

MIXED EXCITATION IN ELECTROLUMINESCENCE*

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Abstract Among the present three types of electric field-induced luminescence we noticed similarities between the inorganic and organic materials in electric field intensity. In this high electric field range SiO_2 has three functions: acceleration, excitation and multiplication of electrons. Based on the acceleration effect, cathodoluminescence-like emission of organic molecules and polymers was found. By using the three functions of SiO_2 or II-VI compounds and the heterojunction of inorganic and organic material we realized different variants of mixed excitation in electroluminescence.

Keywords Cathodoluminescence-like emission, Mixed excitation, Inorganic-organic heterogeneous junction

INTRODUCTION

Luminescence is the only economical way to generate light for human usage. Among the various processes considered, electric field-induced luminescence is the most convenient and direct process to convert electrical energy into light emission and is especially useful in solid flat panel displays. Up to now there are three kinds of electric field induced luminescence in solids, *i.e.*, light emitting diode (LED) based on the p - n junction, inorganic electroluminescence (IEL) excited by impact excitation and organic electroluminescence (OEL) due to charge carrier injection through opposite electrodes and subsequent recombination. In 1994, Pankove proposed a novel kind of electric field-induced luminescence^[1]. He suggested the possibility of direct conversion of electronic potential energy into excitation energy after injection of electrons into a higher energy level in the conduction band. Generally this is impossible due to the strong electron-phonon interaction. But we shall prove that this situation may be possible in special cases in our subsequent work. These three kinds of luminescence differ from each other chiefly because of their differences in carrier mobility. But the electric field intensities for generating IEL or OEL are of the same order of magnitude although the applied voltage in both cases is apparently different. If the complex structure from different materials in the form of heterogeneous junction was prepared and different mechanisms of excitation were used some new devices with interest properties could be obtained. These materials may be excited simultaneously with different mechanisms. We refer to this as the simultaneous excitation mixed excitation.

From the viewpoint of application EL is especially useful in the technology of flat panel displays (FPD). Among the six types of emissive FPDs, IEL and OEL are especially promising because of their several attractive characteristics, namely, active emission, whole solid, large view angle, fast response, wide range of working temperature, distinct outline, high resolution and less labor-intensive processing. But there are still some deficiencies in their behavior. The main problem is the lack of blue colored emission in inorganic EL and the lack of electron transport materials and stability in organic EL. Very interesting is the compensatory properties of

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IEL and OEL. So it is quite natural to develop their superiority and minimize their inferiority. From this analysis, we are convinced that the heterogeneous junction made from organic and inorganic materials as well as the excitations with AC and DC sources may satisfy the above-mentioned requirements. In the following experiments we shall show the realization of this idea.

DISCOVERY OF CATHODOLUMINESCENCE LIKE (CL-LIKE) EMISSION

In IEL we have proposed and investigated carefully the layered optimization^[2-4]. The central point of this scheme is to strengthen the effect of electron acceleration by spatially separated addition of SiO₂ electron acceleration layer to the ordinary EL layer. The semi-conducting property of the thin film of SiO₂ is used for pure electron acceleration. After acceleration the energy of electrons may be raised up to several electron volts^[5-7]. These electrons have sufficient energy to excite centers of luminescence in the visible region by impact excitation. Hence these high-energy electrons are called hot electrons. Because these electrons are accelerated in solid materials instead of in vacuum, the luminescence generated by their bombardment is named CL-like emission. It is difficult but not impossible to observe this phenomenon in inorganic materials due to the imperfections of crystal structure at the interface between SiO₂ and luminescent layer. But to observe this phenomenon in organic materials is much easier because the interactions between the neighboring molecules are very weak and the individual behavior of molecules is sufficiently independent. For this purpose we prepared the combination of ITO/SiO₂/Alq₃/SiO₂/Al (sample 1) in which the thickness of SiO₂ is 40 nm and that of Alq₃ is 50 nm. SiO₂ was evaporated by electron beam heating and Alq₃ was evaporated by thermal heating in vacuum. During deposition, the substrate was kept at 150 °C, under a vacuum of 10⁻⁶ torr. For comparison, an ordinary organic device ITO/Alq₃/Al was also prepared (sample 2). At first, the photoluminescence spectrum of sample 1 (without Al electrode) and the OEL spectrum of sample 2 were measured and sample 1 was excited with AC voltage. The frequency of this sinusoidal voltage ranged from 100 Hz to 200 kHz. The spectrum is also shown in Fig. 1. The peak at 518 nm corresponds to the photoluminescence or the ordinary EL emission of Alq₃ driven by a DC voltage of 10 V. This luminescence peak is attributed to the luminescence of excitons. Obviously, this blue luminescence is not generated from the same injection and recombination process as ordinary OEL. To clarify the origin of the peak at 457 nm, the voltage dependence of AC luminescence was measured the results are shown in Fig. 2. When the applied AC voltage is increased from its threshold value the green peak of luminescence is blue shifted continuously and stopped at 457 nm^[8]. For IEL, we have studied the ionization of excited centers in detail and found that the ionization probability increases with increasing electric field^[9-11]. Thus the decrease of the 518 nm peak with the increase of electric field may be attributed to the dissociation of excitons. To confirm this conclusion the peak at 518 nm was investigated by electric field modulated photoluminescence. Originally, the photoluminescence of Alq₃ appears at 518 nm. By increasing the applied electric voltage below the threshold voltage of EL, the luminescence intensity decreases correspondingly (Fig. 3). Once this center is ionized, all the electrons on levels higher than this excited exciton level will be ionized also. Thus the ultimate blue shift limit 457 nm corresponds to the direct recombination of electrons in LUMO and the holes in HOMO of Alq₃. On the other hand, the energy difference between the LUMO and HOMO is estimated to be 2.7 eV from the absorption measurement, which just corresponds to the emission at 457 nm. We studied the I-V and B-V curves also. Our preliminary result shows good prospects for getting higher efficiency.

This experiment is carried out on electron transport Alq₃, but it shows the same tendency in case of using hole transport materials. For example we used MEH-PPV as the emitting material and prepared the device ITO/SiO₂/MEH-PPV/SiO₂/Al (sample 3). The emitting layer was prepared by means of spin cast method with a spinning velocity of 2000 r/min. Firstly, we investigated the spectra of single layer MEH-PPV under DC and AC excitation, but no difference was found. The spectrum of sample 3 was measured and the voltage applied varied. The result is shown in Fig. 4. At 420 nm and 570 nm there are two luminescence peaks. When the voltage is increased the first peak ascends and the second one descends. If SiO₂ is replaced with Ta₂O₅ no electrons will enter the layer of MEH-PPV from the Al electrode and only one peak near 400 nm can be observed.

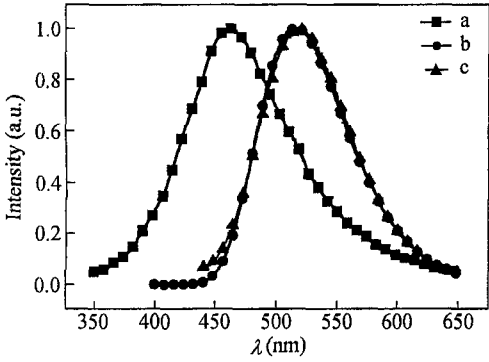


Fig. 1 ACEL spectra of the device ITO/SiO₂/Alq₃/SiO₂/Al (a), ITO/Alq₃/Al (b) and PL spectrum of the stack films ITO/SiO₂/Alq₃/SiO₂ (c)

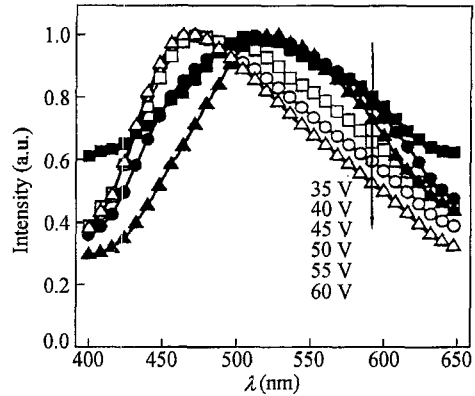


Fig. 2 Dependence of ACEL spectra on applied voltage

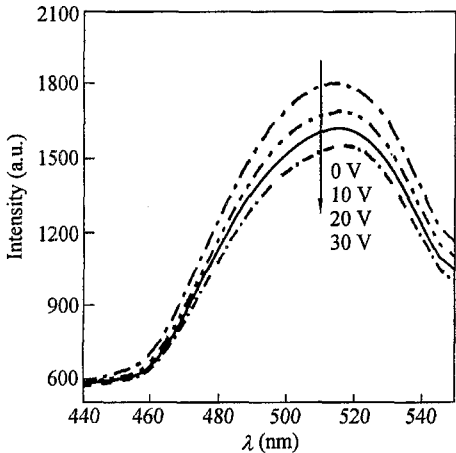


Fig. 3 Dependence of electric field modulated photoluminescence (excited at 400 nm) emitted by sample 1 at room temperature

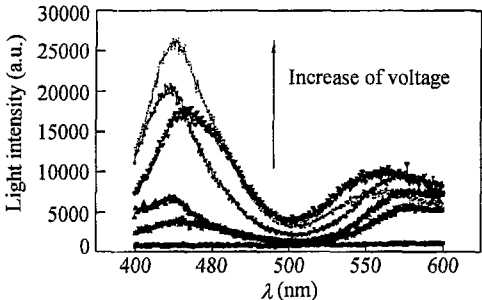


Fig. 4 Dependence of ACEL spectra of ITO/SiO₂/MEH-PPV/SiO₂/Al on applied voltage

MIXED EXCITATION OF CL-LIKE EMISSION AND OEL

In the last experiment we have proved the existence of CL-like luminescence. In this case the impinging energized electrons may have two possibilities. They may excite the centers of luminescence directly and lose their energy or may simply enter the layer of Alq₃. All these electrons will recombine with holes injected from ITO. For this purpose, the device ITO/Alq₃/SiO₂/Al (sample 4) was prepared. The result is a mixed excitation of CL-like emission and OEL. Another example is the device ITO/SiO₂/MEH-PPV/Al (sample 5). There appears also the CL-like emission and the ordinary OEL of MEH-PPV. The resultant spectrum is shown in Fig. 5. When the applied voltage changes from 20 V to 40 V the spectral peak is shifted from 580 nm to 400 nm^[11].

MIXED EXCITATION OF IEL AND OEL

We know that ZnS is also a medium for electron acceleration although its ability is lower than SiO₂. If ZnS:Mn is used instead of SiO₂ to prepare Al/ZnS:Mn/PPV/ITO, the DC luminescence under positive bias shows the superposition of luminescence from ZnS:Mn at 586 nm and that from PPV at 505 nm (Fig. 6). Under negative

DC bias excitation only the 586 peak of Mn emission is observable. That means on this occasion that only the Mn center is excited. This spectrum is also shown in Fig. 6. From the dependence of luminescence of the Mn center on applied voltage, the same behavior of Mn as in DC EL can be seen. Since the electrons lose only the energy of the hot electrons during their collisions with the Mn center, the final number of the hot electrons remains unchanged^[12].

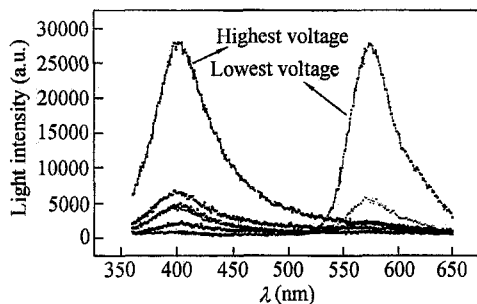


Fig. 5 Dependence of ACEL spectra of ITO/SiO₂/MEH-PPV/Al on applied voltage

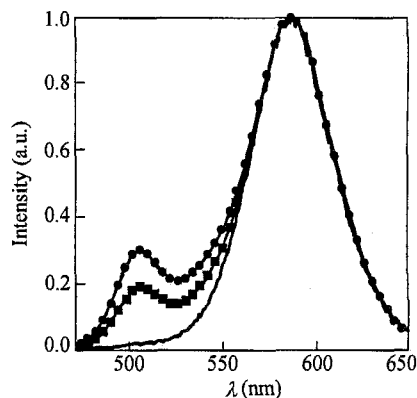


Fig. 6 Normalized DCEL spectra of PPV/ZnS:Mn under (1) positive bias (square: 14 V, dot: 17 V), (2) negative bias (solid curve)

RECOMBINATION OF MULTIPLIED ELECTRONS AND HOLES

As the SiO₂ layer is capable of electron multiplication, the holes will recombine with the multiplied electrons in the heterogeneous junction structures. In our previous works, the electron transport properties of Al/ZnO/PPV/ITO or Al/ZnS/PPV/ITO were used in order to increase the intensity of OEL^[13, 14]. The intensity of EL is really increased more than 10-fold. We calculated the increase of carrier injection probability and compared the intensity of emission with the experimental data. We are convinced that the holes of PPV are recombined not only with the electrons simply coming from the electrode but also with those existing after multiplication.

CONCLUSION

We have found different structures of hybrid integration from inorganic and organic materials and studied their behavior. It is possible to design more than 10 different variants of structures even when the model proposed by Pankove does not come into play. As these kinds of processes are mutually compensatory, additive or one assists the other, the resultant luminescence is undoubtedly enhanced. We can anticipate other new properties or their improvement in this mixed excitation, *e.g.*, color, efficiency, stability and *etc.*.

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