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Degradation processes in encapsulated ZnS:Cu powder electroluminescent phosphors

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Abstract. In this paper we present experimental results of the studying degradation processes in electroluminescent panels, prepared from encapsulated ZnS:Cu powder phosphors and theoretical simulation of energy parameters for the phosphor. Energy band diagrams ZnS, Cu₂S, ZnS-Cu_{2-x}S heterojunction and Cu-ZnS metal-semiconductor junction have been constructed and cohesive energies for Zn-S, Cu-S, Zn-O, Cu-O and Zn-Cu bonds have been calculated by the method based on a linear combination of atomic orbitals and pseudo-potential. Time dependences of brightness have been found to adequately fit a two-component exponential dependence. The first part of the exponential curve has been attributed to the diffusion processes taking place in Cu_{2-x}S, and the second one to the diffusion of Cu in ZnS matrix.

Keywords: electroluminescence, ZnS:Cu powder phosphor, degradation, heterostructure, electronic structure, cohesive energy.

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1. Introduction

The main problem arising in application of electroluminescent (EL) panels prepared from ZnS:Cu powder phosphors is loss in the emission brightness. The respective degradation mechanism in luminescent ZnS phosphors has been the focus of attention for a long time and it is still not clearly understood [1-6]. Different mechanisms of electroluminescence depending on the energy level structure and local field strength, e.g., injection and excitation mechanisms are assumed and confirmed by the experimental studies in ZnS phosphors [7]. The process of brightness decay is thought to be partially related to the structural relaxation at ZnS-Cu_{2-x}S and/or Cu-ZnS interfaces promoting copper diffusion, especially in the presence of sulphur vacancies [6].

The purpose of this work is to determine general relationships for time changes in brightness during operation of EL panels prepared from encapsulated ZnS:Cu powder phosphors, and to gain an understanding of the degradation mechanism. For the latter, we have performed additional theoretical calculations of the energy band diagram for ZnS-Cu_{2-x}S heterostructure, Cu-ZnS metal-semiconductor junction, and also cohesive energy for Zn-S and Cu-S bonds.

2. Experimental and computational details

Degradation processes were investigated on EL panels prepared from ZnS:Cu powder of the following trade marks: ANE, Durel, GG and GGL provided by different manufacturers.

The brightness changes of EL panels have been studied during continuous operation at 400 Hz frequency with voltage of 115 V in the time range from 0 to 2000 hours at intervals of 0.5 hour by using the tailor-made device [8].

Theoretical calculation of the energy band diagram for ZnS-Cu_{2-x}S heterojunction has been performed by the method based on the linear combination of atomic orbitals and pseudo potential [9] with the atomic terms calculated within Hartree-Fock approximation. Details of the computation procedure can be found in our previous paper where we have presented results of calculations of the energy band diagram and gap states for ZnS:Cu, Cl [10]. Energy band diagrams for heterostructures and metal-semiconductor junctions have been computed following the procedure given in Ref. [11].

Cohesive energy was determined as:

$$E_{\text{coh}} = (2 - \alpha_c^2) \sqrt{V_2^2 + V_3^2} + \frac{9}{8} \frac{\alpha_c^4 (V_{1+}^2 + V_{1-}^2)}{\sqrt{V_2^2 + V_3^2}} - E_{\text{pro}}, \quad (1)$$

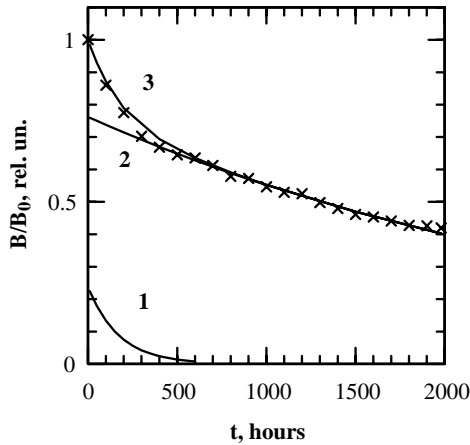


Fig. 1. Time changes in brightness for electroluminescent panel in continuous operation (400 Hz, 115 V) (crosses). Theoretical curves 1, 2 and 3 are the first second, and the sum of 1 and 2 terms in Eq. (2), respectively.

with the promotion energy $E_{pro} = (\epsilon_{p+} - \epsilon_{p-})/2 + V_{1+} + V_{1-}$; α_c – covalency; V_1 , V_2 and V_3 – matrix elements characterizing the metallic energy, covalent energy, and polar energy [9].

3. Results

Fig. 1 shows relative changes in brightness (B/B_0) with time (t) for one of the EL panel types (GG43 pigment). Our graphic analysis of relaxation curves has shown that they can be approximately described by an empiric formula containing at least two components

$$B/B_0 = \alpha \exp(-t/\tau_1) + \beta \exp(-t/\tau_2), \quad (2)$$

with α and β – numerical coefficients ($\alpha + \beta = 1$), τ_1 and τ_2 – relaxation times. These parameters for different types of EL panels are given in Table 1 along with $\tau_{0.5}$ – time interval of the decrease by half of the initial brightness (B_0) for EL panel.

Fig. 2 shows the formation of the energy band from the atomic terms Zn 4p, Zn 4s, S 3p for ZnS (a) and S 3s (Cu s, S p) for Cu₂S (b). Experimental data for the photoemission threshold and optical band gap (in electron-volts) are given in parentheses for comparison.

The results of energy band diagram calculations for ZnS and Cu₂S compounds enabled construction of the energy band diagrams for ZnS-Cu₂S heterostructure and Cu-ZnS metal-semiconductor junction shown in Figures 3a and b, respectively.

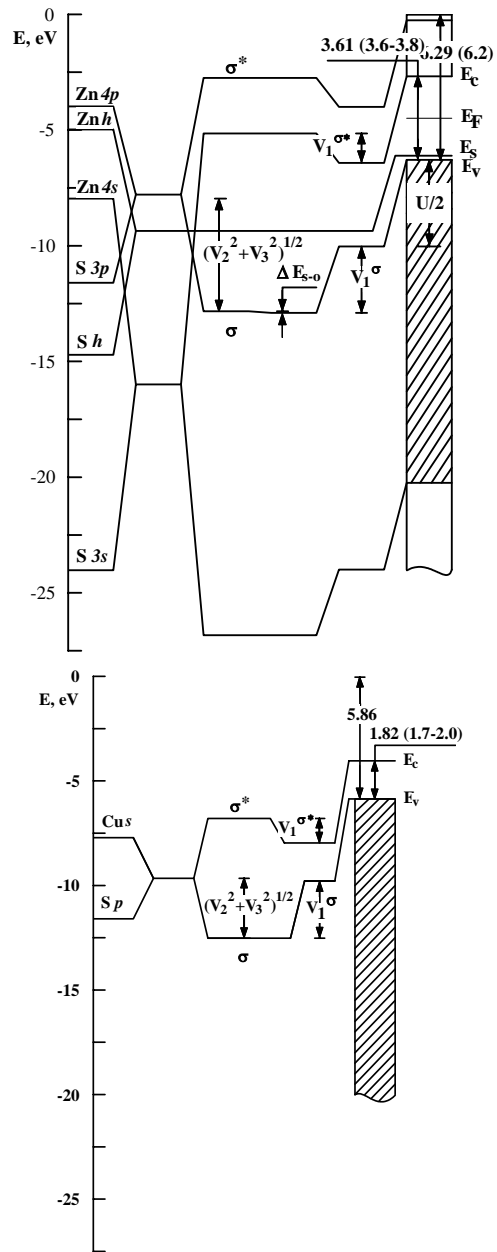


Fig. 2. Formation of the energy band from the atomic terms for ZnS (a) and Cu₂S (b): Zn 4p, Zn 4s, S 3p and S 3s (Cu s, S p) – atomic terms; bonding σ and antibonding σ^* states; spin-orbital splitting ΔE_{s-o} ; the metallicity energy over bonding $V_1\sigma$ and antibonding $V_1\sigma^*$ states; intra-atomic Coulomb repulsion $U/2$. Calculated and experimental (given in parentheses) data for the photoemission threshold and optical band gap are given in electron-volts.

Table 1. Parameters of electroluminescent panels (CM - capsule material, d_1 – phosphor thickness, d_2 – thickness of dielectric, C_0 – initial capacity, B_0 – initial brightness) and relaxation parameters according to Eq. (2).

Pigment	Parameters of EL panels					Relaxation parameters				
	CM	d_1 (μm)	d_2 (μm)	C_0 (nf)	B_0 (Cd/m ²)	α	β	τ_1 (hours)	τ_2 (hours)	$\tau_{0.5}$ (hours)
GG43	Al ₂ O ₃	44	20	4.27	129	0.238	0.762	174	3100	1300
GGL43	Al ₂ O ₃	36	19	4.13	82	0.133	0.867	87	4100	2300
Durel	(Ti-Si)O ₂	45	20	4.20	105	0.262	0.738	145	3100	1200
ANE	AlN	33	22	4.31	79	0.191	0.809	217	3100	1500

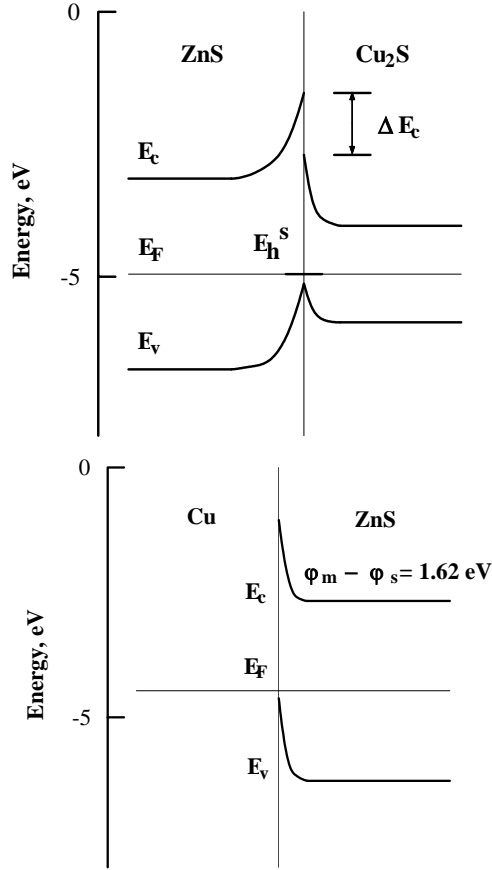


Fig. 3. Energy band diagrams for ZnS-Cu₂S heterostructure (a) and Cu-ZnS metal-semiconductor junction (b).

The results of calculation of the cohesive energy are listed in the Table 2, where summarized are the interatomic distance (d), promotion energy (E_{pro}), covalency (α_c), level splitting energy ($((V_2^2+V_3^2)^{1/2})$), components of cohesive energy and its value for most probable compounds and bondings in the phosphors under investigation. For the Zn-S bond cohesive energy has been found to be 1.14 eV, while the energy of the cohesive bond Cu-S was about 0.77 eV. Therefore, the first part of the relaxation curve (Eq. (2)) is attributed to the diffusion processes taking place in Cu_{2-x}S, when the second one could be attributed to the diffusion of Cu in ZnS matrix.

4. Discussion

Let us discuss the problem of brightness degradation under the assumption that in ZnS: Cu crystals there are linear dislocations arising at the boundary between crystallites with the hexagonal and cubic structures where Cu_{2-x}S inclusions can be found.

It is known that there is an elastic stress field around dislocations in crystal interacting with stress fields arising around impurity atoms [2]. The energy of this interaction is determined by the following expression:

Table 2. Interatomic distance (d), promotion energy (E_{pro}), covalency (α_c), level splitting energy ($((V_2^2+V_3^2)^{1/2})$), components of cohesive energy and its value (E_{coh}).

Parameters	Compound				
	ZnS	Cu ₂ S	ZnO	CuO	ZnCu
d , nm	0.235	0.240	0.198	0.201	0.266
E_{pro} , eV	7.91	8.05	11.70	11.84	2.13
α_c	0.654	0.610	0.588	0.557	0.992
$(V_2^2+V_3^2)^{1/2}$, eV	5.04	5.23	7.91	8.10	2.59
$(2-\alpha_c^2)(V_2^2+V_3^2)^{1/2}$, eV	7.92	8.51	13.09	13.69	2.63
$9\alpha_c^4(V_{1+}^2+V_{1-}^2)/8(V_2^2+V_3^2)$, eV	0.43	0.31	0.33	0.26	0.68
E_{coh} , eV	1.14	0.77	1.72	2.11	1.19

$$E = -\frac{4}{3} \frac{G\varepsilon R^3(1+\gamma)b \sin \vartheta}{1-\gamma r}, \quad (3)$$

with G – shear modulus, $R(1+\varepsilon)$ – impurity atom radius, R – average radius of solvent atoms, b – Burgers vector, γ – Poisson's ratio, r – distance between a dislocation and impurity, θ – polar angle between the direction of sliding and radius-vector. Since the size of the Cu impurity atom is smaller than that for Zn atom ($\varepsilon < 0$), the bonding energy is positive, and these atoms are attracted into the contraction region in the elastic stress field of an edge dislocation. Therefore, in our case we should account both for diffusion flow of Cu atoms towards the dislocation as binding boundary and drift flow in the elastic stress field with the same direction as the diffusion one.

Allowing for diffusion and drift flows, we derive the differential equation describing the impurity concentration (N) changes in the volume of semiconductor when impurity is condensed on dislocations as:

$$\frac{1}{D} \frac{\partial N}{\partial t} = \frac{\partial^2 N(r,t)}{\partial r^2} + \left(\frac{1}{r^2} + \frac{1}{r} \right) \frac{\partial N(r,t)}{\partial r} - \frac{L}{r^3} N(r,t), \quad (4)$$

with D – diffusion coefficient and $L = Er/kT$. The first term of this equation describes the diffusion flow, the other two describe the drift one.

An approximate solution of the Eq. (4) with long times ($t \rightarrow \infty$) and allowance for the probability of Cu impurity atom extraction from dislocation and their turning back into the semiconductor can be described by the expression [12]:

$$N_t = N_0 \left[e^{-\alpha t} - (1 - e^{-\alpha t}) e^{-E/kT} \right], \quad (5)$$

where $\alpha = 2\pi N_D D$, N_D is the dislocation density, N_0 and N_t are impurity concentrations in semiconductor, initial and in t moment, respectively.

The given relationship adequately describes the observed experimental time and temperature

dependences for brightness degradation of EL panels (Fig. 1). In terms of this model, at the initial stage of degradation when Cu atoms are settled at dislocations the binding energy between a Cu atom and dislocation is high [$\exp(-E/kT) \ll 1$] and concentration decrease is described only by the first term of Eq. (5). Then, as Cu atoms are precipitated farther and farther from the dislocation centre (r increases) the value of E decreases and the degradation rate goes down. This results in at least two exponential parts in dependences of brightness on the operation time (Fig. 1). To obtain more precise interpretation of the experimental result, it is necessary to take into consideration the changes in concentration of the emitting centres at the vacancy associations, some complexes, etc.

5. Conclusions

Degradation processes in electroluminescent panels prepared from encapsulated ZnS: Cu powder phosphors in continuous operation (400 Hz, 115 V) in the time range from 0 to 2000 hours have been studied. It has been found that operation time dependences of brightness adequately fit a two-component exponential dependence. Calculated energy band diagrams and cohesive energy allowed inference that the first part of the relaxation curve may be attributed to the diffusion processes taking place in Cu_{2-x}S , and the second one to the diffusion of Cu inside the ZnS matrix.

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