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Novel Problems in the Solid State Cathodoluminescence of Organic Materials

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1. Introduction

Luminescence is the unique efficient supplementary technology to make up a constant deficit of solar light. Among all kinds of luminescence the electric field induced luminescence is especially attractive due to its feasibility of manipulation and direct transformation of electrical energy into light. For this trend cathodoluminescence is used for display already approximately 100 years. But the trend of contemporary display is to make flat panel display. For this reason many efforts were made to use cathodolumunescence, e.g., VFD and FED although the latter achieves still no practical success. At the same time EL finds applications in a certain field. In order to obtain blue color inorganic EL we proposed layered optimization scheme, and very soon we convinced the energy of hot electrons from the acceleration layer is high enough to excite luminescence directly. We realized this idea by using insulator phosphors. But the probability is very low because the environment of luminescent center is not regular near surface. In the layered optimization scheme we used the secondary property of electrons (hot electrons) of inorganic materials in order to raise the electron energy before they are accelerated in EL layer. In this acceleration layer, both the number of electrons and the energy of electrons are increased. The correctness and reasonableness of this idea was fully realized [1]. We tried to use organic materials to substitute the inorganic materials in the layered optimization scheme [2-3], thus discovered the solid state cathodoluminescence of organic luminescent materials. We call it as solid state cathodoluminescence (SSCL) because the hot electrons are accelerated in solids instead of in vacuum. SSCL is an independent branch of electric field induced luminescence. Soon we found also the possibility of integrating SSCL with OEL[4], i.e., using a single electrical source and a single luminescent material we can get two kinds of excitations for SSCL and OEL, which is the unique integrated excitation among all kinds of luminescence.

2. Classification of electric field induced luminescence according to mode of excitation

SSCL is a new kind of electric field induced luminescence. Up to now, electric field induced luminescence play an import role in the field of flat panel display, for example field emission display (FED), vacuum Fluorescent Display (VFD), electroluminescence (EL), light-emitting diode(LED) and organic electroluminescence(OEL), even though some technologies such as FED are still not practical at present. Their excitation mechanism is basically classified as two types, impact excitation and carrier injection.

2.1 Impact excitation

In the impact excitation mechanism, the luminescence center is excited by hot electrons collision which provides an efficient means of producing electronic transition to excited states of the luminescence centers. Based on impact excitation, some technologies of field emission display, vacuum fluorescence display, solid state cathodoluminscence, inorganic electroluminescence are produced.

2.1.1 Field emission display (FED)

A field emission display (FED) is a low power, flat cathodoluminescence display that uses a matrix-addressed cold cathode. Field emission display is a high-voltage display with a triode structure consisting of anode, cathode, and gate electrodes to achieve high illumination by applying a high voltage and a low current. In the field emission display, a strong electric field is formed between a field emitter and gate electrodes disposed on a cathode at a constant interval, so that electrons are emitted from the field emitter so as to impact on phosphors of an anode, thereby emitting light. Field emission display technology makes possible the thin panel as today's liquid crystal displays (LCD), offers a wider field-of-view, provides the high image quality of today's cathode ray tube (CRT) displays, and requires less power than today's CRT displays. However, FED display requires a high level vacuum which is difficult maintain.

2.1.2 Vacuum fluorescent display (VFD)

The VFD is composed of three basic electrodes: the cathode (filaments), anodes (phosphor) and grids under a high vacuum condition in a glass envelope. Electrons emitted from the cathode are accelerated with positive potential applied to both grid and anode, which upon collision with the anode excites the phosphor to emit light. The desired radiative patterns can be achieved by controlling the positive or negative potentials on each grid and anode. This voltage can be as low as 10V DC. The principle of operation is identical to that of a vacuum tube triode. Electrons can only reach (and "illuminate") a given plate element if both the grid and the plate are at a positive potential with respect to the cathode. This allows the displays to be organized as multiplexed displays where the multiple grids and plates form a matrix, minimizing the number of signal pins required. Compared to LCDs, they have relatively high power consumption. Other problems include some segments of a VFD display gradually becoming brighter or dimmer than others (caused by the phosphors glowing less brightly as they get older) and flickering.

2.1.3 Solid state cathodoluminescence (SSCL)

Organic materials for example, Alq_3 [5-6] , MEH-PPV [2], $Ir(ppy)_3$[7], etc, were used to substitute the inorganic materials in the layered optimization scheme and discovered two peaks of luminescence under AC bias. One is the typical organic electroluminescence peak with longer wavelength. Another one is a new luminescence peak with short wavelength. Both peaks constitutes the solid state cathodoluminescence (SSCL). The excitation mechanism of two emission peaks is impact excitation by hot electrons. The emission is not due to the typical recombination electroluminescence of injected carriers because no holes are injected to the organic materials in this kind of device. After primary electrons tunneled into the insulator layer, they are accelerated in the insulator layer and then have the high energy. These hot electrons collide organic materials to excite electrons from HOMO to LUMO like the excitation by photons. These excited electrons relax fast to form excitons with holes in HOMO. Then formed excitons recombine and emit light. Under high electric field, parts of formed excitons should be dissociated and then the light should be emitted directly recombined from electrons in LUMO and holes in HOMO. The excitation mechanism of SSCL is same to that of typical vacuum cathodoluminscence except that the hot electrons are accelerated not in vacuum but in solids.

2.1.4 Electroluminescence (EL)

Electroluminescence is the result of radiative recombination of electrons and holes in a material, usually a semiconductor. The excited electrons release their energy as photons - light. Electroluminescent devices are fabricated using either organic (OEL) or inorganic electroluminescent (IEL) materials. It is well known that the sandwich type thin-film IEL. The phosphor in these devices is not a powder but a thin continuous film prepared by sputtering or vacuum evaporation. The luminescence activators are manganese or rare-earth ions, atomic species doped in ZnS or other host materials with internal electronic transitions that lead to characteristic luminescence. A thin film luminescence (TFEL) device generally has a double insulator structure of electrode/insulator layer/active layer/insulator layer/electrode. For excitation process of luminescence centers in TFEL, the hot electron has been known to be the dominant carrier. Under AC bias, the accumulated electrons in the interface region of the electrode and the insulator layer are accelerated to become hot electrons. These hot electrons impact luminescence centers and EL results. A TFEL device acts like a pure capacitor at low applied voltage; no light is emitted until the voltage reaches a threshold value determined by the dielectric properties of the insulator and phosphor films. Above this threshold a dissipative current flows, and light emission occurs. The brightness increases very steeply with the applied voltage but is finally saturated. The light output, or average brightness, is roughly proportional to the frequency up to at least 5 kHz, and also depends on the waveform of the applied voltage.

Traditional IEL displays are bright, very fast in video response time and highly tolerant of environmental extremes. However, the lack of full-color has limited their application for the mainstream consumer television market. In order to get efficient inorganic electroluminescence, we have proposed the layered optimization scheme. The correctness and reasonableness of this idea was fully realized [1].

2.2 Inject electroluminescence

Injection electroluminescence results when an inorganic semiconductor *pn* junction (LED) or a point contact is biased in the forward direction. This type of emission is the result of radiative recombination of injected minority carriers, with majority carriers in a material. Such emission has been observed in a large number of semiconductors. The wavelength of the emission corresponds to an energy equal, at most, to the forbidden band gap of the material. If a *pn* junction is biased in the reverse direction, so as to produce high internal electric fields, other types of emission can occur, but with very low efficiency. LEDs present many advantages over incandescent light sources including lower energy consumption, longer lifetime, improved robustness, smaller size, faster switching, and greater reliability. For room lighting LED are powerful enough and relatively expensive and require more precise current and heat management than compact fluorescent lamp sources of comparable output.

Electroluminescence in organic materials may be observed in a single organic layer sandwiched between two electrodes, but the efficiency is not high. In order to enhance the efficiency of OLED, multilayer structure devices are introduced. To explain the operation of a typical multilayer OLED, the physical processes have to be identified [8]. Firstly Charge carriers are injected from electrodes on the top and bottom of the OLED and transport in organic materials. A minimum layer thickness has to be retained in order to prevent minority carriers to migrate to the opposite contact. Opposite space charges extend from the two contacts into the device. The zone in which they overlap and where recombination takes place is only a few nanometers wide. The recombinative process is strongly influenced by traps. It results in a charge-transfer complex or an excited molecule, which is called a (Frenkel-)exciton. Due to the spin multiplicity, excited singlet and triplet states are formed with a ratio of one to three. The excitation energy can be transferred to neighboring or more distant molecules of the same type or to molecules with a lower excitation energy. While triplet excitons decay nonradiatively, luminescence is caused by the radiative decay of singlet excitons. Nonradiative decay may take place at contacts and impurities.

2.2.1 Integrated excitation of SSCL and OEL

SSCL of organic materials is resulted from the recombination emission and exciton emission. When the acceleration layer is an suitable material in which electrons can be accelerated and holes can inject to the organic layer, it is possible to detect the luminescence of organic materials due to the electron impact excitation(SSCL) and carrier injection (OEL). The integration of the excitation of SSCL and OEL was achieved [5].

2.2.2 Mixed luminescence of EL and OEL

Electric field induced luminescence provides the way of direct transformation of electric energy into light. According to the materials, there are two kinds of electroluminescence, inorganic electroluminescence and organic electroluminescence. The inorganic electroluminescence (IEL) suffers from the lack of bright blue luminescence, and the organic electroluminescence (OEL) suffers from its stability. But they have their own advantageous to be used in flat plate display. For example, OLED is widely considered as the potential display technology. Therefore we hope to combine their superiority and minimize their inferiority in order to improve their performance. To combine IEL and OEL, We tried to use organic materials to substitute the inorganic materials in the layered optimization scheme [2-3]. Firstly we used the primary property (simple electron conduction) of ZnO or ZnS [9] as the electron transport material for enhancing the electroluminescence of organic layer and achieved positive results. In both of these two kinds of electroluminescence the required electric field is almost of the same order of magnitude. We tried to combine ZnS:Mn and

PPV layers together and really obtained the simultaneous emission from both layers[9]. On the other hand, we successfully applied the layered optimization scheme to improve the overall performance of IEL.

3. Characterization of SSCL

The spectral characteristics of SSCL of organic luminescent materials are the appearance of two light emission peaks when the applied electric field increases. More detailed examination of these two peaks shows that the longer wavelength peak is originated from excitons and the shorter wavelength peak is attributed to transitions from LUMO to HOMO levels directly. When the applied electric field increases, the longer wavelength peak increases at first, then passes a maximum and monotonically drops down to zero. The shorter wavelength peak gradually increases monotonically after the diminishing of the longer wavelength peak. The reason of the variation lies in the ionization of excitons in an electric field.

3.1 When the applied voltage increases，the two bands varies according to ionization of excitons

We used a series of organic phosphors, such as Alq_3, PPV, MEH-PPV, C_9-PPVto substitute the inorganic layer in the layered optimization scheme. The device structure is Al/insulator layer/organic layer/insulator layer/ITO. The methods to prepare different organic layers were different. For example the sample of MEH-PPV with the structure Al/SiO_2/MEH-PPV/SiO_2/ITO was prepared by means of spin casting. The thickness of MEH-PPV is about 50nm. The thin film SiO_2 was obtained by electron beam evaporation (EVA450, alliance concept Co. Ltd., France) at the growth rate of 1Å/s under the high vacuum of 2×10^{-6} Torr with a thickness of about 200nm. The other sample of Alq_3 within the structure Al/SiO_2/ Alq_3 /SiO_2/ITO was prepared by means of thermal evaporation of Alq_3. Excited by AC voltage, these samples showed a similar spectral behavior of having dual spectral peaks and shifting to short wavelength when the applied voltage was increased.

The spectrum of ITO/SiO_2/Alq_3/SiO_2/Al is shown in Fig.1. It is a wide band emission which can be fitted by the Gaussian fitting to two peaks [6]. One peak is 510nm, another one is 451nm. In Fig.1, the electroluminescence of ITO/Alq_3/Al is observed also under DC bias. The peak locates at 510nm which is the emission from the singlet exciton recombination of Alq_3. In a typical OLED, electrons and holes inject to the fluorescent material from the cathode and anode respectively, then they meet each other and singlet and triplet excitons are formed. The recombination of singlet excitons gives the electroluminescence. In our study, SiO_2 is used in this new kind of devices. As we known SiO_2 is an insulator. So it is difficult to transfer electrons, especially holes. In such case, the mechanism of electroluminescence of ITO/SiO_2/Alq_3/SiO_2/Al is different to that of the typical OLED. This means that the electroluminescence of ITO/SiO_2/Alq_3/SiO_2/Al is not originated from the carrier injection recombination.

According to above simulation, electrons which enter to Alq_3 layer have been accelerated in SiO_2 of the device of ITO/SiO_2/Alq_3/SiO_2/Al under AC bias. These electrons with high energies should bombard Alq_3, then Alq_3 is excited by this electron bombardment as excited by light directly. In this case, more singlet excitons are formed. Along with the increasing of the electric field on Alq_3, singlet excitons should be dissociated into free electrons and holes to LUMO and HOMO respectively. If these free electrons and holes recombine, they emit 450nm light. Therefore, we observed a new emission peak in the electroluminescence spectrum of ITO/SiO_2/Alq_3/SiO_2/Al besides the singlet exciton emission of 510nm. Theoretically, in this kind of devices, the quantum efficiency is higher than that of typical OLED devices because the impact excitation likes the excitation by light. There are almost no triplet exciton formations under electron impact excitation. Therefore, the efficiency of this kind device is larger than that of the typical OLED.

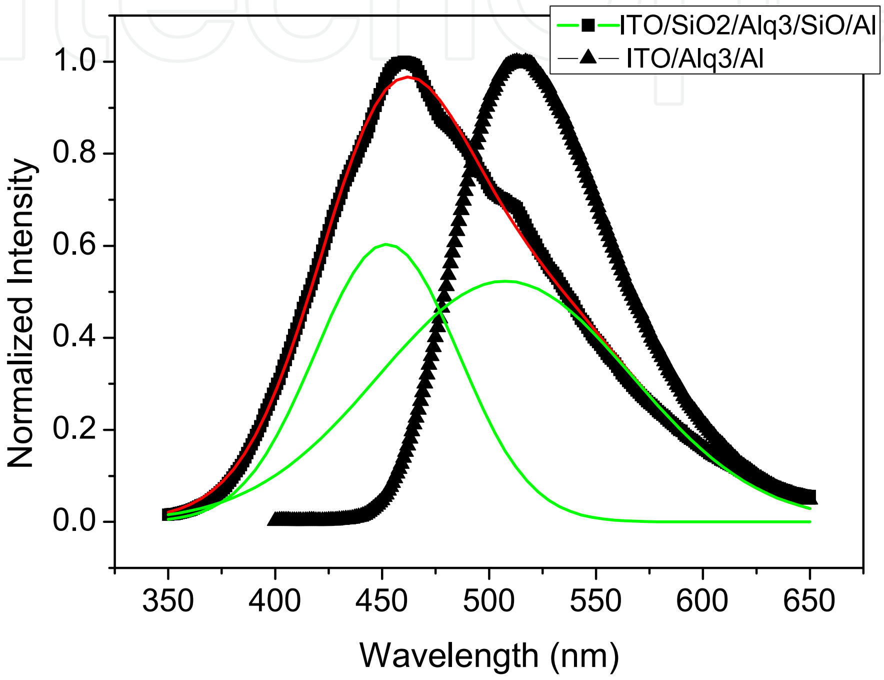

Fig. 1. The electroluminescence spectrum of ITO/SiO_2/Alq_3/SiO_2/Al (square) and ITO/Alq_3/ Al (triangle) under AC bias

The spectrum of Al/SiO_2/MEH-PPV/SiO_2/ITO consists of two peaks at 405 nm and 580 nm (Fig.2)[10]. In ordinary organic electroluminescence we have only the long wavelength peak. In SSCL, the spectrum shifts from the long wave length peak to blue one when the applied voltage increases. The apperance of short wave length peak is a characteristic phenomenon for SSCL due to the appearance of short wave length peak. The voltage range is divided into three different parts according to the spectrum: short wavelength peak at 405 nm only, a mixture of the two spectral components 405 nm and 580 nm, the long wavelength peak at 580 nm only. The 580 nm peak is attributed to the exciton emission, the 405nm peak corresponds to the radiation related to the recombination of carriers in conduction and valence band. When the applied voltage is increased, the spectrum shifts to blue.

We have also observed the solid state cathodoluminescence in organic phosphors, for example, $Ir(ppy)_3$ [7]. $Ir(ppy)_3$ is a well known organic phosphor. Its phosphorescence emission is a green emission with a peak at 520nm. We doped $Ir(ppy)_3$ in PVK, then prepared PVK:$Ir(ppy)_3$ thin film on SiO_2 by the method of spin coating. SiO_2 layers and Al cathode were prepared as before. Then the device of ITO/SiO_2/ PVK:$Ir(ppy)_3$/SiO_2/Al was realized. Under AC bias, the electroluminescence of this device which locates at

520nm was observed under different bias, as shown in Fig.3. This emission corresponds to the triplet excition emission of Ir(ppy)$_3$. As discussed above, the electroluminescence essentially is the solid state cathodoluminescence, that is, the emission from the bombardment of high energy electrons accelerated in SiO$_2$. It is very surprise that there is no the singlet exciton emission from PVK. It is possible that PVK is excited also by electrons and singlet excitons are formed. These singlet excitons do not give the radiative emission but transfer their energy to Ir(ppy)$_3$ directly. According to our previous study, there is the spectrum overlap between the emission spectrum of PVK and the excitation spectrum of Ir(ppy)$_3$. So the Forster energy transfer is possible between PVK and Ir(ppy)$_3$. Therefore, there are two ways for the excitation of Ir(ppy)$_3$. One is the directly excitation of the high energy electrons, another one is the energy transfer from PVK. Therefore, the efficiency should be very high theoretically.

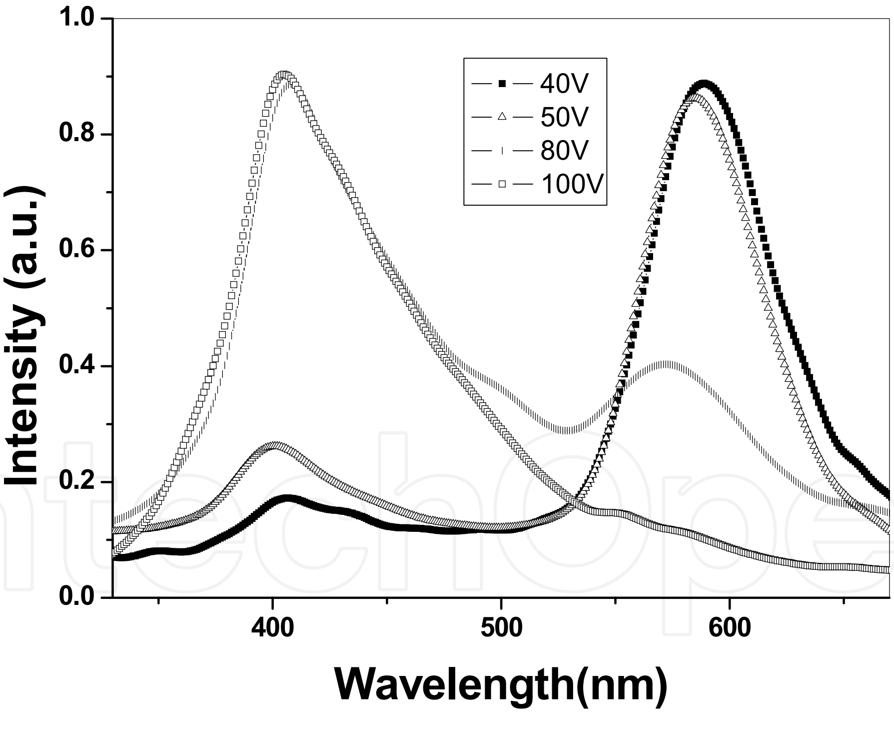

Fig. 2. The electroluminescence spectrum of ITO/SiO$_2$/MEH-PPV/SiO$_2$/Al under AC bias

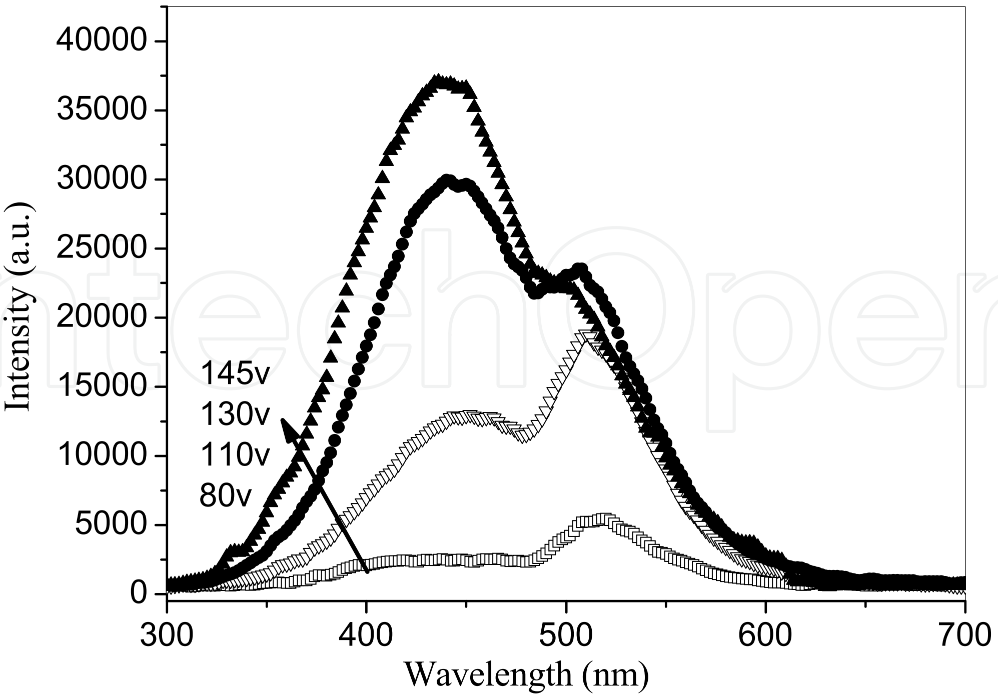

Fig. 3. The electroluminescence spectrum of ITO/SiO_2/PVK:Ir$(ppy)_3$/SiO_2/Al under AC bias

3.2 What is the nature of this emission? Cross proof of this emission being really a new kind of luminescence

We prepared a sample of the structure Al/SiO_2/MEH-PPV/ITO and discussed its emission mechanism under AC bias. If the emission is originated from gaseous discharge, the luminescence excited by it should be observed at both half periods of the applied voltage because the light may propagate ether in front direction, or in tail direction. This is simply because the amplitude of applied voltage remains the same in each of both half periods, the gaseous discharge might occur equally during each half period although their amplitude may be different. But experiment showed that emission occurs only when Al electrode is negative. Really during this half period the accelerated electrons may bombard MEH-PPV and in the opposite half period the electrons can not. Only the direct bombardment produces luminescence. This spoke of the impossibility of gaseous discharge. The same conclusion is true for symmetric structure.

This emission is not the injection luminescence as in p-n junction of LED and organic EL also. Because the energy barrier for holes on the interface of Al/SiO_2 is higher than 5.2eV and on the interface of ITO/ SiO_2 is 4.7eV, no holes can be injected into organic phosphor in a symmetric structure and consequently no recombination of electrons with holes, i.e., no LED or OEL is possible.

This emission is not also the self developed EL as in inorganic materials, in which the acceleration of hot electrons, collision excitation and luminescence proceed in the same layer, because the carrier mobility in organic phosphors is less than 10^{-2} $cm^2/v.s$ or in special case less than $1cm^2/v.s$. The kinetic energy of hot electrons accumulated in this material is lower than the value required for excitation. More than this, the ordinary IEL may be observed only in very limited class of semi-conductors, but the above mentioned new emission occurs not only in semiconductors but also in insulators if it is an ordinary luminescent phosphors.

All these exclusions of trivial phenomena from these aspects stick out the SSCL as a new type of luminescence.

3.3 In brightness waveforms the traditional method for determining phase relation fails to be effective[11]

In order to make the SSCL mechanism clear, we measured the temporary changes in the emission intensity along with the AC bias, which is the emission waveform, as shown in Fig 4. The line with the triangle symbol is the excitation AC bias with the amplitude of 60 V and frequency of 500 Hz. The lines with square and circle symbols are the waveforms of the emissions of 405 nm and 580 nm, respectively. It is found that the waveforms of these two emissions are different. The maximum intensity of 405 nm occurs under forward voltage, but the maximum intensity of 580 nm occurs under reverse voltage. According to the traditional phase detection method, the position of the maximum intensity is taken as the phase of the emission. Apparently 405 nm is emitted before 580 nm according to their waveforms if we take the position of the maximum brightness peak in the forward direction. When the bias is increased to another higher value, the order of these two SSCL peaks appears to be reversed. Certain important fact should be hidden behind this uncertainty of phase.

The detected intensities of 580 nm and 405 nm with increases in voltage are shown in Fig. 5. The threshold bias of this device is 20 V. When the AC voltage increases, 580 nm first enhances and then decreases. In the meantime, 405 nm is detected at the point which corresponds to the voltage of the maximum intensity of 580 nm. Then, 405 nm increases along with the increase in the voltage. We have concluded before that 405 nm emission is due to the direct recombination of electrons and holes which results from the decomposition of excitons. Their changes with changes in voltage can be described by the rate equation. The intensity of 405 nm is:

$$B^{s} = \sigma_1 \upsilon G^{*}[G + \alpha(E) n_0] \tag{1}$$

where $\alpha(E)$ is the exciton decomposition velocity under electric field E, σ_1 is the cross section of the recombination emission, υ is the average electron velocity in the conduction band, G is the excitation rate, and G^{*} is the number of holes. The simplest condition is G^{*} = G. They are functions of the electric field E.

The exciton formation rate is

$$\frac{dn_0}{dt} = \sigma_2 \upsilon G^{*}[G + \alpha(E) n_0] - \frac{1}{\tau} n_0 - \alpha(E) n_0 \tag{2}$$

Here, σ_2 is the cross section of the exciton formation. Because of the weak interaction between molecules, σ_1 and σ_2 can be considered as constants. But but according to the experiment, the recombination emission is difficult to detect in typical organic electroluminescence devices, so σ_1 is much less than σ_2. n_0 is the exciton concentration, and τ is the lifetime characteristic parameter of exciton emission.

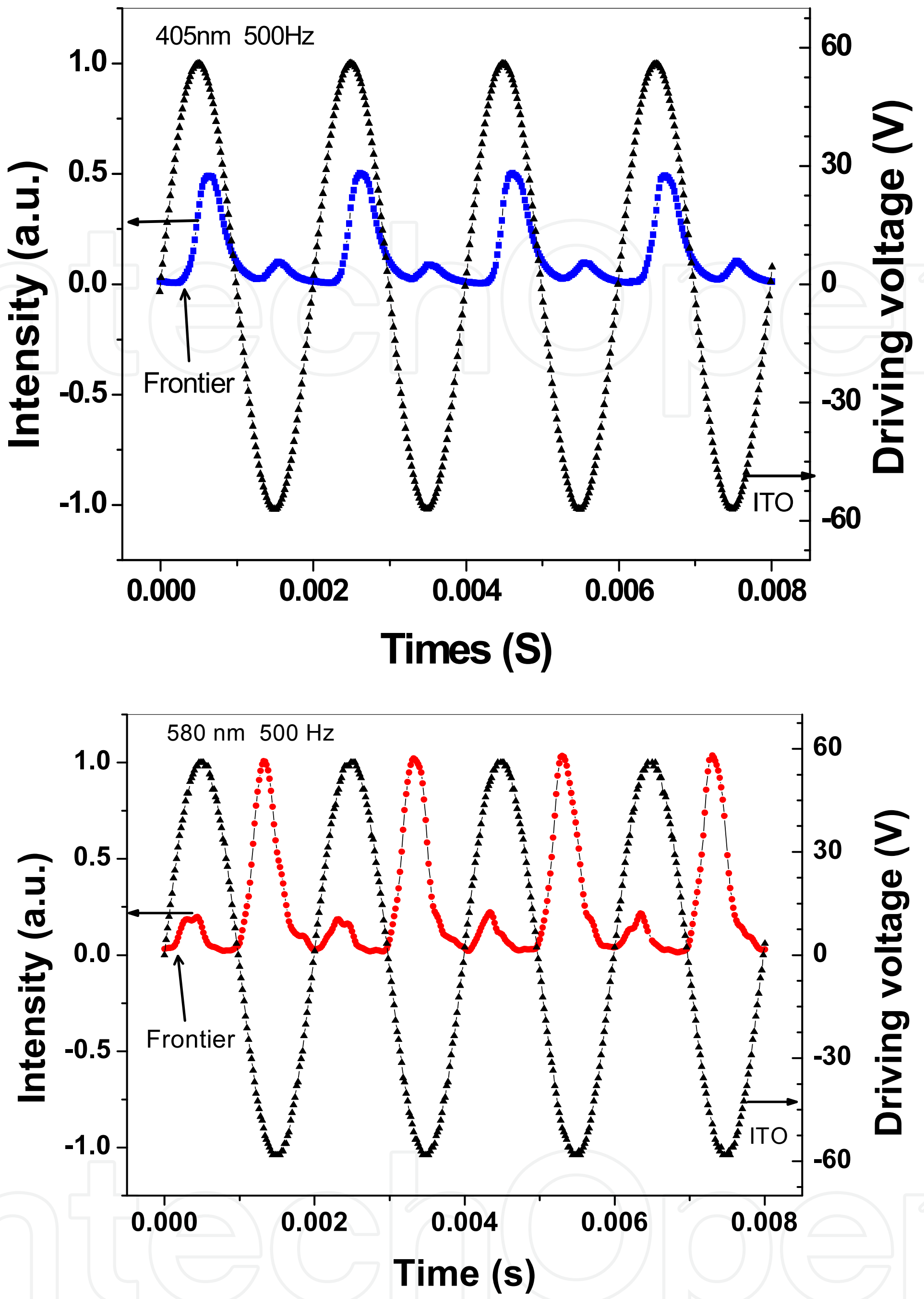

Fig. 4. The emission waveform of ITO/SiO_2/MEH-PPV/SiO_2/Al

The intensity of exciton emission is

$$B^l = \frac{1}{\tau} n_0 = \sigma_2 \upsilon G^* [G + \alpha(E) n_0] - \alpha(E) n_0 \qquad (3)$$

Under forward bias, the electron injection from the cathode is very effective and electrons are accelerated in the SiO_2 layer. So the voltage on MEH-PPV is relatively high. But for reverse bias, the electron injection from ITO is not effective, and most of the voltage falls on the SiO_2

layer. The electric field on MEH-PPV is low. The simulation of the electric field on MEH-PPV is shown in Fig. 6. At low electric fields, $\alpha(E)$ is nearly equal to zero. E increases, and G and G* increase too. So the exciton emission increases. When E reaches a certain value, $\alpha(E)$ begins to increase along with E. As E increases, the exciton emission increases slowly, then decreases because of the decomposition of excitons. Meanwhile, the recombination emission is detected thanks to the decomposition of excitons. The bias on the device is sine wave, and should be changed from low to high. In such cases, 580 nm is detected firstly and then 405 nm is detected along with the increase in the bias. The AC bias put on the device is a changing bias. The voltage is not a constant but changes with time. We take V+ as the average voltage of the organic layer in forward bias, and V– as the average voltage in reverse bias. The actual bias ΔV+ and ΔV– on the organic layer is less than V+ and V– because those other layers take part of the bias, as shown in Fig. 6. The bias changes, and the injection current changes. Therefore, the bias ΔV+ and ΔV– changes and results in a changed electric field on the organic layer. This is critical for the exciton decomposition which relates to the exciton emission and band-band recombination.

Therefore, if we denote the phase of the emissions according to the fact shown in Fig.5, the phase corresponding to the maximum intensity in Fig. 4 is not the actual phase of the emissions. It is contrary to that found by the traditional phase detection method, which means that the traditional phase detection method is not suitable for the SSCL. It is found that the frontiers of their waveforms are consistent with their emission order. Thus if we use the phase of the frontier to denote the phase or the valley phase (minimum intensity) of the SSCL, we will obtain the right results. Therefore, the frontier phase instead of the maximum intensity phase is the true phase of the SSCL.

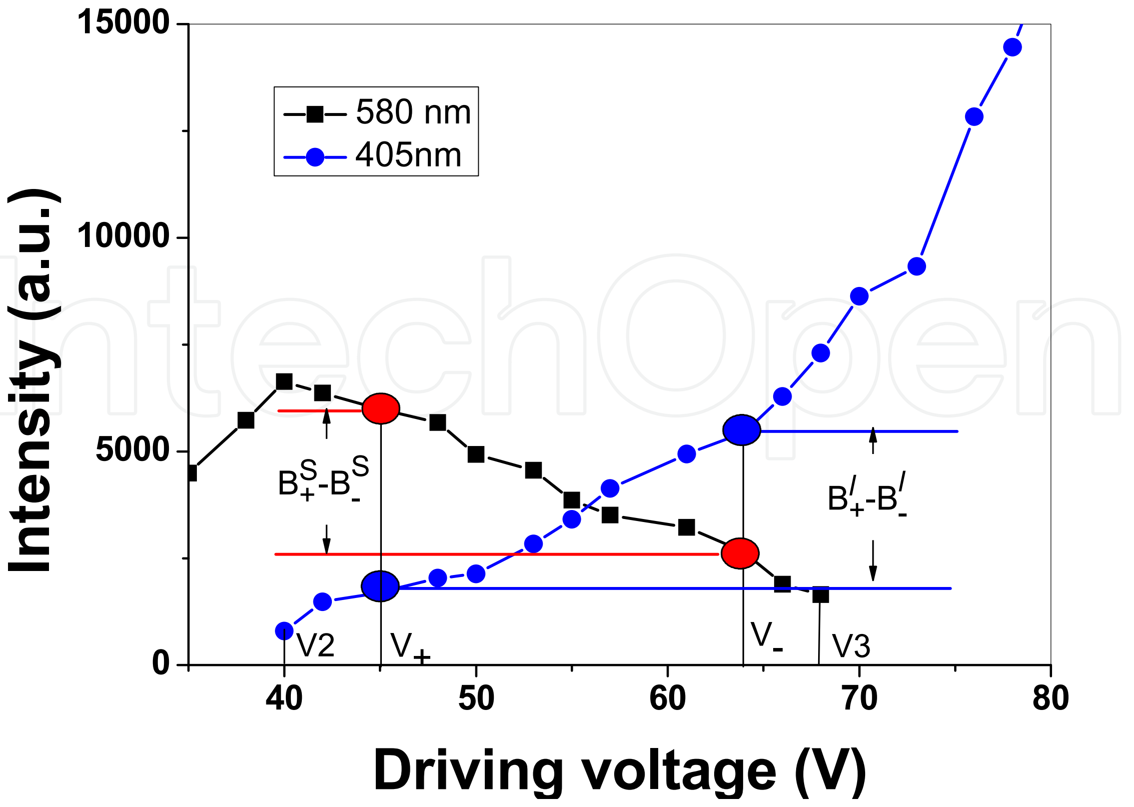

Fig. 5. The dependence of SSCL on the driving voltage

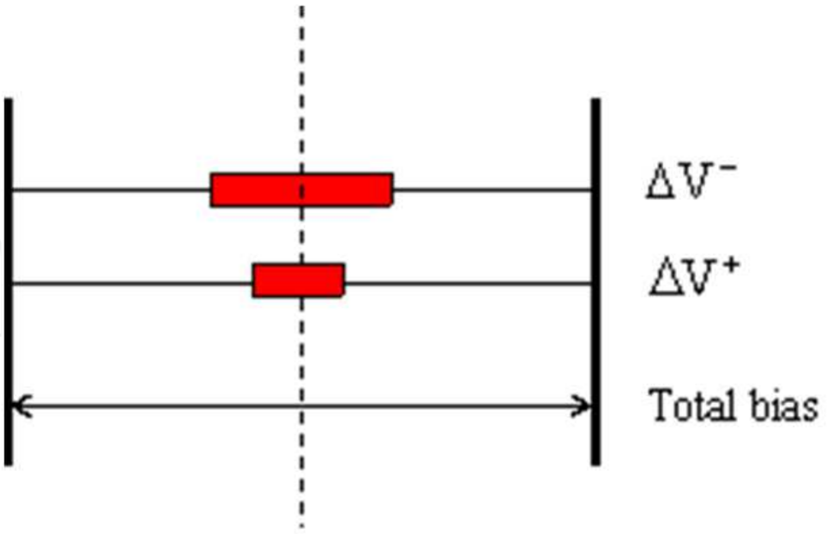

Fig. 6. The simulative bias on the organic layer

4. The special feature of SSCL lies in the accumulation of hot electrons energy

It is known that the SSCL are related to the electric field. The detected intensities of 580 nm and 405 nm of MEH-PPV with increases in voltage are shown in Fig. 5. The threshold bias of this device is 20 V. When the AC voltage increases, 580 nm first enhances and then decreases. In the meantime, 405 nm is detected at the point which corresponds to the voltage of the maximum intensity of 580 nm. Then, 405 nm increases along with the increase in the voltage. We have concluded that 405 nm emission is due to the direct recombination of electrons and holes which results from the decomposition of excitons. All these emissions are due to the electron impact excitation. In this way, the SSCL are depending on the hot electron energy.

4.1 Increment of hot electron energy in a stepwise way along the increase of electric field intensity

Since the excitation of electroluminescence originates from impact by hot electrons, the behavior of electroluminescence (EL) is chiefly determined by the energy of hot electrons. Thus the diverse phenomena in EL inspire the study of electron energy. In the scheme of layered optimization in which we used an acceleration layer located at the front of the luminescent layer in order to form a thrust for the acceleration of hot electrons in the electroluminescent layer, and hence enhance the energy of hot electrons. We observed really the obvious superiority of energy enhancement of this layered optimization scheme over the conventional sandwich structure. The intensity, efficiency, and percentage of short wave length emission are increased [12-14]. Moreover, a second jump of light intensity appears at higher electric field [15]. Here, three problems arise: 1) Does the additional acceleration layer plays the role of providing thrust to the acceleration of electrons in luminescent layer really? 2) How does the density of energy states changes with electric field strength? 3) how is the distribution of electron energy in dependence on electric field strength. Is it in accordance with the experimental result of second jump of luminescence? We limited our research to inorganic electroluminescence and investigated the behavior of electron energy (EE) to clarify the reason for these obvious improvements of performance. In order to find the energy distribution, the Boltzman equation should be solved. However, as it has no rigorous analytical solution we need to ask help of calculation techniques such as numerical calculation or Monte Carlo simulation. We chose the latter route. The initial electron energy and electric field intensity in electroluminescent layer were assumed to vary in a large scope. First, an analytical model [16] of the conduction band is used. It consists of three valleys (Γ, L, X) of the first conduction band, a Valley (X valley) of the second conduction band, and also a valley of still higher energy. For the latter band we proposed a higher conduction band for free electrons instead. The parameters for the free electron band are taken from reference [17].

Second, once the analytical band structure is constituted, we calculated the electron energy density state, as shown in Fig.7, which is defined as $N(E) = \lim_{\Delta E \to 0} \frac{\Delta Z}{\Delta E}$, where ΔZ is the number of energy states between E and $E + \Delta E$ [17]. In this process we took into account the anisotropy of dispersion and averaged the weighted result obtained along different directions.

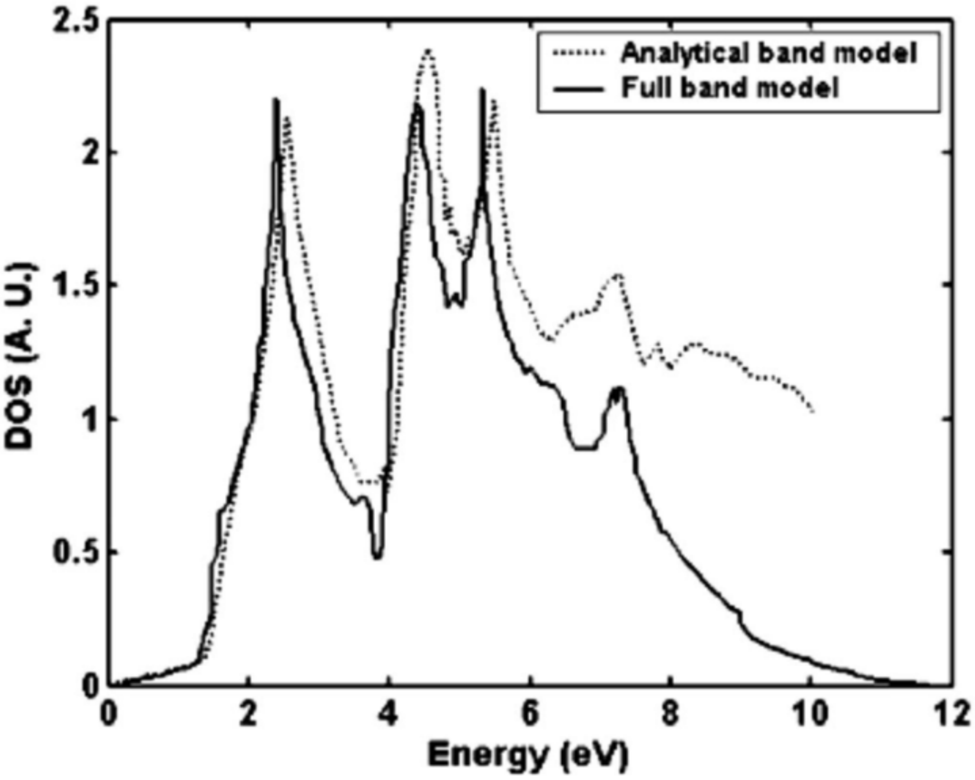

Fig. 7. Comparison of the overall density of states for our new analytical model of conduction band and for full band model

Third, we found out the different scattering rates:

1. The acoustic and optic phonon scattering rates for lower and higher electron energies.
2. The equivalent and non-equivalent inter-valley scattering rates were cited from reference[18].

3. The approximate scattering rate owing to the ionization of valence electron into the conduction band was cited from [19, 20].

$$\lambda_{ion} = R(E - E_{\hbar})^{\alpha}$$

Where $R = 5.14 \times 10^{10} s^{-1}(ev)^{-\alpha}$, $E_{\hbar} = 3.5ev$, and $\alpha = 5.183$

This process dominates the approach to energy stabilization and the beginning of electron multiplication. Based on these kinds of scattering rates, we carried out the Monte Carlo simulation. Electrons have a free flight time which may be determined stochastically according to the total scattering rate. From the total scattering rates we may work out a random number r (0<r<1) from the equation $\int_0^t S(\vec{k}.t')dt' = r$. $S(\vec{k}.t')$ represents the probability of the existence of $\vec{k}$ state within t. Because the variation of the total scattering rates with time is very complicated, the idea of self-scattering proposed by Rees is used. Then the free flight time is simplified to $t_f = -\frac{1}{\Gamma}\ln r$, where Γ is the total scattering rate (including self-scattering). During this free flight time the electron accumulates energy until this electron energy is balanced by scattering. At this time this flight is ended. The scattering which is active in this flight is chosen according to its relative magnitude. In the second flight we again chose a free flight time and new dominant scattering process.

The temporary variation of electron energy shows that after nearly 300fs the energy of hot electrons reaches a stationary value, which is responsible to the luminescence intensity. Thus, we calculated the stationary value of hot electron energy and get the following important results:

1. Initial electron energy might improve the stationary brightness only when the initial electron energy in ZnS attains 8eV in an electric field either lower than 0.6Mv/cm or greater than 4Mv/cm, as shown in Fig.8.
2. The distribution of hot electron energy under different electric fields is shown in Fig.9. The energy of hot electrons centralizes at higher energy valleys and the position of centralized energy consequently moves to the higher energy end when the electric field is increased owing to the increase in electron energy after the acceleration in the electric field and the balance with high energy scattering, including inter-valley scattering,. This tendency is very important and greatly increases the effectiveness of hot electrons in excitation.
3. The growth of hot electron energy proceeds in a stepwise way as shown in Fig. 10. From Fig. 10, we can see that if the initial electron energy ε_0 attains 8eV, the first plateau in EE appears at an average energy of hot electrons of more than 2.0eV, then after a sloping variation a second plateau in EE appears at an average energy of electrons above 4.8eV. The first and second plateaus constitute a stepwise growth in the electron energy. This behavior of EE is fully reflected in EL[15].

The complicated behavior of EE demonstrates the close dependence of electron transport on material properties, including conduction band structure, different scattering characteristics, the concrete structure of the device, and electric field strength. We obtained the satisfactory answers to the previous three problems.

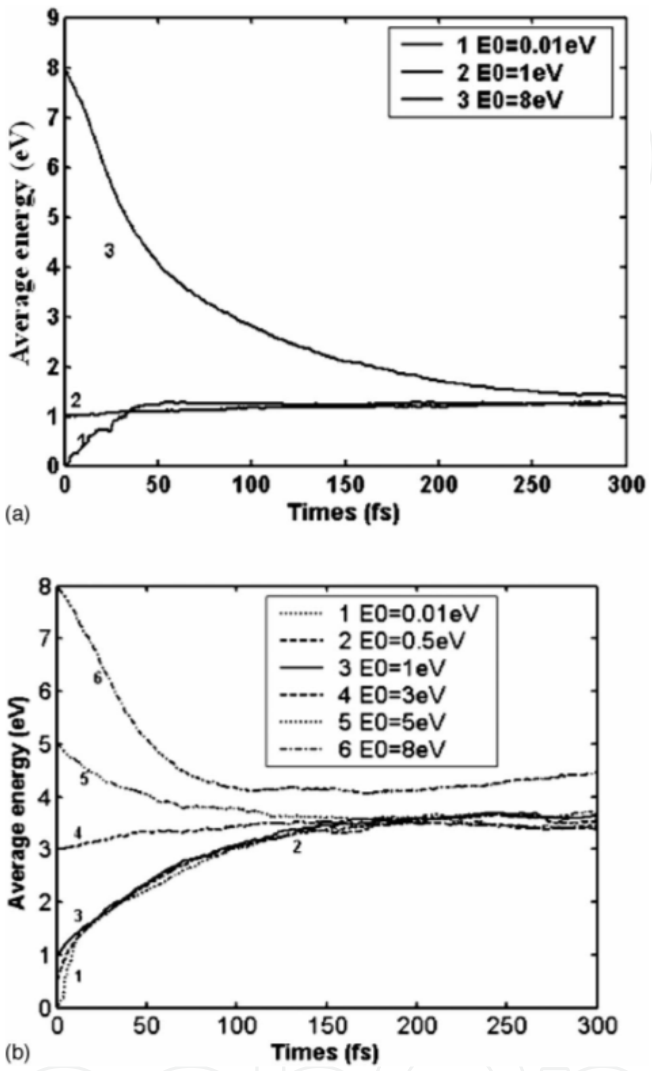

Fig. 8. Time evolution of electron energy at 0.6MV/cm (a) and 4MV/cm (b) field strength for different initial energies of electrons ε_0 in luminescent layer

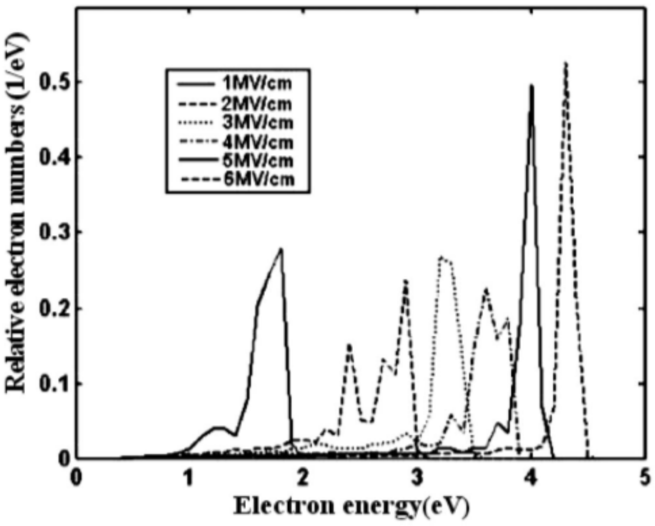

Fig. 9. Distribution of electron energy in different electric fields

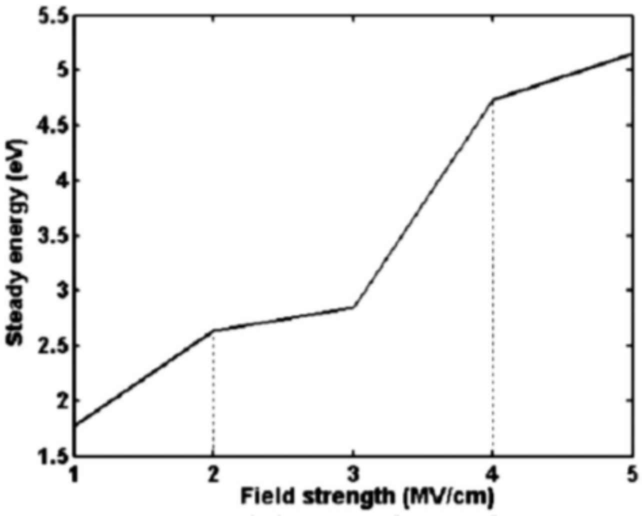

Fig. 10. Dependence of stationary electron energy on electric field strength when initial electron energy attains 8eV

The reason of all these behaviors or physical processes may be understood as follows:

1. When the electric field strength is less than 0.6MV/cm, the strength of scattering is not strong enough, and hence a part of the initial electron energy may be reserved and the stationary energy of hot electrons is raised. When the electric field strength is greater than 4MV/cm, although the strength of scattering is much increased, the free flight of electrons is also strengthened correspondingly. As only a part of the initial electron energy is required for energy balance, the stationary electron energy is thus increased. When the electric field is in between 0.6MV/cm and 4 MV/cm, no influence of 8eV

initial electron energy is detected. That means the sum of free flight energy and initial energy were balanced by total scattering.

2. In the process of electron transport the inter-valley scattering transfers the electrons from lower energy valleys to higher energy ones. This process leads to the concentration of hot electrons at a higher energy valley. During the further increase in the electric field, these hot electrons will be transferred to another even higher valley. Thus, the hot electron energy will be concentrated and shifted to another higher energy valley simultaneously. This tendency agrees with the distribution of density of states shown in Fig.7. When the electric field is high, most of electrons are evacuated from lower states and moved to higher energy states and the result appears in Fig.9.
3. When the electric field strength increases, the electron energy increases correspondingly. We observed a sloping energy increase, but when the field strength is high enough to start inter-valley scattering, the energy is concentrated and we observed a plateau. After the valley is fulfilled, the increase in the slope starts again. Thus we obtain a stepwise growth in hot electron energy. This phenomenon was observed in [15].

4.2 Choice of better acceleration material

The energy of hot electrons depends on the electric field and used materials. We have compared different materials as the acceleration materials and then compared the SSCL of a same emission layer. The acceleration materials used are Si_3N_4, SiO_2, ZnS or complex accelerated layer SiO_2/ZnS respectively [21-23]. The structure of all devices is same as ITO/accelerated layer/MEH-PPV/ accelerated layer/Al. In these devices, two luminescence peaks corresponding to the exciton emission and the extended band emission respectively are observed. The electron acceleration ability of SiO_2 is better than that of ZnS and Si_3N_4, but ZnS is better than SiO_2 when the ability of injection charges (as shown in Fig. 11 and 12) is compared. In Fig.11, under same bias, the intensity of short wavelength of MEH-PPV in the device of ITO/ SiO_2/MEH-PPV/SiO_2 /Al is stronger than that of ITO/ZnS/MEH-PPV/ ZnS/Al. So it is concluded that the acceleration ability of SiO_2 is better than that of ZnS. We investigated the complex accelerated layer SiO_2/ZnS. The results showed that under low voltage, the performance of the complex accelerated layer is superior than that of SiO_2 and inferior than that of ZnS. Under high voltage, the complex accelerated layer is the best among different devices. Thus, SiO_2 is the main accelerated layer, and ZnS is very useful to improve the performance of electrons injection of SSCL device.

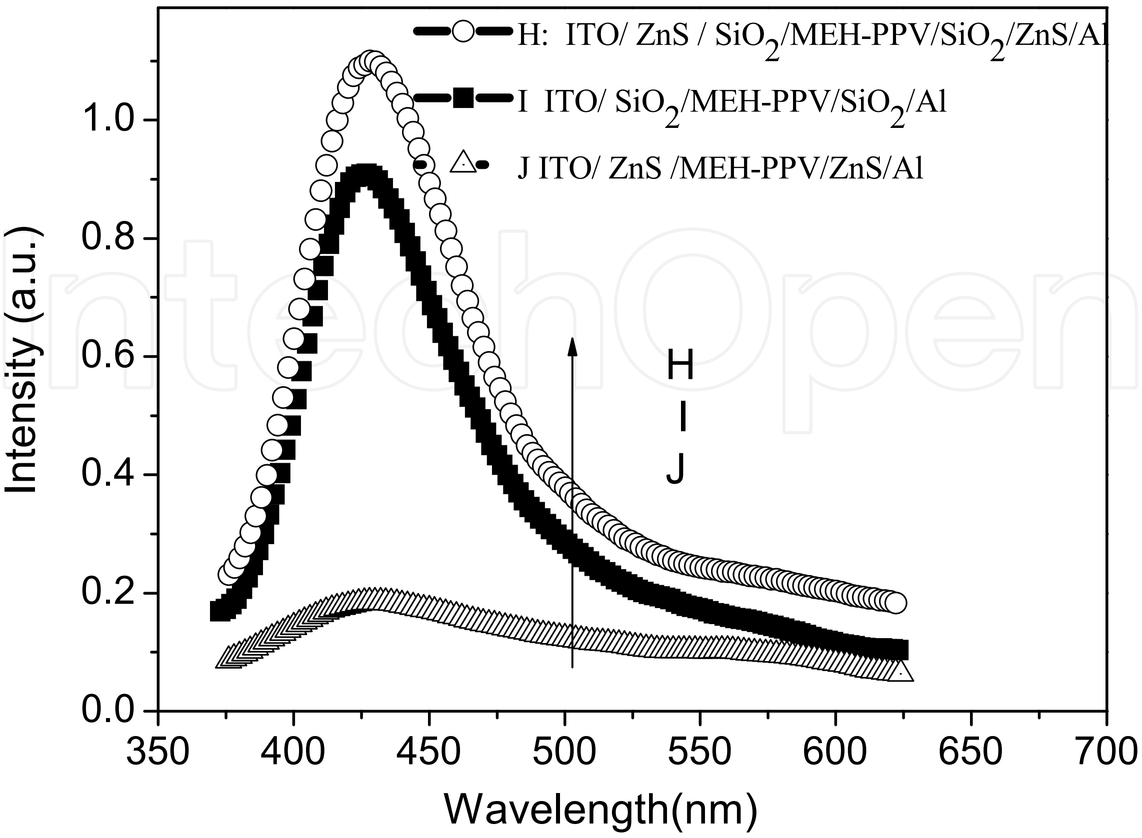

Fig. 11. The contrast of three devices on AC 65V

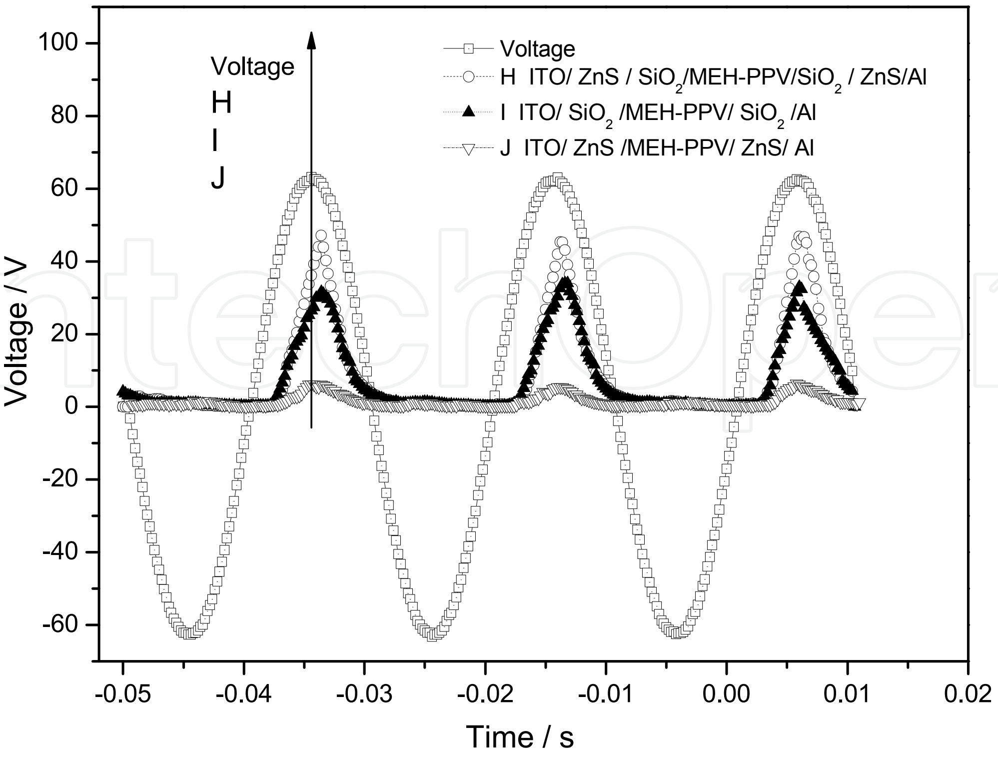

Fig. 12. The waveform of derivative luminescence (405nm) with applied voltage

5. The prospect of SSCL

Concerning above discussion, it is concluded that SSCL have more potential in the display field. The excitation mechanism of SSCL is superior to the organic electroluminescence. In organic electroluminescence, the maximum of the internal quantum efficiency is not more than 1/4 because of the limitation of the photon transition selection rule. After electrons and holes injected to the organic layer, only 1/4 number of electrons and holes can relax to form singlet excitons and give the light emission. But SSCL behaves nearly the photon excitation. In SSCL excitation, more singlet excitons are formed. There are almost no triplet excitons. Therefore, the efficiency of SSCL is better than that of pure OLED. The effort of raising luminescence efficiency is proposed to carry out in 4 aspects:

1. Examination of factors influencing the electron acceleration ability, e.g., crystal orientation of materials.

Using the Monte Carlo simulation method we have found out that the distribution of hot electrons concentrates and moves towards to higher energy end along the increase of energy. This situation is obviously benefit for raising the effectiveness of excitation. Another very important result is that the energy of hot electrons increases with electric field not harmonically but in stepwise way. This result coincides with experimental result of second jump in light intensity at higher electric field. The improvement of acceleration ability of the inorganic layer in the device should enhance SSCL. For example, if electrons transfer along the crystal orientation of the inorganic layer, under electric field, electrons should be accelerated easily.

2. Improvement of light intensity by enlarging the percentage of singlet exciton emission of organic materials.

From the consideration of excitation mechanism, it is beneficial to integrate of SSCL and OEL in the same device and enlarge singlet exciton formations.

3. Extension of complex display panel used in SSCL to FED

We published a paper on Optics Letters proposing the combination of electron source of FED and the complex screen in SSCL to form an improved variant of FED, in order to avoid the gas from the target under electron bombardment, to absorb the incoming high energy electrons b y injecting holes and consequently to hold the vacuum of the device.

4. Determination of trap depth of local electron source.

The release of electron from traps is the main source of the primary electron in SSCL devices. How to enhance the number of primary electrons? We investigated the trap depth of electrons. In luminescence the method of determining trap depth by analyzing glow curve with the assumption of kinetics order being 1 or 2 has been used more than 60 years, we pointed the large error of their results and proposed a quasi-equilibrium method which traces the real physical processes and provide an accurate result.

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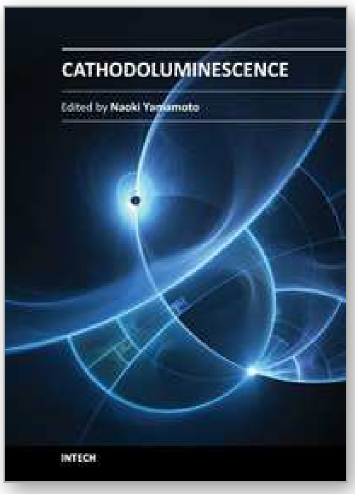

Cathodoluminescence
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Cathodoluminescence (CL) is a non-destructive technique to characterize optical and electronic properties of nanostructures in many kinds of materials. Major subject is to investigate basic parameters in semiconductors, impurities in oxides and phase determination of minerals. CL gives information on carrier concentration, diffusion length and life time of minority carriers in semiconductors, and impurity concentration and phase composition in composite materials. This book involves 13 chapters to present the basics in the CL technique and applications to particles, thin films and nanostructures in semiconductors, oxides and minerals. The chapters covered in this book include recent development of CL technique and applications to wide range of materials used in modern material science.

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