OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 1, No. 8, August 2007, p. 385 -387

# Cathodoluminescence-like phenomenon based on ZnSe

WEIWEI JIANG[a,b*], ZHENG XU[a,b], FUJUN ZHANG[a,b], SULING ZHAO[a,b], JINZHAO HUANG[a,b], YUAN LI[a,b], GUANGCAI YUAN[a,b]

[a]*Institute of Optoelectronics Technology, Beijing Jiaotong University, Beijing 100044，China;*

[b]*Key Laboratory of Luminescence and Optical Information, Ministry of Education，Beijing 100044，China*

The heterojunction of $SiO_2$/ ZnSe /$SiO_2$ was prepared by electron beam evaporation. $SiO_2$ was used as electron acceleration layer and ZnSe was taken as the luminescent material. Luminescence due to direct bombardment by accelerated electrons in a semiconductor thin film adjacent to the phosphor material layer was observed, which was called cathodoluminescence-like (CL-like) because are electrons accelerated in solid but not in vacuum. This new phenomenon can provide a new way to realize blue electroluminescence. The threshold voltage of the device is 40V. The dependence of CL-like intensity on applied voltage and frequency were studied in detail.

(Received June 26, 2007; accepted June 26, 2007)

*Keywords:* Cathodoluminescence-like, CL-like, ZnSe

## 1. Introduction

Cathode ray electrons bombard phosphor and give cathodoluminescence (CL) when they are accelerated by anode voltage. CL had been discovered more than one hundred years ago. Today it still occupies very important place in TV and computer monitors.

In the development of display technology, the solid state color panel display becomes more and more important. Inorganic thin-film electroluminescence (TFEL) plays a very important role for flat plane displays [1-4]. It has many characteristics, such as rapid response, initiative luminescence, widely visual angle. Nowadays, red and green TFEL displays have been widely used in many fields. Though extensive efforts have been made, an efficient blue device is not completely solved. It blocks the development of inorganic full-color flat plane displays seriously. The lack of an efficient blue phosphor [5] and the impact ionization [6] of the excited state electrons were the barier for the development of efficient electroluminescence (EL) devices in the blue.

In this paper, the heterojunction device of $SiO_2$/ZnSe/$SiO_2$ was deposited by electron beam evaporation. It gave blue-green luminescence. The luminescence mechanism of the device called cathodoluminescence-like (CL-like) was discussed. The CL-like spectral properties with driven voltage and frequency were also discussed.

## 2. Experimental

$SiO_2$, ZnSe films were deposited by electron-beam evaporation at a rate of 1 Å/s under high vacuum of $2\times10^{-6}$ Torr. The substrate temperature is kept at 150°. The thickness of $SiO_2$ was 150 nm and the thickness of ZnSe layer was also 150 nm. The thickness was measured by a quartz crystal thickness monitor placed near the substrates. Al was prepared by thermal evaporation under a vacuum of $10^{-5}$ Torr with a thickness of about 200 nm. The structure of the device is shown in Fig. 1. The CL-like spectra were measured with Spex Fluorolog-3 spectrometer.

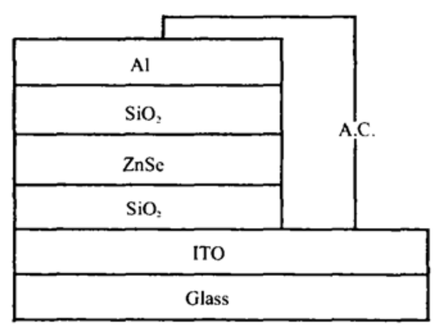


*Fig. 1. Structure of the device.*

## 3. Results and discussion

### 3.1 The mechanism of luminescence

The normalized electroluminescence spectrum of the device is shown in Fig. 2. The device was excited by AC voltage 85 V at 7000 Hz. There are two peaks located at 469 nm and 544 nm.

In the experiment, $SiO_2$ semiconductor film replaces the traditional insulated films, such as $Ta_2O_5$, $BaTiO_3$ and $PbTiO_3$. The electric field distributed to $SiO_2$ layer is higher than ZnSe's because of that the dielectric constant of $SiO_2$ is smaller than ZnSe's, This is different from the traditional device. So electrons are accelerated, multiplied in $SiO_2$ layer and get high energy before entering in the emission layer. These hot electrons have enough energy to impact ZnSe and then the electrons in ZnSe valence band are excited to conduction band. At the same time, ITO/ $SiO_2$/Al device was prepared.It does not emit. So the two peaks come from ZnSe. When the electrons in conduction band transit to valence band and recombine with hole, the 469 nm blue electroluminescence is given. The 544 nm green emission corresponds to self-excited luminescence of ZnSe. The defect of ZnSe includes Zn vacancy, Se vacancy, its interstitial ion defects and other defects caused by impurity. Se vacancy forms double donor level and Zn vacancy is a kind of acceptor defect. According to Phil [7], ZnSe can be p-type conduction due to Zn vacancy existence. So 544 nm emission corresponds to Zn vacancy defect.

The acceleration ability of $SiO_2$ has already been discussed in detail in layered optimization structure TFEL device. In electroluminescence of organic materials there is always short wavelength emission because hot electrons bombard organic molecules when the applied bias is sufficiently high, e.g., ITO/$SiO_2$/$Alq_3$/$SiO_2$/Al, etc. [8,9]. This is called cathodoluminescence-like (CL-like) because the electrons are accelerated in a solid but not in vacuum [10]. Yoshiki Nakajima reported a similar result where the electrons could be accelerated to 8 eV in porous silicon but they only obtained the emission of excitons [11]. This new phenomenon can provide a new way to realize blue electroluminescence.

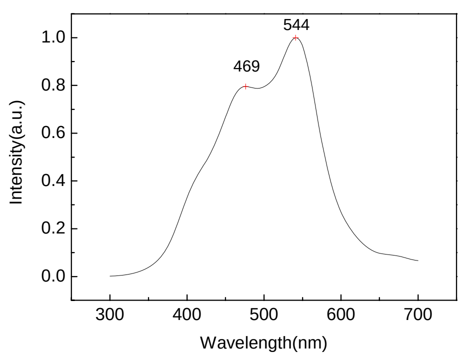


*Fig. 2. The normalized CL-like spectrum of the device.*

## 3.2 The effect of driving voltage on CL-like intensity

The CL-like spectra of the device driven by different AC voltage at 1000 Hz were measured. The relationship between voltage and CL-like intensity of the device is shown in Fig. 3. The threshold voltage is about 40 V and two peaks are located at 469 nm and 544 nm. The CL-like intensity increases with voltage of the device at fixed frequency (1000 Hz). Until 100 V, the intensity does not exhibit a decreasing trend.

The relation between brightness and voltage of ACEL nearly fits the follow equation:

$$B = B_0 \exp[-(V_0 / V)^{\frac{1}{2}}]$$

where B is brightness, V is driving voltage, B0 and V0 are constants independent of driving voltage. B0 and V0 will change with materials and devices. According to the above equation, it is known that brightness increases with increasing voltage. The relationship between luminescence intensity and voltage has the same trend with the relationship between brightness and voltage.

In addition, the process of CL-like is as follows: luminescence centers are bombarded by hot electrons under the action of electric field, the electrons stayed at ground state are excited to excited state. When they transit back to ground state, the emission is given. So if driving voltage increases, more electrons get higher energy, that is to say, the quantity and energy of hot electrons which have enough energy to bombard luminescence centers increase. This results in CL-like intensity increases with driving voltage increasing.

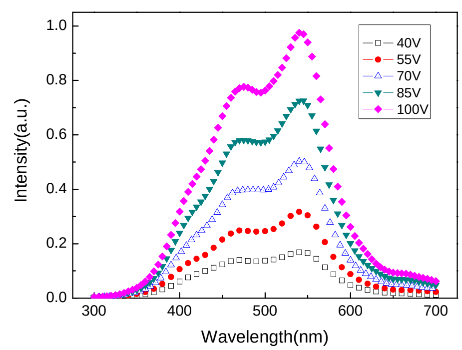


*Fig. 3. The normalized CL-like spectrum of the device under various voltages at fixed frequency(1000 Hz).*

## 3.3 The effect of driving frequency on CL-like intensity

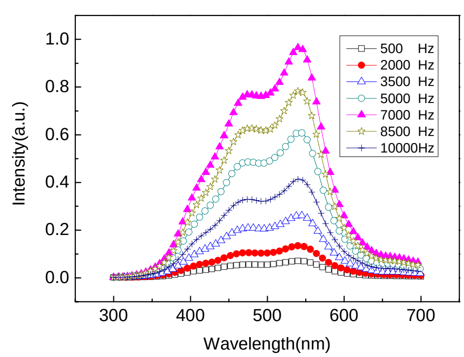


*Fig. 4. The normalized CL-like spectrum of the device under various frequencies at fixed voltage (85 V).*

The CL-like spectra of the device driven by different frequency at fixed voltage (85 V) were measured. The frequency ranges from 500 Hz to 10000 Hz. Fig. 4 shows the relationship between frequency and CL-like intensity. At first, we can see from this graph that the CL-like intensity increases with the frequency increase under fixed voltage (85 V) in this frequency range, but when frequency is higher than 7000 Hz, the CL-like intensity decreases.

The CL-like appears every half voltage cycle. When the frequency is low, those electrons which are not excited or being excited can be accumulated near the positive pole and form reversal electric field. This results in that electrons' rate decreases. So the number of injected hot electrons, that knock the luminescence centers and give emission in unit time is relatively few. The CL-like intensity is low. The number of hot electrons impact the luminescence centers in unit time increases with frequency. So the emission times in unit time increases and luminescence intensity also increases. Intensity will increases with frequency only when the time corresponding to the arrival of hot electrons at luminescence centers is shorter than half of the voltage cycle of excitation [12]. Thus, if the frequency exceeds certain value, the intensity will decrease.

## 4. Conclusion

The heterojunction of $SiO_2$/ZnSe/$SiO_2$ was prepared by electron beam evaporation. $SiO_2$ was used as electron acceleration layer and ZnSe was taken as the luminescent material. Luminescence due to direct bombardment by accelerated electrons in a semiconductor thin film adjacent to the phosphor material layer was observed, which was called cathode-luminescence-like (CL-like) because electrons accelerating in solid but not in vacuum. This new phenomenon can provide a new way to realize blue electroluminescence. The threshold voltage of the device is 40 V. There are two peaks in the CL-like spectrum located at 469 nm and 544 nm. The two peaks' intensity strengthens with increasing applied voltage in measuring range. Their intensity increases at first and then decreases with increasing frequency. The 469 nm blue emission was attributed to ZnSe band-band transition and 544 nm emission is probably caused by defects in ZnSe film.

**Acknowledgments**

The authors express their thanks to the National Natural Science Foundation of China under Grant No. 60576016, 10374001; The National High Technology Research and Development Program of China under Grant No. 2006AA03Z0412; the Beijing Natural Science Foundation of China under Grant No. 2073030; the National Grand Fundamental Research 973 Program of China under Grant No.2003CB314707; National Natural Science Foundation of China under Grant No. 10434030.

## References

[1] Y. A. Ono, Electroluminescent Displays, Word Scientific, Singapore (1995).
[2] W. A. Barrow, R. C. Coovert, C. N. King, SID'84 Digest, 1984, p.249.
[3] W.A. Barrow, R.C. Coovert, E. Dickey, C. N. King, C. Laakso, S.-S. Sun, R.T. Tuenge, R. Wentross, J. Kane, SID'93 Digest, 1993, p.761.
[4] Noboru Miura, Mitsuhiro Kawanishi, Hironaga Matsumoto, et al., Japanese Journal of Applied Physics, 1999, 11B
[5] S.-S. Sun, Display **19**,145 (1999).
[6] E. Bringuier, J. Appl. Phys. **67**, 7040 (1990).
[7] Yu Phil Won, Park Y. S., Appl. Phys. Lett. **22**, 345 (1973).
[8] X. L. Xu, Z. Xu, Y. B. Hou, et al., J. Appl. Phys. **89**, 1082 (2001).
[9] Xiaofeng Wang, Zheng Xu, Xiaohong Cheng, Journal of Optoelectronics·Laser **l2**, 477 (2001) (in Chinese).
[10] Xurong Xu, Xiulai Xu, Xiaofeng Wang, et a1., Chinese Journal of Polymer Science **l9**, 579 (2001).
[11] Yoshiki Nakajima, Akira Kojima, Nobuyoshi Koshida, Appl. Phys. Lett. **81**, 2772(2002).
[12] Xurong Xu, Chin. J. Lumin. **24**, 553 (2003) (in Chinese).

*Corresponding author: rosejiangwei@126.com