Journal of Crystal Growth 101 (1990) 1004–1008
North-Holland

PRELIMINARY TRIAL OF THIRD GENERATION ELECTROLUMINESCENCE (EL) *

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A preliminary trial involving the enhancement of the brightness of an EL cell is presented. Based on the experimental facts that the most important and inevitable process in EL is impact excitation or ionization, we attempt at enlarging the brightness by widening the impact excitation cross-section. By calculation, this cross-section is found to be dependent on the energy distribution and incident direction of the impinging electrons. In this calculation we take into account the conduction band structure. In order to overcome the loss in the initial acceleration phase, we preheat carriers and inject them into the high field acceleration zone, in which the production of streaming carriers is expected. In this way, we vary the energy distribution toward higher energy and really observe a several-fold enhancement of brightness.

1. Introduction

Since the discovery of EL, two generations have been developed: the dispersion type and the thin film. Now the brightness of EL is expected to be enhanced and the driving voltage to be lowered. This should be the most demanding characteristic of third generation EL. Experiment shows that there is no other process which is more probably than impact excitation or ionization in a high electric field [1]. So an effective reasonable method of enhancing the brightness of EL is by widening the cross-section of impact excitation as much as possible [2].

2. Theory: dependence of impact excitation cross-section on the energy and incident direction of impinging electrons

In the process of scattering, the hot electrons are scattered from the upper state ϕ_u into the lower states ϕ_ℓ, and the luminescence centers are excited from the ground state ψ_g to the excited states ψ_e. ϕ_u and ϕ_ℓ may correspond to energies in the same conduction band as shown in the right-hand side of fig. 1 or in different energy bands as shown in the left-hand side of fig. 1. The excita-

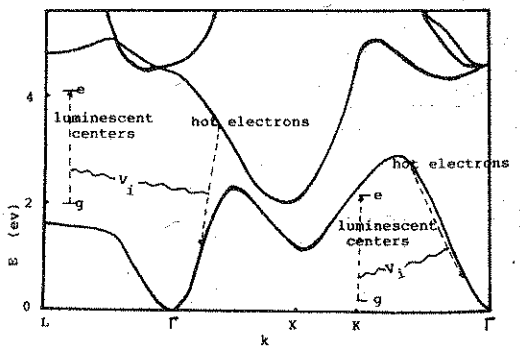

Fig. 1. Hot electrons from the upper states are scattered down to the lower states, and the luminescence centers are excited to the excited states from the ground state. Here the energy position of the luminescence centers is not the real position.

* Work supported by the National Science Foundation of China.

0022-0248/90/$03.50

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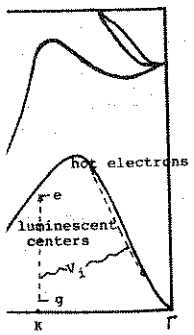

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tion rate for the luminescence center in this process is

$$P = \frac{2\pi}{\hbar}\rho(E)\,|\langle\psi_g(r_j)\phi_u(k, r)\,|\,V_i\,|\,\psi_e(r_j) \times \phi_\ell(k', r)\rangle\,|^2,$$

where $\rho(E)$ is the density of final states and

$$E_u - E_\ell = E_e - E_g,$$

E_u and E_ℓ are the electron energies for states ϕ_u and ϕ_ℓ. $E_e - E_g$ is the transition energy of the luminescence center from the ground state to the excited state. Suppose that the final states of the hot electron transition are in the vicinity of the Γ point, we have

$$\rho(E) = 4\pi V\left(2m_c/h^2\right)^{3/2} E_\ell^{1/2},$$

where m_c is the effective mass of the electrons at the bottom of the conduction band and V is the crystal volume.

The interaction V_i between the hot electron and the luminescence center is

$$V_i(r, r_j) = \sum_j^Z \frac{e^2}{\epsilon\,|r - r_j|} - \frac{Ze^2}{\epsilon r},$$

where r is the position vector of the hot electron and r_j is that of the jth electron of the luminescent center. Then

$$\frac{1}{|r - r_j|} = \sum_{l=0} \frac{1}{r^{l+1}} r_j^l\, P_l(\cos\theta_j),$$

and

$$V_i(r, r_j) \approx \sum_j^Z \frac{e^2 r_j \cos\theta_j}{r^2} = \frac{e^2}{\epsilon r^2}\sum_j^Z Z_j,$$

so that

$$P = \frac{2\pi}{\hbar} 4\pi V\left(\frac{2m_c}{h^2}\right)^{3/2} \times E_\ell^{1/2}\left|\langle\phi_u(k, r)\,|\,\frac{e^2}{r^2}\,|\,\phi_\ell(k', r)\rangle\right|^2 \times \left|\langle\psi_g\,|\,\sum_j Z_j\,|\,\psi_e\rangle\right|^2.$$

In this expression the term

$$\left|\langle\psi_g\,|\,\sum_j Z_j\,|\,\psi_e\rangle\right|^2$$

is related to the lifetime τ_e of the excited states of the luminescence center. The other term

$$\langle\phi_u(k, r)\,|\,\frac{1}{r^2}\,|\,\phi_\ell(k', r)\rangle$$

depends on the wavefunctions $\phi_u(k, r)$ and $\phi_\ell(k', r)$ which are necessarily to be determined. For this purpose we must find the wavefunctions corresponding to the band structure.

From the different approaches we choose the pseudopotential method. In this method the Hamiltonian for an electron in the crystal is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(r),$$

and the potential U is expanded in terms of reciprocal lattice vectors k_l and expressed in the

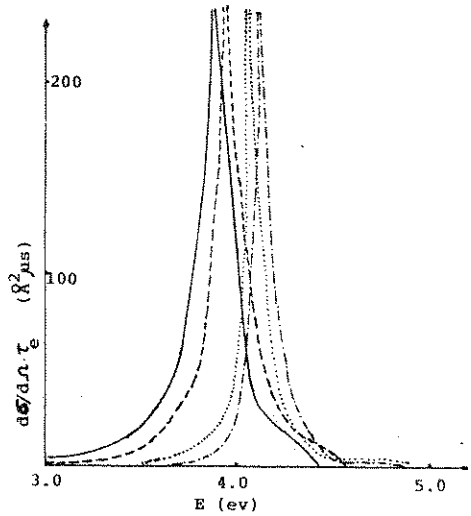

Fig. 2. The variation of $(d\sigma/d\Omega)\tau_e$ for incident direction of hot electrons along [100] with energy of hot electrons. Here only the differential cross-section for [100] scattered direction of the electron are given because the differential cross-sections for [111] and [110] scattered directions are much smaller than those for [100]. (———) Energy levels of 1.88 eV, (— — —) of 2.1 eV, (· · · · · ·) of 2.5 eV and (— · — · —) of 2.75 eV.

form of the product of a structural factor $S(k_l)$ and a pseudopotential factor U_{k_l}. Then

$$U(r) = \sum_l \left[S^s(k_l) U^s_{k_l} + \mathrm{i}\, S^a(k_l) U^a_{k_l} \right] e^{-\mathrm{i}k_l \cdot r}$$

is expressed by symmetric and antisymmetric parts. The base states forming the Hamiltonian matrix are plane waves with wave vector $k_l + k$

$$\phi(k, r) = \sum_l a(k_l) \frac{1}{V^{1/2}} e^{-\mathrm{i}(k_l + k)\cdot r}.$$

Then we obtain the wave functions corresponding to different energies of the conduction band

$$\phi_\ell(k', r) = \sum_n a_\ell(k_n) \frac{1}{V^{1/2}} e^{-\mathrm{i}(k_n + k')\cdot r},$$

$$\phi_u(k, r) = \sum_m a_u(k_m) \frac{1}{V^{1/2}} e^{-\mathrm{i}(k_m + k)\cdot r}.$$

The differential cross-section

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{48\pi^3 C^3 m_c e^2 (E_\ell / E_u)^{1/2}}{n_r (\epsilon_{\mathrm{eff}}/\epsilon_0)^2 \epsilon^2} \frac{1}{(E_e - E_g)^3} \times \left| \sum_{nm} a_\ell(k_n) a^*_u(k_m) \right. / \left| (k + k_n) - (k' + k_m) \right| \Big|^2 \frac{1}{\tau_e},$$

where n_r is the refractive index and $\epsilon_{\mathrm{eff}}/\epsilon_0$ is the effective field ratio. From this expression we can see that the cross-section depends not only on the scattered direction of the electron, but also depends on the incident direction of the hot electron.

Numerical calculation for luminescence centers in ZnS shows the dependence of $\mathrm{d}\sigma/\mathrm{d}\Omega$ on the energy of hot electrons along the direction [100] for the case of transition between different bands. In fig. 2 the product of differential cross-section to lifetime of luminescence is given along the scattered direction [100] only. This value is much larger than that along [110] and [111] directions. There are sharp peaks between 3.5 and 4.5 eV, the peak value reaches 10^3 Å^2 μs. The dependences of $(\mathrm{d}\sigma/\mathrm{d}\Omega)\tau_e$ on hot electron energy for different energy levels are similar to each other.

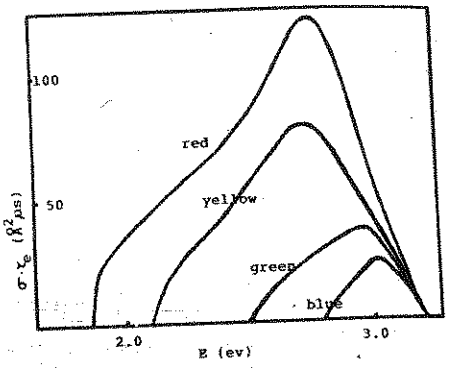

Fig. 3. Variation of $\sigma\tau_e$ for [110] incident direction of hot electron with energy of hot electron showing the emission colour.

Fig. 3 shows the dependence of $\sigma\tau_e$ for the [110] incident direction of electrons on its energy for the case when the hot electron transition is in the same conduction band. Along different directions the magnitude of the cross-section is of the same order. Therefore the total cross-section is summed over different scattered directions. From these results it is shown that the cross-section passes a maximum and then drops down to zero at about 3.2ev.

3. Experiment

The next problem is to control the energy of hot electrons to the energy range in which the cross-section of impact excitation is optimum. In general the energy of hot electrons may be increased by applying a higher bias. But this is seriously prohibited by the scattering processes. So that in conventional EL cells there is only a small probability for hot electrons to reach the threshold value of impact excitation. From the dependence of cross-section on energy of hot electrons we realize that the energy of hot electrons must be increased because σ increases with increasing energy of hot electrons in the low energy range. For this purpose we use two contiguous layers as suggested in ref. [3]. In the first layer the electrons are preheated and injected into the second layer of polar material in which the electrons are accelerated up to higher energy.

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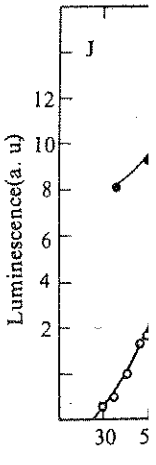

Fig. 4. Ratio of gre
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We choose the structure $SiO/SiO_2/ZnS:ErF_3/SiO_3/SiO$, the contiguous layer SiO/SiO_2 is used for accelerating electrons [3] and the $ZnS:ErF_3$ is used for a qualitative estimate of the energy distribution with the ratio of the green ($^2H_{11/2}-{}^4I_{15/2}+{}^4S_{3/2}-{}^4I_{15/2}$) to red emission ($^4F_{9/2}-{}^4I_{15/2}$) of Er^{3+} [4]. Exciting the thin film with an AC source (4 kHz, 45 V), the ratio R and brightness J of this new cell as a function of applied voltage is measured, and the results are shown in fig. 4. These quantities are compared with those observed for conventional cells, e.g. $Y_2O_3/ZnS:ErF_3/Y_2O_3$. It is found that J and R are several times larger and the $R-V$ relation increases much more steeply than in the conventional cells. It is worth noting that the operation voltage is lowered considerably. For example, the threshold voltage (AC, 30 V) is lower than that in conventional cells (AC, 70 V) by 30 V. The increment of R indicates the increment of electron energy. So that we can get more energetic electrons than that in conventional cells by means of this structure at the same applied voltage. This also explains the fact that the brightness of EL increases several fold, according to the dependence of σ with electron energy.

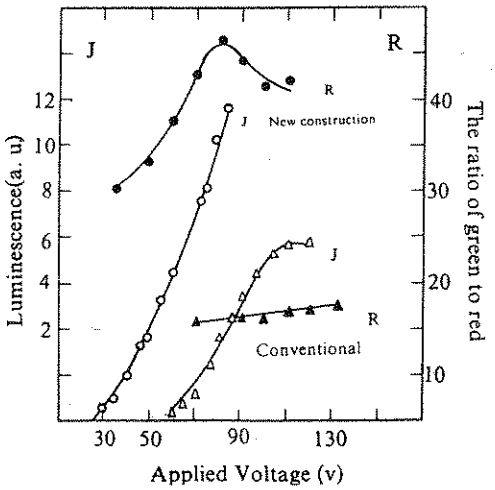

Fig. 4. Ratio of green to red emission and brightness of this new device and its dependence on applied voltage in comparison with a conventional device.

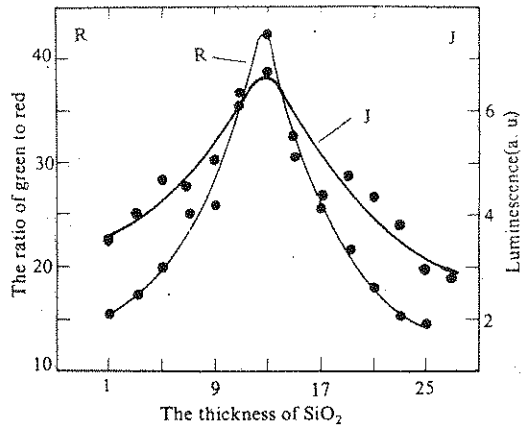

Fig. 5. Ratio of green to red emission of Er^{3+} and integrated luminescence as a function of SiO_2 thickness (in arbitrary units).

We prepared a group of samples from the same evaporation. The positions of the substrate and the source of evaporation were fixed, but the thickness of the SiO_2 layer was changed continuously.

Measuring the quantity R or J at different positions, we obtain their variation with the thickness of the SiO_2 layer. Fig. 5 shows the dependence of R and J on the thickness of the SiO_2 layer. (The excitation is also 4 kHz, 45 V.) When the thickness of the SiO_2 layer increases, both the R and the J curve increase to a maximum and then drop down.

4. Discussion

The slope of R in figs. 4 and 5 indicates that the energy of hot electrons is really increased. From the experimental data we want to clarify whether the maximum of the cross-section is really reached or only the maximum electron energy is obtained. If the maximum cross-section is improved upon, the curves of R and J in fig. 5 should not be parallel to each other, because, if the energy of the electrons is larger than that corresponding to the maximum brightness, the brightness may drop down, but the ratio of green to red emission will be increased continuously,

and not in a parallel fashion. Therefore, fig. 5 provides information only on the existence of the maximum electron energy in a given structure. But what part of the curve in fig. 4 this electron energy corresponds to is still unknown. Even so, we are sure that the electron energy is much higher than that in conventional cells.

In order to increase the brightness of EL, we must enlarge the cross-section as well as the number of electrons. This can be done by electron multiplication or with a rich source of primary electrons. It is worth comparing all the proposed methods for increasing the energy of electrons: use of a single or multistate graded gap structure [5], use of tunnelling electrons [6] through a thin dielectric and the above method using two contiguous layers. In all these methods the principle in the same: separate the process of acceleration and excitation. The process of electron multiplication as reported in ref. [8] should also be considered.

The cross-section for impact excitation depends also on the nature of the centers, e.g., their charge state, discrete or recombination centers, etc. The anisotropy of cross-section is to be checked by experiment, which may partly interpret the mechanism of ref. [7].

5. Conclusion

(1) The cross-section of impact excitation is calculated for different crystal directions as a function of the incident impinging electrons. Anisotropy of the cross-section reveals the favourable crystallographic direction: if the energy transition of hot electrons is in the same conduction band, i.e, below 3.2 eV, the [110] incident direction of hot electrons is favourable; if the transition is between different conduction bands, i.e., in the interval of 3.5 to 4.5 eV, the [110] incident direction of hot electrons is favourable.

(2) The energy of hot electrons is enhanced by the use of two contiguous layers; the second layer is responsible for the acceleration of electrons preheated in the first layer. An optimum thickness of the second layer of polar materials is found in order to obtain the highest electron energy.

(3) A several-fold enhancement of J or several tens of volts decrease of driving voltage has so far been observed. These are the most important properties of the third generation EL.

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