Thermofield $Cr^+ \rightarrow Cr^{2+}$ recharging resulting in anomalous intensification of Cr^{2+} emission in ZnS:Cr thin-film electroluminescent structures

N.A. Vlasenko, P.F. Oleksenko, Z.L. Denisova, M.A. Mukhlyo, L.I. Veligura
V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine
41, prospect Nauky, Kyiv 03028, Ukraine

Abstract. For the first time, an anomalous strong increase of the Cr^{2+} emission intensity (I) with increasing the applied voltage (V) has been discovered in ZnS:Cr thin-film electroluminescent structures (TFELS) instead of the $I(V)$ dependence saturation typical of TFELS of the MISIM type, where M is an electrode, I is an insulator layer and S is an EL film. The dependence of I on the transferred charge (Q) is very superlinear, whereas the luminance of the emission of hot electrons, which takes place simultaneously with the Cr^{2+} emission, increases proportionally to Q as it happens usually in TFELS. The increase of I and Q is accompanied by rising the sample temperature up to $30 - 50$ °C. However, the emission spectrum that is inherent to the $^5E \rightarrow {}^5T_2$ transition in the 3d shell of a Cr^{2+} ion is not changed in this case. The above effects are explained by $Cr^+ \rightarrow Cr^{2+}$ thermofield recharging, which results in an increase of the number not only of free electrons, but also of Cr^{2+} radiation centers. The most probable mechanism of such a recharging is the Frenkel-Pool field-stimulated thermal ionization of Cr^+ ions, whose ionization energy is $0.65…0.82$ eV.

Keywords: electroluminescence, thin films, ZnS:Cr, thermofield ionization, $Cr^+ \rightarrow Cr^{2+}$ recharging.

1. Introduction

An intensive emission in the near-infrared region from 1.7 to 2.8 μm takes place in ZnS(Se):Cr thin-film electroluminescent structures (TFELS) [1-3]. The same emission is observed in photoluminescence of ZnS(Se):Cr crystals [4]. This emission is due to the $^5E \rightarrow {}^5T_2$ transition in the 3d shell of Cr^{2+} ions. In the spectrum of ZnS(Se):Cr TFELS, there is also a week emission in the region of 0.4–1.0 μm that results from intraband indirect transitions of hot electrons [1, 3, 5]. It is known that some number of Cr^+ ions is side-by-side with Cr^{2+} ions in ZnS(Se):Cr. The photo-stimulated appearance of Cr^+ ions in ZnS(Se):Cr crystals has been revealed by investigating the electronic paramagnetic resonance (EPR) at low temperatures This has been explained by $Cr^{2+} \rightarrow Cr^+$ photorecharging [6-10]. It has been reported in [7] that Cr^+ ions are present in ZnS:Cr crystals even without any illumination. The existence of these ions in ZnS:Cr TFELS has been confirmed by studying the magnetic field effect on the emission of hot electrons at 4.2 K [5]. It has been shown that a decrease of the intensity of this emission in the magnetic field

results from the exchange scattering of electrons on Cr^+ ions. In addition, a band connected with Cr^+ ions has been found in the photodepolarization spectrum of ZnS:Cr TFELS (see below). The reverse $Cr^+ \rightarrow Cr^{2+}$ recharging, which leads to a decrease of the Cr^+ EPR signal, has been revealed when ZnS(Se):Cr crystals were heated [8-10] or illuminated by infrared light simultaneously with the photo-stimulation [6, 8-10]. The maximum of the photoquenching was observed at photon energies of 0.7 [6, 8], 0.9 [9], and 1.1 eV [8, 10]. The thermal and optical ionization energies of Cr^+ ions equal to 0.65 - 0.82 eV and 0.7 – 1.1 eV, respectively, have been determined from these data. In this paper, it is reported on the discovery of an effect that evidences, on author's opinion, the existence of the thermofield $Cr^+ \rightarrow Cr^{2+}$ recharging in ZnS:Cr TFELS under certain excitation conditions.
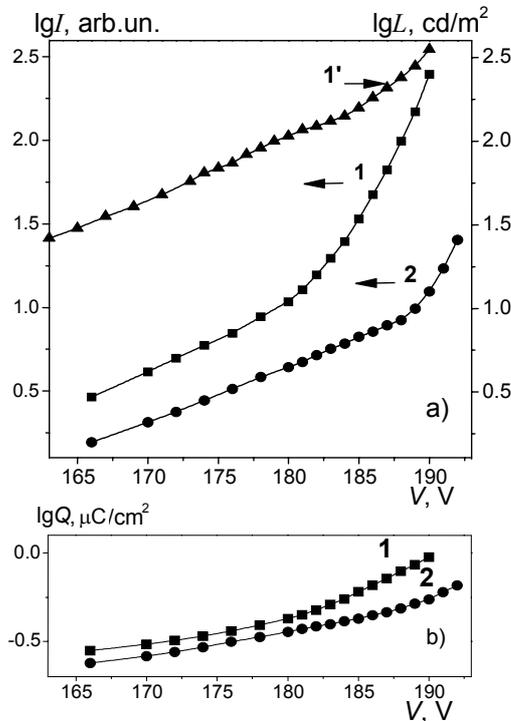
2. Experimental procedures

Samples under study consist of MISIM structures deposited on a glass substrate, where M are ITO and Al electrodes, I are insulator layers (SiO_2/Al_2O_3, ~270 nm),

and S is a ZnS:Cr El film (~650 nm). To increase the transparency of the lower electrode in the near-infrared region, the thin ITO films (60–80 nm) with rather high resistance (−300 Ohm/□) were used. The I layers and ZnS film were deposited by electron-beam evaporation. The latter was doped during the deposition by simultaneous thermal evaporation of Cr. The Cr concentration was >10^{20} cm^{-3}. Annealing in vacuum was performed after the ZnS:Cr film deposition at 550°C for 1 h.

Electroluminescence was excited by a sinusoidal voltage of 10–20 kHz. The emission in the region from 1.5 to 3 μm was recorded by a PbS photodetector set up beyond an MDR-12 monochromator. In the visible region, a FPI luminance meter was used. The charge (Q) transferred through the EL film for the applied voltage cycle was measured with a Sawyer-Tower circuit commonly used for TFELS [11]. The sample temperature (7) was measured by a thermocouple. The flow of cold air was used to cool the sample.

3. Results and discussion

For the first time, the following effect has been revealed in the voltage dependence of the intensity (I) of the Cr^{2+} emission at high frequencies ($f > 10$ kHz). A very strong increase of I takes place at high voltages (Fig. la, curve 1) when a saturation in the $I(V)$ dependence of TFELS is usually observed [11]. Some larger increment of the transferred charge also arises simultaneously, but it is much less than that of I (Fig. 1b, curve 1). The luminance (L) of the emission of hot electrons has the tendency to saturation with voltage increasing at first (Fig. 1a, curve 1′). However, the $L(V)$ dependence becomes steeper after that. It should be noted that the intensification of the emission of hot electrons in this case is significantly weaker than that of the Cr^{2+} emission.

The comparison of the dependences of I and L on the transferred charge (Fig. 2, curve 1 and 1′) shows that both values increase with Q identically up to the voltage, at which the steeper increase of I, L, and Q begins. The essentially different character of the $I(Q)$ and $L(Q)$ dependences takes place at higher voltages. The former becomes more superlinear with the exponent (n) equal to $4 - 6$, whereas the dependence of L on Q is nearly linear, which should be expected. It is known that the luminance of TFELS is proportional to Q at high V when the field in an EL film almost does not increase due to the redistribution of the applied voltage between I and S layers due to an increase of the active current passing through the latter.

It was supposed that the above-mentioned increase of Q is connected with some rising of the sample temperature. The rather high capacitive and active currents in the TFELS under study at $f = 10$–20 kHz (0.1–0.3 A/cm) cause a significant voltage drop (10–20 V) on the high-resistance ITO electrode and consequently its heating. As a result, the whole sample can be also heated. Indeed, the measurement of the sample temperature shows that the effect described above is accompanied by the rising of T from room temperature (~20 °C) up to $30 - 50$ °C. The cooling of the sample by a cold air flow results in a significant decrease of the effect (Fig. 1, 2, curve 2).
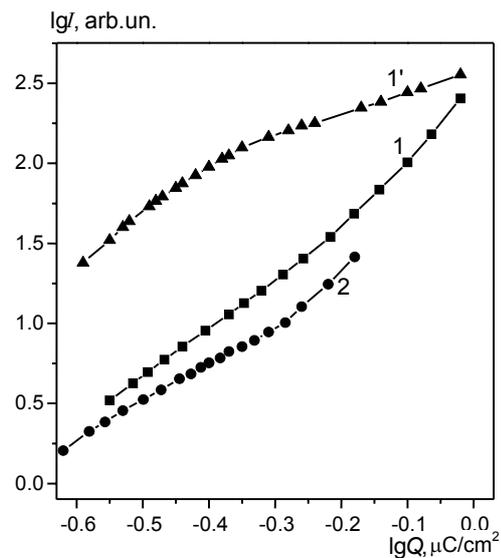

Fig. 1. (a) Voltage dependence of Cr^{2+} emission intensity (1, 2) and luminance of hot electrons emission (1′). (b) Voltage dependence of transferred charge $f = 20$ kHz. Measurement was without sample cooling (1, 1′) and with cooling it by air flow (2).

Fig. 2. Dependence of Cr^{2+} emission intensity and luminance of hot electrons emission on transferred charge. $f = 20$ kHz. Numeration of curves is the same as in Fig. 1.
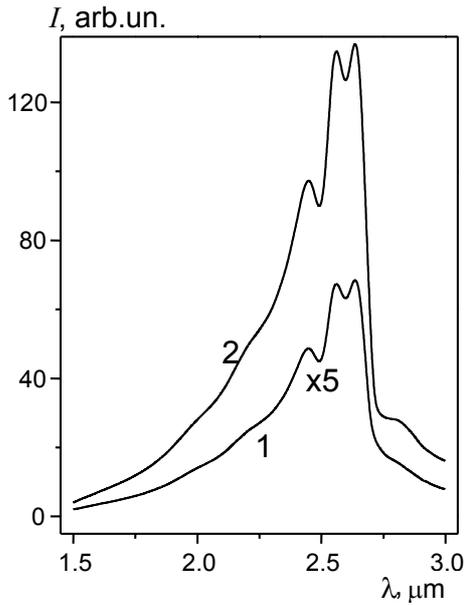
Fig. 3. Emission spectrum of ZnS:Cr TFELS in near-infrared region at 175 V (1) and 187 V (2). $f = 20$ kHz. Spectrum was not corrected for spectral sensitivity of PbS detector.

It should be emphasized that the EL spectrum in the region from 1.7 to 3 μm, in which there is the emission band of Cr^{2+} ions, is the same before and after the appearance of the above effect (Fig. 3).

The increase of I, Q, and T takes also place in time after applying a sufficiently high fixed voltage (Fig. 4). The larger increase is observed for the first minute. It becomes less after this and stops. The increase of the Cr^{2+} emission intensity in this case is much more than the increase of Q. The quantity I increases in time as Q^n where $n \approx 6$ (see insertion in Fig. 4) in accordance with the $I(Q)$ dependence at increasing voltage (Fig. 2).

From the experimental results described above, we can draw the following conclusion concerning the mechanism of the observed effect. The heating of the ZnS:Cr film up to $30 - 50$ °C in the presence of a high electric field, which is ≥ 2 MV/cm when the effect takes place, results in the thermofield ionization of some rather deep centers with an ionization energy (E_i) of 0.5–0.9 eV. Consequently, the number of free electrons, *i.e.*, Q, increases. This only assumption (without one more suggestion about the nature of deep centers) is sufficient to explain the linear increase of the luminance of the emission of hot electrons with increasing Q. However, the very superlinear $I(Q)$ dependence can be explained by assuming also that the thermofield ionization causes an increase of the number not only of free electrons, but also the radiation centers, *i.e.*, Cr^{2+} ions. This means that the thermofield $Cr^+ \rightarrow Cr^{2+}$ recharging takes place. This conclusion is also confirmed by the following. First, the effect enhances with increasing the Cr concentration in the ZnS:Cr film. Secondly, a superlinear increase of the EL intensity when Q increases and T rises up to ~50 °C

was not observed in any from a great number of studied TFELS with such activators as Mn, Tb, Er, and Ce [11].

The presence of Cr^+ ions in the ZnS:Cr films is confirmed, as was noted above, by the dependence of the intensity of the emission of hot electrons on the magnetic field [5]. This is also borne out by the photodepolarization (PDP) spectra of the ZnS:Cr TFELS. The typical PDP spectrum is given in Fig. 5. It is seen that there is an impurity photocurrent in the region of $0.7 - 2$ eV, which increases relative to the main maximum at ~3.5 eV with increasing the Cr concentration. The main maximum is due, as was supposed previously [2], to the ionization of the $\left[Cr_{Zn}^{2+}\right]^0$ isovalent trap that arises when Cr^{2+} ions substitute for Zn^{2+} ions in ZnS. The near-infrared region
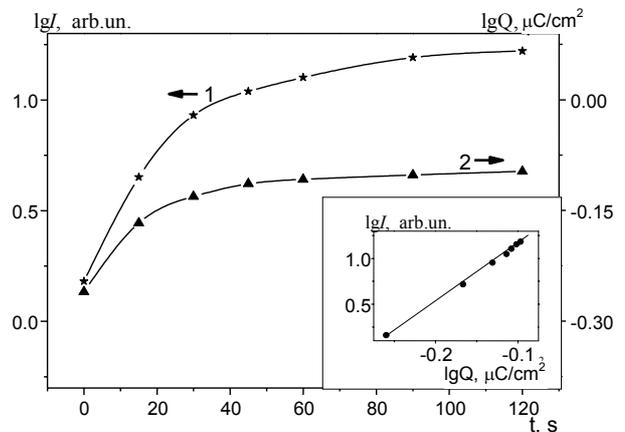
Fig. 4. Dependence of Cr^{2+} emission intensity (1) and transferred charge (2) on time after applying of fixed rather high voltage. $V = 187$ V; $f = 20$ kHz. In insertion: dependence of Cr^{2+} emission intensity on transferred charge in this case.
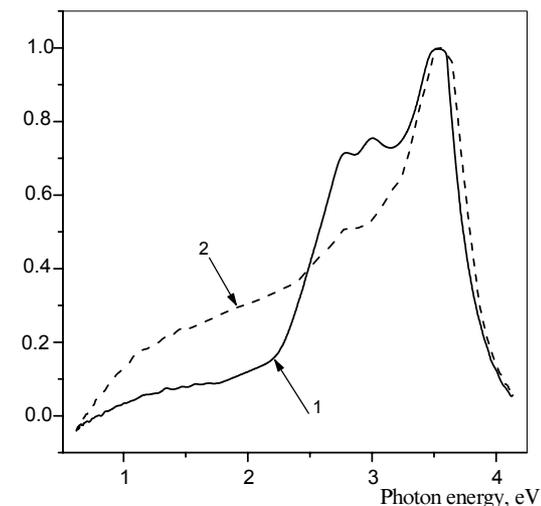
Fig. 5. Normalized PDP spectrum of ZnS:Cr TFELS with Cr concentration of 0.4 wt.% (1) and 1.4 wt.% (2). Charging of sample was by DC voltage of 70 V with +Al polarity. Spectrum was not corrected for equal number of testing photons.

of the impurity photocurrent coincides with the spectral region, in which the photoquenching of the Cr^+ EPR signal was observed [6, 8–10], *i.e.*, $Cr^+ \rightarrow Cr^{2+}$ photo-recharging takes place. In addition, the energy of the long-wavelength edge of this region in the PDP spectrum (0.7–0.75 eV) coincides well with the thermal ionization energy of Cr^+ ions that was determined from the thermal quenching of the Cr^+ EPR signal (0.65 – 0.82 eV) [6, 8-10]. The nature of other peaks observed in the PDP spectrum of the ZnS:Cr TFELS will be a subject of another paper.

The possible mechanism of the thermofield ionization of centers with $E_i = 0.65$–0.82 eV in the field (F) of ≥2 MV/cm and the temperature up to 50 °C can be the Frenkel-Pool field-stimulated thermal ionization [12] or multiphonon assisted tunneling [13]. According to the former, the ionization energy of a center with Coulomb potential well is lower in a high field than in a low field by $\Delta E = e\sqrt{\dfrac{eF}{\pi\varepsilon}}$, where e is the electron charge and ε is the dielectric constant. At $F = 2$ MV/cm, $\Delta E \approx 0.4$ eV. Thus, the Cr^+ ionization energy in such a field can be 0.3–0.35 eV according to the Frenkel-Pool mechanism. The probability of thermal ionization of centers with such potential barrier at $T = 30$–50 °C is rather high, whereas the multiphonon assisted processes have usually a low possibility. The decisive conclusion concerning the mechanism of the discovered thermofield $Cr^+ \rightarrow Cr^{2+}$ recharging needs an additional study.

4. Conclusions

For the first time, the unusually strong intensification of the Cr^{2+} emission has been discovered in the ZnS:Cr TFELS with an increase of the voltage at $F \geq 2$ MV/cm. This emission intensifies very superlinearly with the transferred charge that also increases due to some heating of the sample. The increasing Q at such a field when T rises up to ≤330 K evidences that the thermo-field ionization of some rather deep centers takes place. This explains the observed linear with Q increase of the luminance of the emission of hot electrons without one more additional assumption about the nature of these centers. The anomalous superlinear dependence of the Cr^{2+} emission intensity on Q can be only explained with the additional assumption that the ionized centers are Cr^{2+} ions. These ions are present alongside with Cr^{2+} ions in the ZnS:Cr films and have a thermal ionization energy of 0.65 - 0.82 eV. The thermofield $Cr^+ \rightarrow Cr^{2+}$

recharging results in the increase of the number of both free electrons and radiative centers. The exponent equal to 5–6 in the $I(Q)$ dependence can be explained taking into account that each of the electrons passing through the EL film is capable of the impact excitation of several Cr^{2+} ions. Two mechanisms of thermofield $Cr^+ \rightarrow Cr^{2+}$ recharging are possible: namely, the Frenkel-Pool field-stimulated thermal ionization and the multiphonon assisted tunneling. The estimation of a decrease of E_i of Cr^+ ions in the field that there is in the ZnS:Cr film allows us to conclude preliminarily that the former has advantage over the latter. The decisive conclusion concerning the mechanism of thermofield $Cr^+ \rightarrow Cr^{2+}$ recharging discovered in the ZnS:Cr TFELS needs an additional study.

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