A novel fluorinated Eu(III) β-diketone complex as thin film for optical device applications

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Abstract

We discuss the synthesis and spectroscopic characteristics of a thin film ($\sim$30–90 nm) based on lanthanide europium (III) complexes as the emitter layers, to shift the UV portion of light spectrum into the visible region. The complex presents high quantum efficiency ($\sim$65%), is highly volatile and thermodynamically stable. In addition, the thin film is used as an alternative antireflection coating on a silicon solar cell, allowing for an improvement of about 21% on cell efficiency. The high absorption and luminescence properties in the UV–visible region and its compatibility with device fabrication processes make this material of great potential for use in advanced optical device technologies. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In the past decade, luminescent lanthanide complexes have been intensively studied with particular interest in applications as high efficient light conversion molecular devices (LCMD), as described by Lehn [1]. They embrace a class of new materials with potential applications in a wide range of processes and new technologies, such as luminescent materials [2], sensors for bioinorganic applications [3], luminescent labels in bioaffinity assays [4], europium complex supported on y zeolite [5], and high technology optics and optoelectronic applications [1–4], among others. The design of new attennas [2,6] capable of forming stable and highly luminescent complexes aims at achieving strong ligand-centered absorption in the UV region, efficient ligand-to-metal energy transfer rates and intense lanthanide centered emission in the visible range (Eu(III): red, Tb(III): green, Tm(III): blue).

The approach we have followed to design the europium LCMD is based upon both theoretical [6,7] and experimental [8,9] work, through the investigation of a large number of possibilities involving different Eu(III) and Tb(III) complexes. The fluorinated complexes of this β-diketones of europium (III) and terbium (III) make an ideal family of compounds to study the effects of various parameters on emission and the efficiency of luminescence. This is a consequence of the fact that

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these complexes present a strong ligand-centered absorption, an efficient energy transfer from the ligands to metal, a sensitized metal-centered luminescence, and long-lived excited states.

In this work we present the first experimental results on thin film device structures of the complex Eu(btfa)$_3$bipy, where 4,4,4-trifluoro-1-phenyl-1,3-butanedione (btfa) and bipiridyne (bipy) was used as a second ligand aiming at increasing the quantum yield of the Eu(III) luminescence, by reducing the multiphonon non-radioactive losses, increasing the energy transfer rates and the UV absorption. These properties are restricted to a few lanthanide complexes, and in the case of Eu(btfa)$_3$bipy it presents the additional properties of being highly volatile and thermodynamically stable not only in the powdered form but also as thin film. These characteristics suggest the Eu(btfa)$_3$bipy as a strong candidate for device applications in a variety of areas. As an example, we present the case of a thin film of the Eu(btfa)$_3$bipy complex used as an antireflection coating (ARC) on a silicon solar cell, as discussed later, and that allows for an improvement of about 21% on the cell efficiency. To our knowledge this is the first time that this complex is produced as a thin film and its optical and photon conversion properties are used to demonstrate the beneficial effects on microelectronic device characteristics.

2. Experimental details

2.1. Synthesis of Eu(btfa)$_3$ bipy

The starting materials to synthesize the complex were high purity Eu$_2$O$_3$ (99.999%), btfa (99%) and bipy (99%) supplied by Aldrich, recrystallized twice in high grade ethanol supplied by Merck, and subsequently sublimated. Here, btfa stands for 4,4,4-trifluoro-1-phenyl-2,4-butanedione and bipy stands for 2,2′-bipiridyne. Then, the europium adduct was prepared in a similar procedure as described elsewhere [10]. The synthesis was accomplished by adding a stochiometric quantity of an ethanolic solution of hydrated nitrate of europium(III) dropwise to an ethanolic solution of the btfa anion (prepared by neutralization with an

aqueous solution of NaOH) and bipy, in a three to one ratio over a 2 h period. The product compound precipitates and was separated by filtration and washed with a small amount of alcohol. The complex was then dried at 60°C over P$_2$O$_5$ at a pressure of less than 1 mm Hg in an Abderhalden drying apparatus. The process yields crystals suitable for X-ray structure determination that coupled to micro-analysis and IR vibrational data allowed for a consistent determination of the expected formula Eu(btfa)$_3$bipy. The adduct crystallizes in a monodinic space group (P2$_{1/n}$) with four molecules in the unit cell. The complex is eight-coordinate and all six oxygen atoms average an Eu–O distance of 2.582 Å [10].

2.2. Instrumentation and physical measurements

The absorption spectra were obtained using a Pekin–Elmer UV–visible Spectrophotometer, Lambda-6 model 2688-002. The luminescence and excitation spectra were obtained by scanning a 1 m double-grating Jobin–Yvon Ramanor U-1000 Spectrophotometer with a slit width of 0.05 mm. Excitation was effected using a 150 W xenon lamp and a 0.25 m holographic grating monochromator for wavelength selection. The light detection was performed by a water-cooled RCA C311034 photomultiplier tube, with the photocurrent signal being acquired through a EG & G discriminator model 1182 and digitally stored by a Jobin–Yvon Spectralink interface and a personal computer. Lifetime measurements were made at 300 K using a nitrogen laser as the excitation source and monitored at 337 nm. The quantum yield (q_x) of the $^5D_0$ luminescence of the Eu(III) complex was determined by comparison with standard phosphorous (viz. sodium salicylate), whose efficiencies have been previously determined by absolute measurements [11–13] as described in Section 3.

2.3. Thin film and device processing

The Eu(btfa)$_3$bipy thin films used in the absorption, luminescence and lifetime measurements were prepared by the deposition of the complex on a slide of quartz substrate previously cleaned and degreased to assure proper film adhesion. Films

with thickness approximately 30–90 nm were thermally co-evaporated from an alumina crucible onto the quartz substrate surface and photolitographically defined to form rectangular structures with an area of about 1 cm^2. The thickness of the films were monitored during deposition by a quartz crystal thickness meter and by posterior ellipsometry measurements at several wavelengths to assure film quality and uniformity. The refraction index of the Eu(btfa)$_3$bipy thin films was determined by ellipsometry to be 1.611 ± 0.04 at 6328 nm.

To further test the optical properties of the Eu(btfa)$_3$bipy thin films as potential candidate for use in silicon devices as antireflection coatings of solar cells, p-n junctions were fabricated using simple fabrication techniques [14]. Silicon wafers (1 0 0) p-type oriented (2 in. of diameter) of 1Ω-cm resistivity were cleaned following a standard cleaning process [11], except for the last step, where the wafers were immersed in a 3% HF dip solution, prior to furnace loading. The p-n junctions were formed (after diffusion of a high concentration phosphorous silica glass spun onto specific regions of the wafer surface) in a Thermco MB-80 furnace at 1000°C for 70 min to a depth of about 1 μm. Aluminum films approximately 200 nm thick were thermally evaporated from a W boat on to the wafer surface, and photolitographically defined to form circular gates with area of 1×10^{-4} cm^2, within the effective solar cell area of 1×10^{-2} cm^2. After backside metallization, the wafers were annealed in forming gas at 400°C for 30 min. The solar cells were characterized in a HP 4155A semiconductor parameter analyzer, before and after the Eu(btfa)$_3$bipy ARC deposition. After initial characterization some solar cells were covered by an appropriated Eu(btfa)$_3$bipy complex thin film deposited by thermal evaporation.

3. Results and discussion

In order to evaluate its potential for device applications and to better understand the optical characteristics of the Eu(btfa)$_3$bipy complex, we perform absorption and luminescence measurements, in particular for the thin films deposited on

a quartz substrate. Fig. 1 presents the UV–visible absorption spectra of the complex in (a) ethanolic solution (where it shows high molar absorption coefficients) and in (b) solid state (as a thin film). In these spectra one can notice intensity bands which are characteristic of the chromophoric group (bipy). In addition to these common properties of the complex, the absorption spectrum of the thin film presents significant differences from those in solution. In particular, the thin film spectrum shows invariably a line broadening and shift towards red from ∼20 nm. This may be due to the presence of isomers of the complex and/or the packing effect in the thin film as a result of changes in the microsymmetry around the Eu(III) and/or solvent effect.

Fig. 2 shows the luminescence spectrum of a 40 nm thin film of Eu(btfa)$_3$bipy at 300 K, taken with a slit opening of 0.05 mm. The results show that the $^5D_0 \rightarrow {}^7F_2$ transition (the overwhelming predominant emission line) is approximately ten times more intense than the $^5D_0 \rightarrow {}^7F_1$ transition, resulting in a highly red emission. On the other hand, the $^5D_0 \rightarrow {}^7F_4$ transition has a considerable intensity, when compared to the same line in complexes of the same family [10]. The transition $^5D_0 \rightarrow {}^7F_0$ is a singlet and transition $^5D_0 \rightarrow {}^7F_1$ is a triplet, indicating the presence of a single site, in
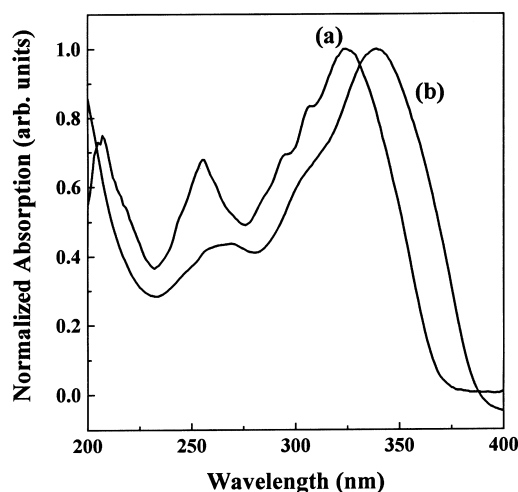

Fig. 1. Absorption spectrum of the Eu(btfa)$_3$bipy complex in (a) ethanolic solution, and (b) as a thin film of thickness 40 nm on a quartz substrate.
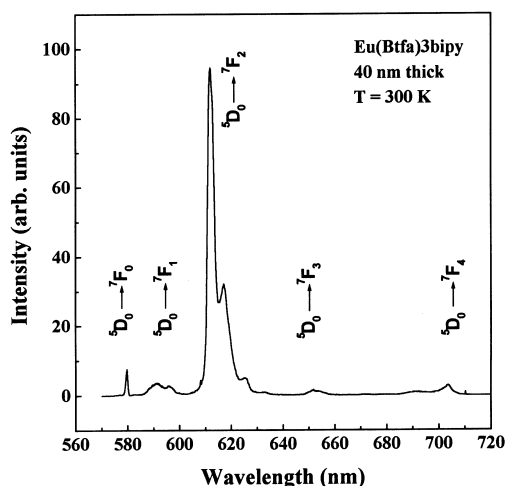
Fig. 2. Luminescence spectrum of a 40 nm thin film of the Eu(btfa)$_3$bipy complex at 300 K, upon ligand excitation (370 nm).

agreement with the X-ray data which recognizes a single species [10]. We have also obtained the decay curve of the luminescent $^5D_0$ state by monitoring the $^5D_0 \rightarrow {}^7F_2$ emission line for a 40 nm thin film of Eu(btfa)$_3$bipy complex as shown in Fig. 3. The decay of luminescence is often a double exponential line [2,7] but for the thin films of Eu(btfa)$_3$bipy complex the two exponentials

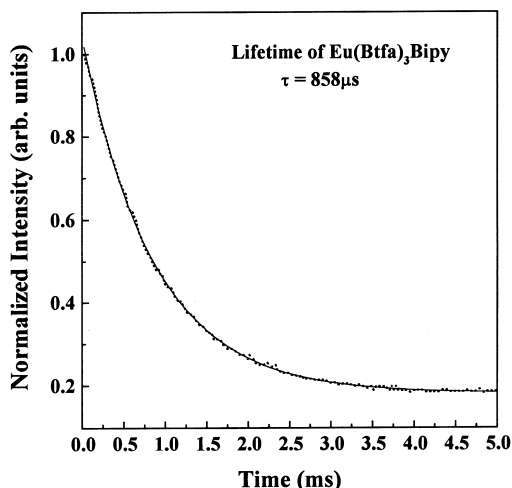Fig. 3. The decay curve of the luminescent $^5D_0$ state for the Eu(btfa)$_3$bipy complex and its least square fitting into a single exponential function. Thin film thickness is 40 nm.

present very close time constants (within 2%) allowing for the least square fitting to a single curve. The lifetime for the single exponential is found to be $\tau \sim 858$ μs and this value is the highest among the complex family, which suggests it to be the strongest candidate to date for use as LCMD. It is important to mention that in the luminescence decay curve of Fig. 3 the time base used does not allow for clear evaluation of the background signal, which is very low and limited in our experiments by the background noise of the photomultiplier tube used in the light detection system.

The quantum efficiency of this complex is in general a result of optimizing absorption, non-radioactive decay, energy transfer and emission rate. For the Eu(btfa)$_3$bipy complex the luminescence quantum yield was obtained by the method described by Bril and co-workers at the Phillips Research Laboratories [12,13], using sodium salicylate (Merck) as a standard phosphorous. The quantum yield is defined as the ratio between the number of photons emitted by the Eu(III) ion and the number of photons absorbed by the ligand. The quantum yield q_x of a sample was calculated by using the expression as follows:

$$q_x = \left(\frac{1 - r_{st}}{1 - r_x} \right) \times \left(\frac{\Delta\Phi_x}{\Delta\Phi_{st}} \right) \times q_{st},$$

where r_{st} and r_x are the amount of exciting radiation reflected by the standard and by the sample respectively, and q_{st} is the quantum yield of the standard. The terms $\Delta\Phi_x$ and $\Delta\Phi_{st}$ give the integrated photon flux (counts/s) respectively for the sample and the standard phosphorous. The quantum yield standard Φ-values are the average of at least two sets of three measurements, with the sample being removed and replaced in the sample holder for every other measurement. This method provides absolute efficiencies while avoiding absolute measurements, and has been described in detail elsewhere [15]. The quantum yield standard (sodium salicylate) has a broad band emission with a maximum at 450 nm and $q = 60\%$. The highest quantum yield is observed for the complex Eu(btfa)$_3$bipy with $q_x \sim 65\%$, which is comparable with recently developed phosphorous materials [16].

The long-term stability of the Eu(btfa)$_3$bipy complex in the thin film form has been observed over a six month period, exposed to atmospheric pressure, and no noticeable change in its properties was found. All the above characteristics, allied to the compatibility with standard device processing techniques (for thin film production) suggest the possibility of using the material in device applications. One of the simplest approaches that comes immediately to mind would be its use as ARC of photovoltaic devices such as solar cells and photo detectors or sensors associated to silicon technology.

Fig. 4 illustrates the use of a thin film of the Eu(btfa)$_3$bipy complex deposited over a silicon p-n junction solar cell. Two effects are expected, from this experiment, to affect the solar cell efficiency due to the presence of the thin film: (a) an improvement in efficiency is expected due to less reflection of incident light (we refer to the mid-visible spectral range ~ 550 nm for silicon average optical response) when the thin film thickness is equal to $\lambda/4n$, and (b) due to the luminescent properties of the complex some further improvement of the solar cell efficiency is expected as a result of the ultraviolet $\rightarrow$ visible (red) photon

energy conversion as evident from the absorption and luminescent spectra presented in Figs. 1 and 2. The latter is a consequence of the better photon response of silicon cells in the visible, in opposition to the UV spectral region. The curves in Fig. 4 represent the solar cell current–voltage ($I \times V$) characteristics (a) in dark, (b) illuminated without ARC and (c) illuminated with a 85.5 nm thick ARC of the Eu(btfa)$_3$bipy thin film. The improvement obtained in the solar cell efficiency is $\sim 21\%$ when the ARC is used. The curve (b) indicates an efficiency of 4.3%, while in curve (c) the efficiency is improved to 5.2% for the same solar cell after the ARC layer deposition. It is important to notice that the results presented in Fig. 4 are mainly illustrative and more elaborate optimization in processing is needed for use with higher efficiency solar cell devices produced with more complex cell structures.

4. Conclusions

The synthesis and optical characterization of thin films of a newly developed Eu(btfa)$_3$bipy complex were discussed. Compared to a wide family of fluorinated volatile β-diketones with Eu(III) ions, this material can be easily produced as a thin film, due to its high volatility and thermodynamic stability. The complex shows very high quantum efficiency ($\sim$65%) and compared to recently developed phosphorous materials it is a strong candidate for the development of new optical device technologies. Light conversion molecular devices and photovoltaic devices are examples of such applications. Presently we are in the process of developing multilayer structures of different β-diketone thin films in order to design electroluminescent devices using these lanthanide complexes.
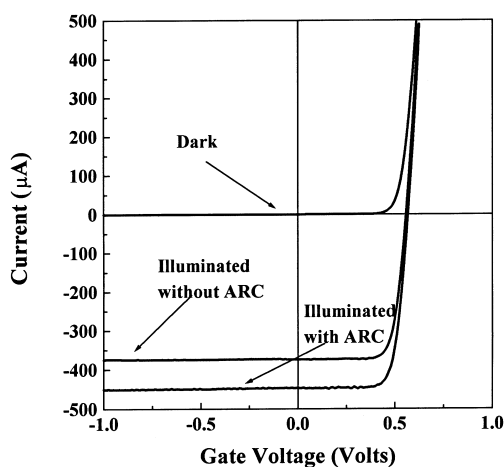

Fig. 4. Current versus voltage characteristics of a silicon p-n junction solar cell without and with an antireflection coating (ARC) of Eu(btfa)$_3$bipy thin film of thickness 85.5 nm. (a) Dark, no ARC; (b) illuminated, no ARC, and (c) illuminated, with ARC. Improvement of about 21% in the solar cell yield is achieved with the Eu(btfa)$_3$bipy ARC layer.

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