

Solid State Cathodoluminescence and Co-existence of Different Mechanisms of Excitation in EL of Organic-inorganic System

XU Xue-rong, XU Xi-lai, YANG Xiao-hui, XU Zheng, HOU Yan-bing

(*Institute of Optoelectronics, Northern Jiaotong University, Beijing 100044 China*)

摘要: 在有机-无机复合体系的电致发光中发现了固态阴极射线发光, 并证明了不同激发过程的共存现象。这些激发过程可附加、放大并相互补偿, 其综合效应肯定可进一步增强电致发光的性能。

关 键 词: 发光; 多色显示; 稳定性

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1 Introduction

In contemporary technology, the application of luminescence in flat panel displays (FPD) becomes much more important and urgent when the communication becomes personalized. There appear six types of FPD based on emissive displays. Among them inorganic and organic electroluminescence (EL) is especially perspective because of its several attractive characteristics, namely active display, solid state, large view angle, fast response, large range of working temperature, sharp figure and high resolution. But there are still some deficiencies in their displays. The principal problem is lack of brightness especially that of blue color emission in inorganic EL and lack of electronic transport materials and stability in organic EL. We prepared thus an organic-inorganic heterogeneous junction (complex system) for developing their priorities and minimizing their deficiencies. In the field of EL there have been found several kinds of excitations. In this paper, we found a new kind of excitation—solid state CL, and a new phenomenon of co-existence of different mechanisms of excitations in addition to these kinds of excitations. It is very important that all these effects are additive, amplifying or compensatory and lead to reinforce the luminescence intensity and to make the spec-

trum of luminescence wider.

2 Experiments and results

2.1 Discovery of solid-state cathodoluminescence

In solid state materials we used SiO_2 as acceleration layer, which will send the accelerated electrons to excite directly the luminescent materials in the adjacent luminescent layer just like CL. The difference lies in that the energetic electrons are accelerated not in vacuum but in solids. To prove the direct impact excitation of luminescent layer by electrons or CL from the accelerating layer, we choose the phosphor Alq_3 as luminescent layer. This is adequate because Alq_3 is a typical organic electroluminescent material with very small carrier mobility and its EL is proved to be the result of recombination of electrons and holes tunneled from opposite electrodes. We prepared a luminescent cell $\text{ITO}/\text{SiO}/\text{SiO}_2/\text{Alq}_3/\text{SiO}_2/\text{SiO}/\text{Al}$ (a). When an AC voltage is applied to this cell, we get the light emission from Alq_3 . The spectrum of which is shown in Fig. 1. Obviously, this is not coming from the recombination of carriers from opposite electrodes as in ordinary organic electroluminescence because all the layers are electronic transport. This is also not coming from the acceleration of hot electrons within Alq_3 and consequent impact excitation as in ordinary inorganic EL because the mobility of

electrons in Alq_3 is small. Thus the only possibility is direct impact excitation by electrons from outside of Alq_3 , i. e. CL. It is very interesting that the spectrum is in the region of blue light, that means the energy of hot electrons accelerated in SiO_2 is large enough to excite the center to an excited level which is capable of giving blue emission.

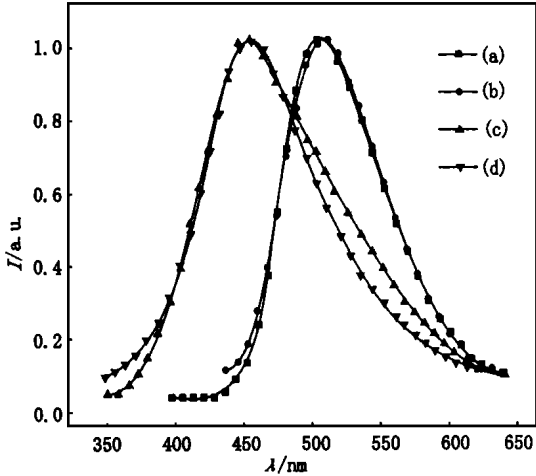


Fig. 1 Normalized emission spectra of AC EL from devices (a) $\text{ITO}/\text{SiO}/\text{SiO}_2/\text{Alq}_3/\text{SiO}_2/\text{Si}/\text{Al}$ () at 40V, (b) $\text{ITO}/\text{Alq}_3/\text{SiO}_2/\text{Al}$ () at 30V, (c) $\text{ITO}/\text{SiO}_2/\text{Alq}_3/\text{Al}$ () at 25V, Normalized photoluminescence spectrum from (a) ().

To make sure this conclusion we measured the photoluminescence (PL) spectrum of sample (a) and the EL spectrum of the samples $\text{ITO}/\text{Alq}/\text{SiO}_2/\text{Al}$ (b) and $\text{ITO}/\text{SiO}_2/\text{Alq}/\text{Al}$ (c). We got two separate peaks at 460 and 530 nm. The 530nm peak is attributed to emission of excitons in Alq_3 and appears in case of PL of (a). When the sample is subjected to high electric field, the excitons will be dissociated. The 530nm peak is diminished and another peak 460nm appears corresponding to direct recombination of electrons with holes. These are observed in cases of (a) and (b). In case of (c) the accelerated electrons may leak into the opposite electrode and no recombination in high electric field can be realized and thus we can observe only the 530 peak. This process can also be verified obviously from the electrophotoluminescence experiment. If we increase the voltage applied to a photoluminescent sample, we can see a gradual shift of the emission peak from 530nm to 460nm as shown

in Fig. 2. These phenomena agree with the consideration of energy of excitons and recombination emission. The former corresponds to 530nm and the latter corresponds to the difference of energy between lowest unoccupied molecular orbit (LUMO) and highest occupied molecular orbit (HOMO) or 460nm. The behavior of excitons in Alq_3 in high electric field will be discussed in other papers which is important in estimation of efficiencies of EL.

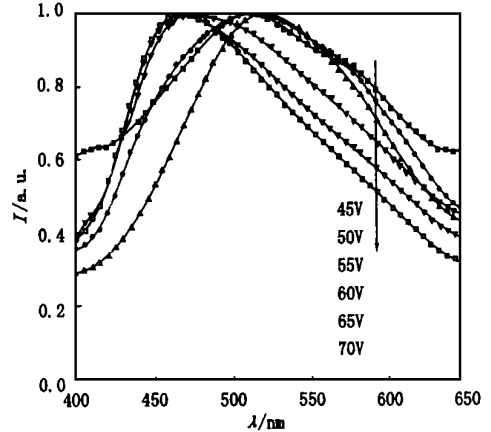


Fig. 2 Shift of AC EL spectra from 517nm towards 457nm when the driving voltage is increased from 45V to 70V.

If we substitute Alq_3 with $\text{Y}_2\text{O}_2\text{S:Eu}$ which is a typical cathodoluminescent phosphor, we obtain a uniform red emission from $\text{Y}_2\text{O}_2\text{S:Eu}$ only occasionally. This difference lies in the requirement of crystallinity of host material for the luminescence center in inorganic phosphors. All these experiments speak of the possibility of direct excitation of luminescent centers from electrons accelerated in the outside of phosphor layer.

2 2 Proof of co-existence of different excitation

Ordinarily polymers are hole conducting material, an electron conducting layer is required to increase the tunneling injection^[1]. Most of compounds, such as ZnS , CdS and ZnO are of electron conductivity. Thus we choose the structure $\text{ITO}/\text{PPV}/\text{ZnO}/\text{Al}$ and use Al as the cathode. The EL in DC electric field with ITO as anode is fairly good^[2]. And from the spectrum of luminescence we confirm that the emission shows characteristic of PPV. The mechanism of luminescence is ordi-

nary injection and recombination. Now we substitute ZnO with ZnS, the result is similar.

When PPV emits light by injection, the electric field is nearly 10^6 V/cm and in such a high field the process of impact excitation is entirely possible. Thus we use ZnS Mn as the electron conducting and emissive material and make a cell in the form of ITO/PPV/ZnS Mn/Al. The electric voltage is applied with Al as cathode. In this case we observe both the emission from PPV and from Mn. The Mn center has energy level beneath valence band according to most of literature reports and may be excited only by impact excitation. It is quite interesting that in the process of impact excitation we lose only the energy of hot electrons, not the number of hot electrons. So that the emission of PPV remains nearly the same as in the case of no impact excitation. Hence we obtained an additional Mn luminescence. Further we examined the variation of emission from PPV and Mn when the electric field was increased and found that the dependence of Mn luminescence on the voltage applied. It is similar to the relation of intensity to voltage in case of ordinary DC EL of ZnS Mn thin film (cf. the inset of Fig. 3). The emission spectrum is shown in Fig. 3. We see that the emission of PPV is much weaker than that of Mn. But in another case of ITO/LPPP/ZnS Mn/Al, we get a spectrum with the intensity of LPPP stronger than that of ZnS Mn (cf. Fig. 4). That means we can adjust the relative intensities of polymer layer to that of ZnS Mn layer by means of optimizing the parameters of preparation. In all these cases the effects of different mechanisms of excitation are additive, amplifying or compensatory. Thus the resultant effect is always positive for getting better performance.

References:

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- 2] Yang Xiaohui, *et al.* Organic light emitting diode using inorganic material as electro transport layer [J]. *Chin. Phys. Lett.*, 1997, 14: 946 (in Chinese).

Key words: Luminescence; multi-colour display; stability

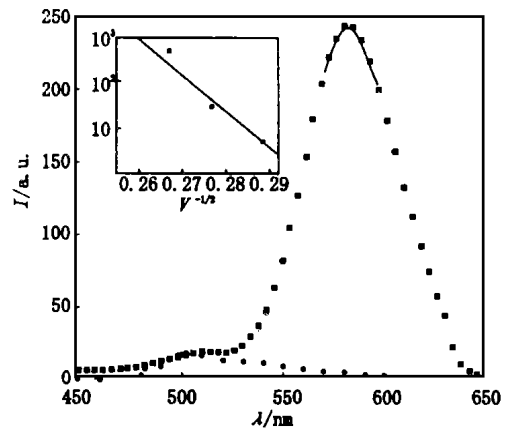


Fig. 3 The spectra of DCEL of ITO/PPV/ZnS Mn/Al () and the DCEL of ITO/PPV/Al () with ITO as anode. The inset shows the dependence of the intensity of ZnS Mn emission on the applied voltage.

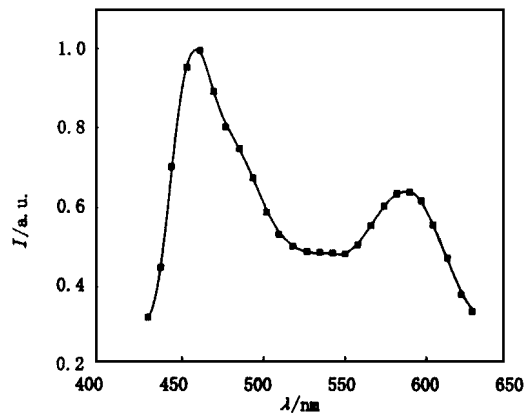


Fig. 4 The spectrum of DCEL of ITO/LPPP/ZnS Mn/Al with ITO as anode. The intensity of LPPP is stronger.

3 Conclusion

The solid-state cathodoluminescence is discovered and the co-existence of different mechanisms of excitation are proved in EL of organic-inorganic complex. The effects of these excitations are additive, amplifying and compensatory and the resultant effect is consequently reinforcement of performance of EL.