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Publication Date
1973
Submitted to Chemical Physics Letters

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January 1973

Prepared for the U.S. Atomic Energy Commission under Contract W-7405-ENG-48

For Reference

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LUMINESCENCE OF ZnO CRYSTALS. ELECTRODE POTENTIAL AND LIGHT
INTENSITY DEPENDENCE

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Abstract

The intensity of the green photoluminescence of ZnO as a function of
the excitation intensity and externally applied voltages was investigated.
In the absence of an external voltage a linear dependence between emission
and excitation intensities was observed. Upon application of reverse bias
the dependence changes gradually to quadratic. This behavior provides the
basis for a new model of the voltage quenching of photoluminescence. The
model proposes that the electron concentration on the surface is reduced
by the formation of a space charge layer.

Under these conditions, electrons and trapped holes which have photo-
produced recombine with second order kinetics, which leads to the observed
quadratic dependence.

(Henkel Z10), Germany.
The influence of bias voltage on the photoluminescence of inorganic phosphors has been investigated in some detail. Stimulation (Gudden-Pohl effect [1] and Destriau effect [2]) as well as quenching of the photoluminescence (Dechène effect [3]) have been observed.

The quenching effect, which is the topic of this paper, has been variously explained either by emptying of the luminescence activator centers under the influence of the electric field or by extraction of carriers from the region of recombination, or both. Most such experiments were performed on single crystals of zinc- and cadmium sulfides, but polycrystalline thin layers have also been employed. See Ivey [4] for a review of these and related experiments.

The quenching of the green photoluminescence of ZnO crystals was described by Petermann et al. [5] and an influence of an electric potential on the photoluminescence could also be observed for polycrystalline layers of ZnO [6]. Experimental results concerning the dependence of the green luminescence of ZnO crystals on the light intensity at different voltages will be presented here. The experiments were performed in an electrochemical cell in which the surface of the ZnO crystal under observation was in contact with an electrolyte solution. The opposite surface of the crystal was ohmically contacted and the circuit completed through the voltage source and a Pt-wire counter electrode immersed in the electrolyte. The potential was measured against a Calomel electrode. The green luminescence of the ZnO was excited with light in the 310-390 nm range.

Fig. 1 shows the dependence of the luminescence intensity upon excitation intensity for different positive voltages, i.e., the ZnO positive with respect to the electrolyte. With the circuit open, a linear dependence is
obtained; this linear dependence changes gradually to a square dependence upon application of a positive voltage and seems to assume an even higher order of dependence at "high" voltage combined with low light intensities. Similar departures from a linear to quadratic and higher orders of dependence have been reported. Measurements on ZnS:Cu and Zn:Ni revealed such effects when temperature and dopants were the parameters [7]. In anthracene the ratio of delayed light emission to excitation light intensity showed departures from the quadratic as the temperature was varied [8].

We present here a qualitative formulation of a model which will account for the observations shown in Fig. 1. A detailed quantitative presentation, together with additional experimental work, will be presented elsewhere.

We assume that the green fluorescence originates from recombination of trapped holes with electrons from the conduction band. We assume further that the fluorescence observed is the sum of contributions from the space charge layer and from the bulk. In the situation where the number of electrons in the conduction band far exceeds the number of photoinduced carriers, as in n-type ZnO, the luminescence intensity will be proportional to the concentration of photoinjected and then trapped holes only, and hence linearly dependent on the exciting light intensity. A quadratic dependence on the light intensity can result when the concentrations of electrons and trapped holes are equivalent, a situation which is likely to exist when only photoinjected carriers recombine. In order to change from a linear to a square dependence the excess electrons must be removed from the recombination zone. This zone is approximately
equivalent to the penetration depth of the light which extends about $10^{-5}$ cm from the surface into the crystal at the wavelengths used.

The removal of all or part of the excess electrons from this area can be attributed to the build-up of a space charge layer, which in this material has a voltage dependent penetration depth of approximately the same magnitude as the penetration depth of the light.

It is assumed that the voltage changes with the distance according to the following relation: $V(x) = \frac{2\pi}{\varepsilon} (a + bI_0)(x-L)^2$ where $\varepsilon$ is the dielectric constant, $I_0$ is the light intensity, $L$ the limit of the space charge layer, $x$ is the distance from the crystal surface, $a$ is related to the number of charge carriers in the absence of light, and $b$ is a parameter which relates the change in number of charge carriers to the light intensity.

It is also assumed that at equilibrium the number of electrons in the space charge layer is related to the number of electrons in the bulk by the Boltzmann distribution. The assumptions so far made are common [9], and were shown to be true in a number of independent experiments. An assumption which is somewhat novel in this treatment is that following absorption of photons, the dominant mode for decay of the charge carriers is to their thermal equilibrium value.

A satisfactory agreement between theory and experiment was found up to the second order dependence on the light intensity. We have no satisfactory explanation for the higher order dependence on light intensity. Experiments are in progress to clarify this region.

Two of the authors gratefully acknowledge the grant of fellowships by the Max Kade Foundation, New York (G.P.) and the National Institutes of Health (M.T.). This work was supported, in part, by the U. S. Atomic Energy Commission.
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FIGURE CAPTION

Fig. 1. The intensity of the green luminescence of ZnO versus the intensity of the exciting light (310-390 nm) for several values of the reverse-bias voltage applied to the illuminated surface of the crystal.
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