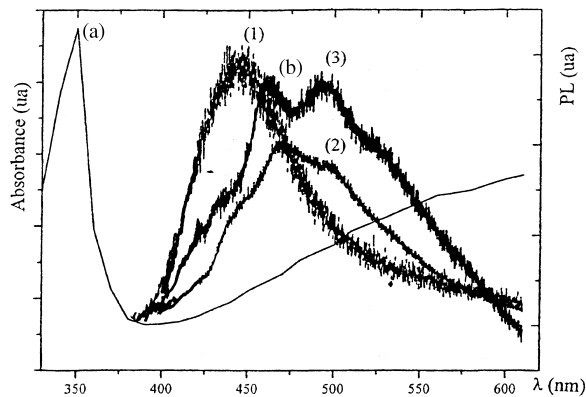


Fig. 1. Optical spectra of PVK and vinylcarbazole: (a) absorption spectrum of PVK; (b) emission spectra of PVK thin film (2), PVK powder (1) and vinylcarbazole powder (3).

Using a band diagram with values taken from the literature [8–10], the characteristics could be explained by the injection of both types of charge from the electrodes. The polarity of the sample in light emitting configuration suggests that holes are majority carriers, while the electron injection efficiency is the limiting factor of the light emission, which explains the better efficiency in the presence of Alq₃ since, there is a better adequation of the work function of Al with the electron affinity of Alq₃. When Schottky model $I = I_0 \exp(-qV/nkT)$ is used a good fit between the theoretical and experimental curves is obtained, however, some series resistance effect appears when the tension increases (Fig. 5), moreover, sometime the value of the ideality factor is higher than two which does not agree with the model since, theoretically *n* cannot be higher than two. May be, some current tunnels through the barrier following the Fowler–Nordheim equation ($I \propto -E^2 \exp(-k/E)$) with ($E = V/t$).

The reproducibility improvement should be related to the same better ad equation of the band structure: the turn on voltage is smaller, the puissance necessary to obtain

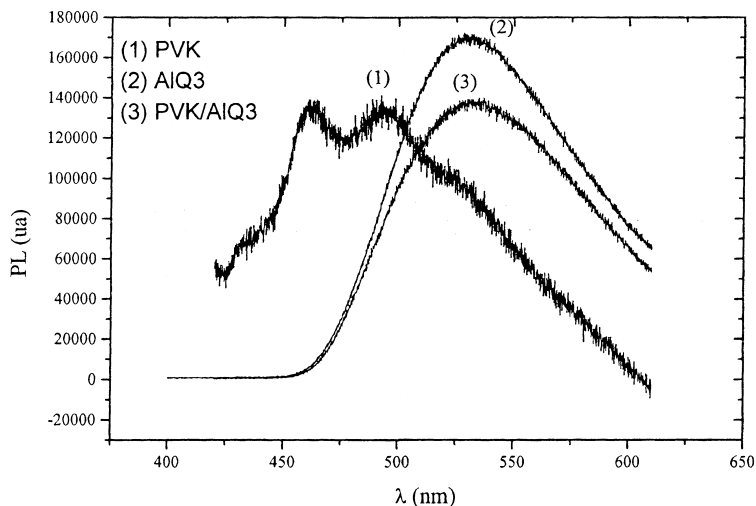
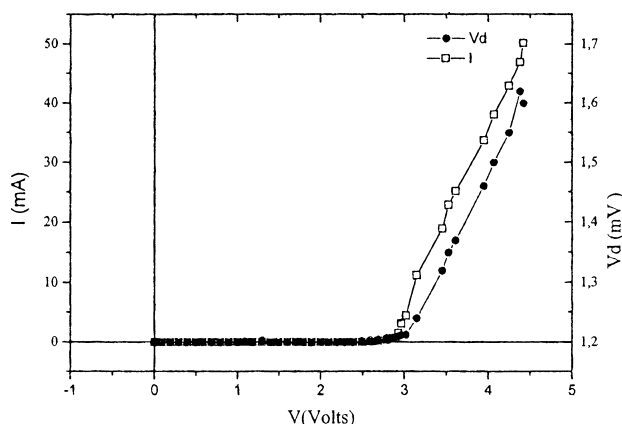
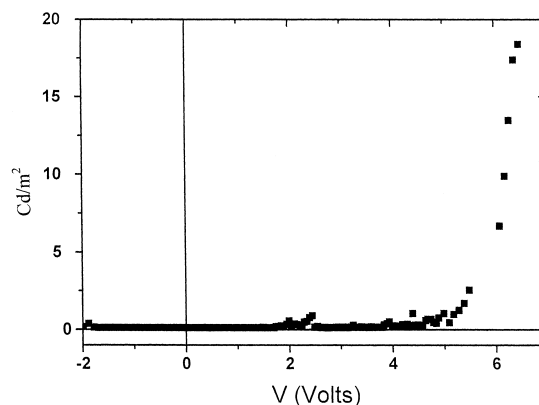
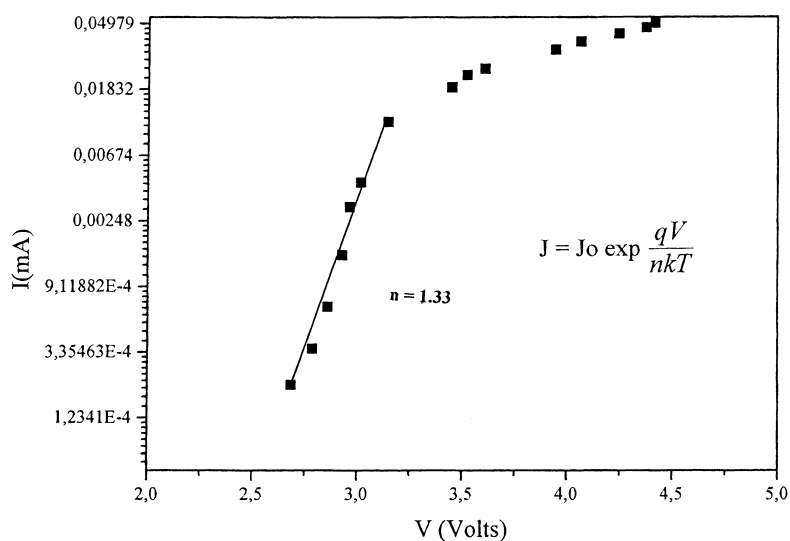


Fig. 2. Photoluminescence spectrum of an Alq₃ film (2); a PVK film (1); a PVK/Alq₃ bilayer (3).

Fig. 3. (I - V) and (EI - V) characteristics of a $\text{SnO}_2/\text{PVK}/\text{Al}$ diode.Fig. 4. (EI - V) characteristics of a $\text{SnO}_2/\text{PVK}/\text{Alq3}/\text{Al}$ diode.Fig. 5. $\ln I = f(V)$ of a $\text{SnO}_2/\text{PVK}/\text{Alq3}/\text{Al}$ diode.

electroluminescence decreases and therefore, heating of the sample is smaller than in the case of the series 1 of diodes.

4. Conclusion

In the present work, we have shown that after evaporation PVK films are formed of vinylcarbazole oligomers with an emission spectrum corresponding to a mixture of PVK and vinylcarbazole. We have demonstrated that the use of bilayer can significantly enhance the light emission of evaporated OLED and simultaneously improve their stability. The first improvement is induced directly by the better band ad equation and the red shift of the emission spectrum, which corresponds to Alq3 emission, while the second derives indirectly from the same fact since, the heating of the sample is smaller, which allows better reproducibility.

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