Red electroluminescence from Tb$_2$O$_3$: Eu/PEDOT: PSS heterojunction light-emitting diodes

Guangmiao Wan 1, Shenwei Wang 2, Ling Li 2, Xue Yin 2, Guangyao Mu 2, and Lixin Yi 2

1School of Electronic and Computer Engineering, Peking University, Shenzhen 518055, China
2School of Science, Beijing Jiaotong University, Beijing 100044, China

Abstract-In this work, heterojunction light-emitting diodes made of Tb$_2$O$_3$: Eu and PEDOT: PSS were prepared and the impact of PEDOT: PSS on luminous intensity of the devices was studied. The electrical and optical properties of the devices were tested. Five luminescence peaks at 544, 585, 610, 648, and 695 nm, corresponding to Tb$^{3+}$ 5D$_4$ → 7F$_5$ and Eu$^{3+}$ 5D$_0$ → 7F$_1$, 5D$_0$ → 7F$_2$, 5D$_0$ → 7F$_3$ and 5D$_0$ → 7F$_4$ transitions were observed. The PEDOT: PSS film has an enhancement effect on electroluminescence.

1. Introduction

In recent years, silicon-based light sources have received extensive attention and research due to their applications in integrated photonics. [1-3]. Among them, rare earth doped light-emitting devices have attracted great interest due to their wide spectral range and high luminous efficiency. [4, 5]. Ce-related emissions at 390 and 410 nm due to 4f-5d transitions are used in blue light-emitting devices [6, 7]. Er$^{3+}$ is researched because of its emission at 1.54 μm, which is widely used in the communication field [8, 9].

Since energy transfer can be performed between different rare earth ions, devices based on rare earth doping are widely studied. Li et al. gained multicolor emission from Ga$_2$O$_3$/Tb$_2$O$_3$: Re/Si structure [10]. Mu et al. reported near-infrared emissions from Yb$^{3+}$-doped CeO$_2$ and Ce$_2$Si$_2$O$_7$ films [11]. Compared with inorganic materials, organic materials are easy to realize p-type conductivity and are widely used in electroluminescence [12]. And some organic-inorganic hybrid light-emitting devices have been reported [13, 14]. Therefore, Tb$_2$O$_3$: Re/polymer heterojunction light-emitting devices are well worth studying. However, related light-emitting devices have not been reported.

In this paper, we prepared heterojunction light-emitting devices made of Tb$_2$O$_3$: Eu and PEDOT: PSS. The electrical and optical properties of the devices were tested, and the electroluminescence mechanism was analyzed. The effect of the PEDOT: PSS film on performance was studied.
2. Experimental

Figure 1 The structure diagram of the Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device.

The cross-sectional schematic of a Tb$_2$O$_3$: Eu/PEDOT: PSS heterojunction light-emitting diode is shown in Figure 1. A Tb$_2$O$_3$: Eu thin film was prepared on N-type (100) silicon substrate by magnetron co-sputtering. The targets used were Tb target (99.95%) and Eu$_2$O$_3$ target (99.99%). The sputtering power was 200 W. The gas flow rate of argon and oxygen were kept at 15 sccm and 5 sccm, respectively. The working pressure was 0.5 Pa. The thickness of Tb$_2$O$_3$: Eu film was 100 nm and the doping concentration of Eu$^{3+}$ was 1 at.%. In order to reduce defects in the film, the film was annealed. The annealing atmosphere, temperature and time were air, 800°C and 40 minutes, respectively. Afterwards, a PEDOT: PSS film was deposited on the Tb$_2$O$_3$: Eu film by spin coating. The concentration of the PEDOT: PSS aqueous solution used was 1.4%, the spin coating atmosphere was air, the speed of the homogenizer was 4000 revolutions per minute, and the spin coating time was 30 seconds. The thickness of the PEDOT: PSS film was 80 nm. In order to evaporate the solvent in the PEDOT: PSS film and improve its conductivity, the film was dried. Drying atmosphere, temperature and time were air, 120°C and 20 minutes, respectively. After that, 200 nm of ITO and silver were prepared on the upper surface of the PEDOT: PSS thin film and the lower surface of the silicon substrate as electrodes of the electroluminescent device, respectively.

Current–voltage (I-V) characteristics and electroluminescent spectra of the devices were measured by a Keithley 2410 and a charge coupled device, respectively. All these measurements were taken at room temperature.

3. Results and discussion

Figure 2 The I-V characteristic of the Tb$_2$O$_3$: Eu electroluminescent device and the Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device.
The electroluminescence performance of the device was tested and compared with the Tb$_2$O$_3$: Eu electroluminescence device without PEDOT: PSS layer. Figure 2 shows the I-V curve of Tb$_2$O$_3$: Eu electroluminescent device and Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device. It can be seen from the figure that these two I-V curves are relatively smooth and have obvious rectification characteristics. Compared with the Tb$_2$O$_3$: Eu electroluminescent device, the Tb$_2$O$_3$: Eu/PEDOT: PSS device has a higher turn-on voltage (from 15 V to 16 V) and a smaller current.

The electroluminescence spectrum and photo of Tb$_2$O$_3$: Eu electroluminescent device and Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device at 26V are shown in Figure 3. It can be seen from the figure that the Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device and the Tb$_2$O$_3$: Eu electroluminescent device have the same shape of the electroluminescence spectrum. There are five luminescence peaks at 544, 585, 610, 648 and 695 nm, respectively. The peaks correspond to $^5$D$_4 \rightarrow ^7$F$_5$ of Tb$^{3+}$ and $^5$D$_0 \rightarrow ^7$F$_1$, $^5$D$_0 \rightarrow ^7$F$_2$, $^5$D$_0 \rightarrow ^7$F$_3$ and $^5$D$_0 \rightarrow ^7$F$_4$ transitions of Eu$^{3+}$, respectively [15, 16]. Among them, the $^5$D$_0 \rightarrow ^7$F$_1$ transition of Eu$^{3+}$ corresponds to the magnetic dipole transition, which occurs when Eu$^{3+}$ is located at the symmetric lattice point of the inversion center, and its transition probability has nothing to do with the crystal field environment; the $^5$D$_0 \rightarrow ^7$F$_2$ transition corresponds to the electric dipole transition, occurring when Eu$^{3+}$ is located at a center-symmetric lattice without inversion. The transition probability is easily affected by the crystal field environment [17, 18]. After Eu$^{3+}$ doping in the Tb$_2$O$_3$ layer, only the Tb$^{3+}$ emission peak at 544 nm was observed, and the Tb$^{3+}$ emission was significantly weaker than the Eu$^{3+}$ emission, indicating that energy transfer from Tb$^{3+}$ to Eu$^{3+}$ occurred. Because the PEDOT: PSS layer has the function of blocking electrons and injecting holes in the device, the Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device is superior to the Tb$_2$O$_3$: Eu electroluminescent device in terms of luminous intensity, which is about 2 times of the latter.

![Electroluminescence spectra and images of the Tb$_2$O$_3$: Eu electroluminescent device and the Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device at the forward bias of 26V.](image)

Through the luminescence spectrum of Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device, the color coordinate of the device can be calculated as (0.60, 0.40). Figure 4 shows the corresponding CIE chromaticity diagram.
Figure 4 Chromaticity diagram of CIE of the Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device.

Figure 5 Schematic luminescence mechanism diagram of the Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device.

The luminescence mechanism of PEDOT: PSS/Tb$_2$O$_3$: Eu electroluminescent device is shown in Figure 5. When the device is in forward bias, the electrons in the N-type Si substrate tunnel through the SiO$_x$ layer and enter the conduction band of Tb$_2$O$_3$. Meanwhile, the holes in the ITO electrode and PEDOT: PSS hole injection layer enter the valence band of Tb$_2$O$_3$. After that, the electrons in the conduction band recombine with the holes in the valence band and release energy, thereby exciting the electrons in Tb$_2$O$_3$ from the valence band to the 4f$^{11}$ excited energy level. Excited state electrons reach the $^5$D$_4$ energy level after a series of non-radiative relaxations, and then transition downward, which can produce characteristic luminescence peaks Tb$^{3+}$ at 488 ($^5$D$_4 \rightarrow ^7$F$_{5}$), 544 ($^5$D$_4 \rightarrow ^7$F$_{4}$), 584 ($^5$D$_4 \rightarrow ^7$F$_{3}$) and 618 nm ($^5$D$_4 \rightarrow ^7$F$_{2}$). After doping Eu$^{3+}$ in the Tb$_2$O$_3$ layer, Tb$^{3+}$ can efficiently transfer energy to Eu$^{3+}$ through resonance transmission. Therefore, the electrons relaxed to the $^5$D$_4$ energy level of Tb$^{3+}$ and reached the $^5$D$_0$ energy level of Eu$^{3+}$ after the non-radiative relaxation process. Then the energy transfer process resulted in Eu$^{3+}$ luminescence at 585 ($^5$D$_0 \rightarrow ^7$F$_{1}$), 610 ($^5$D$_0 \rightarrow ^7$F$_{2}$), 648 ($^5$D$_0 \rightarrow ^7$F$_{3}$) and 695 nm ($^5$D$_0 \rightarrow ^7$F$_{4}$), respectively.
4. Conclusions

Tb$_2$O$_3$: Eu/PEDOT: PSS heterojunction light-emitting diodes were prepared by magnetron co-sputtering. The electrical and optical properties of the devices were tested. The Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent devices have five luminescence peaks at 544, 585, 610, 648, and 695 nm, corresponding to Tb$^{3+}$ $^5$D$_4$ $\rightarrow$ $^7$F$_5$ and Eu$^{3+}$ $^5$D$_{0}$ $\rightarrow$ $^7$F$_{1}$, $^5$D$_{0}$ $\rightarrow$ $^7$F$_{2}$, $^5$D$_{0}$ $\rightarrow$ $^7$F$_{3}$ and $^5$D$_{0}$ $\rightarrow$ $^7$F$_{4}$ transitions, respectively. The luminescence of Tb$^{3+}$ is significantly weaker than that of Eu$^{3+}$, indicating that energy transfer from Tb$^{3+}$ to Eu$^{3+}$ has occurred. Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device is superior to Tb$_2$O$_3$: Eu electroluminescent device in terms of luminous intensity, which is about 2 times of the latter. The PEDOT: PSS film has an enhancement effect on electroluminescence. At a doping concentration of 1 at. %, the color coordinates of the Tb$_2$O$_3$: Eu/PEDOT: PSS electroluminescent device is (0.60, 0.40).

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 61275058). It was also supported by the School of Electronic and Computer Engineering, Peking University.

References

[1] S. Pillai, K.R. Catchpole, T. Trupke, G. Zhang, J. Zhao, M.A. Green, Enhanced emission from Si-based light-emitting diodes using surface plasmons, Applied Physics Letters, 88 (2006) 161102.
[2] T. Sunohara, K. Kobayashi, T. Suemasu, Epitaxial growth and characterization of Si-based light-emitting Si/beta-FeSi$_2$ film/Si double heterostructures on Si(001) substrates by molecular beam epitaxy, Thin Solid Films, 508 (2006) p. 371-375.
[3] M. Modreanu, M. Gartner, E. Aperathitis, N. Tomozetu, M. Androulidaki, D. Cristea, P. Hurley, Investigation on preparation and physical properties of nanocrystalline Si/SiO$_2$ superlattices for Si-based light-emitting devices, Physica E-low-dimensional Systems & Nanostructures, 16 (2003) 461-466.
[4] M.E. Castagna, S. Coffa, M. Monaco, Si-based rare-earth-doped light-emitting devices, Proceedings of Spie the International Society for Optical Engineering, 5366 (2004) 137-148.
[5] J.M. Sun, L. Rebohle, S. Prucnal, M. Helm, W. Skorupa, Giant stability enhancement of rare-earth implanted SiO$_2$ light emitting devices by an additional SiON protection layer, Applied Physics Letters, 92 (2008) 071103.
[6] L. Chen, J. Li, M. Ge, Promotional Effect of Ce-doped V2O5-WO3/TiO2 with Low Vanadium Loadings for Selective Catalytic Reduction of NOx by NH3, Journal of Physical Chemistry C, 113 (2009) 21177-21184.
[7] W. Trabelsi, P. Cecilio, M.G.S. Ferreira, M.F. Montemor, Electrochemical assessment of the self-healing properties of Ce-doped silane solutions for the pre-treatment of galvanised steel substrates, Progress in Organic Coatings, 54 (2005) 276-284.
[8] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, K. Yamamoto, 1.54 μm photoluminescence of Er3+ doped into SiO2 films containing Si nanocrystals: Evidence for energy transfer from Si nanocrystals to Er$^{3+}$, Applied Physics Letters, 71 (1997) 1198-1200.
[9] M. Nishi, S. Tanabe, M. Inoue, M. Takahashi, K. Fujita, K. Hirao, Optical-telecommunication-band fluorescence properties of Er3+-doped YAG nanocrystals synthesized by glycothermal method, Optical Materials, 27 (2005) 655-662.
[10] L. Li, S.W. Wang, G.Y. Mu, X. Yin, L.X. Yi, Multicolor light-emitting devices with Tb$_2$O$_3$ on silicon, Scientific Reports, 7 (2017) 42479.
[11] G. Mu, S. Wang, L. Li, X. Yin, M. Huang, L. Yi, Near-infrared emissions from Yb$^{3+}$-doped CeO2 and Ce2Si2O7 films based on silicon substrates subjected to thermal treatment, Applied Physics A, 5 (2016) 1-5.
[12] J. Meyer, S. Hamwi, S. Schmale, T. Winkler, H.H. Johannes, T. Riedl, W. Kowalsky, A strategy
towards p-type doping of organic materials with HOMO levels beyond 6 eV using tungsten oxide, Journal of Materials Chemistry, 19 (2009) 702.

[13] Y.H. Kim, H. Cho, J.H. Heo, T.S. Kim, N. Myoung, C.L. Lee, S.H. Im, T.W. Lee, Multicolored Organic/Inorganic Hybrid Perovskite Light-Emitting Diodes, Adv. Mater., 27 (2015) 1248-1254.

[14] G. Wan, S. Wang, M. Huang, Y. Zhang, K. Ou, L. Yi, Green electroluminescence from Tb2O3/polymer heterojunction light-emitting diodes, Journal of Materials Science, 53 (2018) 13949–13954.

[15] T. Wang, H. Li, A simple and green strategy for preparing luminescent Tb3+ complex-based nanocomposite with stable luminescence in water, Mater. Res. Bull., 93 (2017) 28-34.

[16] J. Heikenfeld, M. Garter, D.S. Lee, R. Birkhahn, A.J. Steckl, Red light emission by photoluminescence and electroluminescence from Eu-doped GaN, Applied Physics Letters, 75 (1999) 1189.

[17] S.A. Naidu, U.V. Varadarajuz, Electric dipole red emission in Eu3+-doped low bandgap oxide LiInO2, Electrochemical & Solid State Letters, 11 (2008) J40-J42.

[18] A.K. Banerjee, A.K. Mukhopadhyay, R.K. Mukherjee, M. Chowdhury, 7F0-5D1 transition in Eu3+—hexakisantipyrene-triiodide single crystal. A magnetic dipole transition, Chemical Physics Letters, 67 (1979) 418-419.