Injection light-emitting diodes based on low-resistance ZnS with blue and green emission

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(Submitted March 11, 1974)

ZhETF Pis. Red. **19**, 513–516 (April 20, 1974)

In metal-semiconductor diodes based on low-resistance ZnS single crystals, we observed at room temperature a sufficiently intense and stable blue and green electroluminescence, registered when a positive bias $U \geq 2$ V was applied to the diodes and apparently due to injection of holes into the ZnS from the metallic contact. In the dc interval 10^{-5}–10^{-1} A, the external quantum yield of the luminescence was 10^{-4} quantum/electron when Au was used as the injecting contact.

The bright luminescence of zinc sulfide at room temperature in the visible band has long attracted interest to this semiconductor as a possible material for the development of visible-radiation sources. Unfortunately, the development of a p-n or heterojunction based on this substance and capable of ensuring effective injection electroluminescence is a rather complicated matter. [1]

At the same time, as suggested by the results of[2], ZnS has a low electron affinity. This, in our opinion, justifies attempts of producing a barrier-type band bending on the interface between low-resistance zinc sulfide and a metal, and to ensure with its aid injection of minority carriers (holes) into the semiconductor.

We note that to produce a light-emitting diode on the basis of such injection it is no less important to make the second contact with the semiconductor ohmic. The latter, on the other hand, (obviously, owing to the small electron affinity of ZnS) is far from a simple matter. This is apparently one of the reasons why injection electroluminescence in systems consisting of metals and low-resistance zinc sulfide has hardly been investigated to this day.

We have succeeded in developing, on the basis of low-resistance ZnS single cyrstals, light-emitting diodes having at room temperatures and low voltages a sufficiently intense and uniform, and stable emission in the blue or green spectral regions. The samples were single crystals ($\rho = 1-10\ \Omega$-cm) measuring $\sim 3 \times 2 \times 1$ mm on the "rear" surface of which we deposited, using a procedure developed by us, an indium-base alloy that ensured the ohmic contact; on the "front" surface, after treatment, we deposited a rectifying contact. The latter was a layer of metal (Pt, Au, Im, Mn, Cu), for which the work function apparently exceeded the electron affinity of ZnS. [2] The rectification coefficient of such diodes was high enough, 10^4-10^5 at $U \approx 2$ V.

A sufficiently intense electroluminescence was observed in the diodes when a voltage $U \gtrsim 2$ V was applied to them in the conduction direction (i.e., with the positive potential on the frontal electrode). Depending on the conditions under which the rectifying contact was deposited, the maximum of the electroluminescence band was either in the blue or in the green region of the spectrum (Fig. 1).

The voltage-brightness characteristics of the light-emitting diodes with different rectifying contacts are shown in Fig. 2a. As seen from the figure, at low voltages ($U < 4-6$ V), the electroluminescence brightness increases with increasing voltage exponentially, but at larger U it becomes proportional to the voltage. It has been observed that at $U =$ const the radiation brightness depends on the material of the rectifying contact, namely, it is maximal in the case of a gold contact and

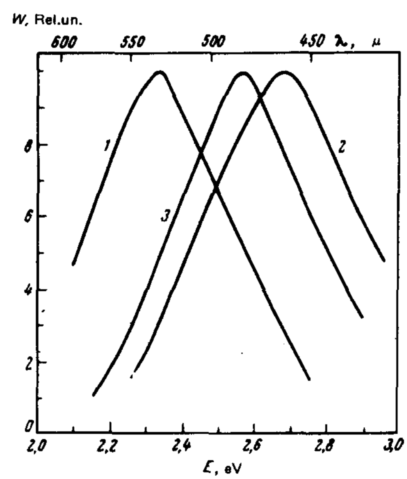

FIG. 1. Spectral distribution of the green (curve 1) and blue (curve 2) electroluminescence in different Au-Zn diodes (at $i = 30-40$ mA), as well as the spectral distribution of the photoluminescence (curve 3) measured on a section of the same ZnS single crystals but free of contacts; $T = 300$ °K.

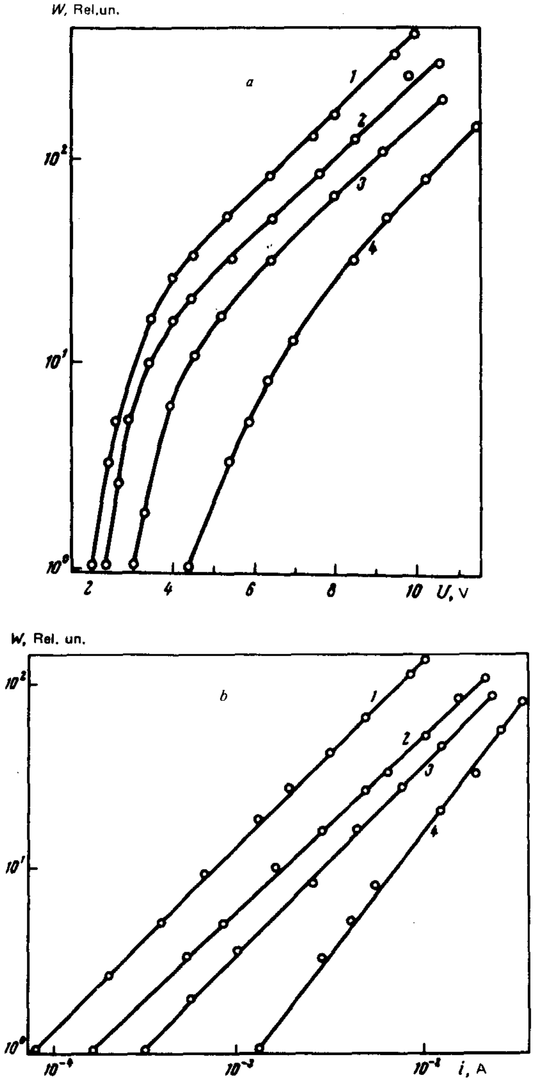

FIG. 2. Emission spectrum vs the forward bias (*a*) and current (*b*) for diodes obtained on the basis of one and the same ZnS single crystal with different injecting contacts: 1—Au, 2—Pt, 3—In, 4—Mn; $T = 300$ °K.

decreases with increasing height of the barrier that is produced, according to[2], by the metal with the zinc sulfide (Fig. 2b).

The presented facts allow us to propose that the described emission is due to injection of holes into the ZnS from the rectifying metallic contact. We note that at sufficiently high negative bias ($U \gtrsim 20$ V) emission is also observed in the diodes; this emission is quite weak, yellow-orange in color, and, just as the value of the reversed current, frequently unstable. Emission of this type was observed earlier in metal-semiconductor diodes based on ZnS and was attributed to impact ionization.[3]

For most metals used as injecting contacts, the emission intensity increased in proportion to the current in the entire investigated range of forward currents (10^{-5}–10^{-6} A) (Fig. 2b). The external quantum yield of the luminescence in samples with Au contacts was 10^{-4} quantum/electron, and in the preparation of the experimental samples no measures were taken at all to decrease the scattering of the radiation in the sample, to ensure optimal crystal shape, etc.

The results allow us to conclude that a metal in conjunction with low-resistance zinc sulfide is a promising system for the production of injection sources of blue and green light. This is all the more important, since, in so far as we know, there has been no success as yet in the development of sufficiently effective light-emitting diodes based on other materials (GaN[4] and SiC[5], at which blue electroluminescence can be observed at room temperature.

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