

Red light emission from ZnO:Eu³⁺/CuSCN hetero-junction under cathodic polarization

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Introduction

Recently a considerable interest has been shown on the studies of photo-luminescence (PL) of lanthanides doped oxide ceramics. The group of rare-earth ions exhibits unique PL bands at particulate wavelengths that are highly independent from the host matrix. However, width and intensity of PL bands frequently change with the host material. Eu³⁺ ions are one of the best candidates to study luminescence properties compared to other lanthanide elements (Nogami, 2002). In this study, Eu³⁺ ions were bonded to ZnO ceramic via organic molecules. Further enhancement of luminescence bands was observed by coupling with selected oligomers to Eu³⁺ ions. A hetero-junction was prepared by depositing copper-thiocyanate on surface modified zinc oxide ceramic. Red light emission was observed from the surface bounded Eu³⁺ ions of ZnO:Eu³⁺/CuSCN hetero-junction under reverse bias.

Methodology

ZnO was deposited on Fluorine doped tin oxide (FTO) coated glass substrates as previously discussed (Sirimanne et al, 2011). ZnO thin films were kept immersed in 2,2'-bipyridyl 4,4'-dicarboxylic acid (abbreviated as dcbpy, 200 µM in ethanol), EuCl₃ (1 mM in ethanol) and 2-thenoyltrifluoroacetone (abbreviated as TTA, 200 µM in ethanol) for one hour in each solution in order. Temperature of solutions was maintained as 80°C. ZnO|dcbpy|Eu³⁺|TTA electrodes were films dried at 60°C for 30 min. 0.1g of CuSCN was dissolved in propylsulfide and centrifuge the solution for separate residue. Small amount of this solution was spread on the surface of modified ZnO electrodes pre-heated at 150°C. A thin layer of graphite was finally coated on p-CuSCN layer by painting carbon powder on the electrode. Characteristics of ZnO|dcbpy|Eu³⁺|TTA|CuSCN hetero-junction were studied.

Results and Discussion

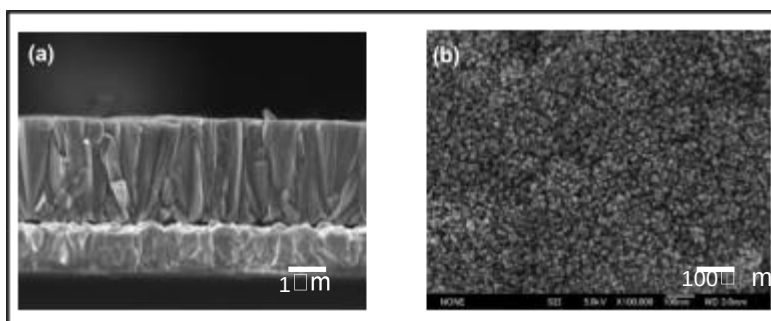


Figure 1. Morphology of (a) cross section and (b) surface of the ZnO film.

Morphology of ZnO films utilized for this investigation is shown in Fig. 1. As is shown ZnO films exhibited nano-rods like a structure. This structure occupies higher surface area than its geometrical area and also exhibited high degree of crystallinity with the predominant orientation of (002) crystal plane. Doping of Eu³⁺ ions in metal oxide ceramics is known to increase the luminescence especially in visible region (Lu et al, 2007). A simple technique is chosen to link

Eu^{3+} ions to ZnO films by using organic molecules. Organic molecule dcbpy has a capability of bonding with ZnO via carboxylic groups and also with other cations by excess electrons at nitrogen sites in the same molecule. Similar, techniques have been used to bind Ru^{3+} ions with TiO_2 substrates in dye-sensitized solar cells.

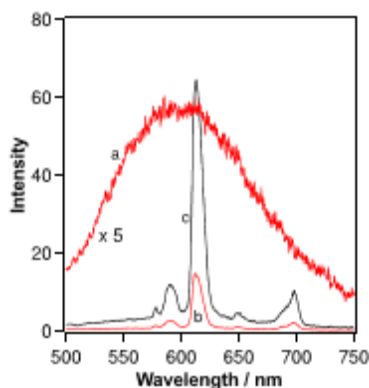


Figure 2. Emission spectra for (a) ZnO, (b) ZnO|dcbpy| Eu^{3+} and (c) ZnO|dcbpy| Eu^{3+} |TTA electrodes, excitation was carried out at 370, 315 and 374 nm, respectively.

Luminescence spectrum of (a) ZnO, (b) ZnO|dcbpy| Eu^{3+} is shown in Fig. 2. ZnO exhibits a feeble photoluminescence with the maximum at 600 nm due i.e; oxygen vacancies in the host matrix. Eu^{3+} doped ZnO electrodes exhibit several luminescence bands at 578, 590, 612, 650 and 699 nm with different intensities. These luminescence bands are due to electron transitions from f-f intraconfigurational transitions and can be assigned as $(j=0,1,2,3,4)$ (Zhao et al, 2007). The band at 612 nm exhibited highest intensity among those luminescence bands.

Several attempts were made to increase intensity of ZnO|dcbpy| Eu^{3+} electrodes. TTA was found as a candidate to couple with Eu^{3+} ligand that helps to enhance luminescence of ZnO|dcbpy| Eu^{3+} electrodes. Coupling of organic compounds belonging to oligomers with cations is a well-established phenomenon. Luminescence spectrum of ZnO|dcbpy| Eu^{3+} |TTA electrode is also shown as curve c in Fig. 2. The enhancement of luminescence in the presence of TTA on the electrode is known as antenna effect. Once TTA molecules are attached to Eu^{3+} ions less possibility is to absorb water molecules on the electrode, thus resulting higher luminescence on the electrode.

A semiconductor hetero-junction was fabricated by depositing CuSCN on ZnO|dcbpy| Eu^{3+} |TTA electrodes. Current-voltage characteristics clearly indicated the formation of a semiconductor hetero-junction in electronically between CuCNS and ZnO via S-S bonds. Formation of S-S bonds among compounds has been observed previously. Formation of bonds between CuCNS and ZnO is shown in the inset of Fig. 3. When the opposed potential is negatively increased (more than -6.5 V) a weaker red light emission at 613 nm where the highest luminescence is detected; is observed from the device. The emission spectrum of ZnO|dcbpy| Eu^{3+} |TTA|CuSCN device is shown in Fig. 3.

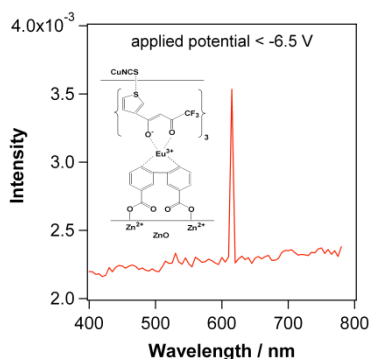


Figure 3. Light emission of ZnO|dcbpy|Eu³⁺|TTA|CuSCN device under reverse bias. Active area of the device is 0.75 cm². Inset shows formation of bonds between CuSCN and surface modified ZnO.

The mechanism of red light emission of ZnO|dcbpy|Eu³⁺|TTA|CuSCN device can be explained as follow, the minority carries gathered large kinetic energy under reverse bias especially at higher negative potentials. These hot electrons move toward the junction with a higher velocity and get collapse with Eu³⁺ ions and get excited. Excited inner core electrons especially in the 5d orbital reach to their ground status by emitting light. Thus results red light emission from the device.

Conclusions

An enhancement of luminescence is observed by doping Eu³⁺ in ZnO matrix. Further enhancement in luminescence is observed by coupling selected oligomers to the Eu³⁺ ions. A hetero-junction is prepared by depositing CuSCN on Eu³⁺ bonded ZnO electrodes. Red light emission is observed under reverse bias from the ZnO|dcbpy|Eu³⁺|TTA|CuSCN device.

References

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