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On the Mechanism and Kinetics of Electroluminescence of Cuprous Oxide

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The present communication contains the results of an investigation of certain features of the infrared electroluminescence of Cu_2O under various excitation conditions. For the first time, an ohmic contact between cuprous oxide and a metal was used to excite the luminescence. New information has been obtained on the kinetics of the phenomenon. It is shown that the idea of the existence of two different kinds of electroluminescence (1) is unfounded.

The electroluminescence of Cu_2O was first described by Frerichs and Gandy (2). In their experiments, a layer of cuprous oxide was situated between the parent copper and a front transparent electrode (a layer of SnO_2). The luminescence arose when the voltage on the parent copper had a positive sign, i.e., for the blocking direction of the current through the barrier layer Cu—Cu_2O, and was correlated by the authors with the presence of a strong field in the mentioned layer. Luminescence of the second kind, observed by Frerichs and Liebermann (3) and by Gol' dman and Toropkova (4) on specimens separated from the parent copper, arises when the voltage at the metallic electrode is negative, i.e., for the forward direction of current through the rectifying contact of Cu_2O with the metal.

We investigated both specimens separated from the parent copper and specimens not separated from it. The latter were prepared by the method for obtaining nonvalve Cu_2O photocells described by V. E. Lashkarev and K. M. Kosonogova (4). The specimens exhibited a condenser photoeffect, indicating the existence of an antibarrier layer at the surface of Cu_2O (positive on the illuminated electrode). A semitransparent layer of gold was deposited on the surface by evaporation in vacuum; in this case the near-surface antibarrier layer was preserved, as can be judged from the sign of the photo-emf observed on these specimens. At the Cu—Cu_2O boundary, as usual, there existed a blocking layer (the ratio of forward and reverse currents at a voltage of 30 V was about 2). Such specimens possessed electroluminescence whose characteristics were completely analogous to those described by Frerichs and Gandy (2) (luminescence with positive voltage on Cu, a superlinear dependence of brightness on the applied voltage, the shape of the luminescence pulses under sinusoidal excitation, and the change in luminescence intensity with time under excitation by a constant field).

Fig. 1. Oscillogram of the electroluminescence pulse of Cu2O excited by a rectangular voltage pulse of duration 2 μsec. Marks every 0.05 μsec.

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After the measurements, a strip of the parent copper together with the adjoining Cu_2O layer, about $50\,\mu$ thick, was separated from the specimen; an electrode of Wood' s alloy was soldered onto the cleaned side (in some cases a pressure electrode of tin foil was used), and the electroluminescence was measured again. It turned out that removal of the blocking layer (on the cleaned specimens the currents in the two directions did not differ to within an accuracy of 1%) leads to a considerable increase in the radiation intensity. Thus, the blocking layer at the boundary of Cu_2O with the copper anode does not play a determining role in the occurrence of electroluminescence of the first kind.

The radiation of specimens separated from Cu and of specimens on the parent copper has identical characteristics. Replacing the cathode that gives an ohmic contact (Au, Wood' s alloy) by a cathode forming a rectifying con-

contact (for example, Al) does not change the character of the radiation, but increases its intensity. Replacement of the anode has practically no effect on the glow.

Frerichs and Liberman [3] showed that electroluminescence of the second type should be associated with the injection of electrons into the semiconductor through a rectifying contact with a metallic electrode connected in the forward direction. Our experiments show that the presence of a blocking layer at the contact is not necessary. The intensity of the glow is determined by the level of electron injection from the metal. Therefore, the use of a metallic electrode with a small work function $\Delta\varphi$, forming a blocking layer (Frerichs and Liberman used Zn, Goldman and Toropkova Al; in both cases $\Delta\varphi = 3.7$ eV), leads to an increase in the brightness of the glow.

Fig. 1. Oscillogram of the electroluminescence pulse of Cu_2O, excited by a rectangular voltage pulse of duration $2\,\mu$sec. Marks every $0.05\,\mu$sec.

Taking the above into account, it appears obvious that radiation of the first kind is also associated with the injection of electrons from the cathode (in our case Au, in Frerichs and Gandy SnO_2). From this point of view, the absence of radiation under current in the forward direction (minus on Cu) through a Cu–Cu_2O contact [2] may seem incomprehensible. However, this fact can be explained if one considers that the cuprous-oxide layer near the parent Cu contains excess copper and practically has no vacancies of Cu^+ ions, which are responsible for infrared luminescence [5]. The Cu_2O samples investigated by us on parent copper, oxidized for 5 min, i.e., possessing a weakly developed blocking layer, exhibited radiation also with minus on Cu.

The common nature of the electroluminescence of different samples is confirmed by investigation of the kinetics of the phenomenon. Frerichs and Gandy [2] indicate that in their experiments a relaxation time of the glow τ of the order of 10^{-3} sec was observed. Goldman and Toropkova [1], studying the delay of the glow relative to the exciting voltage, estimated the relaxation time at several tens of microseconds. It should be noted that neither the first nor the second value of τ agrees with the injection mechanism, which, in particular, the authors of [1] also support, since in the case of injection τ must be determined by the mean lifetime of free electrons; the latter, according to the data of Lashkarev and Kosonogova [6], is of the order of $5\,\mu$sec in the volume of Cu_2O; the influence of the surface can only reduce τ. It may be assumed that the delay of the glow noted in the cited works is determined not by electronic processes in the semiconductor (i.e., by the kinetics of the glow itself), but by side effects (for example, by the influence of the capacitance of the blocking layer at the injecting contact). To eliminate the influence of such effects, we selected the output resistance of the source of injecting pulses (a 26I generator) in such a way that the rectangular voltage pulse from the 26I was distorted by no more than $0.1\,\mu$sec; moreover, some of the samples investigated had no blocking layers.

It turned out that the proper relaxation time of the glow τ in different samples varies from $1.5 \cdot 10^{-7}$ to $8 \cdot 10^{-7}$ sec; τ of Cu_2O samples on parent copper did not differ from τ for samples separated from Cu. The constants

the decay and rise times of the signal sometimes differed. The decay law in many cases is well represented by one, sometimes by two, exponentials. An oscillogram of an electroluminescence pulse for one of the samples is shown in Fig. 1.

It seemed of interest to compare the relaxation time of electroluminescence with the relaxation time of infrared photoluminescence for the same samples. In order to select conditions of photoexcitation of the glow analogous to the excitation conditions for electroluminescence, the dependence of the photoluminescence τ^{ϕ} on the wavelength λ of the exciting light was investigated. A typical dependence $\tau^{\phi}(\lambda)$ is presented in Fig. 2. As is seen, τ^{ϕ} decreases with decreasing λ (i.e., with increasing absorption coefficient), which may be explained by the influence of surface recombination. In the region $\lambda < 460$ mμ, τ ceases to depend on λ (τ^{ϕ}_{min}). Evidently, here "surface" excitation takes place, in which the thickness of the layer excited by the light is extremely small, and the relaxation time is determined by recombination at the surface and in the near-surface layer of thickness of the order of the diffusion length. Electroluminescence should also be associated with "surface" excitation ([1]). It is therefore natural to compare τ_{e} of electroluminescence with τ^{ϕ}_{min} of photoluminescence. It turned out that, for all the samples investigated, these values of τ coincided to within an accuracy of 10–20%.

Fig. 2. Spectral dependence of the photoluminescence kinetics of Cu_2O. Sample No. 1

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Yu. I. Karkhanin and V. E. Lashkarev (^{5}) showed that the photoluminescence of Cu_2O is caused by excitons. The coincidence of τ_{e} with $\tau^{\phi}_{\mathrm{min}}$ makes it possible to suggest that excitons and free electrons in cuprous oxide have a common recombination mechanism through vacancies of Cu^+ ions.

N. A. Tolstoy and co-workers (^{7}) observed that τ of the photoluminescence of Cu_2O at room temperature is inversely proportional to the content of Cu^+ vacancies. This is manifested, in particular, in the fact that τ^{ϕ} differs noticeably for different faces of one and the same sample. Our measurements showed that the τ of electroluminescence differs in the same way.

The comparison of the kinetics of photo- and electroluminescence, carried out by us for samples of different types, is another argument in favor of the previously expressed assumption that the electroluminescence of cuprous oxide is in all cases connected with the injection of electrons from the cathode.

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