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K. V. TAGANTSEV and Academician A. N. TERENIN

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Abstract

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K. V. TAGANTSEV and Academician A. N. TERENIN

THE EFFECT OF GAS ADSORPTION ON THE LUMINESCENCE OF ZINC OXIDE*

In the present work, measurements of luminescence intensity were carried out in two regimes: 1) under continuous illumination; 2) under brief illuminations, each 10 sec in duration, with dark intervals of no less than 5 min. The need for two illumination regimes is connected with the fact that prolonged illumination can cause, and indeed, as our experiments established, does cause, a change in the state of the adsorbent surface, for example as a result of photodesorption of gas. With brief illuminations it is possible to record changes in the state of the adsorbent surface caused only by dark adsorption of gases.

Method. Zinc oxide was prepared by burning metallic zinc in air in a crucible furnace at a temperature of 900° and was deposited on a glass plate in the form of an aqueous suspension. The plate with the sample was placed in a glass vessel, where it was trained in high vacuum at 200° or 400° C for several hours.

The luminescence of ZnO was excited by the light of an ARK-4 mercury lamp (220 W) through a UFS-3 ultraviolet light-filter plate. The differential photoelectric photometer used to measure the luminescence intensity consisted of two antimony-cesium vacuum photocells, TsSV-3, connected opposite to each other. The differential current was amplified by a direct-current amplifier. The greenish-yellow luminescence light from the zinc oxide sample was focused by a glass lens onto one photocell, and onto the other was focused the luminescence light of a comparison standard—a uranium-glass plate.

In the figures presented here, as a rule, (I_0) denotes the initial value of the luminescence intensity in vacuum before admission of gas under brief illumination, and (I) denotes the changed value of the luminescence intensity under the influence of the introduced factors (gas adsorption, prolonged illumination).

Results. 1. It was established by means of brief illuminations that dark adsorption, by a sample trained in vacuum, of water vapor, as well as adsorption of dry oxygen alone, has a noticeable quenching effect on luminescence (Fig. 1). A ZnO sample quenched by water vapor is additionally quenched by oxygen (Fig. 1, curve 3).

On one of the ZnO samples, prepared from other starting materials and possibly containing traces of organic substances, very weak quenching of luminescence

Figure 1

Figure 1: Figure 1

by dry oxygen and significant quenching by oxygen only in the presence of water vapor were observed ((^{11})).

2. A particularly strong quenching effect under brief illuminations is caused by adsorption of quinone vapor, which quenches the luminescence of ZnO even at a pressure of 0.1 torr (see Fig. 2). The quinone molecule has an electron affinity comparable to that of oxygen.

3. If oxygen at a pressure of 1.5 torr is subjected to the action of a weak electrodeless discharge from a Tesla transformer, normally used for checking the vacuum, and then immediately or after 1 min admitted into a vessel with a luminescent ZnO sample, strong quenching occurs. Apparently, the principal quenching action of active oxygen is associated with ozone formed in the discharge.

Fig. 1. Quenching of ZnO luminescence upon dark adsorption of gases (short-term illuminations). 1 –oxygen, 2 –H(_2)O vapor; 3 –action of oxygen on a sample already preliminarily quenched by water vapor (vapor pressure 16 torr) in their presence.

4. Measurements of luminescence intensity carried out under prolonged illumination of the ZnO sample under study, which had adsorbed gases, revealed a strong effect of light on this system. In the presence of oxygen (pressure 80 torr), a rekindling of the luminescence of ZnO, quenched by oxygen, is observed upon transition from short-term illumination to prolonged illumination (Fig. 3). This phenomenon is reversible: after the light is switched off, the luminescence, measured by short-term illuminations, again falls to the initial value. This phenomenon should be attributed to photodesorption of oxygen, detected by other methods (4, 5), in particular by direct manometric measurements by Solonitsyn (6).

Analogous rekindling of quenched luminescence upon transition from short-term illuminations to continuous illumination is shown by ZnO that has adsorbed activated oxygen, water vapor, and quinone vapor. Evidently, here too we have the phenomenon of photodesorption.

Fig. 2. Course of quenching of ZnO luminescence by quinone vapor with time

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* Brief contents of a report at the 5th All-Union Conference on Luminescence in Tartu in June 1956. The present work is a direct continuation of a series of works begun by Terenin, Gachkovskii, and Kasparov ((^{1-3})) in the 1930s at the Physics Institute of Leningrad University, on the study of quenching of the luminescence of solids by vapors and gases.

Figure 2

Figure 2: Figure 2

under short-term illuminations. Arrows directed downward indicate the moment of admission of quinone vapor; arrows directed upward indicate the moment at which pumping out and freezing out of the vapor began.

Fig. 4 presents a band scheme of the energy levels according to current views. The upper local levels, denoted in the figure as Zn (Zn(^+)–e), are created by excess zinc atoms which, according to Mollwo and Stöckmann (7), as well as Bergunas and Konovalov (8), are centers from which electrons of dark conductivity are separated. The lower local levels, denoted in the figure as Zn(^+) (Z(^{++})–e), belong to excess singly charged zinc ions, which, according to the views of the same authors, are centers of photoconductivity and luminescence. In other words, under the action of light, electrons are detached from Zn(^+), enter the conduction band, and recombination of an electron with Zn(^{++}) leads to the excited level and emission of luminescence light (process (E_m) in Fig. 4).

Upon adsorption of electronegative molecules (O(_2), H(_2)O, O(_3)), quinone on the ZnO surface, additional electron-capture levels are created. These levels are already filled in the dark by electrons transferred to them from local levels of Zn atoms, as shown in the figure.

According to the concepts currently widespread, in this way a double layer is created at the semiconductor surface, leading–

leading to the bending of the bands shown in the figure. Under the action of an absorbed light quantum, probably migrating in the form of an exciton to the surface, electrons are detached from the photoeffect centers Zn^+ with transfer of the electrons into the conduction band (arrow (E_{xc}) in the figure).

The potential barrier decreases the concentration of electrons in the boundary layer, as a result of which the process of their recombination with the ionized center, accompanied by luminescence emission, is suppressed. Ionized luminescence centers Zn^{++} recombine nonradiatively with electrons sitting on trapping levels created by the adsorption of electronegative molecules.

The indicated process leads, on the one hand, to quenching of luminescence and, on the other, to an increase in the photoeffect owing to the lengthening of the lifetime of electrons in the conduction band. The latter was experimentally found by Putseiko and Terenin (^{6}) upon adsorption of electronegative gases on ZnO. As electrons leave the adsorbed trapping levels, the height of the barrier will decrease, which makes possible the migration of electrons to the surface and the replenishment by electrons of the emptied levels created by adsorption.

Fig. 3. Flare-up of ZnO luminescence, quenched by oxygen (80 torr), upon transition from short-time illuminations (*a*) to continuous illumination (*b*).

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

The flare-up of luminescence upon transition to continuous illumination is explained by photodesorption, in accordance with the photoelectric and manometric effects on ZnO mentioned above. It may be supposed that a light quantum absorbed by the crystal, migrating to the surface in the form of an exciton, discharges negative molecular ions of the surface with transfer of an electron into the conduction band. The change in the potential energy of binding of the ion with the surface occurs in this quantum transition according to the Franck-Condon principle. The excess kinetic energy imparted to the neutral molecule formed, along the coordinate perpendicular to the surface, is evidently sufficient to overcome its bond with the adsorbent and to cause desorption (6). Photodesorption destroys the surface levels that caused quenching of luminescence.

Fig. 4. Scheme of electronic transitions. It is assumed that the absorption centers ((E_{xc})) in the photoeffect and in luminescence are Zn^+((Zn^{++}-e)) and that the emission ((E_m)) arises upon recombination with them of electrons from the conduction band.

A water molecule can also create a trapping level, since in the free state it has an electron affinity of the order of 1 eV (9), while in the hydrated state its affinity, i.e. the affinity of liquid water, is still higher (10).

The absence, observed by us on some samples, of quenching by dry (O_2) and the appearance of quenching by oxygen only in the simultaneous presence of adsorbed water can be explained as follows. On a given sample the surface trapping levels created by adsorption of (O_2) turn out to be situated so high that they cannot capture electrons from local levels of Zn atoms. Upon additional adsorption of water, especially upon formation of capillary-adsorbed water, hydration of the (O_2) molecules takes place, as it were, leading, as is known (10), to a lowering of the energy level of the negative ion, which is equivalent to an increase in the affinity of the initial (O_2) molecule. As a result the vacant (O_2) level on the surface

decreases sufficiently to cause the electron transition and the process of luminescence quenching, as described above.

Physical Institute
of Leningrad State University
named after A. A. Zhdanov

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