Light emission in forward and reverse bias operation in OLED with amorphous silicon carbon nitride thin films

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Abstract. Amorphous silicon carbon nitride (a-SiC:N) thin films deposited by magnetron sputtering were used in the structure of an organic light emitting diode (OLED), obtaining an OLED operating in forward and reverse bias mode. The device consist of the heterojunction structure ITO/a-SiC:N/Hole Transport Layer (HTL)/ Electron Transport Layer (ETL)/a-SiC:N/Al. As hole transporting layer was used a thin film of 1-(3-methylphenyl)-1,2,3,4 tetrahydroquinoline – 6 – carboxyaldehyde - 1,1' diphenylhydrazone (MTCD), while the tris(8-hydroxyquinoline aluminum) (Alq3) is used as electron transport and emitting layer. A significant increase in the voltage operation compared to the conventional ITO/MTCD/Alq3/Al structure was observed, so the onset of electroluminescence occurs at about 22 V in the forward and reverse bias mode of operation. The electroluminescence spectra is similar in both cases, only slightly shifted 0.14 eV to lower energies in relation to the conventional device.

Keyword: amorphous carbon films, OLED, electroluminescence

1. Introduction
Amorphous carbon films are being extensively studied in the last few years due to their commercial applications in optoelectronics. In particular, electron emission from a cold cathode induced by an electric field has attracted much attention due to its potential application in vacuum microelectronic devices including field emission displays and in this area, electron field emission from thin films of amorphous carbon nitride (a-C:N) [1] and silicon carbon nitride (SiCN) [2] have been reported. However, together with a large quantity of experimental work in photoluminescence (PL) [3], results about the electroluminescence (EL) in these materials also are reported [4]. Also, amorphous carbon nitride thin films (a-C:N and a-SiC:N) were used as electron injection layer in organic LEDs (OLEDs) [5], while that the a-C:N thin film was also used as buffer layer in OLEDs [6]. So, the application of amorphous carbon films in OLEDs can be realized and this can produce interesting results in the OLEDs comportment. On the other hand, in some cases of a light emitting diode made with a semiconductor polymer, light emission in reverse bias mode can be obtained [7]. However, the light emission of the OLEDs made with small molecules, is usually obtained only in the forward bias mode.

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(ITO positive), while in the reverse bias mode (ITO negative) light emission is not obtained. But by using amorphous carbon films (a-SiC:N) in the OLED structure can be showed that the OLED so fabricated can emit light in forward bias and reverse bias mode too.

In this work, thin films of a-SiC:N deposited by rf magnetron sputtering (13.56 MHz) were used to produce OLEDs with light emission in the forward bias and the reverse bias mode, inclusive. The amorphous carbon films present the advantage of being stable and chemically inert in contact with metals and organic materials. Preliminary study on the applications of the amorphous carbon films in OLEDs with organic molecules of low molecular weight was performed [5, 6]. Different techniques were used in order to characterize the composition and the optical characteristics of the deposited amorphous carbon films.

2. Experimental

In this work, the 1-(3-methylphenyl)-1,2,3,4 tetrahydroquinoline – 6 – carboxyaldehyde - 1, 1’ - diphenylhydrazone (MTCD) [8] was used as Hole Transport Layer (HTL) [9], while the tris(8-hydroxyquinoline aluminum) (Alq3) as the Emitting and Electron Transport Layer (ETL). Depositing amorphous carbon films, OLED with hetero-structure was fabricated and is shown in the figure 1. Organic materials were sequentially deposited by thermal evaporation onto glass/ITO/a-SiC:N substrates at room temperature. The base pressure was 5 × 10⁻⁴ Pa and during the evaporation, the pressure was ~9 × 10⁻⁴ Pa. The rates of deposition of the organic compounds were in the range of 0.1-0.3 nm/s. The organic layer thicknesses were 50 nm for MTCD and 70 nm for Alq3. Then a film of a-SiC:N was deposited onto the Alq3 layer and finally an Al thick layer of 180 nm was thermally deposited with a rate of 1 nm/s.

![Figure 1. Structure of the OLED device studied in this work. Forward bias (+ on ITO, – on Al) and reverse bias (– on ITO, + on Al).](image_url)

The a-SiC:N films were deposited by rf magnetron sputtering of high purity (99.95%) SiC target onto the substrates mounted over a copper block at a distance of 5.5 cm from the target. The r.f. power was kept constant and equal to 370 W. The base pressure of the vacuum system was in the range of 2.0 x 10⁻⁴ Pa and Pd was 2 x 10⁻¹ Pa. The gas flow rate was 1.5 sccm for the N₂ and 10 sccm for Ar. The deposition rate was approximately 25 nm/min. The deposition rates of the a-SiC:N was previously determined so that deposition time could be adjusted in order to produce the desired
thickness. Low temperature plasmas was used to avoid introducing significant surface modifications of the organics films due to the initial ion bombardment with consequent changes in the emission properties of the Alq₃ films [10].

The chemical composition of the a-SiC:N films was controlled by Auger Electron Spectroscopy (AES). Their optical absorption spectrum was measured through a Si (100) substrate using a Perkin-Elmer spectrophotometer. The OLED brightness was measured using a radiometer/photometer United Detector Technology (UDT-350) and their electroluminescence spectra were measured with a Photon Technology International (PTI) fluorescence spectrophotometer. The electrical characteristics of the OLED devices were measured in air at room temperature and at atmospheric pressure.

3. Results and discussion

The chemical composition of the a-SiC:N film used in this work was realized using a 100 nm thick film deposited onto silicon Si(100) substrate. The Auger spectra is shown in figure 1 and the analysis confirmed a content of Si(30):C(29):N(40):O(1) in at.%. 

![Figure 1. Auger spectra of 100 nm thick a-SiC:N film deposited onto Si(100) substrate.](image)

In order to use these kinds of films in optoelectronic devices, it is fundamental to know their optical properties. For that, the absorption spectrum of 100 nm thick a-SiC:N film was measured in the range 200 to 800 nm and is reported in figure 3 together with a typical Alq₃ electroluminescence (EL) spectra of an conventional OLED, without a-SiC:N films, working in forward bias. This figure demonstrate the possibility of the application of the a-SiC:N films as optical layer in OLED devices. Indeed, because the relatively good optical transparence of this film in the visible spectrum region, the OLED emission peaked at 575 nm we can to say that is very little affected by the presence of the amorphous carbon layer. So, the emission light produced by the OLED can cross the amorphous carbon layer and to be detected.
Figure 3. Absorption spectra (dashed) of 100 nm thick a-SiC:N film deposited onto Si(100) substrate together with the electroluminescence (EL) spectra of the Alq3 in conventional OLED without a-SiC:N layers working in forward bias.

From the absorption spectra of this film it is also possible to determine a value for the optical gap ($E_g$) sometimes called Tauc gap. For this purpose, a function of the absorption coefficient $\alpha$ is plotted against the photon energy using the well known relation $(\alpha(E)E)^{1/2} = B(E - E_g)$ for amorphous materials, where $E$ is the photon energy, and $B$ is a constant [11]. Using the graphic interpolation shown in figure 4 it is possible to found a value for $E_g$ of about 1.70 eV.

Figure 4. Tauc plot used to determine the energy bandgap of a-SiC:N film. The dashed line meets the energy axis at about 1.70 eV, that is the $E_g$ value.

Figure 5a show the current density behavior as a function of applied voltage in forward (+V) and reverse (–V) bias mode. It is quite evident the typical rectifier junction behavior starting from approximately +20 V in forward and –20 V in reverse bias operation. The introduction of the a-SiC:N layers in the OLED structure does not produce a correspondent increase in the current value in comparison with a conventional device without a-SiC:N layers. The only effect obtained by
introducing the amorphous carbon layers is to increase the working voltages, allowing the device to support higher values. Figure 5b show the OLED luminance as a function of applied voltage in both cases, forward and reverses bias operation. The luminance comportment is similar to a conventional OLED without a-SiC:N layers, except that the device begin to emit light at +20 or −20 V approximately, according to each bias mode operation, whereas in conventional OLED light emission is detected as soon the voltage is about 3-4 V typically. This difference may be due, for example, that the wide-band gap of the a-SiC:N may form higher interfacial barriers increasing the “resistance” to the electron injection [5]. By other hand, the figure 5b suggest that in forward mode of operation the holes and electrons is a more balanced process, since the light output is higher at the same voltage or same current density, as under reverse bias operation.

Figure 5. Current density-voltage (a) and electroluminescence intensity-voltage (b) characteristics of OLED with a-SiC:N layers.

The electroluminescence spectra of the fabricated OLED with a-SiC:N layers are reported in figure 6. The EL spectra were obtained for different voltage values and with the device working under forward and reverse bias mode. From these spectra it seems that the EL bands of the OLED working with forward or reverse bias do not show large differences between them, except a slight shift of about 0.04 eV in the peak of the EL spectra with reverse bias mode in relation with the EL spectra in forward bias mode, probably due to conformational energy changes on reverse electrical excitation [12]. On the other hand, the EL spectra of OLED with a-SIC:N layer is shifted at 0.14 eV to lower energies with respect to the EL spectra of conventional OLED without a-SiC:N layers, showing that possible changes in the exciton energies levels in the Alq3 may occur due to some kind of mechanism induced by the ion bombarding process [10].
4. Conclusion
In this work was studied the possibility of using amorphous carbon films type a-SiC:N in an optical device as OLED. First was measured their absorption in the optical range showing that the light visible can be transmitted by the film and their optical band gap was measured obtaining a value of 1.70 eV. Then we have presented experimental results of introduce amorphous carbon layers a-SiC:N in the structure of an OLED, obtaining a device that can operate at forward and reverse mode bias mode and was showed that this type of OLED have characteristics of current and light emission very similar to conventional OLED without a-SiC:N layers. The advantage of the OLED with a-SiC:N of working under forward and reverse bias may be interesting to fabricate OLEDs that can operate with alternating current, and so eventually may be important in the applications for displays or for other optoelectronics devices. Further investigations are in progress to better understand the mechanisms and possible modifications to the holes and electrons transport properties once a-SiC:N is present.

Acknowledgement The authors wish to acknowledge Prof. Sung-Hoon Kim of the Department of Dyeing and Finishing, of the Kyunpook National University (South Korea) for the MTCD material and Professor Sonia Renaux W. Louro for the use of the spectrofluorimeter equipment. This work was supported by RENAMI, CNPq, CAPES and FAPERJ.

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