

EFFECT OF OXYGEN ADSORPTION ON THE KINETICS OF RADICAL-RECOMBINATION LUMINESCENCE OF PHOSPHORS

Yu. A. Sivov, V. V. Styrov,
and L. I. Yagnova

UDC 535.373.2

One way to study the surface properties of semiconductors is to study the effect of gas adsorption on the various types of luminescence. A very convenient luminescence for this type of study is radical-recombination luminescence, because the luminescence of the solid in this case is largely superficial [1].

We report here a study of the effect of preliminary adsorption of gases on the buildup kinetics of the radical-recombination luminescence of phosphors. We used molecular oxygen as adsorbate, since the effect of its adsorption on other types of luminescence, particularly photoluminescence, has been studied thoroughly (see, e.g., [2, 3]). We used powdered phosphors of the following compositions: "self-activated" ZnS, ZnS-Mn [10^{-4} g/g], ZnS-Mn [10^{-1} g/g], and CaO-Mn. The latter material was used for comparison because of its broad energy gap and because it is supposed to have a different mechanism for the excitation of radical-recombination luminescence [4].

The experiments were carried out on an apparatus similar to that described in [5], but incorporating certain structural changes for these experiments. Radical-recombination luminescence was excited by atomic hydrogen produced in molecular hydrogen by a high-frequency discharge. The electrodes were conditioned as in [6] (procedure "a"). The first kinetic curve of the luminescence buildup was thus obtained from the sample conditioned in vacuum. Then the sample was again degassed in vacuum, and oxygen was admitted into the working volume at the selected temperature (T_{ads}), to a pressure of $P = 0.3$ torr. The adsorption time was ~ 15 min. Then the oxygen was evacuated at T_{ads} , the desired temperature (T_{lum}) was established, and a second kinetic curve of the luminescence buildup was recorded. Two curves were thus recorded: "before" and "after" adsorption; the curves were compared.

This sample was not used again, since it was difficult to remove the tightly bound chemisorbed oxygen, and it was difficult to restore the original state of the sample by conditioning. Oxygen adsorption at a different T_{ads} was therefore studied on a fresh sample, conditioned under identical conditions.

Figure 1 shows the effect of preliminary oxygen adsorption on the radical-recombination luminescence of self-activated ZnS at two temperatures. For clarity, the curves showing the luminescence buildup for two phosphor samples before adsorption at room temperature are brought into coincidence by changing the ordinate scale (curve 1). Curves 1' and 2' show the isotherms after adsorption. Even at room temperature (1'), oxygen adsorption quenches the luminescence in such a manner that it cannot thereafter be restored to its previous level, i.e., irreversibly. The irreversible quenching is more pronounced at higher T_{ads} (2').

Figure 2 shows the analogous family of kinetic curves for the ZnS-Mn [10^{-4} g/g] sample. In this case the luminescence quenching by oxygen is completely reversible at T_{ads} not too high (1', 2'); at $T_{\text{ads}} = 360^\circ\text{K}$, the quenching becomes irreversible (3').

The following factors must be taken into account in order to understand these results.

1. Adsorption of an acceptor gas (oxygen) charges a surface negatively and reduces the Fermi level. As a result, the equilibrium coverage by a charged chemisorbed species (H^+) increases; if we neglect the chemical interaction between adsorbed oxygen and hydrogen and blocking of hydrogen

S. M. Kirov Tomsk Polytechnical Institute. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 9, pp. 124-126, September, 1970. Original article submitted September 17, 1969.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

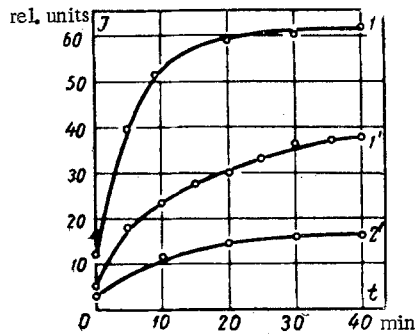


Fig. 1

Fig. 1. Kinetic isotherms showing the buildup of radical-recombination luminescence of self-activated ZnS samples at $T_{lum} = 300^{\circ}K$. 1) Before adsorption; 1', 2') after adsorption of oxygen at $T_{ads} = 300$ and $330^{\circ}K$, respectively.

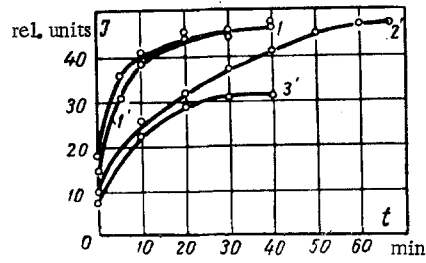


Fig. 2

Fig. 2. Kinetic isotherms for the luminescence of ZnS-Mn [10^{-4} g/g] samples at $T_{lum} = 300^{\circ}K$. 1) Before adsorption; 1'-3') after oxygen adsorption at 300, 330, and $370^{\circ}K$, respectively.

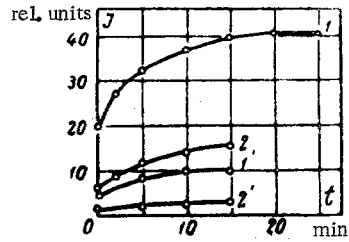


Fig. 3

Fig. 3 Kinetic isotherms for the luminescence of ZnS-Mn [10^{-1} g/g] samples (1, 1') and CaO-Mn samples (2, 2') at $T_{lum} = 300^{\circ}K$. 1, 2) Before adsorption; 1', 2') after adsorption of oxygen at $T_{ads} = 300^{\circ}K$.

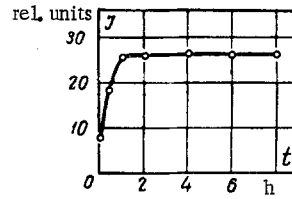


Fig. 4

Fig. 4. Kinetic isotherm for the luminescence of ZnS-Mn [10^{-4} g/g] at $T_{lum} = 330^{\circ}K$.

from adsorption centers by oxygen, we conclude that the intensity of radical-recombination luminescence should increase after adsorption, according to the mechanism described for this luminescence in [8].

2. Electrons which appear in the conduction band as a result of the adsorption and recombination of hydrogen atoms can recombine at oxygen traps and leave the radiative-recombination process. As a result, the luminescence intensity should decrease (there may also be afterglow and thermoluminescence).
3. Blocking of atomic hydrogen from adsorption centers by oxygen reduces the luminescence intensity.
4. Finally, a previously adsorbed gas can actively interact with atomic hydrogen, so that adsorption of atomic hydrogen and thus luminescence excitation becomes improbable.

Accordingly, only the first of these factors has a "positive" effect, i.e., increases the luminescence intensity. If this effect is to be observed (if this observation is at all possible), the effects of the other factors would have to be eliminated; i.e., it would be necessary to resort to an extremely low surface coverage by adsorbed oxygen.

Experimentally we observed only quenching of luminescence, apparently due to factors 2-4. The blocking should be particularly important for those phosphors whose luminescence centers are excited

by immediate recombination of atoms at luminescence centers (in the case of phosphors having a broad energy gap, e.g., CaO-Mn, or phosphors having a narrow energy gap but a high activator concentration, e.g., ZnS-Mn [10^{-1} g/g]). In fact, both types of phosphors display an equally pronounced quenching of luminescence by oxygen (Fig. 3). Factor 2 also operates during photoexcitation, but in the case of radical-recombination luminescence its effect should be greater because of the superficial nature of the luminescence. Finally, that a chemical reaction does occur between adsorbed oxygen and hydrogen cannot be denied, in view of the complete or partial restoration of the steady-state luminescence intensity after quenching by adsorption.

The possibility of monitoring a chemical reaction on the basis of the kinetics of the luminescence restoration after adsorption would seem to be a highly interesting application of radical-recombination luminescence. In this case the reaction "tells us about itself, using the language of light," in the graphic words of B. Ya. Sveshnikov. For example, the irreversibility of the quenching observed in several cases (Figs. 1-3) implies that the oxygen adsorption is inhomogeneous: some of the oxygen adsorbed at a given T_{ads} does not react with atomic hydrogen at the given T_{lum} , while another part actively interacts with it. In addition to the qualitative information about the existence of various chemisorbed species, about the temperatures at which they appear on the surface, and about the temperatures at which they begin to interact with the gaseous medium which can be extracted from the kinetic curves, it would in principle be possible to calculate the cross sections for chemical reactions.

We previously pointed out the possibility of using a phosphor as a probe for determining the concentration of active particles in a gaseous medium [7]. Such an application would require that the probe retain its properties (that it not age) for a sufficiently long time. Aging might be caused, in particular, by the adsorption of slight amounts of foreign impurities from the working gas (e.g., an oxygen impurity in hydrogen) or products of chemical reactions. Pertinent experiments which we carried out showed that the "steady-state" intensity of radical-recombination luminescence was retained in "electrolytic" hydrogen for an extremely long time under certain conditions. These results are illustrated in Fig. 4 for the case of ZnS-Mn [10^{-4} g/g] sample. Under these conditions, this sample could thus be used to detect the concentration of atomic hydrogen.

LITERATURE CITED

1. V. V. Styrov, Candidate's Dissertation [in Russian], TGU, Tomsk (1968).
2. A. N. Terenin and V. A. Tagantsev, Dokl. Akad. Nauk SSSR, 112, 2 (1957).
3. S. H. Liebson, J. Chem. Phys., 23, 1723 (1965).
4. A. I. Bazhin, V. A. Sokolov, and V. V. Styrov, Izv. Akad. Nauk SSSR, Ser. Fiz., 33, No. 5, 921 (1969).
5. V. V. Styrov and V. A. Sokolov, Zh. Prikl. Spekt., 8, 809 (1968).
6. V. V. Styrov, Yu. A. Sivov, Yu. A. Markin, and Yu. M. Nasledinkov, Izv. VUZ, Fizika, No. 8, 33 (1970).
7. V. A. Sokolov, V. V. Styrov, A. I. Bazhin, and O. G. Brik, Zh. Prikl. Spekt., 11, 546 (1969).
8. F. F. Vol'kenshtein, V. A. Sokolov, and A. N. Gorban', Kinetika i Kataliz, 4, 24 (1963).