NEGATIVE RESISTANCE AND A STIMULATED STATE IN ELECTROLUMINESCENT ZINC-SULFIDE FILMS AT 77°K

PHYSICS

1966

SovietRxiv

Abstract

Full Text

UDC 535.376 + 535.377 + 537.226.8

PHYSICS

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NEGATIVE RESISTANCE AND A STIMULATED STATE IN ELECTROLUMINESCENT ZINC-SULFIDE FILMS AT 77°K

1. In recent years many investigators have studied the state of “negative resistance” that arises in dielectrics or semiconductors under double injection, i.e., when electrons are injected into a crystal from the cathode and, simultaneously, holes from the anode (1). A justification of this process was given in Lampert’ s theory (2). Less attention has been paid to the state with increased conductivity and, in the case of an electroluminophor, with substantially increased brightness, which arose after the stage of negative resistance.

In a preliminary study of such a state (we shall call it stimulated) in zinc-sulfide films at 77°K, its great stability was found: in the dark and without applied voltage it could persist for a long time. The stimulated state could be completely eliminated, for example, by heating to room temperature, and restored after cooling by the action of a sufficiently high “critical” voltage, or by preliminary ultraviolet irradiation (3). At low temperature the phosphor could stably retain either the unstimulated or the stimulated state. In the latter, its conductivity was 2–3 orders of magnitude higher, and the electroluminescence brightness 3-5 orders of magnitude higher, than in the unstimulated state.

2. In all measurements the electroluminescent cell was in a cryostat with a window, in liquid nitrogen. The luminescence was recorded with an FEU-17 photomultiplier connected to an M-95 galvanometer or to an EPPV-60 recorder. Spectral measurements were made with an SF-4 spectrophotometer.

Figure 1 gives the emission spectrum of the cell, measured twice:
a) in the unstimulated state of the cell (room temperature), and
b) in the stimulated state. The two spectra practically coincided. The maximum is located at 465 mμ; the half-width of the band is 76 mμ. No differences in the spectrum caused by stimulation were found.

3. For a more precise determination of the stimulated state and to eliminate the possible influence of redistribution of the voltage between the phosphor

Fig. 1 and Fig. 2: normalized electroluminescence spectra and current dependence plots.

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and the near-electrode regions during stimulation, it was necessary to measure the voltage drop across the phosphor with probes.

The cells in which negative resistance and the stimulated state were obtained consisted of a zinc-sulfide layer about 20–30 μ thick, produced by sublimation on a glass plate (4). Aluminum electrodes were deposited on top by evaporation in vacuum. To determine the voltage directly on the phosphor, probes were used whose potentials were measured with electrostatic voltmeters. The probes were set in place, and the distance between them read, with the aid of a large binocular microscope. The probes were made of tungsten wire 0.2 mm in diameter; their ends were sharpened by electrolytic etching to a thickness of the order of 10 μ.

The stimulated state was obtained by the action of the critical voltage, i.e., the voltage was raised to the value at which the current began to rapidly—

to increase with a simultaneous decrease in voltage. This process of negative resistance lasted several minutes and ended with the establishment of a new state. Fig. 2 gives the results of the measurement (cell No. 12K; distance between the electrodes 0.72 mm; distance between the probes 0.27 mm). The measurement was begun at a voltage of 428 V with a current of $3 \cdot 10^{-9}$ A and, gradually increasing the voltage to 640 V, the current-voltage characteristic I was obtained (Fig. 2). The current began to rise rapidly and increased from $0.45 \cdot 10^{-6}$ to $41 \cdot 10^{-6}$ A, while the voltage decreased to 605 V. The current stabilized at the level $65 \cdot 10^{-6}$ A at 630 V. Then the current-voltage characteristic of the stimulated state was obtained. The current values on this branch were on average 200 times greater than on I. Curves I and II (Fig. 2) are described by the equations

Fig. 1. Normalized electroluminescence spectra of the cell: *a*—unstimulated at 300 K; *b*—stimulated at 77° K

Fig. 2. Dependence of the current in the cell on the potential difference of the probes. I—characteristic of the unstimulated state, II—characteristic of the stimulated state

$$I_I = 1.66 \cdot 10^{-38} V^{11.2},$$

$$I_{II} = 3.25 \cdot 10^{-33} V^{10.1}.$$

Fig. 3. Thermoluminescence of a cell—preliminarily stimulated by the critical voltage (I) and excited by ultraviolet irradiation (II)

Figure 2: Fig. 3. Thermoluminescence of a cell—preliminarily stimulated by the critical voltage (I) and excited by ultraviolet irradiation (II)

Fig. 4. Decay of the phosphorescence of a cell after switching off the critical voltage

Figure 3: Fig. 4. Decay of the phosphorescence of a cell after switching off the critical voltage

If the conductivity of the film is denoted by σ, and the average field strength is defined as $E_{\text{av}} = \Delta V/\Delta l$, where ΔV is the potential difference of the probes and Δl is the projection of the distance between them onto the direction of the field, then expressions of the form $\sigma = Ae^{bE}$ describe curves I and II approximately as well as those given above.

Measurements using probes established that the increase in the conductivity of the phosphor is determined by its special state after stimulation. On the other hand, it had been shown earlier that the action of the critical voltage and the action of preliminary UV irradiation lead to one and the same steady current-voltage characteristic and to an identical electroluminescence brightness characteristic (^{3}). Therefore, we are justified in considering the physical state of the phosphor after the action of the critical voltage and after the action of UV irradiation to be identical and in drawing the conclu-

that the stimulated state is determined by the filling of recombination centers with holes: the arrival of holes creates a positive space charge, partially compensating the injected negative space charge and therefore strengthening the injection current.

Thus, a stimulated stable state with very high conductivity and, correspondingly, bright electroluminescence is determined by a considerable excitation of luminescence centers, produced either by short-wave irradiation or by the negative-resistance process at the critical voltage.

Fig. 3. Thermoluminescence of a cell—preliminarily stimulated by the critical voltage (I) and excited by ultraviolet irradiation (II)

Fig. 4. Decay of the phosphorescence of a cell after switching off the critical voltage

4. These considerations are supported by certain experimental data.

a) A cell cooled in the dark to 77° K showed no luminescence upon reheating. The same cell, cooled in the dark to 77° K and subjected to a voltage below the critical value, likewise gave no luminescence on heating. The same cell, cooled in the dark to 77° K and subjected to the critical voltage during heating (6 deg/min), gave luminescence with 4 characteristic peaks, recorded by a chart recorder (Fig. 3, I). The cell was not exposed to irradiation. It is evident that excitation of recombination centers by holes occurred during the action of the voltage in the negative-resistance stage.

Curve II in Fig. 3 gives a recording of the thermoluminescence of the same cell, excited by ultraviolet irradiation. The positions of the peaks in curves I and II coincide, so that under the critical voltage the same trapping centers and recombination centers are filled as under ultraviolet excitation.

b) As is known, the afterglow of electroluminescence decays in a small fraction of a second. After excitation of the cell by the critical voltage at 77° K and switching off the voltage, an afterglow was obtained that was recorded by a chart recorder for more than 10 min (Fig. 4), which indicates a substantial filling of deep trapping centers and recombination centers.

Conclusions

The critical voltage without the participation of irradiation, or ultraviolet irradiation by itself, creates in sublimated electroluminescent zinc sulfide films at 77° K the same stable stimulated state, which manifests itself (a) in an increase in pro-

conductivity by several orders of magnitude, (b) in the amplification of the brightness of electroluminescence by a correspondingly greater number of orders of magnitude, (c) in the current-voltage characteristics, identical in both cases, (d) in thermoluminescence with identical peaks, and (e) in phosphorescence.

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Received
26 IV 1966

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