JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 9, September 2009, p. 1316 - 1318

Ultraviolet range optical properties of fullerenes in contact with microcrystalline ZnS:Cu♣

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In the present work, results are presented on the optical properties of composite layers of blue-luminescent ZnS:Cu in an epoxy oligomer. The addition of small quantities of fullerenes, with concentrations in the range W_f = 0.001 to 0.01] wt.%, results in the emergence of a new wavelength region of increased electroluminescence. This effect is probably due to the high activity of dimers and trimers of $(C_{60})_n$ associates of microcrystalline ZnS at high dissolution rates.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: Fullerenes, Oligomer polymerization, Transmission spectra, Diffuse reflectivity, Electroluminescence.

1. Introduction

In recent years, there has been a growing interest in the studies of thin films from fullerenes and films containing fullerenes on different semiconducting and dielectric materials, including polymers. Before film deposition, fullerenes are dissolved in xylene which are then introduced into an epoxy oligomer material.

The fullerenes change the optical and electrophysical properties of the thin film /media interface, in a number of cases. The photo and electroluminescent properties of luminophors are improved considerably, especially in the case of ZnS:Cu blue emission. The aim of the present work is to investigate the transmission spectra of fullerenes in xylene, the diffuse reflectivity (R_D) of the oligomer layers and the electroluminescent brightness (B) of the films at very low fullerene concentration $W_f < 0.01$ wt.% [1,2].

2. Experimental

The samples investigated were layers of polyepoxy oligomer (with microcrystalline ZnS:Cu and fullerenes) about 20 μm thick, coated on glass substrates with a thickness of 1mm and dimensions of 15x30 mm. Fullerenes of the type C_{60}/C_{70} at a ratio of 85 % to 15 % were used [3].

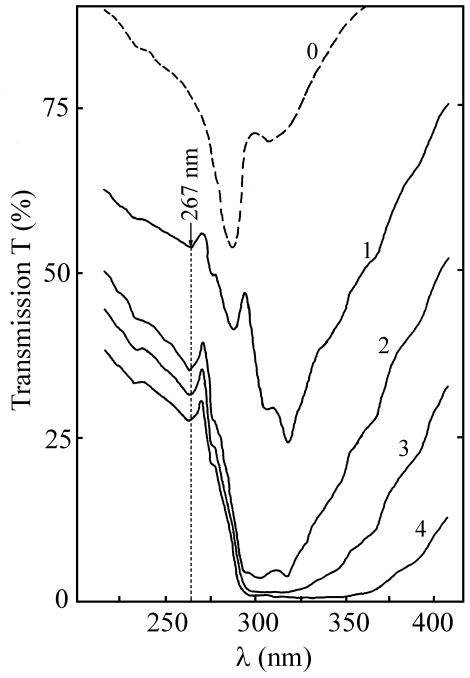

Fig. 1. *Effect of UV transmission T(%) spectra of fullerenes in xylene with different fullerene concentrations in(wt.%): curve 0 – pure xylene; curve 1 - 0.02 wt.%; curve 2 – 0.04 wt.%; curve 3 -0.08 wt.%; curve 4 -0.16 wt.%.*

♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008

For the complete oligomer polymerization, the layers were annealed at 120 ^{0}C.

The measurements of the optical transmission (T) spectra were performed using a double-beam spectrometer (Shimadzu UV-190) in spectral range λ = 220 to 420 nm. For the measurements of the diffuse optical reflectivity (R_D) spectra, an attachment was used, consisting of an integrating sphere with an R 446 V photomultiplier [4].

The brightness measurements of the electroluminescent layers were performed using a Radiometer/Photometer Model 550 EG&G-Electro-optics division, USA.

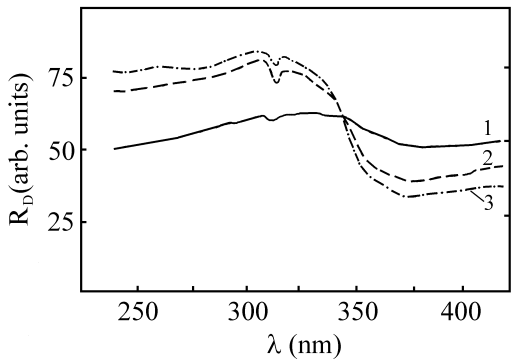

Fig. 2. UV diffuse reflection R_D spectra of fullerenes in a polyepoxy oligomer with microcrystalline ZnS :Cu: curve 1 - 0.02 wt.% ; curve 2 - 0.04 wt.% ; and curve 3 - 0.08 wt.%. The reference electrode was a standard white plate.

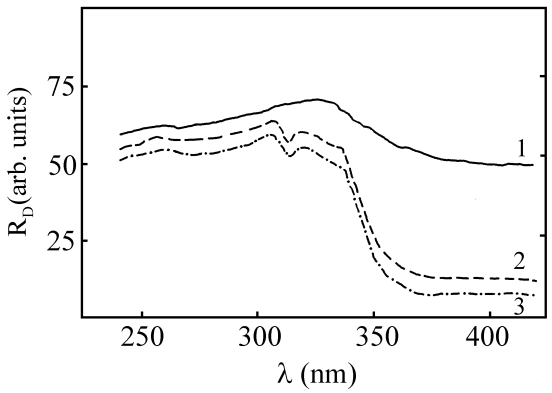

Fig. 3. UV diffuse reflection R_D spectra of carbon black in a polyepoxy oligomer with microcrystalline ZnS: curve 1 - 0.01wt.%; curve2 - 0.02 wt.% and curve 3 - 0.04 wt.%. The reference electrode was a standard white plate.

3. Results and discussion

The obtained transmission spectra of the fullerenes in xylene (Fig. 1) demonstrate the presence of

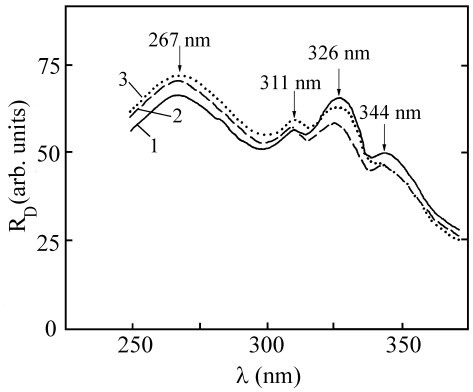

Fig. 4. UV diffuse reflection R_D spectra of fullerenes in a polyepoxy oligomer with microcrystalline ZnS:Cu: curve 1 - 0.02 wt.%; curve 2 - 0.04 wt.% and curve 3 - 0.08 wt.%. The reference electrode was a polyepoxy oligomer with microcrystalline ZnS:Cu on a glass substrate.

maxima for all studied concentrations, probably related to the presence of fullerene clusters. This effect is most clearly expressed for λ=267 nm, i.e. well exceeding the associated values for $(C_{60})_n$, where n is ≤ 4 [5,6].

The diffuse reflectivity spectra of light $R_D=f(\lambda)$ in the UV range λ = 220 to 420 nm (Fig. 2) show a considerable increase of R_D in the shorter wavelength range. An increase in the fullerene concentration leads also to a R_D increase for λ < 345 nm.

After introducing finely dispersed carbon black into the composite layer [4], there is a considerable decrease in R_D with increasing carbon black concentration, for the whole studied UV range (Fig. 3).

If the reference electrode of pressed MgO is substituted by a layer of polyepoxy oligomer with microcrystalline ZnS:Cu, then the R_D spectra (Fig. 4) become much more clear and allow one to distinguish four maxima, changing with the increasing fullerene concentration in the composite.

In the range of very low fullerene concentrations W_f = 0.001 to 0.01 wt. % in the polymer composite, there is (Fig. 5) a considerable increase in the electroluminescent brightness (B). This effect is probably due to the high activity of dimers and trimers of $(C_{60})_n$ associates on the surface of microcrystalline ZnS at high dissolution rates [7,8].

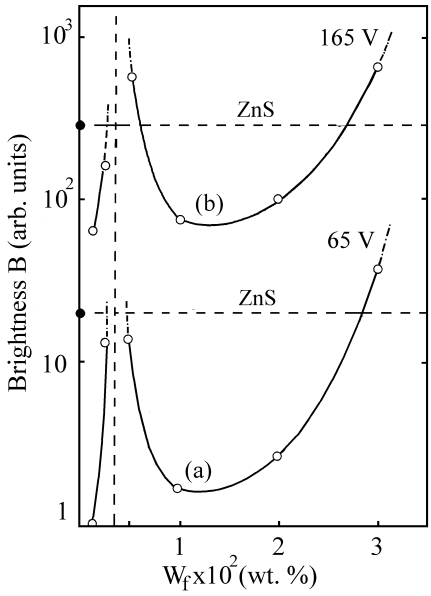

Fig. 5. Dependence of brightness on the fullerene weight percentage additives(W_f) in the ranges 0.1 to3 x 10^2 wt. %: (a) brightness at 65 volts, frequency 1kHz; (b) brightness at 165 volts, frequency 1 kHz.

3. Conclusions

The observed strongly expressed absorption maximum in the transmission spectra for C_{60}/C_{70} at λ = 267 nm is manifested as the main maximum in the diffuse reflection spectra $R_D = f(\lambda)$.

In the diffuse reflection spectra R_D, apart from the maximum at λ_0=267 nm, there are other three clearly expressed maxima at λ_1=311 nm, λ_2=326 nm and λ_3=344 nm, which are also increasing with fullerene concentration increase.

In the range of very low fullerene concentrations, W_f = 0.001 to 0.01 wt. % in the oligomer matrix of microcrystalline ZnS:Cu, a new region of increased electroluminescence has been observed.

The obtained results are related to the problem of obtaining stable and highly effective multilayer systems with fullerene activation, for photovoltaic or electroluminescent devices.

Acknowledgements

The present work is realized with financial support from the National Council "Scientific Investigation" at the Ministry of Education and Science in Bulgaria, under contract LME 294/06.

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