Field-induced ionization of excited luminescent centers at high electric field strengths

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Abstract

In this paper we discuss the mechanism of field-induced ionization of the excited luminescent centers in rare-earth doped ZnS TFEL devices and estimate the upper-level positions of the centers according to Franz–Keldysh effect. Effects of impact and room temperature on ionization of the centers are also considered.

Keywords: Field-induced ionization; Excited luminescent centers; Franz–Keldysh effect

1. Introduction

TFEL devices with rare-earth-doped zinc sulfides, such as ZnS : Er, ZnS : Tm and ZnS : Ce are used to obtain green or blue light. It is believed that in these devices, the dominant excitation mechanism of phosphor ZnS is the direct impact excitation of the luminescent centers. However, the appearance of sharp spikes [1] at the leading edge of the exciting pulse voltage in Er-, Tm- and Ce-doped ZnS TFEL devices for different transitions from upper levels of dopants are understood to be due to the recombination of electrons from the conduction band with the ionized luminescent centers. Ranta-aho [2] investigated electric-field quenching of photoluminescence under the threshold voltage, which indicates that field-induced

ionization of excited luminescent centers exists at the voltage range of electroluminescence in thin film ZnS : Tm. The existence of ionization of the excited rare-earth centers in ZnS TFEL devices is disadvantageous for getting blue electroluminescence when there is quenching effect when electrons stay in the conduction band.

2. Results and discussion

Effects of electric field on the luminescent centers have been investigated by comparison with Franz–Keldysh effects [3] in Er-, Tm- and Ce-doped ZnS TFEL devices. F–K effects were investigated through reflection spectra, since the back electrodes of the devices are not transparent. According to F–K effect the energy deficiency of the absorption edge $\Delta E(F)$ is given by [4]

$$\Delta E(F) = 1.5(m^*)^{-1/3} \times (e\hbar F)^{2/3}, \qquad (1)$$
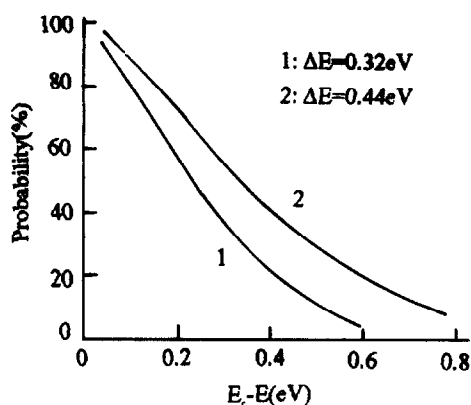
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Fig. 1. Dependence of the probabilities of finding conduction electrons in the forbidden band in the depths of the excited levels of the centers at different electric field strength.

where $\hbar$ is the Dirac constant, e the charge of a free electron, m^* the effective mass of the electron at the bottom of the conduction band which is 0.39 for β-ZnS, and F the electric field strength. The experimental data for ΔE fit the calculated values from Eq. (1) well. For ZnS : Er at the electric field from 1.8 to 3.0 MV/cm, the device is luminescent and the absorption edge moves from 0.32 to 0.44 eV towards the lower-energy side in the absorption spectrum, namely, the probability of finding a conduction electron in the forbidden band near the conduction band edge increases. In the same way, the energy deficiencies of the absorption edges in the experimental range are 0.28–0.37 eV for ZnS : Tm and 0.38–0.48 eV for ZnS : Ce, respectively.

It is expected that at high electric field strengths there exists an overlap between the s-like conduction electron wave function of Zn^{2+} and the 5d or 4f wave function of Er^{3+} or Tm^{3+} and Ce^{3+}. The probability of finding a conduction electron at E in the forbidden band is proportional to [4]

$$\exp\{ - [(E_c - E)/(\Delta E(F)]^{3/2}\}, \qquad (2)$$

where E_c is the energy of the bottom of the conduction band, E as a fixed level equals the energy of the upper levels of luminescent centers and $\Delta E(F)$ is the deficiency of energy for a parametric electric field. In Fig. 1, the probability decreases with the depth of the excited state of the centers at a constant field

strength. The lower the excited state level is, the weaker the interaction between a s-like conduction electron of Zn^{2+} and a 5d or 4f electron of the centers becomes. When the deficiency of energy in F–K effect becomes equal to $(E_c - E)$, the probability is $1/e$ or 37%. Thus, from the probability we can estimate $(E_c - E)$. If assuming that 37% is a critical value on which no field-induced ionization occurs, we conclude that the energy differences between the conduction band edges and the excited states of luminescent centers are approximately at the range 0.32–0.44 eV for ZnS : Er, 0.28–0.37 eV for ZnS : Tm and 0.38–0.48 eV for ZnS : Ce, respectively.

Besides field-induced ionization, there are two other possible factors responsible for the ionization of the excited states of the luminescent centers [5]: impact ionization and thermally assisted ionization. The rates of impact ionization and thermally assisted ionization are 10^{10} and $10^7 \, s^{-1}$, respectively, while the field-induced ionization rate is $10^{13} \, s^{-1}$. This indicates that field-induced ionization is dominant in the ionization of excited luminescent centers at room temperature.

3. Conclusion

Field-induced ionization is responsible for ionization of the excited states of the luminescent centers at room temperature. This effect may be understood as interaction between the electrons at the bottom of the conduction band in ZnS and the electrons in the higher excited states of the luminescent centers in the form of overlapping of the wave function.

References

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